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(54) **HARD-SURFACE CLEANING COMPOSITIONS**

REINIGUNGSZUSAMMENSETZUNGEN FÜR HARTE OBERFLÄCHEN

COMPOSITIONS DE NETTOYAGE DE SURFACES DURES

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EP 0 971 997 B1

Description**Technical Field**

5 **[0001]** The present invention relates to general purpose, hard surface, liquid cleaning compositions comprising non-ionic surfactants and polymeric components.

Background of the Invention

10 **[0002]** Compositions for cleaning hard surfaces generally comprise one or more nonionic surfactants as cleaning agents involved in the removal of soil from the surface. Nonionic surfactants have far better fatty soil detergency than charged surfactants and are typically used in general purpose cleaning compositions for hard surfaces such as kitchen worktops, bathroom fittings, floors and the like.

15 **[0003]** A broad range of nonionic surfactants are known and used in cleaning compositions. For example, these surfactants typically comprise alkoxylated alcohols described as compounds produced by the condensation of alkylene oxide groups, which are hydrophilic in nature, with an organic hydrophobic compound which may be aliphatic 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. Particular examples include the condensation product of aliphatic alcohols having from 8 to 22 carbon atoms in either straight or branched chain configuration with ethylene oxide, such as a coconut oil ethylene oxide condensate having from 2 to 15 moles of ethylene oxide per mole of coconut alcohol; alternatives include condensates of alkylphenols whose alkyl group contains from 6 to 12 carbon atoms with 5 to 25 moles of ethylene oxide per mole of alkylphenol.

25 **[0004]** It is known to incorporate components into a nonionic surfactant-based composition with the intention that deposition of such components onto surfaces will provide a protective layer against soiling in a one step cleaning operation. Our published application WO 94/26858 discloses how certain anionic polymers can be used, together with nonionic surfactants, both to improve initial cleaning and to prevent soil redeposition on hard surfaces which have been cleaned with compositions comprising these polymers. It is believed that the polymer not only improves the initial detergency of the formulation but is also deposited on the surface during the cleaning process, leaving a protective film which either prevents soil adhesion or assists in soil removal. In addition to the anionic polymers it is known to deposit silicone materials and fluorosurfactants so as to achieve the same end.

30 **[0005]** WO 94/26858 discloses how cleaning compositions which deposit a protective film of polymer may be prepared at acid pH's. As is noted in WO 94/26858, the benefit of these polymers was lost as the pH of the prior products was increased. Furthermore, one recognised difficulty with acid products is that they have the potential to damage certain surfaces, particularly enamels such as those used on baths. It is also preferred that cleaning compositions should be formulated at high pH so as to give particularly good fatty soil detergency. It is therefore desirable to be able to formulate products across the entire pH range 3-11 while maintaining the soil release and low effort cleaning benefits outlined in the above mentioned case.

35 **[0006]** WO 89/12673 discloses liquid fabric cleaning compositions comprising nonionic and cationic surfactants and polyacrylate builder. The pH of the compositions is 7.5-12 or 3-5. Although the mol weight of the polymers is not specified, it is known that polyacrylate builders have mol weights well below 100,000, see e.g. US 3,922,230 and US 4,797,223.

Brief Description of the Invention

45 **[0007]** We have now determined that the presence of cationic surfactant enables the pH of nonionic and polymer containing products to be increased, without the loss of the benefits due to polymers. While it is believed that this enables the difficulties associated with low pH formulations to be overcome the incorporation of cationic surfactants has additional advantages as set out below.

50 **[0008]** Accordingly the invention provides a hard surface cleaning composition of pH 3-12 comprising:

a) 1-30% nonionic surfactant,

55 b) 0.005-5% of a water soluble, anionic polymer having an average molecular weight of above 100,000 and less than 1000000, said polymer being free of quaternary nitrogen groups, wherein, the ratio of polymer:nonionic is 0.1:1 or less, and,

c) 0.005-5% of a cationic surfactant.

[0009] A further aspect of the present invention relates to a method for cleaning hard surfaces which comprises the step of treating the surface with a cleaning composition of pH 3-12 comprising:

a) 1-30% nonionic surfactant,

b) 0.005-5% of a water soluble, anionic polymer having an average molecular weight of above 100,000 and less than 1000000, said polymer being free of quaternary nitrogen groups, wherein, the ratio of polymer:nonionic is 0.1:1 or less, and,

c) 0.005-5% of a cationic surfactant.

[0010] Without wishing to limit the present invention by reference to any theory of operation it is believed that enhanced detergency of nonionic surfactants, at acid pH, in the presence of polymer is due to the formation of a hydrogen bonded complex between the nonionic surfactant and the uncharged, undissociated carboxylic acid groups of the polymer. As the pH is raised, the acid groups of the polymer dissociate and the hydrogen-bonded complex is no longer formed. It is believed that in the presence of the cationic surfactant required by the present invention, negatively charged (i.e. carboxylic dissociated) polymer can interact with the cationic surfactant and the nonionic surfactant to form a three-component complex which deposit the nonionic surfactant upon the soil and/or surface being cleaned. While the mechanism is not entirely clear, this may possibly be due to the interaction of the charged polymer with mixed micelles of cationic and nonionic surfactant.

[0011] It is believed that the deposition of the complex on the surface has two results. Firstly the concentration of the surfactant at the surface is increased, resulting in improved cleaning in the initial cleaning cycle and a reduction in the so-called primary cleaning effort. It is also believed that the complex, or at least some part of it, remains on the surface after cleaning and prevents or reduces the reattachment of soil to the surface thereby making the surface easier to clean in second and subsequent cleaning cycles, i.e. it reduces the 'secondary' cleaning effort.

[0012] The presence of a cationic surfactant in the compositions of the invention can also provide an antimicrobial effect during primary cleaning where the cationic is antimicrobial. Using compositions according to the invention it is possible to achieve a log 5 reduction in populations of bacteria. Surprisingly, we have determined that compositions according to the invention which contain antimicrobial cationic surfactants show longer lasting hygiene on surfaces which have been treated with the compositions and can maintain the antimicrobial effect even after the surfaces have been rinsed. This is believed to be due in part to the retention of antimicrobial components of the formulation at the surface and may be due in part to the formulation preventing re-adhesion of microbes on the surface.

[0013] Accordingly, a third aspect of the present invention relates to the use, in a surface cleaning composition comprising nonionic surfactant and an antimicrobial cationic surfactant, of a water soluble, anionic polymer having an average molecular weight of above 100,000 and less than 1000,000, said polymer being free of quaternary nitrogen groups, to prolong the antimicrobial effectiveness of the antimicrobial cationic surfactant on said surface.

[0014] As will be explained in further detail below, the compositions of the invention can comprise other benefit components which become deposited at the surface during a cleaning operation performed with such a composition.

Detailed Description of the Invention

[0015] Various preferred and essential features of the invention are described in further detail below.

Polymers

[0016] The water soluble polymer is an essential component of the compositions according to the present invention.

[0017] As noted above the polymers according to the invention are water soluble polymers having an average molecular weight of above 100,000 and less than 1000,000, and being free of quaternary nitrogen groups. Typically, these polymers are polymers bearing carboxylate functional groups although the use of other anionic polymers is not excluded. In the context of the present invention, anionic polymers are those which carry a negative charge or similar polymers in protonated form. Mixtures of polymers can be employed.

[0018] The preferred polymers in embodiments of the present invention are those which are readily available in the marketplace. These are polymers of acrylic or methacrylic acid or maleic anhydride, or a co-polymer of one or more of the same either together or with other monomers.

[0019] Particularly suitable polymers include polyacrylic acid, polymaleic anhydride and copolymers of either of the aforementioned with ethylene, styrene and methyl vinyl ether.

[0020] The most preferred polymers are maleic anhydride co-polymers, preferably those formed with styrene, acrylic acid, methyl vinyl ether and ethylene.

[0021] The molecular weight of the polymer is in excess of 100,000. VERSICOL E-11 [RTM] (ex. Allied Colloids) which is a polyacrylic acid, has been found to be a suitable polymer for use in compositions according to the invention.

[0022] Typically, the surfactant based cleaning compositions comprise at least 0.01wt% polymer, on product. The positive benefit of the presence of polymer as regards the improvement in cleaning properties can be identified even when very low levels of polymer and surfactant are present. This property of a low concentration threshold is particularly advantageous in applications of the invention where considerable dilution is expected, such as in floor cleaning.

[0023] Preferably the level of polymer is 0.05-5.0wt% at which level the anti-resoiling benefits become particularly significant. More preferably 0.2-2.0wt% of polymer is present. We have determined that higher levels of polymer do not give significant further cleaning advantages with common dilution factors, while increasing the cost of compositions. It is believed that high levels of polymer increase the viscosity of the product and hinder product wetting and penetration of the soil. However, for concentrated products which are significantly diluted prior to use, the initial polymer level can be as high as 5%wt.

[0024] As mentioned above, the molecular weight of the polymer is below 1 000 000 Dalton. It is believed that as the molecular weight increases the cleaning benefit of the polymer is reduced.

Surfactants

[0025] It is essential that compositions according to the present invention comprise at least one nonionic surfactant. The composition according to the invention comprise detergent actives which can be chosen from commercially available nonionic detergent actives. Suitable nonionic detergent active compounds can be broadly described as compounds produced by the condensation of alkylene oxide groups, which are hydrophilic in nature, with an organic hydrophobic compound which may be aliphatic or alkyl aromatic in nature. Alkoxylated alkanols are particularly preferred.

[0026] 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. In general, the compounds will be alkoxylated alcohols having C8-C22 alkyl chains and 1-20 molar equivalents of ethylene oxide and/or propylene oxide residues attached thereto.

[0027] Particular examples include the condensation product of aliphatic alcohols having from 8 to 18 carbon atoms in either straight or branched chain configuration with 2-15 moles of ethylene oxide. Examples of such materials include a coconut oil ethylene oxide condensate having from 2 to 15 moles of ethylene oxide per mole of coconut alcohol; condensates of alkylphenols whose alkyl group contains from 6 to 12 carbon atoms with 5 to 25 moles of ethylene oxide per mole of alkylphenol.

[0028] The preferred nonionic surfactants are the condensation products of 9-15 carbon alcohols with 3-10 moles of ethylene oxide. In embodiments of the invention we have found that DOBANOL [RTM] series ethoxylated alcohol nonionic surfactants (ex. Shell) are suitable. Preferred materials include DOBANOL 91-5 [TM] (C9-C11 alkyl, 5 EO alkyl ethoxylate ex. Shell) and DOBANOL 91-8 [TM] (C9-C11 alkyl, 8 EO alkyl ethoxylate ex. Shell).

[0029] It is possible to use mixtures of nonionic surfactants. As will be described in more detail below these mixed systems have some advantages in antifoaming the products.

[0030] Alternative nonionic surfactant materials which are envisaged include condensates of the reaction product of ethylenediamine and propylene oxide with ethylene oxide, the condensates containing from 40 to 80% of polyoxyethylene radicals by weight and having a molecular weight of from 5,000 to 11,000; tertiary amine oxides of structure R_3NO , where one group R is an alkyl group of 8 to 18 carbon atoms and the others are each methyl, ethyl or hydroxyethyl groups, for instance dimethyldodecylamine oxide; tertiary phosphine oxides of structure R_3PO , where one group R is an alkyl group of from 10 to 18 carbon atoms, and the others are each alkyl or hydroxyalkyl groups of 1 to 3 carbon atoms, for instance dimethyldodecylphosphine oxide; and dialkyl sulphoxides of structure R_2SO where the group R is an alkyl group of from 10 to 18 carbon atoms and the other is methyl or ethyl, for instance methyltetradecyl sulphoxide; fatty acid alkylolamides; alkylene oxide condensates of fatty acid alkylolamides and alkyl mercaptans. In addition, it is believed that alkyl polyglycoside surfactants can be employed as the nonionic surfactant.

[0031] The amount of nonionic detergent active to be employed in the composition of the invention will be from 1 to 30%wt, preferably from 3 to 15%wt. Levels of above 15% active show little increase in neat-use cleaning performance, although such higher levels can be employed in products intended to be considerably diluted prior to use. Typical compositions will comprise 5-10%wt nonionic active on product. Anionic surfactant can be present in relatively small proportions, however it is preferable that anionic surfactant is absent from composition. As described in further detail below small amounts of anionic detergents may be present in the form of soaps as part of an antifoam system. It is preferred that the compositions of the invention comprise less than 2%wt, preferably less than 1% of anionic surfactant.

[0032] Typically the cationic surfactants are materials of the general formula $R_1R_2R_3R_4N^+X^-$, wherein all of the radicals are hydrocarbons with or without hydroxy substitution, at least one of the radicals R1-R4 is a C6-C22 alkyl, alkaryl or hydroxyalkyl, at least one of the radicals R1-R4 is a C1-C4 alkyl or hydroxy alkyl and X is a monovalent anion equivalent.

[0033] The cationic surfactants are preferably, quaternary nitrogen compounds of the general formula $R_1R_2R_3R_4N^+X^-$, where R_1 and R_2 are the same or different C1-C4 alkyl or hydroxy alkyl, R_3 is a C6-C22 alkyl, alkaryl or hydroxyalkyl, R_4 is a C1-C22 alkyl, alkaryl or hydroxyalkyl and X is a monovalent anion equivalent.

[0034] Preferably X is a halogen, most preferably chloride or bromide.

[0035] Preferably R_1 and R_2 are methyl. In embodiments of the invention R_3 is preferably C8-C18 alkyl, more preferably C10-C16 alkyl. In embodiments of the invention R_4 is preferably methyl, C8-C18 alkyl or benzyl. Thus, the cationic surfactants used can have three 'short chain' radicals such as methyl and one fatty-soluble 'long chain' radical or two 'short' chains and two fatty-soluble 'long chains', wherein the 'long chains' can be either linear or branched hydrocarbons or contain aromatic rings.

[0036] A further advantage of including a cationic surfactant in the compositions of the invention is that preferred cationic surfactants confer antimicrobial properties on the formulation. Surprisingly, we have determined that compositions according to the invention which contain antimicrobial cationic surfactants show longer lasting hygiene on surfaces which have been treated with the compositions.

[0037] Particularly suitable cationic detergent-active compounds include cetyltrimethyl ammonium bromide (CTAB), hardened ditallow di-methyl ammonium chloride (available in the marketplace as BARDAC 2250), benzalkonium chloride and mixtures thereof.

[0038] The cationic surfactants which comprise one aryl substituent are especially preferred as they are believed to give particularly good antimicrobial effects.

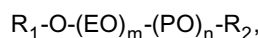
[0039] Typical levels of cationic surfactant will lie in the range of 0.05-3%wt on product. Preferred levels of cationic surfactant are around 1-3%wt.

[0040] The total amount of detergent active compound to be employed in the detergent composition of the invention will generally be from 1.5 to 30%, preferably from 2 to 20% by weight, most preferably from 5-20wt%.

Solvents

[0041] Solvents may be present in the compositions of the invention.

[0042] It is preferred that the compositions of the present invention comprise not more than 2%wt of solvents of the general formula:



wherein R_1 and R_2 are independently C2-6 alkyl or H, but not both hydrogen, m and n are independently 0-5. It is believed that the use of polymers in compositions according to the present invention can offset the otherwise deleterious effects of any solvent which is present when the product is used on certain plastics materials.

[0043] More preferably, no more than 2%wt of solvent selected from the group comprising di-ethylene glycol mono n-butyl ether, mono-ethylene glycol mono n-butyl ether, propylene glycol n-butyl ether and mixtures thereof is present. Advantageously, effectively no solvent other than water is present.

Metal ion binding agents

[0044] Preferably the composition contain either detergent builders or non-building metal ion sequesterants, collectively these are known as metal ion binding agents.

[0045] Suitable metal ion binding agents include nitrilotriacetates, polycarboxylates, citrates, dicarboxylic acids, water-soluble phosphates especially polyphosphates, mixtures of ortho- and pyrophosphate, zeolites and mixtures thereof. Such agents can additionally function as abrasives if present in an amount in excess of their solubility in water as explained herein. In general, where the metal ion binding agent is a builder it will preferably will form from 0.05 to 25% by weight of the composition.

[0046] Metal ion binding agents such as ethylenediaminetetraacetates (e.g. EDTA), amino-polyphosphonates (e.g. those available as the 'DEQUEST' (TM) series of materials) and phosphates and a wide variety of other poly-functional organic acids and salts (including materials such as methyl glycine diacetate (MGDA)), can also optionally be employed.

[0047] A particular, further advantage of including metal ion binding agents, preferably organic acetates, more preferably MGDA or EDTA is believed to be that the microbiocidal properties of the cationic surfactants are improved especially against Gram-negative bacteria particularly under hard water conditions.

[0048] Preferred levels of metal ion binding agents are 0.05-5%wt, preferably 0.1-3.0%wt, most preferably 1.5-3%wt. In preferred compositions containing around 2% cationic surfactant, 1.5-3% of an organic acetate sequesterant will give a log five reduction in viable bacteria even against recalcitrant bacterial strains such as *Pseudomonas aeruginosa*.

[0049] Preferred compositions according to the invention contain 1.5-3%wt of MGDA or EDTA.

[0050] In addition to the cleaning benefit we have determined that the formulation containing polymer, alcohol, ethoxylate, cationic surfactant and sequestering agent has the additional benefit that it reduces the adhesion of fungal and/or bacterial spores to surfaces. This is described in further detail below with reference to examples.

Minors

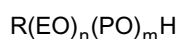
[0051] The composition according to the invention can contain other ingredients which aid in their cleaning performance and general utility.

[0052] Typically, a further optional ingredient for compositions according to the invention is a suds regulating material, which can be employed in compositions according to the invention which have a tendency to produce excessive suds in use. One example of a suds regulating material is soap. Soaps are salts of fatty acids and include alkali metal soaps such as the sodium, potassium, ammonium and alkanol ammonium salts of higher fatty acids containing from about 8 to about 24 carbon atoms, and preferably from about 10 to about 20 carbon atoms. Particularly useful are the sodium and potassium and mono-, di- and triethanolamine salts of the mixtures of fatty acids derived from coconut oil and ground nut oil. When employed, the amount of soap can form at least 0.005%, preferably 0.5% to 2% by weight of the composition.

[0053] Further example of a suds regulating materials are organic solvents, hydrophobic silicas, silicone oils and hydrocarbons.

[0054] An alternative suds regulating material comprises a mixed EO/PO nonionic surfactant. Suitable ethoxylated/propoxylated nonionic detergents include the condensation product of aliphatic alcohols having from 8 to 22 carbon atoms in either straight or branched chain configuration with ethylene oxide and propylene oxide, such as a coconut oil ethylene oxide/propylene oxide condensate having from 2 to 15 moles in total of ethylene oxide and propylene oxide per mole of coconut alcohol. It is preferable that the mole ratio of ethylene oxide to propylene oxide lies in the range 1:5-5:1.

[0055] Particularly preferred ethoxylated/propoxylated nonionics include molecules of the general formula:



wherein: R is an alkyl residue having an average carbon chain length of C8-C14, preferably C9-C11, EO is an ethylene oxide residue, n is 1-10, PO is a propylene oxide residue and m is 1-5. A particularly preferred material is C9-11 5-8EO 1-3PO, most preferably C9-11 6EO 2PO.

[0056] The amount of ethoxylated/propoxylated nonionic detergent active to be employed in the composition of the invention will generally be from 2 to 10%wt, and most preferably from 3-6%wt.

[0057] Preferred ratios of the ethoxylated to the ethoxylated/propoxylated surfactant fall into the range 4:1-2:1 with the ethoxylated surfactant being present in weight excess over the ethoxylated/propoxylated surfactant.

[0058] Compositions according to the invention can also contain, in addition to the ingredients already mentioned, other optional ingredients such as pH regulants, sunscreens, colourants, optical brighteners, soil suspending agents, enzymes, compatible bleaching agents, gel-control agents, freeze-thaw stabilisers, additional biocides, preservatives, detergent hydrotropes, perfumes and opacifiers.

[0059] Hydrotropes, are useful optional components. It is believed that the use of hydrotropes enables the cloud point of the compositions to be raised without requiring the addition of anionic surfactants.

[0060] Suitable hydrotropes include, alkali metal toluene sulphonates, urea, alkali metal xylene and cumene sulphonates, short chain, preferably C₂-C₅ alcohols and glycols. Preferred amongst these hydrotropes are the sulphonates, particularly the cumene and toluene sulphonates.

[0061] Typical levels of hydrotrope range from 0-5% for the sulphonates. Correspondingly higher levels of urea and alcohols are required. Hydrotropes are not generally required for dilute products.

[0062] Given that the compositions of the invention effectively comprise a means for deposition of a surfactant/polymer complex at the surface being cleaned, it is envisaged that the compositions of the invention can further comprise components which it is desirable to deposit upon a surface. Three preferred classes of additional components are perfumes, non-cationic surfactant antimicrobial components and insect repellents and/or insecticides.

[0063] Given that the compositions of the invention already comprise a cationic surfactant and are alkaline, some antimicrobial activity is already found in the compositions. Suitable additional non-cationic non-surfactant antimicrobial components are known in the art. Typical examples of this class of materials includes antimicrobial perfume oils and oil components.

[0064] Typical levels of the non-cationic antimicrobial agent in formulations range from 0.01 to 8%, with levels of 0.05-4wt%, particularly around 2% being preferred for normal compositions and up to two or four times that concentration being present in so called, concentrated products. For sprayable products the concentration of the antimicrobial

agent will be in the range 0.05-0.5%wt.

[0065] Particularly suitable insect repellents include essential oils such as those of genus *Mentha*, particularly *Mentha arvensis*, *mentha piperita*, *Mentha spicata* and *Mentha cardica*; Lemongrass East Indian oil, Lemon oil, Citronella, Cedarwood and Pine oil; terpenoids, particularly limonene, carvone, cineole, linalool, Gum Camphor, citronellal, alpha and beta terpenol, fencholic acid, borneol, iso borneol, bornyl acetate and iso bornyl acetate. The most preferred insect repellants are the terpenoids, particularly limonene. Of the above-mentioned oils many are known to show antimicrobial effects as well as being insect repellents and/or perfumes.

[0066] The level of insect repellent required will vary with the nature of the material used. For essential oils and terpenoids, preferred levels are 0.1-5% on product.

[0067] It is preferable that the compositions of the present invention are essentially free of abrasive particles.

[0068] The preferred pH of the neat products is 7-12 with a pH in the range of 7-11 being more preferred and a pH of around 10-11 being particularly preferred so as to balance cleaning and hygiene effectiveness.

[0069] Particularly preferred compositions according to the present invention are mobile aqueous liquids, having a pH of 7-12 (preferably 7-11) which comprise:

a) 5-20%wt of a ethoxylated, 2-15EO, C8-C18 alcohol, nonionic surfactant,

b) less than 1%wt of anionic surfactants,

c) 0.2-2%wt of a water soluble, anionic polymer having an average molecular weight of above 100,000 and less than 1,000,000, said polymer being a polymer of at least one of acrylic acid, methacrylic acid or maleic anhydride, with at least one of acrylic acid, methacrylic acid, maleic anhydride, ethylene, styrene and methyl vinyl ether, and ,

d) 0.05-5%wt (preferably 0.05-2%wt) of a cationic surfactant which is a quaternary nitrogen compounds of the general formula $R_1R_2R_3R_4N^+X^-$, where R1 and R2 are the same or different C1-C4 alkyl or hydroxy alkyl, R3 is a C6-C22 alkyl, alkaryl or hydroxyalkyl, R4 is a C1-C22 alkyl, alkaryl or hydroxyalkyl and X is a monovalent anion equivalent, and,

e) not more than 2% of a solvent selected from the group comprising di-ethylene glycol mono n-butyl ether, mono-ethylene glycol mono n-butyl ether, propylene glycol n-butyl ether and mixtures thereof.

[0070] More particularly preferred compositions according to the invention are as described in the above paragraph but contain a cationic surfactant which has antimicrobial properties (such as benzalconium chloride) and a metal ion binding agent which is an organic acetate. These compositions exhibit improved primary and secondary cleaning at high pH as well as having effective and persistent antimicrobial properties against a broad range of microbes.

[0071] Compositions can be manufactured which comprise an essentially dry powder and which form the compositions of the invention on the addition of water.

[0072] In order that the present invention may be further understood it will be described hereafter by way of the following nonlimiting examples.

EXAMPLES

Examples 1-6: primary and secondary cleaning

[0073] In all the cleaning examples described below a specified level (based on non-volatiles) of soil were deposited on an 'A4' sized area of 'DECAMEL' (RTM ex Formica) test surface by spraying. The soil comprised 1% glycerol tripalmitate, 0.5% glycerol trioleate, 0.5% kaolin, 0.2% liquid paraffin, 0.1% palmitic acid, 0.02% carbon black in methylated spirits. The soil was allowed to age for a specified time at room temperature prior to cleaning. The initial effort required to clean the surface is referred to below as the primary cleaning effort.

[0074] Where secondary cleaning benefits were examined, in order to investigate the anti-resoiling performance, the DECAMEL sheets were pretreated with the test composition and copiously rinsed prior to soiling. The effort required to clean the re-soiled surfaces is known as the secondary cleaning effort.

[0075] In both primary and secondary cleaning the total effort used to remove the soil from the test surface using a cellulosic sponge cloth was measured using a rig fitted with force measuring means to determine the total effort applied to the surface. Due to variability in the experimental conditions, in the data which follows results should not be compared between series of experiments presented in different tables.

[0076] Formulations comprised nonionic surfactant and water with and without polymer and with and without cationic surfactant.

The nonionic surfactants employed were DOBANOL 91-5 [TM] (C9-C11 alkyl, 5 EO alkyl ethoxylate ex. Shell) and DOBANOL 91-8 [TM] (C9-C11 alkyl, 8 EO alkyl ethoxylate ex. Shell). The polymers illustrative of the present invention were a polyacrylic acid (VERSICOL E11 [TM] ex Allied Colloids) which had an average molecular weight of 250,000 Daltons. The cationic surfactants used were C_n-alkyl trimethyl ammonium bromide (C_nTAB: where n is 12,14 and 16), dicetyldimethyl and tricetylmethyl ammonium bromides (DTAB and TTAB respectively). The pH of the compositions was regulated with sodium hydroxide or a carbonate/bicarbonate buffer system as indicated.

[0077] Example 1a-1d in Table 1 below show the primary cleaning effort required using compositions which contained the formulations given, on the soil given above, aged for a period of two days after application of the soil at a coverage of 0.5mg/cm².

Table 1

	1a	1b	1c	1d
Dobanol 91-5	7%	7%	7%	7%
Cetyl TAB	-	-	1%	1%
Versicol E11	-	0.5%	-	0.5%
Carbonate/bicarbonate	pH9	pH9	pH9	pH9
Cleaning Effort (N/s)	1036	769	689	412

[0078] From table 1 it can be seen that the primary cleaning effort is minimised at alkaline pH in the presence of both the cationic surfactant and the polymer (example 1d), while higher effort is required if either or both of these components is absent (compare with comparative examples 1a, 1b and 1c). It is believed that this is due to the formation of a polymer/surfactant complex which increases the surfactant concentration at the surface.

[0079] Table 2 below shows the effect of the cationic type on primary cleaning effort. Experiments were performed on the soil given above aged for a period of one day after application of the soil at a coverage of 0.25mg/cm².

Table 2

	2a	2b	2c	2d	2e	2f	2g	2h
Dobanol 91-8	7%	7%	7%	7%	7%	7%	7%	7%
TTAB	-	-	1%	1%	-	-	-	-
DTAB	-	-	-	-	1%	1%	-	-
CTAB	-	-	-	-	-	-	1%	1%
Versicol E11	-	0.5%	-	0.5%	-	0.5%	-	0.5%
Hydroxide to	pH9	pH9	pH9	pH9	pH9	pH9	pH9	pH9
Cleaning Effort (N/s)	1754	1408	1520	399	1728	617	1324	442

[0080] From table 2 it can be seen that compared with the control (comparative example 2a) primary cleaning effort is in all cases markedly reduced by the combination of surfactant, polymer and cationic (examples 2d, 2f and 2h) as compared with systems in which only the cationic is added (comparative examples 2c, 2e and 2g). Addition of the polymer alone, in the absence of the cationic surfactant, (comparative example 2b) gives no significant reduction in primary cleaning effort at this pH. It can be seen that of the different cationics used the TTAB and CTAB materials give the lowest cleaning effort.

[0081] Table 3 below further illustrates the effect of pH for compositions which comprise 7% Dobanol 91-5 and 0.5% Versicol E11 in the presence of differing levels of CTAB at the pH indicated. pH was regulated with hydroxide and the experiments were performed on the soil given above aged for a period of one day after application of the soil at a coverage of 0.25mg/cm². Results are given in total primary effort to clean in N/s.

Table 3

	3a	3b	3c
pH	pH6	pH8	pH10
0% CTAB	213	262	-
25% CTAB	163	195	193
0.5% CTAB	142	180	175
1% CTAB	151	131	190

[0082] From Table 3 it can be seen that through this pH range the primary cleaning effort generally falls as the level of the cationic surfactant level is increased.

[0083] Table 4 below provides additional data on the effect of pH for compositions which comprise 8% active in total and 0.5% Versicol E1 in the presence of differing levels of CTAB (C) and DTAB (D) at the pH indicated. The non-cationic active material is Dobanol 91-5. pH was regulated with hydroxide and the experiments were performed on the soil given above aged for a period of one day after application of the soil at a coverage of 0.25mg/cm². Results are given in total primary cleaning effort in N/s.

Table 4

	4a	4b	4c	4d
pH	pH4	pH7	pH4	pH7
type of cationic	C	C	D	D
0.00% cationic	162	749	162	749
0.13% cationic	171	399	171	308
0.25% cationic	188	288	173	227
0.50% cationic	190	403	162	269

[0084] From Table 4 it can be seen that compositions show poor cleaning performance at the higher pH unless the cationic surfactant is present. In the lower pH range (examples 4a and 4c) the effect disclosed in WO 94/26858 is believed to be acting to reduce the primary cleaning effort requirement and there is no significant effect of adding cationic (if anything the compositions get slightly worse) although useful cleaning results are still attained.

[0085] In the higher pH range (examples 4b and 4d) it can be seen that the addition of cationic surfactant significantly lowers the cleaning effort and enables the nonionic/polymer systems to achieve similar results to those obtained in more acidic products.

[0086] Table 5 below show the effect on the primary cleaning energy effort requirement and the cloud point of modifying the nonionic surfactant present. The compositions comprise 7% of a mixture of Dobanol 91-5 and Dobanol 91-8, 1% CTAB and 0.5% Versicol E11. The table lists the percentage of Dobanol 91-8 in the nonionic portion of the surfactant mixture, the remainder of the mixture being the Dobanol 91-5.

Table 5

	% Dobanol 91-8	Effort (N/s)	Cloud Point
5a	0	331	30
5b	25	401	42.5
5c	50	479	53

Table 5 (continued)

	% Dobanol 91-8	Effort (N/s)	Cloud Point
5d	75	809	64
5e	100	876	75

[0087] From Table 5 it can be seen that the compositions which are rich in the Dobanol 91-5 surfactant (for example 5a) give the best reduction in primary cleaning effort, whereas while the compositions which are rich in Dobanol 91-8 (for example 5e) also give a useful reduction in primary cleaning effort this is less marked than for the other surfactant. It is clear from the table that the selection of an appropriate combination of surfactants enables the cloud point of the compositions to be controlled.

[0088] Table 6 below shows the effect on the secondary cleaning effort requirement in subsequent cleaning cycles for the compositions of the invention, using two different cationics. The 'VARI' material is Varisoft 442-100P (TM: ex. Sherex-Witco) a dihardened tallow dimethyl ammonium chloride.

Table 6

	6a	6b	6c	6d
	CTAB	CTAB	VARI	VARI
	primary	resoiled	primary	resoiled
pH6	886	203	846	364
pH8	679	257	745	460
pH10	969	426	958	602
pH12	637	211	501	408

[0089] From Table 6 it can be seen that in all cases the surfaces proved more easy to clean in the second cleaning cycle (compare 6a with 6b and compare 6c with 6d). It is believed that this demonstrates that the one or more components of the composition are being deposited on the surface and leaving a residual film which either retards the attachment of soil or aids in its removal, i.e. the secondary cleaning effort after re-soiling of the surfaces is reduced.

[0090] The above examples illustrate how the compositions of the present invention enable a reduction of both primary and secondary cleaning effort over a broad pH range.

Example 7-9: Biocidal effects

[0091] Table 7: below shows the result of a biocidal efficacy test using the following bacteria (from the National Collection of Type Cultures or American Type Culture Collection). Cultures were maintained on beads in a cryopreservative at -80/C.

<i>Staphylococcus aureus</i>	NCTC 10788
<i>Pseudomonas aeruginosa</i>	ATCC 15442
<i>Saccharomyces cerevisiae</i>	ATCC 9763

[0092] To prepare inoculum a bead was removed from the storage vial and aseptically transferred to 100ml Nutrient Broth and incubated at 37/C in a shaking waterbath for 24 hours (bacteria). After incubation, the culture suspensions were aseptically transferred into two 50ml centrifuge tubes and centrifuged at 2180g for 10 minutes (Mistral 1000, MSE) in order to harvest the cells. The supernatants were poured off and the pellets resuspended in peptone diluent (0.1 percent peptone and 0.85 percent sodium chloride, pH 7.0). The suspensions were kept at 4/C until needed, and before use in the test were left on the bench at ambient temperature for at least 30 minutes.

[0093] The test used was a microtitre plate assay, which is comparable to 'Method for the test for the antimicrobial activity of disinfectants in food hygiene', more commonly known as the European Suspension Test (EST). Bovine albumin at a low level (0.03 percent) or a high level (0.3 percent) was included in some of the tests. A 1/15 dilution of the formulation was made in 'Water of Standard Hardness' as referred to in the above method.

[0094] Microtitre plates (Bibby Sterilin, sterile 96-well, flat-bottom) were prepared by adding 270ml quenching solution in row B of each plate and 270ml peptone diluent into rows C-G. The quench solution was composed of Tween 80 (3.0 percent), lecithin (0.3 percent), L-histidine (0.1 percent), sodium thiosulphate (0.5 percent) and 0.25N KH_2PO_4 buffer (1 percent) in sterile distilled water (1 litre). Sterile distilled water or bovine albumin as appropriate (120ml) was added to the test wells of row A. Then the formulation (150ml 1/15 dilution) was added to the appropriate test wells. The formulations were randomised across the plates. The plates were placed on a stainless steel 'plate incubator' tray attached to a circulating waterbath, held at 20/C.

[0095] An aliquot of microbial suspension (30ml) was then added simultaneously to all the wells of row A of the microtitre plate using a multichannel pipette. The test mixture was left at 20/C for a contact time of 5 minutes $\pm$ 5 seconds, after which time an aliquot (30ml) was transferred into row B (quench), giving a 10^{-1} dilution. After 5 ± 1 min, an aliquot (30ml) was transferred to row C (peptone diluent). Further serial dilutions were performed in the same manner until row G (10^{-6} dilution). The bacteria were enumerated using the Miles-Misra technique. Three aliquots (10ml) from each dilution were spotted onto pre-dried Tryptone Soya Agar plates which had been divided into 6 sectors. The spots were allowed to dry and the plates incubated at 37/C for 24 hours. Plates were counted by selecting a dilution segment with 3-50 cfu per spot and the average of the 3 spots was calculated. The decadic logarithm of this number was calculated and subtracted from the decadic logarithm of the initial count to give the log (reduction).

[0096] All formulations contained Dobanol 91-8 (8 percent) and polymer (polyacrylic acid 0.5wt percent), and were adjusted to pH9. Formulations were diluted 1/30 in test in presence of WSH (water of standard hardness) and soil (bovine albumin). Examples are provided both for formulations containing CTAB and benzalkonium chloride.

Table 7

ORGANISM	CTAB (%)	BAAC (%)	MEAN LOG (REDUCTION) (2 replicates)	
			LOW SOIL	HIGH SOIL
<i>Staph. aureus</i>	1.0	-	4.5	4.7
	2.0	-	7.4	7.6
	-	1.0	7.2	7.2
	-	2.0	7.2	7.2
<i>Pseudomonas aeruginosa</i>	1.0	-	0.1	0.03
	2.0	-	0.04	0.01
	-	1.0	2.3	2.6
	-	2.0	3.5	3.1
<i>Saccharomyces cerevisiae</i>	1.0	-	4.4	3.5
	2.0	-	7.0	2.7
	-	1.0	6.0	6.0
	-	2.0	6.0	6.0

[0097] From the results given in Table 7 it can be seen that the levels of cationic used in the compositions of the present invention are sufficient to give a biocidal effect. It can also be seen that benzalkonium chloride has an improved biocidal effect even against the normally recalcitrant *Pseudomonas aeruginosa*.

[0098] In order to show the effect of sequesterant in improving bacterial kill, formulations were prepared which contained Dobanol 91-8 (7wt percent) and polymer (VERSICOL E11 polyacrylic acid 0.5wt percent), and were adjusted to pH11. Formulations were diluted 1/20 in the presence of WSH (water of standard hardness) and 0.03% soil (bovine albumin) on final suspension. Examples are provided for formulations containing benzalkonium chloride (BAC) at both 1.0 and 2.0 wt%. Sequesterant, either EDTA or MGDA was used as indicated in table 8. The test bacteria was *Pseudomonas aeruginosa* ATCC 15442, and assays were conducted as described above. Examples which give a log reduction greater than 5 are indicated in bold.

Table 8

BAC %	EDTA %	MGDA %	Log Reduction
1	0.5	0	1.22
1	1	0	1.1
1	1.5	0	5.54
1	2	0	5.66
1	2.5	0	5.66
2	0.5	0	1.86
2	1	0	2.17
2	1.5	0	5.66
2	2	0	5.3
2	2.5	0	5.66
1	0	0.5	0.89
1	0	1	1.23
1	0	1.5	1.44
1	0	2	4.57
1	0	2.5	5.42
2	0	0.5	1.7
2	0	1	2.95
2	0	1.5	3.46
2	0	2	5.48
2	0	2.5	5.74

[0099] The results given in Table 8 show that a log five reduction in viable counts can be obtained by use of appropriate levels of sequestering agents.

[0100] In order to demonstrate the advantages of longer lasting hygiene which accrue with the compositions of the present invention, formulations were prepared which contained Dobanol 91-8 (7wt percent) with and without polymer (VERSICOL E11 polyacrylic acid 0.5wt percent), and were adjusted to pH11. Formulations were diluted 1/20 in the presence of WSH (water of standard hardness) and 0.03% soil (bovine albumin) on final suspension. Examples are provided for formulations containing benzalkonium chloride (BAAC) at both 1.5 and 2.0 wt%. Sequesterant, either EDTA or MGDA was used as indicated in table 9.

[0101] Efficacy was determined against *Staphylococcus aureus* NCTC 6538 by means of the method set out below.

[0102] Glazed ceramic tiles squares (size = 2.5x2.5cm, were cut from plain black glazed Cristal (TM) tiles, ex H & R Johnson with all sloping edges removed. The tiles were cleaned rigorously before application of the test solution or product, so that a uniform coverage on a hydrophilic surface is obtained. Cleaning is undertaken on the day that application of product, and rinsing is carried out no longer than 24 hrs before microbiological testing is undertaken. Tiles were cleaned by applying calcite powder to the tile and rubbing vigorously with a clean, damp sponge cloth. Tiles are rinsed with de-ionised water and it was determined if the tile was hydrophilic all over by allowing a small amount of water to run over it. The water should run smoothly over the tile and form an even film over the entire surface. If any area remained hydrophobic calcite was reapplied and the cleaning process repeated. After cleaning, tiles were dried by wiping with a clean paper tissue (Kimsoft (TM) facial tissue).

[0103] 50µl of cleaning product (whether a formulation according to the invention, a control or a comparative example) was placed on a clean tile and carefully spread it over the whole tile surface using a flattened micropipette tip. The tile was allowed to dry in a 30°C incubator then any rinses were carried out by placing each tile in 100ml of sterile WSH for 30 seconds, removing and placing in a 30°C incubator to dry.

[0104] After treatment with the products according to the invention, comparative examples or controls the tiles were

stored in a microbiological safety cabinet to limit contamination.

[0105] In order to demonstrate the substantive antibacterial effect, each product was tested in duplicate, using 50µl of sterile distilled water as the control formulation for control tiles. At time zero tiles treated according to the present invention were inoculated together with a control tile with 20µl of culture (as described above) so that there were approximately 2×10^7 bacteria/tile in a 0.03% Bovine Albumin soil. The bacteria were spread over the whole tile area using a sterile spreader. After 30 minutes contact time between the bacteria and the tiles, a sterile microbiological cotton swab was wet with quench solution and swabbed thoroughly over the tile in two directions at right angles to each other. The end of the swab was broken off into 10ml of quench solution and the process repeated with a dry swab to remove residual liquid and bacteria. Quench bottles were left for 30 minutes to allow for recovery of injured cells (60 minutes for *E. coli*). After recovery each quench bottle was vortexed for 15 seconds at high speed to resuspend the cells evenly in the quench solution.

[0106] For each tile being tested, a column of wells in a sterile microtitre plate was inoculated with 270µl of Peptone water, leaving the first well empty in each case. The first well was filled with 300µl of the quenched swab solutions. A further 500µl of quenched swab solution was plated directly onto an agar plate and spread using a sterile spreader. This plate is used for enumerating low levels of survivors. Serial 10-fold dilutions of the solutions were prepared by transferring 30µl of solutions in row 1 to row 2; mixing them, then repeating the procedure down to row 6 so that a 10⁻⁶ dilution is achieved (pipette tips are changed between transfers).

[0107] For each tile sample taken an agar plate (dried plate face down with the lid off in a 60°C oven for 15 minutes prior to use and marked into 6 equal segments on its base with a marker pen) was spotted with 10µl volumes of liquid onto the appropriate segment of the plate, placing 3 spots per segment. All plates were left face up to dry and then placed face down in an incubator at 37°C for 24 hrs. Counts were obtained for the plates and log₁₀ reduction obtained by subtracting the log₁₀ count[test] from log₁₀ count[control].

[0108] Results for such a test are shown in table 9 below: all composition contained soil and nonionic surfactant as noted above and the other components of the neat cleaning composition are indicated in the table. As noted above, log reductions are calculated relative to controls which had been treated with sterile water rather than a 'cleaning' composition.

Table 9

Example	BAAC%	Polymer%	EDTA%	MGDA%	Log Red Rinsed	Log Red. Unrinsed
9a	1.5	0.5	-	2.5	1.41	3.49
9b	1.5	-	-	2.5	1.01	4.02
9c	1.5	0.5	1.5	-	1.80	3.87
9d	1.5	-	1.5	-	0.35	4.02
9e	2.0	0.5	-	2.5	2.18	4.02
9f	2.0	-	-	2.5	0.38	4.02
9g	2.0	0.5	1.5	-	2.67	4.02
9h	2.0	-	1.5	-	0.01	2.48

[0109] From the results in table 9 it can be seen that bacteria recovered from a surface which had been previously treated with a composition according to the invention (9a, 9c, 9f or 9h) had a significantly reduced viability of between 2-4 logs when the surface was not rinsed. This reduction in viability would be expected given that the surfaces had been exposed to a biocide-containing solution which had been allowed to dry on the surface.

[0110] For the tiles which had been rinsed, only those treated with formulations which contained polymer (9a, 9c, 9e and 9g) showed markedly better than 1 log reduction (90%) of the recovered bacteria. Formulations using 2%wt BAAC, polymer and sequesterant (9e and 9g) showed the best results in the example with a better than 99% reduction in viable count.

[0111] It is believed that these results show that the compositions of the invention have a persistent antimicrobial effect as compared with the polymer free control compositions.

Example 10: Fungal Spore Adhesion

[0112] Plastic Petri dishes (9cm diameter, 2cm depth) were treated with 20ml of test product at the recommended dilution (1:20, 30 min, room temperature), before decanting the solution and allowing plates to dry. Control plates were

untreated. Prior to dilution the example formulation (10a) contained Dobanol 91-8 (7%wt) with polymer (VERSICOL E11 polyacrylic acid 0.5%wt), cationic surfactant (2%wt BAAC) and sequesterant (2.5%wt MGDA) and was adjusted to pH11 with NaOH. Comparative examples were also performed against Lysoform (TM) a commercially available disinfectant product.

[0113] A suspension of *Aspergillus niger* spores (ATCC 6275), prepared in sterile distilled water, was introduced to the plates (20ml per plate, 3×10^5 spores/ml). Plates were agitated in an orbital shaker to distribute spores evenly (1 min, 100 rpm) and left standing at room temperature for 30 min, before re-agitating (1 min, 100 rpm). Supernatants were discarded and the plates allowed to dry. As the plates had been allowed to dry after pretreatment and prior to exposure to the spores, the spores had not been exposed to relatively high levels of the pre-treatment compositions. Initial attachment of spores to the treated and untreated plates could then be determined by the method given below.

[0114] To show the effect of rinsing, duplicate dishes which had been treated as above (including the exposure to mould spores) were subjected to rinsing by introducing standard hard water (10ml) into each dish and mixing (1 min, 100rpm).

[0115] The supernatant was discarded and the plates dried at room temperature.

[0116] To show the effect of scrubbing duplicate dishes which had been inoculated with spores as described above were scrubbed using an epicyclic scrubbing device. Scrubbing of the surface was achieved through the use of standard, pre-washed sponge cloths, dampened with standard hard water, at a fixed pressure of 80g/cm², (10 cycles, speed 4). Dishes were then allowed to dry at room temperature as before.

[0117] Each of the above plates was viewed under light microscopy (x40 magnification) and the average number of attached spores determined from each of five pre-defined fields of view. Plates from the rinsing and scrubbing experiments were re-counted and the numbers of spores recorded. The percentage attachment following each of the treatments was calculated by the equation:

$$\frac{\text{Average no. spores counted} \times 100}{\text{Average no. spores on untreated control}}$$

[0118] Results are given in table 10 below, a percentage of spores attached as compared with an untreated surface

Table 10

	Initial Attachment	Attachment after rinsing	Attachment after scrubbing
10a	45.05	32.67	5.41
Lysoform (TM)	64.26	53.07	14.74
Control	100.00	77.53	38.83

[0119] As expected, the results show that for untreated surfaces rinsing and scrubbing remove some mould spores, but leave almost 40% of the spores on the surface even after scrubbing. The results show that spores are less likely to attach to a surface treated with the compositions of the present invention, and, when spores do attach, they are not as strongly bound to the surface.

[0120] Statistical analysis of the data showed a significant decrease (95% confidence) in the percentage of spores which attached to the surface in the presence of the polymer-containing formulation, compared to the reference product Lysoform (RTM) and as compared with untreated surfaces. As noted above, this difference was seen at each stage of treatment.

[0121] It is believed that these results show that the compositions of the invention at least partly prevent the adhesion of spores to a surface and consequently, it is believed that the use of a composition according to the present invention would reduce the rate of regrowth on a clean surface of micro-organisms including moulds or bacteria which propagate through spores.

Claims

1. A hard surface cleaning composition of pH 3-12 comprising:

a) 1-30%wt nonionic surfactant,

b) 0.005-5%wt of a water soluble, anionic polymer having an average molecular weight of above 100,000 and

less than 1000000, said polymer being free of quaternary nitrogen groups, wherein the ratio of polymer:non-ionic is 0.1:1 or less, and

c) 0.005-5%wt of a cationic surfactant.

2. Composition according to claim 1 wherein the polymer is a polymer of acrylic or methacrylic acid or maleic anhydride, or a co-polymer of one or more of the same either together or with other monomers.

3. Composition according to claim 2 wherein the polymer is selected from the group comprising polyacrylic acid, polymaleic anhydride and copolymers of either of the aforementioned with ethylene, styrene and methyl vinyl ether.

4. Composition according to claim 1 wherein the cationic surfactants is a material of the general formula $R_1R_2R_3R_4N^+X^-$, wherein all of the radicals are hydrocarbons with or without hydroxy substitution, at least one of the radicals R1-R4 is a C6-C22 alkyl, alkaryl or hydroxyalkyl, at least one of the radicals R1-R4 is a C1-C4 alkyl or hydroxy alkyl and X is a monovalent anion equivalent.

5. Composition according to claim 4 wherein R1 and R2 are the same or different C1-C4 alkyl or hydroxy alkyl, R3 is a C6-C22 alkyl, alkaryl or hydroxyalkyl, R4 is a C1-C22 alkyl, alkaryl or hydroxyalkyl and X is a monovalent anion equivalent.

6. Composition according to claim 5 wherein R1 and R2 are methyl, R3 is C8-C18 alkyl and R4 is methyl, C8-C18 alkyl or benzyl.

7. Composition according to claims 1-6 which further comprises a metal ion binding agent.

8. Composition according to claims 1-7 wherein the pH is 7-12

9. Hard surface cleaning composition of pH of 7-11 which comprise:

a) 5-20%wt of a ethoxylated, 2-15EO, C8-C18 alcohol, nonionic surfactant,

b) less than 1%wt of anionic surfactants,

c) 0.2-2%wt of a water soluble, anionic polymer having an average molecular weight of above 100,000 and less than 1,000,000, said polymer being a polymer of at least one of acrylic acid, methacrylic acid or maleic anhydride, with at least one of acrylic acid, methacrylic acid, maleic anhydride, ethylene, styrene and methyl vinyl ether, wherein the ratio of polymer:nonionic is 0.1:1 or less,

d) 0.05-2%wt of a cationic surfactant which is a quaternary nitrogen compounds of the general formula $R_1R_2R_3R_4N^+X^-$, where R1 and R2 are the same or different C1-C4 alkyl or hydroxy alkyl, R3 is a C6-C22 alkyl, alkaryl or hydroxyalkyl, R4 is a C1-C22 alkyl, alkaryl or hydroxyalkyl and X is a monovalent anion equivalent, and

e) not more than 2% of a solvent selected from the group comprising di-ethylene glycol mono n-butyl ether, mono-ethylene glycol mono n-butyl ether, propylene glycol n-butyl ether and mixtures thereof.

10. A method for cleaning hard surfaces which comprises the step of treating the surface with a cleaning composition according to any one of claims 1-9.

11. The use, in a hard-surface cleaning composition comprising 1-30%wt of a nonionic surfactant and 0.005-5%wt of an antimicrobial cationic surfactant, of 0.005-5%wt of a water soluble, anionic polymer having an average molecular weight of above 100,000 and less than 1000000, said polymer being free of quaternary nitrogen groups and the ratio of polymer:nonionic being 0.1:1 or less, to prolong the antimicrobial effectiveness of the antimicrobial cationic surfactant on said hard-surface.

Patentansprüche

1. Reinigungszusammensetzung für harte Oberflächen mit einem pH-Wert von 3 bis 12 enthaltend:

- a) 1 bis 30 Gew.-% nichtionisches Tensid,
- b) 0,005 bis 5 Gew.-% eines wasserlöslichen anionischen Polymers mit einem mittleren Molekulargewicht von mehr als 100.000 und weniger als 1.000.000, wobei das Polymer frei von quaternären Stickstoffgruppen ist, wobei das Verhältnis von Polymer zu nichtionischem Tensid 0,1:1 oder weniger ist und
- c) 0,005 bis 5 Gew.-% eines kationischen Tensids.

2. Zusammensetzung nach Anspruch 1, wobei das Polymer ein Polymer von Acrylsäure oder Methacrylsäure oder Maleinsäureanhydrid oder ein Copolymer von einem oder mehreren dieser miteinander oder mit anderen Monomeren ist.

3. Zusammensetzung nach Anspruch 2, wobei das Polymer ausgewählt ist aus der Gruppe enthaltend Polyacrylsäure, Polymaleinsäureanhydrid und Copolymere der erwähnten mit Ethylen, Styrol und Methylvinylether.

4. Zusammensetzung nach Anspruch 1, wobei die kationischen Tenside ein Material der allgemeinen Formel $R_1R_2R_3R_4N^+X^-$ sind, wobei alle Reste Kohlenwasserstoffe mit oder ohne Hydroxysubstitution sind, mindestens einer der Reste R_1 bis R_4 ein C_6 - C_{22} -Alkyl-, Alkaryl- oder Hydroxyalkylrest ist, mindestens einer der Reste R_1 bis R_4 ein C_1 - C_4 -Alkyl- oder Hydroxyalkylrest ist und X ein einwertiges anionisches Äquivalent ist.

5. Zusammensetzung nach Anspruch 4, worin R_1 und R_2 gleiche oder verschiedene C_1 - C_4 -Alkyl- oder Hydroxyalkylreste sind, R_3 ein C_6 - C_{22} -Alkyl-, Alkaryl- oder Hydroxyalkylrest ist, R_4 ein C_1 - C_{22} -Alkyl-, Alkaryl- oder Hydroxyalkylrest ist und X ein einwertiges anionisches Äquivalent ist.

6. Zusammensetzung nach Anspruch 5, wobei R_1 und R_2 Methylreste sind, R_3 ein C_8 - C_{18} -Alkylrest ist und R_4 ein Methyl-, C_8 - C_{18} -Alkyl- oder Benzylrest ist.

7. Zusammensetzung nach einem der Ansprüche 1 bis 6, die weiterhin ein Metallionen bindendes Mittel enthält.

8. Zusammensetzung nach einem der Ansprüche 1 bis 7, wobei der pH-Wert 7 bis 12 ist.

9. Reinigungszusammensetzung für harte Oberflächen mit einem pH-Wert von 7 bis 11, die enthält:

- a) 5 bis 20 Gew.-% eines ethoxylierten nichtionischen 2-15 EO, C_8 - C_{18} -Alkoholtensids,
- b) weniger als 1 Gew.-% anionische Tenside,
- c) 0,2 bis 2 Gew.-% eines wasserlöslichen anionischen Polymers mit einem mittleren Molekulargewicht von mehr als 100.000 und weniger als 1.000.000, wobei das Polymer ein Polymer ist aus mindestens einem der Monomere Acrylsäure, Methacrylsäure oder Maleinsäureanhydrid, mit mindestens einem der Monomere Acrylsäure, Methacrylsäure, Maleinsäureanhydrid, Ethylen, Styrol und Methylvinylether, wobei das Verhältnis von Polymer zu nichtionischem Tensid 0,1:1 oder weniger ist,
- d) 0,05 bis 2 Gew.-% eines kationischen Tensids, das eine quaternäre Stickstoffverbindung der allgemeinen Formel $R_1R_2R_3R_4N^+X^-$ ist, worin R_1 und R_2 gleiche oder verschiedene C_1 - C_4 -Alkyl- oder Hydroxyalkylreste sind, R_3 ein C_6 - C_{22} -Alkyl-, Alkaryl- oder Hydroxyalkylrest ist, R_4 ein C_1 - C_{22} -Alkyl-, Alkaryl- oder Hydroxyalkylrest ist und X ein einwertiges anionisches Äquivalent ist und
- e) nicht mehr als 2% eines Lösungsmittels ausgewählt aus der Gruppe umfassend Diethylenglycolmono-n-butylether, Monoethylenglycolmono-n-butylether, Propylenglycol-n-butylether und Mischungen davon.

10. Verfahren zur Reinigung von harten Oberflächen, das die Stufe umfasst, dass die Oberfläche mit einer Reinigungszusammensetzung nach einem der Ansprüche 1 bis 9 behandelt wird.

11. Verwendung von 0,005 bis 5 Gew.-% eines wasserlöslichen anionischen Polymers mit einem mittleren Molekulargewicht von mehr als 100.000 und weniger als 1.000.000 in einer Reinigungszusammensetzung für harte Oberflächen mit 1 bis 30 Gew.-% eines nichtionischen Tensids und 0,005 bis 5 Gew.-% eines antimikrobiellen kationischen Tensids, wobei das Polymer frei von quaternären Stickstoffgruppen ist und das Verhältnis von Polymer zu nichtionischem Tensid 0,1:1 oder weniger ist, um die antimikrobielle Wirksamkeit des antimikrobiellen kationischen Tensids auf der harten Oberfläche zu verlängern.

Revendications

1. Composition nettoyante pour les surfaces dures ayant un pH de 3 à 12 et comprenant :

- a) de 1 à 30 % en poids de tensioactif non ionique ;
- b) de 0,005 à 5 % en poids d'un polymère anionique soluble dans l'eau ayant une masse moléculaire moyenne supérieure à 100.000 et inférieure à 1.000.000, ledit polymère ne contenant pas de groupes azotes quaternaires, dans lequel le rapport entre le polymère et le non ionique est de 0,1 pour 1 ou inférieur ; et
- c) de 0,005 à 5 % en poids d'un tensioactif cationique.

2. Composition selon la revendication 1, dans laquelle le polymère est un polymère d'acide acrylique ou d'acide méthacrylique ou d'anhydride maléique, ou un copolymère d'un ou de plusieurs de ceux-ci, soit ensembles, soit avec d'autres monomères.

3. Composition selon la revendication 2, dans laquelle le polymère est sélectionné à partir du groupe comprenant l'acide polyacrylique, l'anhydride polymaléique et les copolymères de l'un ou l'autre de ceux mentionnés précédemment avec de l'éthylène, du styrène et du méthyle vinyle éther.

4. Composition selon la revendication 1, dans laquelle le tensioactif cationique est un matériau de formule générale $R_1R_2R_3R_4N^+X^-$, dans laquelle tous les radicaux sont des hydrocarbures avec ou sans substitution hydroxy, au moins l'un des radicaux $R_1 - R_4$ est un alkyle, un alkaryle ou un hydroxyalkyle en $C_6 - C_{22}$, au moins l'un des radicaux $R_1 - R_4$ est un alkyle ou un hydroxyalkyle en $C_1 - C_4$, et X est un équivalent d'un anion monovalent.

5. Composition selon la revendication 4, dans laquelle R_1 et R_2 sont un alkyle ou un hydroxyalkyle en $C_1 - C_4$ identiques ou différents, R_3 est un alkyle, un alkaryle ou un hydroxyalkyle en $C_6 - C_{22}$, R_4 est un alkyle, un alkaryle ou un hydroxyalkyle en $C_1 - C_{22}$, et X est un équivalent d'un anion monovalent.

6. Composition selon la revendication 5, dans laquelle R_1 et R_2 sont méthyle, R_3 est un alkyle en $C_8 - C_{18}$ et R_4 est un méthyle, un benzyle ou un alkyle en $C_8 - C_{18}$.

7. Composition selon les revendications 1 - 6 comprenant en outre un agent de liaison des ions métaux.

8. Composition selon les revendications 1 - 7, dans laquelle le pH est de 7 à 12.

9. Composition nettoyante pour les surfaces dures ayant un pH de 7 à 11, comprenant :

- a) de 5 à 20 % en poids d'un tensioactif non ionique éthoxylé 2 - 15 EO, alcool en $C_8 - C_{18}$;
- b) moins de 1 % en poids de tensioactifs anioniques ;
- c) de 0,2 à 2 % en poids d'un polymère anionique soluble dans l'eau ayant une masse moléculaire supérieure à 100.000 et inférieure à 1.000.000, ledit polymère étant un polymère d'au moins parmi l'acide acrylique, l'acide méthacrylique ou l'anhydride maléique, avec au moins un parmi l'acide acrylique, l'acide méthacrylique, l'anhydride maléique, l'éthylène, le styrène et le méthyle vinyle éther, dans lequel le rapport entre le polymère et le non ionique est de 0,1 pour 1 ou inférieur.
- d) de 0,05 à 2 % en poids d'un tensioactif cationique qui est un composé azote quaternaire ayant la formule générale $R_1R_2R_3R_4N^+X^-$, dans laquelle R_1 et R_2 sont un alkyle ou un hydroxyalkyle en $C_1 - C_4$ identique ou différent, R_3 est un alkyle, un alkaryle ou un hydroxyalkyle en $C_6 - C_{22}$, R_4 est un alkyle, un alkaryle ou un hydroxyalkyle en $C_1 - C_{22}$ et X est un équivalent d'un anion monovalent ; et
- e) pas plus de 2 % d'un solvant sélectionné à partir du groupe constitué du mono n-butyle éther de di-éthylène glycol, du mono n-butyle éther de mono-éthylène glycol, du n-butyle éther de propylène glycol et des mélanges de ceux-ci.

10. Procédé de nettoyage des surfaces dures comprenant l'étape consistant à traiter la surface avec une composition nettoyante selon l'une quelconque des revendications 1 - 9.

11. Utilisation, dans une composition nettoyante pour les surfaces dures comprenant de 1 à 30 % en poids d'un tensioactif non ionique et de 0,005 à 5 % en poids d'un tensioactif cationique antimicrobien, de 0,005 à 5 % en poids d'un polymère anionique soluble dans l'eau ayant une masse moléculaire moyenne supérieure à 100.000 et inférieure à 1.000.000, ledit polymère ne contenant pas de groupes azotes quaternaires et le rapport entre le polymère

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et le non ionique étant de 0,01 pour 1 ou inférieur, afin de prolonger l'efficacité antimicrobienne du tensioactif cationique antimicrobien sur ladite surface dure.

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