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(54) **Hard surface cleaners**

(57) Suggested is a hard surface cleaning composition, comprising a blend of two non-ionic surfactants having simultaneously good rinsing, drying, streak-free, anti-filming and anti-spotting performance and excellent wetting on substrates and also showing compared to the state of the art superior water run-off behaviour.

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Description**FIELD OF INVENTION**

5 **[0001]** The present invention belongs to the area of detergents and refers to a new blend of surfactants, hard surface cleaners comprising them and their use as hard surface cleaners.

STATE OF THE ART

10 **[0002]** The cleaning of hard surfaces has not only the hygienic aspect but also an aesthetic side. It is thus desirable that a clean surface dries very rapidly and uniformly in order to avoid the formation of unappealing drop- or streak-like residues ("runs") if possible. However, these can form not only after the cleaning, especially in the case of use of hard water, but also between the cleaning operations when the surface again comes into contact with water, known as the rain effect. For example, this is the case in bathrooms, but in particular for surfaces exposed to the weather, such as windows etc. The rapid drying of the surfaces is therefore generally desirable.

15 **[0003]** It is further advantageous when the surface is wetted over the full surface for a prolonged period instead of the film breaking, which likewise leads to "runs". The full-surface wetting with a thin film likewise contributes to rapid drying; in addition, tiny soil particles are distributed uniformly instead of occurring concentrated in the "runs", so that the surface has a visually cleaner appearance. A further aspect, again in particular for surfaces exposed to the weather, is the reduction of the re-soiling tendency of clean surfaces, since it is desirable for the consumer to allow a maximum period of time between two cleaning operations without the surface appearing dirty to the observer.

20 **[0004]** In addition, an anti-condensation action is desirable to minimise the condensation of water on the surface. In order to satisfy all of these requirements, the cleaner should modify the surface to be cleaned in such a way that the wetting behaviour changes compared to an untreated surface, so that it is soiled less rapidly and dries rapidly without the formation of "runs".

25 **[0005]** Hard surface cleaners found in the market typically contain non-ionic surfactants combining high detergency with low foaming behaviour. The preferred types of non-ionic surfactants encompass in particular all types of ethoxylated and propoxylated fatty alcohols as disclosed for example in WO 1998 014545 A1 or EP 1897933 A1 and the corresponding polyglycol ethers based on alkyl phenols. During the recent years also alkyl polyglucosides have become standard surfactants for cleaner systems, either taken alone (EP 0210220 B1), or in combination with other surfactants, like for example amine oxides (EP 0210270 A1), fatty alcohol ethoxylates (EP 0783560 B1, EP 2049642 B1) or also anionic surfactants (EP 1171557 A2).

30 **[0006]** Nevertheless, market needs and consumer insight are still increasing, so detergent products of today need to fulfil a complex profile:

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- Professional cleaners for cleaning outdoor facade, windows and transportation vehicles need to involve removal of mixture of diverse soil such as of earth soil (minerals), soot, fine dust, grease and traffic film, etc.;
 - Both acidic and alkaline formulations with high performance and long-time stability are needed to target different types of soils;
 - The products must allow good removal of soil by mechanical action via hand cleaning, machine operations, but also without brushing. If applied with highpressure hose, production of high foam volume should be avoided for ease of rinseability;
 - The products must not leave any stain, streak, or marks and should be easily removed or left on the surface without rinsing;
 - The products should leave only a thin layer of water on the surface that dries very fast, leaving a non-streaky surface;
 - Formulations are required for providing more shine, but also avoid creating white visible water spot marking, if the remaining water dries unevenly on the surface;
 - Since antifoaming agent leaves visible films on the surface, products are required which are free of these unwanted additives; in addition silicones are unwanted additives too, since they are responsible for build-up effects;
 - Especially in I&I application, foam and slow drying lead to extra cost and energy consumption, making it less sustainable. Therefore products are needed, which show both low foaming, a rapid drying behaviour, as well as
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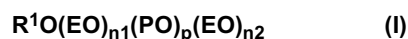
streak-free finish.

[0007] Therefore, the complex problem underlying the present invention has been to provide a new surfactant blend useful for hard surface cleaning that overcomes all or at least most of the problems explained above. In particular, the surfactants should exhibit a lower foaming behaviour, both under alkaline and acidic conditions, when compared to standard non-ionic surfactants, especially in view of alkyl polyglucosides.

DESCRIPTION OF THE INVENTION

[0008] Object of the present invention is a liquid hard surface cleaner composition, comprising a surfactant blend comprising or consisting of

(a) a first non-ionic surfactant of formula (I)



in which

R^1 stands for a linear alkyl radical having 9 to 11 carbon atoms;

$n1$ stands for 0 or an integer of from 6 to 10;

$n2$ stands for 0 or an integer of from 6 to 10;

p stands for 0 or an integer of from 4 to 6;

and

(b) a second non-ionic surfactants of formula (II)



in which

R^2 stands for a linear alkyl radical having 10 carbon atoms;

$m1$ stands for 0 or an integer of from 6 to 10;

$m2$ stands for 0 or an integer of from 6 to 10;

q stands for 0 or an integer of from 4 to 6;

on condition that both sums $(n1+p+n2)$ and $(m1+q+m2)$ is different from 0.

[0009] Surprisingly, it has been observed that surfactants blends comprising the non-ionic surfactants of formula (I) and (II), preferably in a ratio by weight of from about 1:5 to about 5:1 provides superior performance when compared to other non-ionic surfactants typically used for the same purpose. In particular, the cleaners incorporating the new surfactant blend exhibit the following advantages:

- A well-balanced hydrophobicity and hydrophilicity which allows superior quick drying as well as sheeting property, leading to streak-free finish. The invention dries evenly, leaving no streaks or white water spots behind;
- The products according to the present invention represent low foaming hard surface cleaners, which allows aesthetic finish and prevents foam marks during and after drying;
- The products are suitable for various substrates (glass, ceramic, metal, plastic) with especially excellent performance on plastic and metal surfaces;
- Due to minimised foam and quick drying, the use of the products leads to cost and energy saving, especially in I&I applications;
- The products are suitable for a broad range of pH formulations, making it suitable for both acidic and alkaline formulations;
- The products show excellent cold water solubility and do not form gel phase, allowing ease to formulate concentrates and concentrated formulations using wide range of processing conditions;
- The products show excellent wetting performance with regard to the release from fats and oils from hard surfaces and inhibit re-deposition.

[0010] Therefore, the products according to the present invention fulfil the complex profile as set out above to the entire. Moreover, the effect is demonstrated for various substrates in comparison with other non-ionic surfactants known from the state of the art for the same purpose.

[0011] The surfactant blends as proposed by the invention represent a binary mixture of an oxoalcohol and a fatty

alcohol alkoxylated, more particularly component (a) represents an alkoxylated $C_{9/11}$ oxoalcohol of formula (I), wherein n_1 stands for 8 to 9, p stands for 5 to 6 and n_2 stands for 0. On the other hand, component (b) represents a fatty alcohol having 10 carbon atoms (or a pure synthetic decanol) of formula (II), wherein m_1 stands for 8 to 9, q stands for 5 to 6 and m_2 stands for 0.

[0012] The preparation takes place in the manner known to the person skilled in the art by reacting fatty alcohols or oxoalcohols with the alkoxides in the presence of acidic or basic catalysts. The components may show a broad or narrow homologue distribution.

[0013] The hard surface cleaning compositions according to the present invention may contain the components (a) and (b) in a ratio by weight of about 5:1 to about 1:5 and more particular in a ratio by weight of about 2:1 to about 3:1.

HARD SURFACE CLEANING COMPOSITIONS

[0014] The hard surface cleaning compositions of the present invention may further comprise non-ionic surfactants different from components (a) and (b), builders or abrasive compounds, polymers, hydrotropes and/or organic acids and the like.

[0015] In particular such composition may encompass

(a) about 5 to about 15 % b.w. surfactant of formula (I);

(b) about 1 to about 5 % b.w. surfactant of formula (II);

(c) 0 or about 1 to 5 % b.w. co-surfactants;

(d) 0 or about 1 to 65 % b.w. builders, abrasive compounds, sequestrants and/or chelating agents;

(e) 0 or about 1 to 5 % b.w. polymers;

(f) 0 or about 1 to about 15 % b.w. hydrotropes;

(g) 0 or about 1 to about 5 % b.w. organic acids,

on condition that the amounts add with water and optionally usual auxiliary agents to 100 % b.w.

[0016] The compositions are prepared by mixing the different components, optionally with the input of energy by stirring and/or heating of the mixtures. Preferably, after introducing the water as initial charge, the remaining components are added in any order with stirring and then the mixture is further stirred until clear.

[0017] Suitable additives for hard surface cleaning compositions according to the present invention are summarised in the following:

ANIONIC CO-SURFACTANTS

[0018] Preferably, surfactants of the sulfonate type, alk(en)yl sulfonates, alkoxylated alk(en)yl sulfates, ester sulfonates and/or soaps are used as the anionic surfactants. Suitable surfactants of the sulfonate type are advantageously C_{9-13} alkylbenzene sulfonates, olefin sulfonates, i.e. mixtures of alkene- and hydroxyalkane sulfonates, and disulfonates, as are obtained, for example, by the sulfonation with gaseous sulfur trioxide of C_{12-18} monoolefins having a terminal or internal double bond and subsequent alkaline or acidic hydrolysis of the sulfonation products.

[0019] Alk(en)yl sulfates. Preferred alk(en)yl sulfates are the alkali and especially the sodium salts of the sulfuric acid half-esters of the $C_{12}-C_{18}$ fatty alcohols, for example, from coconut butter alcohol, tallow alcohol, lauryl, myristyl, cetyl or stearyl alcohol or from C_8-C_{20} oxo alcohols and those half-esters of secondary alcohols of these chain lengths. Alk(en)yl sulfates of the cited chain lengths that comprise a synthetic straight chain alkyl group manufactured petrochemically are also preferred. The $C_{12}-C_{16}$ alkyl sulfates and $C_{12}-C_{15}$ alkyl sulfates as well as $C_{14}-C_{15}$ alkyl sulfates and $C_{14}-C_{16}$ alkyl sulfates are particularly preferred on the grounds of laundry performance. The 2,3-alkyl sulfates, which can be obtained from Shell Oil Company under the trade name DANTM, are also suitable anionic surfactants.

[0020] Alk(en)yl ether sulfates. Sulfuric acid mono-esters derived from straight-chained or branched C_7-C_{21} alcohols ethoxylated with 1 to 6 moles ethylene oxide are also suitable, such as 2-methyl-branched C_9-C_{11} alcohols with an average of 3.5 mol ethylene oxide (EO) or $C_{12}-C_{18}$ fatty alcohols with 1 to 4 EO.

[0021] Ester sulfonates. The esters of alpha-sulfo fatty acids (ester sulfonates), e.g., the alpha-sulfonated methyl esters of hydrogenated coco-, palm nut- or tallow acids are likewise suitable.

[0022] Soaps. Soaps, in particular, can be considered as further anionic surfactants. Saturated fatty acid soaps are

particularly suitable, such as the salts of lauric acid, myristic acid, palmitic acid, stearic acid, hydrogenated erucic acid and behenic acid, and especially soap mixtures derived from natural fatty acids such as coconut oil fatty acid, palm kernel oil fatty acid or tallow fatty acid. Those soap mixtures are particularly preferred that are composed of 50 to 100 wt. % of saturated C₁₂-C₂₄ fatty acid soaps and 0 to 50 wt. % of oleic acid soap.

[0023] Ether carboxylic acids. A further class of anionic surfactants is that of the ether carboxylic acids, obtainable by treating fatty alcohol ethoxylates with sodium chloroacetate in the presence of basic catalysts. They have the general formula: RO(CH₂CH₂O)_pCH₂COOH with R = C₁-C₁₈ and p = 0.1 to 20. Ether carboxylic acids are insensitive to water hardness and possess excellent surfactant properties.

NON-IONIC (CO-)SURFACTANTS

[0024] Among the group of co-surfactants non-ionic surfactants are preferred due to its low foaming behaviour:

[0025] Alkohol alkoxylates. The added nonionic surfactants are preferably alkoxylated and/or propoxylated, particularly primary alcohols having preferably 8 to 18 carbon atoms and an average of 1 to 12 mol ethylene oxide (EO) and/or 1 to 10 mol propylene oxide (PO) per mol alcohol. C₈-C₁₆-Alcohol alkoxylates, advantageously ethoxylated and/or propoxylated C₁₀-C₁₅-alcohol alkoxylates, particularly C₁₂-C₁₄ alcohol alkoxylates, with an ethoxylation degree between 2 and 10, preferably between 3 and 8, and/or a propoxylation degree between 1 and 6, preferably between 1.5 and 5, are particularly preferred. The cited degrees of ethoxylation and propoxylation constitute statistical average values that can be a whole or a fractional number for a specific product. Preferred alcohol ethoxylates and propoxylates have a narrowed homolog distribution (narrow range ethoxylates/propoxylates, NRE/NRP). In addition to these nonionic surfactants, fatty alcohols with more than 12 EO can also be used. Examples of these are (tallow) fatty alcohols with 14 EO, 16 EO, 20 EO, 25 EO, 30 EO or 40 EO.

[0026] Alkylglycosides (APG®). Furthermore, as additional nonionic surfactants, alkyl glycosides that satisfy the general Formula RO(G)_x, can be added, e.g., as compounds, particularly with anionic surfactants, in which R means a primary linear or methyl-branched, particularly 2-methyl-branched, aliphatic group containing 8 to 22, preferably 12 to 18 carbon atoms and G stands for a glucose unit containing 5 or 6 carbon atoms, preferably for glucose. The degree of oligomerisation x, which defines the distribution of monoglycosides and oligoglycosides, is any number between 1 and 10, preferably between 1.1 and 1.4.

[0027] Fatty acid ester alkoxylates. Another class of preferred nonionic surfactants, which are used either as the sole nonionic surfactant or in combination with other nonionic surfactants, in particular, together with alkoxylated fatty alcohols and/or alkyl glycosides, are alkoxylated, preferably ethoxylated or ethoxylated and propoxylated fatty acid alkyl esters preferably containing 1 to 4 carbon atoms in the alkyl chain, more particularly the fatty acid methyl esters which are described, for example, in Japanese Patent Application JP-A-58/217598 or which are preferably produced by the process described in International Patent Application WO 2012/028435 A1 (KOLB). Methyl esters of C₁₂-C₁₈ fatty acids containing an average of 3 to 15 EO, particularly containing an average of 5 to 12 EO, are particularly preferred.

[0028] Amine oxides. Nonionic surfactants of the amine oxide type, for example, N-coco alkyl-N,N-dimethylamine oxide and N-tallow alkyl-N,N-dihydroxyethylamine oxide, and the fatty acid alkanolamides may also be suitable. The quantity in which these nonionic surfactants are used is preferably no more than the quantity in which the ethoxylated fatty alcohols are used and, particularly no more than half that quantity.

[0029] Gemini surfactants. The so-called gemini surfactants can be considered as further surfactants. Generally speaking, such compounds are understood to mean compounds that have two hydrophilic groups and two hydrophobic groups per molecule. As a rule, these groups are separated from one another by a "spacer". The spacer is usually a hydrocarbon chain that is intended to be long enough such that the hydrophilic groups are a sufficient distance apart to be able to act independently of one another. These types of surfactants are generally characterised by an unusually low critical micelle concentration and the ability to strongly reduce the surface tension of water. In exceptional cases, however, not only dimeric but also trimeric surfactants are meant by the term gemini surfactants. Suitable gemini surfactants are, for example, sulfated hydroxy mixed ethers according to German Patent Application DE 4321022 A1 or dimer alcohol bis- and trimer alcohol trisulfates and ether sulfates according to International Patent Application WO 96/23768 A1. Blocked end group dimeric and trimeric mixed ethers according to German Patent Application DE 19513391 A1 are especially characterized by their bifunctionality and multifunctionality. Gemini polyhydroxyfatty acid amides or polyhydroxyfatty acid amides, such as those described in International Patent Applications WO 95/19953 A1, WO 95/19954 A1 and WO 95/19955 A1 can also be used.

CATIONIC CO-SURFACTANTS

[0030] Tetraalkyl ammonium salts. Cationically active surfactants comprise the hydrophobic high molecular group required for the surface activity in the cation by dissociation in aqueous solution. A group of important representatives of the cationic surfactants are the tetraalkyl ammonium salts of the general formula: (R¹R²R³R⁴N⁺) X⁻. Here R¹ stands

for C_1 - C_8 alk(en)yl, R^2 , R^3 and R^4 , independently of each other, for alk(en)yl radicals having 1 to 22 carbon atoms. X is a counter ion, preferably selected from the group of the halides, alkyl sulfates and alkyl carbonates. Cationic surfactants, in which the nitrogen group is substituted with two long acyl groups and two short alk(en)yl groups, are particularly preferred.

[0031] Esterquats. A further class of cationic surfactants particularly useful as co-surfactants for the present invention is represented by the so-called esterquats. Esterquats are generally understood to be quaternised fatty acid triethanolamine ester salts. These are known compounds which can be obtained by the relevant methods of preparative organic chemistry. Reference is made in this connection to International patent application WO 91/01295 A1, according to which triethanolamine is partly esterified with fatty acids in the presence of hypophosphorous acid, air is passed through the reaction mixture and the whole is then quaternised with dimethyl sulphate or ethylene oxide. In addition, German patent DE 4308794 C1 describes a process for the production of solid esterquats in which the quaternisation of triethanolamine esters is carried out in the presence of suitable dispersants, preferably fatty alcohols.

[0032] Typical examples of esterquats suitable for use in accordance with the invention are products of which the acyl component derives from monocarboxylic acids corresponding to formula $RCOOH$ in which RCO is an acyl group containing 6 to 10 carbon atoms, and the amine component is triethanolamine (TEA). Examples of such monocarboxylic acids are caproic acid, caprylic acid, capric acid and technical mixtures thereof such as, for example, so-called head-fractionated fatty acid. Esterquats of which the acyl component derives from monocarboxylic acids containing 8 to 10 carbon atoms, are preferably used. Other esterquats are those of which the acyl component derives from dicarboxylic acids like malonic acid, succinic acid, maleic acid, fumaric acid, glutaric acid, sorbic acid, pimelic acid, azelaic acid, sebacic acid and/or dodecanedioic acid, but preferably adipic acid. Overall, esterquats of which the acyl component derives from mixtures of monocarboxylic acids containing 6 to 22 carbon atoms, and adipic acid are preferably used. The molar ratio of mono and dicarboxylic acids in the final esterquat may be in the range from 1:99 to 99:1 and is preferably in the range from 50:50 to 90:10 and more particularly in the range from 70:30 to 80:20. Besides the quaternised fatty acid triethanolamine ester salts, other suitable esterquats are quaternised ester salts of mono-/dicarboxylic acid mixtures with diethanolalkylamines or 1,2-dihydroxypropyl dialkylamines. The esterquats may be obtained both from fatty acids and from the corresponding triglycerides in admixture with the corresponding dicarboxylic acids. One such process, which is intended to be representative of the relevant prior art, is proposed in European patent EP 0750606 B1. To produce the quaternised esters, the mixtures of mono- and dicarboxylic acids and the triethanolamine - based on the available carboxyl functions - may be used in a molar ratio of 1.1:1 to 3:1. With the performance properties of the esterquats in mind, a ratio of 1.2:1 to 2.2:1 and preferably 1.5:1 to 1.9:1 has proved to be particularly advantageous. The preferred esterquats are technical mixtures of mono-, di- and triesters with an average degree of esterification of 1.5 to 1.9.

AMPHOTERIC OR ZWITTERIONIC CO-SURFACTANTS

[0033] Betaines. Amphoteric or ampholytic surfactants possess a plurality of functional groups that can ionise in aqueous solution and thereby--depending on the conditions of the medium--lend anionic or cationic character to the compounds (see DIN 53900, July 1972). Close to the isoelectric point (around pH 4), the amphoteric surfactants form inner salts, thus becoming poorly soluble or insoluble in water. Amphoteric surfactants are subdivided into ampholytes and betaines, the latter existing as zwitterions in solution. Ampholytes are amphoteric electrolytes, i.e. compounds that possess both acidic as well as basic hydrophilic groups and therefore behave as acids or as bases depending on the conditions. Especially betaines are known surfactants which are mainly produced by carboxyalkylation, preferably carboxymethylation, of amine compounds. The starting materials are preferably condensed with halocarboxylic acids or salts thereof, more particularly sodium chloroacetate, one mole of salt being formed per mole of betaine. The addition of unsaturated carboxylic acids, such as acrylic acid for example, is also possible. Examples of suitable betaines are the carboxy alkylation products of secondary and, in particular, tertiary amines which correspond to formula $R^1R^2R^3N-(CH_2)_qCOOX$ where R^1 is an alkyl radical having 6 to 22 carbon atoms, R^2 is hydrogen or an alkyl group containing 1 to 4 carbon atoms, R^3 is an alkyl group containing 1 to 4 carbon atoms, q is a number of 1 to 6 and X is an alkali and/or alkaline earth metal or ammonium. Typical examples are the carboxymethylation products of hexylmeth-ylamine, hexyldimethylamine, octyldimethylamine, decyldimethylamine, $C_{12/14}$ -cocoalkyldimethyl-amine, myristyldimethylamine, cetyldimethylamine, stearyldimethylamine, stearylethyl-methylamine, oleyldimethylamine, $C_{16/18}$ -tallow-alkyldimethylamine and their technical mixtures, and particularly dodecyl methylamine, dodecyl dimethylamine, dodecyl ethylmethylamine and technical mixtures thereof.

[0034] Alkylamido betaines. Other suitable betaines are the carboxyalkylation products of amidoamines corresponding to formula $R^1CO(R^3)(R^4)-NH-(CH_2)_p-N-(CH_2)_qCOOX$ in which R^1CO is an aliphatic acyl radical having 6 to 22 carbon atoms and 0 or 1 to 3 double bonds, R^2 is hydrogen or an alkyl radical having 1 to 4 carbon atoms, R^3 is an alkyl radical having 1 to 4 carbon atoms, p is a number from 1 to 6, q is a number from 1 to 3 and X is an alkali and/or alkaline earth metal or ammonium. Typical examples are reaction products of fatty acids having 6 to 22 carbon atoms, like for example

caproic acid, caprylic acid, caprinic acid, lauric acid, myristic acid, palmitic acid, palmoleic acid, stearic acid, isostearic acid, oleic acid, elaidic acid, petroselinic acid, linolic acid linoleic acid, elaeostearic acid, arachidonic acid, gadoleic acid, behenic acid, erucic acid and their technical mixtures with N,N-dimethylaminoethylamine, N,N-dimethylaminopropylamine, N,N-diethylaminoethylamine und N,N-diethylaminopropylamine, which are condensed with sodium chloroacetate. The commercially available products include Dehyton® K and Dehyton® PK (Cognis Deutschland GmbH & Co., KG) as well as Tego® Betaine (Goldschmidt).

[0035] Imidazolines. Other suitable starting materials for the betaines to be used for the purposes of the invention are imidazolines. These substances are also known and may be obtained, for example, by cyclizing condensation of 1 or 2 moles of C₆-C₂₂ fatty acids with polyfunctional amines, such as for example aminoethyl ethanolamine (AEEA) or diethylenetriamine. The corresponding carboxyalkylation products are mixtures of different open-chain betaines. Typical examples are condensation products of the above-mentioned fatty acids with AEEA, preferably imidazolines based on lauric acid, which are subsequently betainised with sodium chloroacetate. The commercially available products include Dehyton® G (Cognis Deutschland GmbH & Co., KG)

[0036] The amount of (co-)surfactant comprised in the inventive compositions is advantageously 0.1 wt. % to 90 wt. %, particularly 10 wt. % to 80 wt. % and particularly preferably 20 wt. % to 70 wt.-%.

ORGANIC SOLVENTS

[0037] Cleaners may comprise organic solvents, preferably those miscible with water. Polydiols, ethers, alcohols, ketones, amides and/or esters are preferably used as the organic solvent for this in amounts of 0 to 90 wt. %, preferably 0.1 to 70 wt. %, particularly 0.1 to 60 wt. %. Low molecular weight polar substances, such as for example, methanol, ethanol, propylene carbonate, acetone, acetonylacetone, diacetone alcohol, ethyl acetate, 2-propanol, ethylene glycol, propylene glycol, glycerin, diethylene glycol, dipropylene glycol monomethyl ether and dimethylformamide or their mixtures are preferred.

ENZYMES

[0038] Cellulase Enzymes. Cellulase enzymes optionally used in the instant cleaner composition are preferably incorporated, when present, at levels sufficient to provide up to about 5 mg by weight, more preferably about 0.01 mg to about 3 mg, of active enzyme per gram of the composition. Unless stated otherwise, the compositions herein preferably comprise from about 0.001% to about 5%, preferably 0.01%-1% by weight of a commercial enzyme preparation.

[0039] The cellulases suitable for the present invention include either bacterial or fungal cellulase. Preferably, they will have a pH optimum of between 5 and 9.5. Suitable cellulases are fungal cellulase produced from *Humicola insolens* and *Humicola* strain DSM1800 or a cellulase 212-producing fungus belonging to the genus *Aeromonas*, and cellulase extracted from the hepatopancreas of a marine mollusk (*Dolabella Auricula Solander*), suitable cellulases are also disclosed in GB 2,075,028 A. In addition, cellulase especially suitable for use herein are disclosed in WO 1992 013057 A1. Most preferably, the cellulases used in the instant detergent compositions are purchased commercially from NOVO Industries A/S under the product names CAREZYMEO and CELLUZYMEO.

[0040] Other Enzymes. Additional enzymes can be included in the cleaning composition for example for removal of protein-based, carbohydrate-based, or triglyceride-based stains, for example, and for the prevention of refugee dye transfer, and for fabric restoration. The additional enzymes to be incorporated include proteases, amylases, lipases, and peroxidases, as well as mixtures thereof. Other types of enzymes can also be included. They can be of any suitable origin, such as vegetable, animal, bacterial, fungal and yeast origin. However, their choice is governed by several factors such as pH-activity and/or stability optima, thermostability, stability versus active cleaners, builders as well as their potential to cause malodors during use. In this respect bacterial or fungal enzymes are preferred, such as bacterial amylases and proteases.

[0041] Enzymes are normally incorporated at levels sufficient to provide up to about 5 mg by weight, more typically about 0.01 mg to about 3 mg, of active enzyme per gram of the composition. Stated otherwise, the compositions herein will typically comprise from about 0.001% to about 5%, preferably 0.01%-1% by weight of a commercial enzyme preparation. Protease enzymes are usually present in such commercial preparations at levels sufficient to provide from 0.005 to 0.1 Anson units (AU) of activity per gram of composition.

[0042] Suitable examples of proteases are the subtilisins which are obtained from particular strains of *B. subtilis* and *B. licheniformis*. Another suitable protease is obtained from a strain of *Bacillus*, having maximum activity throughout the pH range of 8-12, developed and sold by Novo Industries A/S under the registered trade name ESPERASE®. The preparation of this enzyme and analogous enzymes is described in GB 1,243,784 of Novo. Proteolytic enzymes suitable for removing protein-based stains that are commercially available include those sold under the trade names ALCALASE® and SAVINASE® by Novo Industries A/S and MAXATASE® by International Bio-Synthetics, Inc.. Other proteases include Protease A; Protease B and proteases made by Genencor International, Inc., according to US 5,204,015 and US

5,244,791.

[0043] Amylases include, for example, alpha-amylases like RAPIDASE[®], International Bio-Synthetics, Inc. and TER-MAMYL[®], Novo Industries.

[0044] Suitable lipase enzymes for cleaner usage include those produced by microorganisms of the Pseudomonas group, such as Pseudomonas stutzeri ATCC 19154. This lipase is available from Amano Pharmaceutical Co. Ltd., under the trade name Lipase P "Amano". Other commercial lipases include Amano-CES, lipases ex Chromobacter viscosum, e.g. Chromobacter viscosum var. lipolyticum NRRLB 3673, commercially available from Toyo Jozo Co., and further Chromobacter viscosum lipases from U.S. Biochemical Corp. and Disoynt Co., and lipases ex Pseudomonas gladioli. The LIPOLASE[®] enzyme derived from Humicola lanuginosa (commercially available from Novo Industries A/S) is a preferred lipase for use herein.

[0045] Peroxidase enzymes are used in combination with oxygen sources, e.g., percarbonate, perborate, persulfate, hydrogen peroxide, etc. They are used for "solution bleaching," i.e. to prevent transfer of dyes or pigments removed from substrates during cleaning operations to other substrates in the aqueous solution. Peroxidase enzymes are known in the art, and include, for example, horseradish peroxidase, ligninase, and haloperoxidase such as chloro- and bromo-peroxidase. Peroxidase-containing detergent compositions are disclosed, for example, in WO 1989 099813 A1.

[0046] Enzyme Stabilizers. The enzymes employed herein are stabilised by the presence of water-soluble sources of calcium and/or magnesium ions in the finished detergent compositions which provide such ions to the enzymes. (Calcium ions are generally somewhat more effective than magnesium ions and are preferred herein if only one type of cation is being used.) Additional stability can be provided by the presence of various other art-disclosed stabilisers, especially borate species, see US 4,537,706, incorporated herein in its entirety. Typical detergents, especially liquids, will comprise from about 1 to about 30, preferably from about 2 to about 20, more preferably from about 5 to about 15, and most preferably from about 8 to about 12, millimoles of calcium ion per liter of finished composition. In solid cleaner compositions the formulation can include a sufficient quantity of a water-soluble calcium ion source. In the alternative, natural water hardness can suffice.

[0047] It is to be understood that the foregoing levels of calcium and/or magnesium ions are sufficient to provide enzyme stability. More calcium and/or magnesium ions can be added to the compositions to provide an additional measure of grease removal performance. Accordingly, as a general proposition the compositions herein will typically comprise from about 0.05% to about 2% by weight of a water-soluble source of calcium or magnesium ions, or both. The amount can vary, of course, with the amount and type of enzyme employed in the composition.

[0048] The compositions herein can also optionally, but preferably, contain various additional stabilisers, especially borate-type stabilisers. Typically, such stabilisers will be used at levels in the compositions from about 0.25% to about 10%, preferably from about 0.5% to about 5%, more preferably from about 0.75% to about 3%, by weight of boric acid or other borate compound capable of forming boric acid in the composition (calculated on the basis of boric acid). Boric acid is preferred, although other compounds such as boric oxide, borax and other alkali metal borates (e.g., sodium ortho-, meta- and pyroborate, and sodium pentaborate) are suitable. Substituted boric acids (e.g., phenylboronic acid, butane boronic acid, and p-bromo phenylboronic acid) can also be used in place of boric acid.

BUILDERS AND ABRASIVE AGENTS

[0049] Zeolites. Fine crystalline, synthetic zeolites containing bound water can be used as builders, for example, preferably zeolite A and/or P. Zeolite MAP.RTM. (commercial product of the Crosfield company), is particularly preferred as the zeolite P. However, zeolite X and mixtures of A, X, Y and/or P are also suitable. A co-crystallised sodium/potassium aluminum silicate from Zeolite A and Zeolite X, which is available as Vegobond[®] RX. (commercial product from Condea Augusta S.p.A.), is also of particular interest. Preferably, the zeolite can be used as a spray-dried powder. For the case where the zeolite is added as a suspension, this can comprise small amounts of nonionic surfactants as stabilisers, for example, 1 to 3 wt. %, based on the zeolite, of ethoxylated C₁₂-C₁₈ fatty alcohols with 2 to 5 ethylene oxide groups, C₁₂-C₁₄ fatty alcohols with 4 to 5 ethylene oxide groups or ethoxylated isotridecanols. Suitable zeolites have an average particle size of less than 10µm (test method: volumetric distribution Coulter counter) and preferably comprise 18 to 22 wt. %, particularly 20 to 22 wt. % of bound water. Apart from this, phosphates can also be used as builders.

[0050] Layered silicates. Suitable substitutes or partial substitutes for phosphates and zeolites are crystalline, layered sodium silicates. These types of crystalline layered silicates are described, for example, in European Patent Application EP 0164514 A1. Preferred crystalline layered silicates are those obtained for example, from the process described in International Patent Application WO 91/08171 A1.

[0051] Amorphous silicates. Preferred builders also include amorphous sodium silicates with a modulus (Na₂O:SiO₂ ratio) of 1:2 to 1:3.3, preferably 1:2 to 1:2.8 and more preferably 1:2 to 1:2.6. In the context of this invention, the term "amorphous" also means "X-ray amorphous". In other words, the silicates do not produce any of the sharp X-ray reflexions typical of crystalline substances in X-ray diffraction experiments, but at best one or more maxima of the scattered X-radiation, which have a width of several degrees of the diffraction angle. However, particularly good builder properties

may even be achieved where the silicate particles produce indistinct or even sharp diffraction maxima in electron diffraction experiments. This is to be interpreted to mean that the products have microcrystalline regions between 10 and a few hundred nm in size, values of up to at most 50 nm and especially up to at most 20 nm being preferred. This type of X-ray amorphous silicates, which similarly possess a delayed dissolution in comparison with the customary water glasses, are described, for example, in German Patent Application DE 4400024 A1. Compacted/densified amorphous silicates, compounded amorphous silicates and over dried X-ray-amorphous silicates are particularly preferred.

[0052] Phosphates. Also the generally known phosphates can also be added as builders, in so far that their use should not be avoided on ecological grounds. The sodium salts of the orthophosphates, the pyrophosphates and especially the tripolyphosphates are particularly suitable. Their content is generally not more than 25 wt. %, preferably not more than 20 wt. %, each based on the finished composition. In some cases it has been shown that particularly tripolyphosphates, already in low amounts up to maximum 10 wt. %, based on the finished composition, in combination with other builders, lead to a synergistic improvement of cleaning power. Preferred amounts of phosphates are under 10 wt. %, particularly 0 wt. %.

[0053] Suitable water-soluble builders can also act as abrasive components as for example alkali metal carbonates, preferably sodium bicarbonate, with a mean particle size of about 200 μm . The abrasive component is present in a quantity of preferably more than 50% by weight and, more preferably, between 50 and 65% by weight, based on the cleaner according to the invention. To stabilise the abrasive component, the cleaner according to the invention is preferably formulated as a gel. The viscosity and hence the flow properties of the cleaners according to the invention may be positively influenced by an addition of up to 5% b.w. and, preferably, between about 0.3 and 3% b.w. of polyols such as for example, ethylene glycol, n- and iso-propylene glycol and glycerol.

CO-BUILDERS

[0054] Polycarboxylic acids. Useful organic cobuilders are, for example, the polycarboxylic acids usable in the form of their sodium salts of polycarboxylic acids, wherein polycarboxylic acids are understood to be carboxylic acids that carry more than one acid function. These include, for example, citric acid, adipic acid, succinic acid, glutaric acid, malic acid, tartaric acid, maleic acid, fumaric acid, sugar acids, aminocarboxylic acids, nitrilotriacetic acid (NTA) and its derivatives and mixtures thereof. Preferred salts are the salts of polycarboxylic acids such as citric acid, adipic acid, succinic acid, glutaric acid, tartaric acid, sugar acids and mixtures thereof.

[0055] Organic acids. Acids per se can also be used. Besides their building effect, the acids also typically have the property of an acidifying component and, hence also serve to establish a relatively low and mild pH in detergents or cleansing compositions. Citric acid, succinic acid, glutaric acid, adipic acid, gluconic acid and any mixtures thereof are particularly mentioned in this regard. Further suitable acidifiers are the known pH regulators such as sodium hydrogen carbonate and sodium hydrogen sulfate.

[0056] Polymers. Particularly suitable polymeric cobuilders are polyacrylates, which preferably have a molecular weight of 2,000 to 20,000 g/mol. By virtue of their superior solubility, preferred representatives of this group are again the short-chain polyacrylates, which have molecular weights of 2,000 to 10,000 g/mol and, more particularly, 3,000 to 5,000 g/mol. Suitable polymers can also include substances that consist partially or totally of vinyl alcohol units or its derivatives.

[0057] Further suitable copolymeric polycarboxylates are particularly those of acrylic acid with methacrylic acid and of acrylic acid or methacrylic acid with maleic acid. Copolymers of acrylic acid with maleic acid, which comprise 50 to 90 wt. % acrylic acid and 50 to 10 wt. % maleic acid, have proven to be particularly suitable. Their relative molecular weight, based on free acids, generally ranges from 2,000 to 70,000 g/mol, preferably 20,000 to 50,000 g/mol and especially 30,000 to 40,000 g/mol. The (co)polymeric polycarboxylates can be added either as an aqueous solution or preferably as powder. In order to improve the water solubility, the polymers can also comprise allylsulfonic acids as monomers, such as, for example, allyloxybenzene sulfonic acid and methallyl sulfonic acid as in the EP 0727448 B1.

[0058] Biodegradable polymers comprising more than two different monomer units are particularly preferred, examples being those comprising, as monomers, salts of acrylic acid and of maleic acid, and also vinyl alcohol or vinyl alcohol derivatives, as in DE 4300772 A1, or those comprising, as monomers, salts of acrylic acid and of 2-alkylallyl sulfonic acid, and also sugar derivatives. Further preferred copolymers are those that are described in German Patent Applications DE 4303320 A1 and DE 4417734 A1 and preferably include acrolein and acrylic acid/acrylic acid salts or acrolein and vinyl acetate as monomers.

[0059] Similarly, other preferred builders are polymeric aminodicarboxylic acids, salts or precursors thereof. Those polyaspartic acids or their salts and derivatives disclosed in German Patent Application DE 19540086 A1 as having a bleach-stabilising action in addition to cobuilder properties are particularly preferred.

[0060] Further suitable builders are polyacetals that can be obtained by treating dialdehydes with polyol carboxylic acids that possess 5 to 7 carbon atoms and at least 3 hydroxyl groups, as described in European Patent Application EP 0280223 A1. Preferred polyacetals are obtained from dialdehydes like glyoxal, glutaraldehyde, terephthalaldehyde as

well as their mixtures and from polycarboxylic acids like gluconic acid and/or glucoheptonic acid.

[0061] Carbohydrates. Further suitable organic cobuilders are dextrans, for example, oligomers or polymers of carbohydrates that can be obtained by the partial hydrolysis of starches. The hydrolysis can be carried out using typical processes, for example, acidic or enzymatic catalysed processes. The hydrolysis products preferably have average molecular weights in the range of 400 to 500,000 g/mol. A polysaccharide with a dextrose equivalent (DE) of 0.5 to 40 and, more particularly, 2 to 30 is preferred, the DE being an accepted measure of the reducing effect of a polysaccharide in comparison with dextrose, which has a DE of 100. Both maltodextrins with a DE between 3 and 20 and dry glucose syrups with a DE between 20 and 37 and also so-called yellow dextrans and white dextrans with relatively high molecular weights of 2,000 to 30,000 g/mol may be used. A preferred dextrin is described in British Patent Application 94 19 091.

[0062] The oxidised derivatives of such dextrans concern their reaction products with oxidizing compositions that are capable of oxidising at least one alcohol function of the saccharide ring to the carboxylic acid function. Such oxidised dextrans and processes for their manufacture are known for example, from European Patent Applications EP 0232202 A1. A product oxidized at C6 of the saccharide ring can be particularly advantageous.

[0063] Oxydisuccinates and other derivatives of disuccinates, preferably ethylenediamine disuccinate are also further suitable cobuilders. Here, ethylene diamine-N,N'-disuccinate (EDDS), the synthesis of which is described for example, in US 3,158,615, is preferably used in the form of its sodium or magnesium salts. In this context, glycerine disuccinates and glycerine trisuccinates are also particularly preferred, such as those described in US 4,524,009. Suitable addition quantities in zeolite-containing and/or silicate-containing formulations range from 3 to 15% by weight.

[0064] Lactones. Other useful organic co-builders are, for example, acetylated hydroxycarboxylic acids and salts thereof which optionally may also be present in lactone form and which contain at least 4 carbon atoms, at least one hydroxyl group and at most two acid groups. Such cobuilders are described, for example, in International Patent Application WO 1995 020029 A1.

BLEACHING COMPOUNDS, BLEACHING AGENTS AND BLEACH ACTIVATORS

[0065] The cleaning compositions herein can optionally contain bleaching agents or bleaching compositions containing a bleaching agent and one or more bleach activators. When present, bleaching agents will typically be at levels of from about 1% to about 30%, more typically from about 5% to about 20%, of the composition. If present, the amount of bleach activators will typically be from about 0.1% to about 60%, more typically from about 0.5% to about 40% of the bleaching composition comprising the bleaching agent-plus-bleach activator.

[0066] The bleaching agents used herein can be any of the bleaching agents useful for hard surface cleaning, or other cleaning purposes that are now known or become known. These include oxygen bleaches as well as other bleaching agents. Perborate bleaches, e.g., sodium perborate (e.g., mono- or tetra-hydrate) can be used herein.

[0067] Another category of bleaching agent that can be used without restriction encompasses percarboxylic acid bleaching agents and salts thereof. Suitable examples of this class of agents include magnesium monoperoxyphthalate hexahydrate, the magnesium salt of meta-chloro perbenzoic acid, 4-nonylamino-4-oxoperoxybutyric acid and diperoxododecanedioic acid.

[0068] Peroxygen bleaching agents can also be used. Suitable peroxygen bleaching compounds include sodium carbonate peroxyhydrate and equivalent "percarbonate" bleaches, sodium pyrophosphate peroxyhydrate, urea peroxyhydrate, and sodium peroxide. Persulfate bleach (e.g., OXONEO®, manufactured commercially by DuPont) can also be used.

[0069] A preferred percarbonate bleach comprises dry particles having an average particle size in the range from about 500 micrometers to about 1,000 micrometers, not more than about 10% by weight of said particles being smaller than about 200 micrometers and not more than about 10% by weight of said particles being larger than about 1,250 micrometers. Optionally, the percarbonate can be coated with silicate, borate or water-soluble surfactants. Percarbonate is available from various commercial sources.

[0070] Mixtures of bleaching agents can also be used.

[0071] Peroxygen bleaching agents, the perborates, the percarbonates, etc., are preferably combined with bleach activators, which lead to the in situ production in aqueous solution of the peroxy acid corresponding to the bleach activator. The nonanoyloxybenzene sulfonate (NOBS) and tetraacetyl ethylene diamine (TAED) activators are typical, and mixtures thereof can also be used.

[0072] Preferred amido-derived bleach activators include (6-octanamido-caproyl)oxybenzene-sulfonate, (6-nonanamidocaproyl)oxybenzenesulfonate, (6-decanamidocaproyl)oxybenzenesulfonate, and mixtures thereof.

[0073] Another class of bleach activators comprises the benzoxazin-type activators disclosed in US 4,966,723, incorporated herein by reference.

[0074] Highly preferred lactam activators include benzoyl caprolactam, octanoyl caprolactam, 3,5,5-trimethylhexanoyl caprolactam, nonanoyl caprolactam, decanoyl caprolactam, undecenoyl caprolactam, benzoyl valerolactam, octanoyl valerolactam, decanoyl valerolactam, undecenoyl valerolactam, nonanoyl valerolactam, 3,5,5-trimethylhexanoyl valero-

lactam and mixtures thereof, optionally adsorbed into solid carriers, e.g. acyl caprolactams, preferably benzoyl caprolactam, adsorbed into sodium perborate.

[0075] Bleaching agents other than oxygen bleaching agents are also known in the art and can be utilised herein. One type of non-oxygen bleaching agent of particular interest includes photoactivated bleaching agents such as the sulfonated zinc and/or aluminum phthalocyanines. If used, cleaning compositions will typically contain from about 0.025% to about 1.25%, by weight, of such bleaches, especially sulfonate zinc phthalocyanine.

[0076] If desired, the bleaching compounds can be catalysed by means of a manganese compound. Such manganese-based catalysts are well known in the art and include $\text{Mn}^{\text{IV}}_2 (\text{u-O})_3 (1,4,7\text{-trimethyl-1,4,7-triazacyclononane})_2 (\text{PF}_6)_2$, $\text{Mn}^{\text{III}}_2 (\text{u-O})_1 (\text{u-OAc})_2 (1,4,7\text{-trimethyl-1,4,7-triazacyclononane})_2 (\text{ClO}_4)_2$, $\text{Mn}^{\text{IV}}_4 (\text{u-O})_6 (1,4,7\text{-triazacyclononane})_4 (\text{ClO}_4)_4$, $\text{Mn}^{\text{III}}\text{Mn}^{\text{IV}}_4 (\text{u-O})_1 (\text{u-OAc})_2 (1,4,7\text{-trimethyl-1,4,7-triazacyclononane})_2 (\text{ClO}_4)_3$, $\text{Mn}^{\text{IV}} (1,4,7\text{-trimethyl-1,4,7-triazacyclononane})-(\text{OCH}_3)_3 (\text{PF}_6)$, and mixtures thereof.

[0077] As a practical matter, and not by way of limitation, the compositions and processes herein can be adjusted to provide on the order of at least one part per ten million of the active bleach catalyst species in the aqueous cleaning composition, and will preferably provide from about 0.1 ppm to about 700 ppm, more preferably from about 1 ppm to about 500 ppm, of the catalyst species in the compositions.

POLYMERS AND POLYMERIC SOIL RELEASE AGENTS

[0078] Any polymeric soil release agent known to those skilled in the art can optionally be employed in the cleaning compositions and processes of this invention. The polymeric soil release agents useful herein especially include those soil release agents having: (a) one or more nonionic hydrophile components consisting essentially of (i) polyoxyethylene segments with a degree of polymerisation of at least 2, or (ii) oxypropylene or polyoxypropylene segments with a degree of polymerisation of from 2 to 10, wherein said hydrophile segment does not encompass any oxypropylene unit unless it is bonded to adjacent moieties at each end by ether linkages, or (iii) a mixture of oxyalkylene units comprising oxyethylene and from 1 to about 30 oxypropylene units wherein said mixture contains a sufficient amount of oxyethylene units such that the hydrophile component has hydrophilicity great enough to increase the hydrophilicity of conventional hard surfaces upon deposit of the soil release agent on such surface, said hydrophile segments preferably comprising at least about 25% oxyethylene units and more preferably, especially for such components having about 20 to 30 oxypropylene units, at least about 50% oxyethylene units; or (b) one or more hydrophobe components comprising (i) C_3 oxyalkylene terephthalate segments, wherein, if said hydrophobe components also comprise oxyethylene terephthalate, the ratio of oxyethylene terephthalate: C_3 oxyalkylene terephthalate units is about 2:1 or lower, (ii) C_4 - C_6 alkylene or oxy C_4 - C_6 alkylene segments, or mixtures therein, (iii) poly (vinyl ester) segments, preferably polyvinyl acetate, having a degree of polymerisation of at least 2, or (iv) C_1 - C_4 alkyl ether or C_4 hydroxyalkyl ether substituents, or mixtures therein, wherein said substituents are present in the form of C_1 - C_4 alkyl ether or C_4 hydroxyalkyl ether cellulose derivatives, or mixtures therein, and such cellulose derivatives are amphiphilic, whereby they have a sufficient level of C_1 - C_4 alkyl ether and/or C_4 hydroxyalkyl ether units to deposit upon conventional hard surfaces and retain a sufficient level of hydroxyls, once adhered to such conventional hard surface, to increase surface hydrophilicity, or a combination of (a) and (b).

[0079] Typically, the polyoxyethylene segments of (a) (i) will have a degree of polymerisation of from about 200, although higher levels can be used, preferably from 3 to about 150, more preferably from 6 to about 100. Suitable oxy C_4 - C_6 alkylene hydrophobe segments include, but are not limited to, end-caps of polymeric soil release agents.

[0080] Polymeric soil release agents useful in the present invention also include cellulosic derivatives such as hydroxyether cellulosic polymers, copolymeric blocks of ethylene terephthalate or propylene terephthalate with polyethylene oxide or polypropylene oxide terephthalate, and the like. Such agents are commercially available and include hydroxyethers of cellulose such as METHOCEL[®] (Dow). Cellulosic soil release agents for use herein also include those selected from the group consisting of C_1 - C_4 alkyl and C_4 hydroxyalkyl cellulose.

[0081] Soil release agents characterised by poly(vinyl ester) hydrophobe segments include graft copolymers of poly(vinyl ester), e.g., C_1 - C_6 vinyl esters, preferably poly(vinyl acetate) grafted onto polyalkylene oxide backbones, such as polyethylene oxide backbones, see EP 0 219 048, incorporated herein in its entirety. Commercially available soil release agents of this kind include the SOKALAN[®] type of material, e.g., SOKALAN[®] HP-22, available from BASF.

[0082] One type of preferred soil release agent is a copolymer having random blocks of ethylene terephthalate and polyethylene oxide (PEO) terephthalate. The molecular weight of this polymeric soil release agent preferably is in the range of from about 25,000 to about 55,000.

[0083] Another preferred polymeric soil release agent is a polyester with repeat units of ethylene terephthalate units contains 10-15% by weight of ethylene terephthalate units together with 90-80% by weight of polyoxyethylene terephthalate units, derived from a polyoxyethylene glycol of average molecular weight 300-5,000. Examples of this polymer include the commercially available material ZELCON[®] 5126 (from DuPont) and MILEASE[®] T (from ICI).

[0084] Another preferred polymeric soil release agent is a sulfonated product of a substantially linear ester oligomer comprised of an oligomeric ester backbone of terephthaloyl and oxyalkyleneoxy repeat units and terminal moieties

covalently attached to the backbone. These soil release agents are described fully in US 4,968,451. Other suitable polymeric soil release agents include the terephthalate polyesters of US 4,711,730, the anionic end-capped oligomeric esters of US 4,721,580, the block polyester oligomeric compounds of US 4,702,857, and anionic, especially sulfoaroyl, end-capped terephthalate esters of US 4,877,896 all cited patents incorporated herein in their entirety.

[0085] Still another preferred soil release agent is an oligomer with repeat units of terephthaloyl units, sulfoisoterephthaloyl units, oxyethyleneoxy and oxy-1,2-propylene units. The repeat units form the backbone of the oligomer and are preferably terminated with modified isethionate end-caps. A particularly preferred soil release agent of this type comprises about one sulfoisophthaloyl unit, 5 terephthaloyl units, oxyethyleneoxy and oxy-1,2-propyleneoxy units in a ratio of from about 1.7 to about 1.8, and two end-cap units of sodium 2-(2-hydroxyethoxy)-ethanesulfonate. Said soil release agent also comprises from about 0.5% to about 20%, by weight of the oligomer, of a crystalline-reducing stabiliser, preferably selected from the group consisting of xylene sulfonate, cumene sulfonate, toluene sulfonate, and mixtures thereof.

[0086] If utilised, soil release agents will generally comprise from about 0.01% to about 10.0%, by weight, of the detergent compositions herein, typically from about 0.1% to about 5%, preferably from about 0.2% to about 3.0%.

[0087] Naturally occurring polymers and derivatives thereof, such as xanthan gum, other polysaccharides and/or gelatine, may also be added in quantities of up to 2% by weight and preferably in quantities of about 0.1 to 1.0% b.w.

POLYMERIC DISPERSING AGENTS

[0088] Polymeric dispersing agents can advantageously be utilised at levels from about 0.1% to about 7%, by weight, in the detergent compositions herein, especially in the presence of zeolite and/or layered silicate builders. Suitable polymeric dispersing agents include polymeric polycarboxylates and polyethylene glycols, although others known in the art can also be used. It is believed, though it is not intended to be limited by theory, that polymeric dispersing agents enhance overall detergent builder performance, when used in combination with other builders (including lower molecular weight polycarboxylates) by crystal growth inhibition, particulate soil release peptisation, and anti-redeposition.

[0089] Polymeric polycarboxylate materials can be prepared by polymerising or copolymerising suitable unsaturated monomers, preferably in their acid form. Unsaturated monomeric acids that can be polymerised to form suitable polymeric polycarboxylates include acrylic acid, maleic acid (or maleic anhydride), fumaric acid, itaconic acid, aconitic acid, mesaconic acid, citraconic acid and methylenemalononic acid. The presence in the polymeric polycarboxylates herein or monomeric segments, containing no carboxylate radicals such as vinylmethyl ether, styrene, ethylene, etc. is suitable provided that such segments do not constitute more than about 40% by weight.

[0090] 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 polymerised acrylic acid. The average molecular weight of such polymers in the acid form preferably ranges from about 2,000 to 10,000, more preferably from about 4,000 to 7,000 and most preferably from about 4,000 to 5,000. 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 US 3,308,067.

[0091] Acrylic/maleic-based copolymers can also be used as a preferred component of the dispersing/anti-redeposition agent. 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 EP 0193360 A1, which also describes such polymers comprising hydroxypropylacrylate. Still other useful dispersing agents include the maleic/acrylic/vinyl alcohol terpolymers, for example, a 45/45/10 terpolymer of acrylic/maleic/vinyl alcohol.

[0092] Another polymeric material which can be included is polyethylene glycol (PEG). PEG can exhibit dispersing agent performance as well as act as a clay soil removal-antiredeposition agent. Typical molecular weight ranges for these purposes range from about 500 to about 100,000, preferably from about 1,000 to about 50,000, more preferably from about 1,500 to about 10,000.

[0093] Polyaspartate and polyglutamate dispersing agents can also be used, especially in conjunction with zeolite builders. Dispersing agents such as polyaspartate preferably have a molecular weight (avg.) of about 10,000.

FOAM INHIBITORS/SUD SUPPRESSORS

[0094] For certain purposes which do not allow the generation of any foam, for example in the degreasing operations in automotive industry, it can be advantageous to add conventional foam inhibitors to the compositions. Suitable foam inhibitors include for example, soaps of natural or synthetic origin, which have a high content of C₁₈-C₂₄ fatty acids. Suitable non-surface-active types of foam inhibitors are, for example, organopolysiloxanes and mixtures thereof with

microfine, optionally silanised silica and also paraffins, waxes, microcrystalline waxes and mixtures thereof with silanised silica or bis-stearyl ethylenediamide. Mixtures of various foam inhibitors, for example, mixtures of silicones, paraffins or waxes, are also used with advantage. Preferably, the foam inhibitors, especially silicone-containing and/or paraffin-containing foam inhibitors, are loaded onto a granular, water-soluble or dispersible carrier material. Especially in this case, mixtures of paraffins and bis-stearylethylene diamides are preferred.

[0095] Compounds for reducing or suppressing the formation of suds can be incorporated into the cleaning compositions of the present invention. Suds suppression can be of particular importance in the so-called "high concentration cleaning process".

[0096] A wide variety of materials can be used as suds suppressors, and suds suppressors are well known to those skilled in the art. See, for example, Kirk Othmer Encyclopedia of Chemical Technology, Third Edition, Volume 7, pages 430-447 (John Wiley & Sons, Inc., 1979). One category of suds suppressor of particular interest encompasses monocarboxylic fatty acid and soluble salts therein. The monocarboxylic fatty acids and salts thereof used as suds suppressor typically have hydrocarbyl chains of 10 to about 24 carbon atoms, preferably 12 to 18 carbon atoms. Suitable salts include the alkali metal salts such as sodium, potassium, and lithium salts, and ammonium and alkanolammonium salts.

[0097] The cleaning compositions herein can also contain non-surfactant suds suppressors. These include, for example: high molecular weight hydrocarbons such as paraffin, fatty acid esters (e.g., fatty acid triglycerides), fatty acid esters of monovalent alcohols, aliphatic C₁₈-C₄₀ ketones (e.g., stearone), etc. Other suds inhibitors include N-alkylated amino triazines such as tri- to hexa-alkylmelamines or di- to tetra-alkyldiamine chlortriazines formed as products of cyanuric chloride with two or three moles of a primary or secondary amine containing 1 to 24 carbon atoms, propylene oxide, and monostearyl phosphates such as monostearyl alcohol phosphate ester and monostearyl di-alkali metal (e.g., K, Na, and Li) phosphates and phosphate esters. The hydrocarbons such as paraffin and haloparaffin can be utilised in liquid form. The liquid hydrocarbons will be liquid at room temperature and atmospheric pressure, and will have a pour point in the range of about -40°C and about 50°C, and a minimum boiling point not less than about 110°C (atmospheric pressure). It is also known to utilise waxy hydrocarbons, preferably having a melting point below about 100°C. Hydrocarbon suds suppressors are known in the art and include aliphatic, alicyclic, aromatic, and heterocyclic saturated or unsaturated hydrocarbons having from about 12 to about 70 carbon atoms. The term "paraffin," as used in this suds suppressor discussion, is intended to include mixtures of true paraffins and cyclic hydrocarbons.

[0098] Another preferred category of non-surfactant suds suppressors comprises silicone suds suppressors. This category includes the use of polyorganosiloxane oils, such as polydimethylsiloxane, dispersions or emulsions of polyorganosiloxane oils or resins, and combinations of polyorganosiloxane with silica particles wherein the polyorganosiloxane is chemisorbed or fused onto the silica. Silicone suds suppressors are well known in the art.

[0099] Other silicone suds suppressors are disclosed in US 3,455,839, incorporated herein in its entirety, which relates to compositions and processes for defoaming aqueous solutions by incorporating therein small amounts of polydimethylsiloxane fluids.

[0100] Mixtures of silicone and silanated silica are described, for instance, in DE-OS 2124526, incorporated herein in its entirety. Silicone defoamers and suds controlling agents in granular detergent compositions are disclosed in US 4,652,392, incorporated herein in its entirety.

[0101] In the preferred silicone suds suppressor used herein, the solvent for a continuous phase is made up of certain polyethylene glycols or polyethylene-polypropylene glycol copolymers or mixtures thereof (preferred), or polypropylene glycol. The primary silicone suds suppressor is branched/crosslinked and preferably not linear.

[0102] The silicone suds suppressor herein preferably comprises polyethylene glycol and a copolymer of polyethylene glycol/polypropylene glycol, all having an average molecular weight of less than about 1,000, preferably between about 100 and 800. The polyethylene glycol and polyethylene/polypropylene copolymers herein have a solubility in water at room temperature of more than about 2 weight %, preferably more than about 5 weight %.

[0103] The preferred solvent herein is polyethylene glycol having an average molecular weight of less than about 1,000, more preferably between about 100 and 800, most preferably between 200 and 400, and a copolymer of polyethylene glycol/polypropylene glycol, preferably PPG 200/PEG 300. Preferred is a weight ratio of between about 1:1 and 1:10, most preferably between 1:3 and 1:6, of polyethylene glycol:copolymer of polyethylene-polypropylene glycol.

[0104] The preferred silicone suds suppressors used herein do not contain polypropylene glycol, particularly of 4,000 molecular weight. They also preferably do not contain block copolymers of ethylene oxide and propylene oxide, like PLURONIC® L101.

[0105] Other suds suppressors useful herein comprise the secondary alcohols (e.g., 2-alkyl alkanols) and mixtures of such alcohols with silicone oils. The secondary alcohols include the C₆ - C₁₆ alkyl alcohols having a C₁- C₁₆ chain. A preferred alcohol is 2-butyl octanol, which is available from Condea under the trademark ISOFOL® 12. Mixtures of secondary alcohols are available under the trademark ISALCHEM® 123 from Enichem. Mixed suds suppressors typically comprise mixtures of alcohol+silicone at a weight ratio of 1:5 to 5:1.

[0106] The compositions herein will generally comprise from 0% to about 5% of suds suppressor. When utilised as suds suppressors, monocarboxylic fatty acids, and salts therein, will be present typically in amounts up to about 5%, by

weight, of the detergent composition. Preferably, from about 0.5% to about 3% of fatty monocarboxylate suds suppressor is utilised. Silicone suds suppressors are typically utilised in amounts up to about 2.0%, by weight, of the detergent composition, although higher amounts can be used. This upper limit is practical in nature, due primarily to concern with keeping costs minimised and effectiveness of lower amounts for effectively controlling sudsing. Preferably from about 0.01% to about 1% of silicone suds suppressor is used, more preferably from about 0.25% to about 0.5%. As used herein, these weight percentage values include any silica that can be utilised in combination with polyorganosiloxane, as well as any adjunct materials that can be utilised. Monostearyl phosphate suds suppressors are generally utilized in amounts ranging from about 0.1% to about 2%, by weight, of the composition. Hydrocarbon suds suppressors are typically utilised in amounts ranging from about 0.01% to about 5.0%, although higher levels can be used. The alcohol suds suppressors are typically used at 0.2%-3% by weight of the finished compositions.

HYDROTROPES

[0107] Hydrotropes are agents which act as solubility promoter for a second, more sparingly soluble substance.

[0108] The preferred hydrotropes are selected from the group of cumene sulfonates, xylene sulfonates, propylene glycols and their mixtures, and here preferably 1,2-monopropylene glycol, preference being given to cumene- and xylene sulfonates.

[0109] Cumene- and xylene sulfonates are to be regarded as particularly preferred component (d), here in particular the sodium salts of cumene- or xylene sulfonate. Particular preference is given to cumene sulfonate, sodium salt.

ORGANIC ACIDS

[0110] Organic acids show builder functions, but usually are incorporated into the formulations to buffer the pH value. Usually organic hydroxycarboxylic acids are preferred, in particular selected from the group mandelic acid, lactic acid, hydroxysuccinic acid, citric acid, tartaric acid and their mixtures, with particular preference being given to citric acid.

SEQUESTRANTS AND CHELATING AGENTS

[0111] The salts of polyphosphonic acid can be considered as sequestrants or as stabilisers, particularly for peroxy compounds and enzymes, which are sensitive towards heavy metal ions. Here, the sodium salts of, for example, 1-hydroxyethane-1,1-diphosphonate, diethylenetriamine pentamethylene phosphonate or ethylenediamine tetramethylene phosphonate are used in amounts of 0.1 to 5 wt. %.

[0112] The cleaning compositions herein can also optionally contain one or more iron and/or manganese chelating agents. Such chelating agents can be selected from the group consisting of amino carboxylates, amino phosphonates, polyfunctionally-substituted aromatic chelating agents and mixtures therein, all as hereinafter defined. Without intending to be bound by theory, it is believed that the benefit of these materials is due in part to their exceptional ability to remove iron and manganese ions from cleaning solutions by formation of soluble chelates. It is understood that some of the builders described hereinbefore can function as chelating agents and if such builder is present in a sufficient quantity, it can provide both functions.

[0113] Amino carboxylates useful as optional chelating agents include ethylenediamine-tetracetates, N-hydroxyethylethylenediaminetriacetates, nitrilotriacetates, ethylenediamine tetrapropionates, triethylenetetraaminehexacetates, diethylenetriaminepentaacetates, and ethanoldiglycines, alkali metal, ammonium, and substituted ammonium salts therein and mixtures therein.

[0114] Amino phosphonates are also suitable for use as chelating agents in the compositions of the invention when at least low levels of total phosphorus are permitted in detergent compositions, and include ethylenediaminetetrakis (methylenephosphonates) as DEQUEST. Preferred, these amino phosphonates do not contain alkyl or alkenyl groups with more than about 6 carbon atoms.

[0115] Polyfunctionally-substituted aromatic chelating agents are also useful in the compositions herein. Preferred compounds of this type in acid form are dihydroxydisulfobenzenes such as 1,2-dihydroxy-3,5-disulfobenzene.

[0116] A preferred biodegradable chelator for use herein is ethylenediamine disuccinate ("EDDS"), especially the [S,S] isomer.

[0117] If utilized, these chelating agents will generally comprise from about 0.1% to about 10% by weight of the cleaning compositions herein. More preferably, if utilized, the chelating agents will comprise from about 0.1% to about 3.0% by weight of such compositions.

CLAY SOIL REMOVAL/ANTI-REDEPOSITION AGENTS

[0118] The cleaning compositions of the present invention can also optionally contain water-soluble ethoxylated amines

having clay soil removal and antiredeposition properties. Granular detergent compositions which contain these compounds typically contain from about 0.01% to about 10.0% by weight of the water-soluble ethoxylates amines; liquid cleaning compositions typically contain about 0.01% to about 5%.

[0119] The most preferred soil release and anti-redeposition agent is ethoxylated tetraethylenepentamine. Exemplary ethoxylated amines are further described in US 4,597,898. Other groups of preferred clay soil removal-antiredeposition agents are the cationic compounds disclosed in EP 0111965 A1, the ethoxylated amine polymers disclosed in EP 0111984 A1, the zwitterionic polymers disclosed in EP 0112592 A1, and the amine oxides disclosed in US 4,548,744. Another type of preferred antiredeposition agent includes the carboxy methyl cellulose (CMC) materials. These materials are well known in the art.

THICKENERS

[0120] The compositions can also comprise common thickeners and anti-deposition compositions as well as viscosity regulators such as polyacrylates, polycarboxylic acids, polysaccharides and their derivatives, polyurethanes, polyvinyl pyrrolidones, castor oil derivatives, polyamine derivatives such as quaternised and/or ethoxylated hexamethylenediamines as well as any mixtures thereof. Preferred compositions have a viscosity below 10,000 mPa*s, measured with a Brookfield viscosimeter at a temperature of 20°C and a shear rate of 50 min⁻¹.

INORGANIC SALTS

[0121] Further suitable ingredients of the composition are water-soluble inorganic salts such as bicarbonates, carbonates, amorphous silicates or mixtures of these; alkali carbonate and amorphous silicate are particularly used, principally sodium silicate with a molar ratio Na₂O:SiO₂ of 1:1 to 1:4.5, preferably of 1:2 to 1:3.5. Preferred compositions comprise alkaline salts, builders and/or cobuilders, preferably sodium carbonate, zeolite, crystalline, layered sodium silicates and/or trisodium citrate, in amounts of 0.5 to 70 wt. %, preferably 0.5 to 50 wt. %, particularly 0.5 to 30 wt. % anhydrous substance.

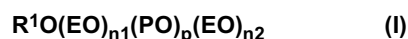
PERFUMES AND COLORANTS

[0122] The compositions can comprise further typical detergent and cleaning composition ingredients such as perfumes and/or colorants. Preferred amounts of the totality of the added colorants are below 1 wt. %, preferably below 0.1 wt. %, based on the composition. The compositions can also comprise white pigments such as e.g., TiO₂.

SURFACTANT BLENDS

[0123] Another object of the present invention relates to a surfactant blend consisting of

(a) a first non-ionic surfactant of formula (I)



in which

R¹ stands for a linear alkyl radical having 9 to 11 carbon atoms;

n₁ stands for 0 or an integer of from 6 to 10;

n₂ stands for 0 or an integer of from 6 to 10;

p stands for 0 or an integer of from 4 to 6;

and

(b) a second non-ionic surfactants of formula (II)



in which

R² stands for a linear alkyl radical having 10 carbon atoms;

m₁ stands for 0 or an integer of from 6 to 10;

m₂ stands for 0 or an integer of from 6 to 10;

q stands for 0 or an integer of from 4 to 6;

on condition that both sums (n_1+p+n_2) and (m_1+q+m_2) is different from 0.

[0124] Preferably the components (a) and (b) are present in said blend in a ratio by weight of from about 1:5 to about 5:1, and preferably about 2:1 to 3:1.

[0125] The surfactant blends according to formulae (I) and (II) can be incorporated into customary cleaners and in particular multipurpose cleaners on their own or in combination with the components (c) to (g). The compositions may be liquid or gel-like. The compounds of the formula (I) are present in ready-formulated hard surface cleaning compositions preferably in amounts of from 1 to 45 percent by weight, in particular in amounts of from 4 to 30 percent by weight and particularly preferably in amounts of from 15 to 30 percent by weight.

INDUSTRIAL APPLICATION

[0126] The cleaner according to the invention can be formulated as ready-to-use solutions, in particular as a spray cleaner. In a preferred embodiment, the cleaner according to the invention is formulated as a pourable concentrate which may additionally contain a water-soluble abrasive component. Cleaners of this type contain a water-soluble salt and are suitable in concentrated form as scourers and in diluted form as multipurpose cleaners. In this embodiment, the cleaners according to the invention are particularly suitable as multipurpose cleaners and spray cleaners, more particularly for heavily soiled hard surfaces.

[0127] The pH value of the cleaning formulations may be varied over a wide range, although the range from 2 to 13 and in particular 2.5 to 10.5 is preferred.

[0128] The cleaners according to the invention are particularly suitable for cleaning hard surfaces such as, enamel, glass, china, PVC and other plastics, linoleum, ceramic tiles, marble and metals. At the commercial level, a distinction is made between manual dishwashing detergents which are generally used for cleaning crockery, glasses, cutlery, pots and pans, etc. and multipurpose cleaners which are generally used for cleaning relatively large surfaces encountered in the home.

[0129] The present application further provides a method for cleaning hard surfaces, wherein said surfaces are brought into contact with the cleaning composition or the surfactant blend of the invention. By using the surfactant blend in a hard surface cleaning composition as defined above, cleaning performance is improved, foam is reduced almost to zero and the drying procedure is significantly shortened. The surfaces are evenly dried and show a streak-free finish, without spots and water marks.

[0130] Preferred areas of application encompass:

- Transportation vehicles, e.g., train, plane, truck, car, public transport;
- Professional cleaning, e.g., window, metal and ceramic floor;
- Public and train toilet made of metal;
- Professional and consumer car wash;
- In general: industrial cleaning, dock ship cleaning, and the like.

EXAMPLES

EXAMPLES 1 to 2, COMPARATIVE EXAMPLES C1 TO C2

[0131] Foam behavior of two surfactant blends according to the present invention and two comparative products was evaluated according to EN 12728 (Foam Beat Method according to GÖTTE) at different temperatures and at different pH values. The results are compiled in Table 1.

Table 1

Foam characteristics				
Composition	1	2	C1	C2
C _{9/11} +8.5EO+5.5PO	10.0	4.0	-	-
C ₁₀ +8.5EO+5.5PO	4.0	10.0	-	-
C _{12/14} +6EO+6PO	-	-	14.0	-

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(continued)

Foam characteristics				
Composition	1	2	C1	C2
C _{10/16} Alkylpolyglucoside	-	-		14.0
Water	Ad 100			
Foam development (deionised water, pH = 5.7)				
T = 25 °C, t = 0	160	70	520	650
T = 25 °C, t = 1 min	20	30	360	600
T = 25 °C, t = 3 min	20	30	300	530
T = 25 °C, t = 5 min	20	20	270	510
T = 25 °C, t = 10 min	10	20	190	500
T = 25 °C, t = 0	0	0	150	630
T = 25 °C, t = 1 min	0	0	60	560
T = 25 °C, t = 3 min	0	0	40	510
T = 25 °C, t = 5 min	0	0	40	490
T = 25 °C, t = 10 min	0	0	30	460
Foam development (2 % HCl, pH = 2)				
T = 25 °C, t = 0	100	120	170	110
T = 25 °C, t = 1 min	10	10	60	60
T = 25 °C, t = 3 min	10	10	50	60
T = 25 °C, t = 5 min	0	0	40	60
T = 25 °C, t = 10 min	0	0	30	40
C _{9/11} +8.5EO+5.5PO	10.0	4.0	-	-
C ₁₀ +8.5EO+5.5PO	4.0	10.0	-	-
C _{12/14} +6EO+6PO	-	-	14.0	-
C _{10/16} Alkylpolyglucoside	-	-		14.0
Water	Ad 100			
Foam development (2 % HCl, pH = 2)				
T = 50 °C, t = 0	0	0	20	30
T = 50 °C, t = 1 min	0	0	10	20
T = 50 °C, t = 3 min	0	0	0	0
T = 50 °C, T = 5 min	0	0	0	0
T = 50 °C, t = 10 min	0	0	0	0
Foam development (2 % NaOH pH = 13)				
T = 25 °C, t = 0	40	50	40	250
T = 25 °C, t = 1 min	10	20	20	130
T = 25 °C, t = 3 min	0	0	0	110
T = 25 °C, T = 5 min	0	0	0	110
T = 25 °C, t = 10 min	0	0	0	110
T = 50 °C, t = 0	0	0	0	180

(continued)

Foam development (2 % NaOH pH = 13)				
T = 50 °C, t = 1 min	0	0	0	90
T = 50 °C, t = 3 min	0	0	0	90
T = 50 °C, T = 5 min	0	0	0	80
T = 50 °C, t = 10 min	0	0	0	80

[0132] The examples clearly demonstrate the superior low foaming behavior of the new surfactant blends at lower and higher temperatures and under neutral, acidic and alkaline conditions.

EXAMPLES 3 TO 4, COMPARATIVE EXAMPLES C3 TO C4

Quick dry effect on PVC flooring

[0133] 2 g of two products according to the present invention and two comparative products were dissolved in 1 L deionised water. PVC flooring material was dipped in freshly prepared test solution. The substrates were left dry vertically. The drying progress was evaluated 1 min after the start of the process according to following scheme: (++) = level drying, no foam or water marks; (+) level drying, but few foam or water marks; (#) level drying, but significant number of foam and water marks; (-) uneven drying with significant number of foam and water marks. The results are reflected in the following **Table 2**.

Table 2

Composition and drying performance on PVC				
Composition	3	4	C3	C4
C _{9/11} +8.5EO+5.5PO	10.0	4.0	-	-
C ₁₀ +8.5EO+5.5PO	4.0	10.0	-	-
C _{12/14} +6EO+6PO	-	-	14.0	-
C _{10/16} Alkylpolyglucoside	-	-		14.0
Water	Ad 100			
Drying performance	++	+	#	-

EXAMPLES 5 TO 6, COMPARATIVE EXAMPLES C5 TO C6

Quick dry effect and streak-free finish on polypropylene

[0134] 2 g of two products according to the present invention and two comparative products were dissolved in 1 L deionised water. PP plates were dipped in freshly prepared test solution. The substrates were left dry vertically. The drying progress was evaluated 4 min after the start of the process according to following scheme: (++) = streak-free finish, no water spots; (+) streak-free finish, but few water spots; (#) streak-free finish, but significant number of water spots; (-) uneven finish with significant number of water spots. The results are reflected in the following **Table 3**.

Table 3

Composition and drying and streak-free performance on PP				
Composition	5	6	C5	C6
C _{9/11} +8.5EO+5.5PO	10.0	4.0	-	-
C ₁₀ +8.5EO+5.5PO	4.0	10.0	-	-
C _{12/14} +6EO+6PO	-	-	14.0	-
C _{10/16} Alkylpolyglucoside	-	-		14.0

(continued)

Composition and drying and streak-free performance on PP				
Composition	5	6	C5	C6
Water	Ad 100			
Drying & streaking performance	++	++	+	-

EXAMPLES 7 TO 8, COMPARATIVE EXAMPLES C7 TO C8

Streak-free finish on metal

[0135] 2 g of two products according to the present invention and two comparative products were dissolved in 1 L deionised water. Steel plates were dipped in freshly prepared test solution. The substrates were left dry vertically. The drying progress was evaluated 4 min after the start of the process according to following scheme: (++) = streak-free finish, no water spots; (+) streak-free finish, but few water spots; (#) streak-free finish, but significant number of water spots; (-) uneven finish with significant number of water spots. The results are reflected in the following **Table 4**.

Table 4

Composition and streak-free performance on metal				
Composition	7	8	C7	C8
C _{9/11} +8.5EO+5.5PO	10.0	4.0	-	-
C ₁₀ +8.5EO+5.5PO	4.0	10.0	-	-
C _{12/14} +6EO+6PO	-	-	14.0	-
C _{10/16} Alkylpolyglucoside	-	-		14.0
Water	Ad 100			
Drying & streak-free performance	++	++	+	-

EXAMPLES 9 TO 10, COMPARATIVE EXAMPLES C9 TO C10

Streak-free finish on lacquered metal

[0136] 2 g of two products according to the present invention and two comparative products were dissolved in 1 L deionised water. Lacquered metal plates were dipped in freshly prepared test solution. The substrates were left dry vertically. The drying progress was evaluated 4 min after the start of the process according to following scheme: (++) = streak-free finish, no water spots; (+) streak-free finish, but few water spots; (#) streak-free finish, but significant number of water spots; (-) uneven finish with significant number of water spots. The results are reflected in the following **Table 5**.

Table 5

Composition and streak-free performance on lacquered metal				
Composition	9	10	C9	C10
C _{9/11} +8.5EO+5.5PO	10.0	4.0	-	-
C ₁₀ +8.5EO+5.5PO	4.0	10.0	-	-
C _{12/14} +6EO+6PO	-	-	14.0	-
C _{10/16} Alkylpolyglucoside	-	-		14.0
Water	Ad 100			
Streak-free performance	++	+	-	-

EXAMPLE 11, COMPARATIVE EXAMPLES C11 TO C12

Emulsifying capacity

- 5 **[0137]** 30 ml of a surfactant solution with 2 % b.w. in deionized water was blended with the same amount of olive oil. The mixture was stirred at 1.200 rpm for 2 minutes and the level of the recovered aqueous phase was determined after 1, 2 and 4 hours. The lesser the recovering aqueous phase volume, the better the emulsification power of the test solution. The results are reflected in **Table 6**.

10 **EXAMPLE 12, COMPARATIVE EXAMPLES C13 TO C14**

Cleaning efficacy

- 15 **[0138]** 0.25g of a soil composition consisting of used motor oil (55%), a flushing medium (40%) and soot (5%) was applied on galvanised steel. To evaluate the cleaning capacity the steel substrate was weighed, the soil applied and the substrate weighed again. The substrate was immersed with the soil in test solution (200 mL with a concentration 2% b.w. surfactant in deionised water) for 3 min and then dried in an oven at 105 °C to evaporate the aqueous solution. The substrate was weighed again and the amount of removed soil in % calculated from the difference. The results are compiled in **Table 7**.

Table 6

Composition and emulsifying capacity			
Composition	11	C11	C12
C _{9/11} +8.5EO+5.5PO	10.0	-	-
C ₁₀ +8.5EO+5.5PO	4.0	-	-
C _{12/14} +6EO+6PO	-	14.0	-
C _{10/16} Alkylpolyglucoside	-		14.0
Water	Ad 100		
<i>Recovered water phase [ml]</i>			
After 1 h	11	14	10
After 2 h	19	22	18
After 4 h	23	28	22

Table 7

Cleaning efficacy			
Composition	12	C13	C14
C _{9/11} +8.5EO+5.5PO	10.0	-	-
C ₁₀ +8.5EO+5.5PO	4.0	-	-
C _{12/14} +6EO+6PO	-	14.0	-
C _{10/16} Alkylpolyglucoside	-		14.0
Water	Ad 100		
<i>Soil removal [%]</i>	79.8	59.5	50.5

EXAMPLE 13, COMPARATIVE EXAMPLES C15 TO C16

Cleaning efficacy in all-purpose cleaner formulation

[0139] A soil was applied in an amount of about 0.25 g with an airbrush on a pre-defined floor tile on an area of 8 * 26 cm. 5 mL of a test product was applied on the cleaning cloth (Wecovi cloth). A wiping motion was carried out using Sheen Wet Abrasion Scrub tester Ref. 903/PG. It was determined that 7 strokes provide a sufficient differentiation between the performance of the tested products. The substrates were dried for an hour at room temperature before the performance could be visually assessed. The detailed test method is described in SÖFW-journal, 130, 10/2004. The results are shown in **Table 8** and represent median values over 3 trials. The scale is (0) = worst; (10) = best.

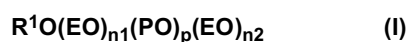
Table 8

Cleaning efficacy			
Composition	12	C13	C14
C _{9/11} +8.5EO+5.5PO	10.0	-	-
C ₁₀ +8.5EO+5.5PO	4.0	-	-
C _{12/14} +6EO+6PO	-	14.0	-
C _{10/16} Alkylpolyglucoside	-		14.0
Water	Ad 100		
Performance	9	7	8

Claims

1. A liquid hard surface cleaner composition, comprising a surfactant blend comprising or consisting of

(a) a first non-ionic surfactant of formula (I)



in which

R¹ stands for a linear alkyl radical having 9 to 11 carbon atoms;

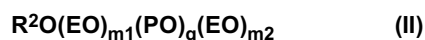
n₁ stands for 0 or an integer of from 6 to 10;

n₂ stands for 0 or an integer of from 6 to 10;

p stands for 0 or an integer of from 4 to 6;

and

(b) a second non-ionic surfactants of formula (II)



in which

R² stands for a linear alkyl radical having 10 carbon atoms;

m₁ stands for 0 or an integer of from 6 to 10;

m₂ stands for 0 or an integer of from 6 to 10;

q stands for 0 or an integer of from 4 to 6;

on condition that both sums (n₁+p+n₂) and (m₁+q+m₂) is different from 0.

2. The composition of Claim 1, wherein n₁ stands for 8 to 9, p stands for 5 to 6 and n₂ stands for 0.

3. The composition of Claim 1, wherein m₁ stands for 8 to 9; q stands for 5 to 6 and m₂ stands for 0.

4. The composition of Claim 1, wherein the components (a) and (b) are present in a ratio by weight of about 5:1 to about 1:5.

5. The composition of Claim 1, further comprising non-ionic surfactants different from components (a) and (b), builders or abrasive compounds, polymers, hydrotropes and/or organic acids and the like.

6. The composition of Claim 1, comprising

- (a) about 5 to about 15 % b.w. surfactant of formula (I);
- (b) about 1 to about 5 % b.w. surfactant of formula (II);
- (c) 0 or 1 to 5 % b.w. co-surfactants;
- (d) 0 or about 1 to 65 % b.w. builders, abrasive compounds, sequestrants and/or chelating agents;
- (e) 0 or about 1 to 5 % b.w. polymers;
- (f) 0 or about 1 to about 15 % b.w. hydrotropes;
- (g) 0 or about 1 to about 5 % b.w. organic acids,

on condition that the amounts add with water and optionally usual auxiliary agents to 100 % b.w.

7. The composition of Claim 5 and/or 6, wherein said co-surfactants are selected from the group consisting of non-ionic surfactants.

8. The compositions of Claim 5 and/or 6, wherein said builders are selected from the group consisting of zeolites, layered silicates, amorphous silicates, phosphates, polycarboxylic acids and their mixtures.

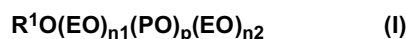
9. The compositions of Claim 5 and/or 6, wherein said polymers represent polymeric soil release polymers.

10. The composition of Claim 5 and/or 6, wherein said hydrotropes are selected from the group consisting of cumene sulfonates, xylene sulfonates, propylene glycols and their mixtures.

11. The composition of Claim 5 and/or 6, wherein said organic acids are selected from the group consisting of mandelic acid, lactic acid, hydroxysuccinic acid, citric acid tartaric acid, and their mixtures.

12. A surfactant blend consisting of

- (a) a first non-ionic surfactant of formula (I)



in which

R¹ stands for a linear alkyl radical having 9 to 11 carbon atoms;

n₁ stands for 0 or an integer of from 6 to 10;

n₂ stands for 0 or an integer of from 6 to 10;

p stands for 0 or an integer of from 4 to 6;

and

- (b) a second non-ionic surfactants of formula (II)



in which

R² stands for a linear alkyl radical having 10 carbon atoms;

m₁ stands for 0 or an integer of from 6 to 10;

m₂ stands for 0 or an integer of from 6 to 10;

q stands for 0 or an integer of from 4 to 6;

on condition that both sums (n₁+p+n₂) and (m₁+q+m₂) is different from 0.

13. The surfactant blend of Claim 12, wherein n₁ and m₁ both stand for 8.5, p and q both for 5.5, and n₂ and m₂ both for 0.

14. A method for cleaning a hard surface, wherein said surface is brought into contact with the composition of Claim 1 or the surfactant blend of Claim 12.

15. The use of the surfactant blend of Claim 12 for making liquid hard surface cleaners.



EUROPEAN SEARCH REPORT

Application Number
EP 14 18 7013

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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	EP 1 023 431 A1 (PROCTER & GAMBLE [US]) 2 August 2000 (2000-08-02) * paragraphs [0004], [0222] - [0225]; claims; examples *	1-15	INV. C11D1/825 C11D1/72 C11D1/722
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