

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
21 June 2007 (21.06.2007)

PCT

(10) International Publication Number
WO 2007/068939 A1

(51) International Patent Classification:

C11D 17/00 (2006.01) *B82B 3/00* (2006.01)
C11D 7/20 (2006.01) *B05D 5/08* (2006.01)
C11D 3/12 (2006.01) *B08B 17/06* (2006.01)
C11D 3/37 (2006.01)

(21) International Application Number:

PCT/GB2006/004692

(22) International Filing Date:

14 December 2006 (14.12.2006)

(25) Filing Language:

English

(26) Publication Language:

English

(30) Priority Data:

0525714.2 17 December 2005 (17.12.2005) GB

(71) Applicant (for all designated States except US):
RECKITT BENCKISER (UK) LIMITED [GB/GB];
103-105 Bath Road, Slough, Berkshire SL1 3UH (GB).

(72) Inventors; and

(75) Inventors/Applicants (for US only): **CHADWICK, Madeleine** [GB/GB]; c/o Reckitt Benckiser Corporate Services Limited, Dansom Lane, Hull HU8 7DS (GB).
KULKE, Torsten [DE/GB]; c/o Reckitt Benckiser Corporate Services Limited, Dansom Lane, Hull HU8 7DS (GB).

(74) Agents: **BOWERS, Craig, M.** et al.; Legal Department, Patents Group, Reckitt Benckiser plc, Dansom Lane, Hull HU8 7DS (GB).

(81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LV, LY, MA, MD, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RS, RU, SC, SD, SE, SG, SK, SL, SM, SV, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

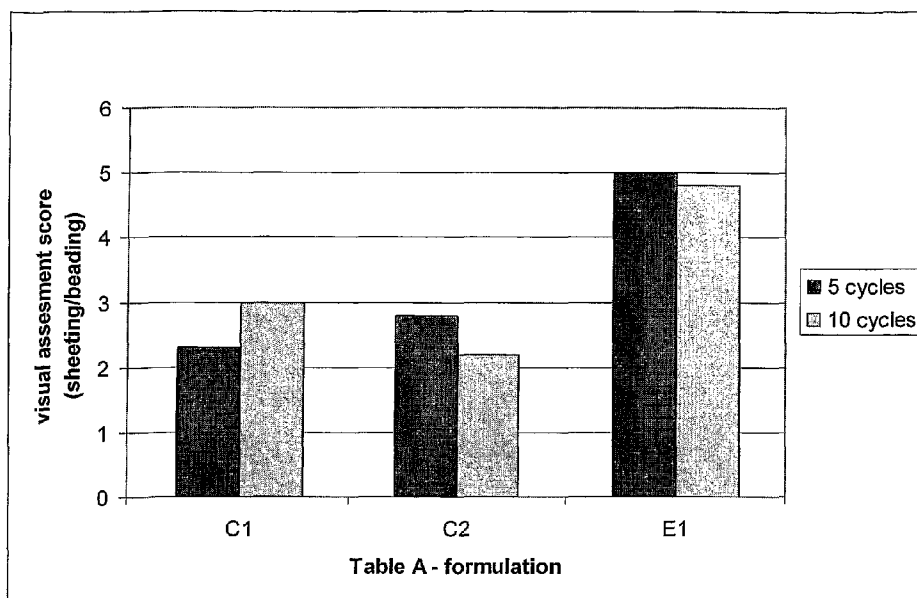
(84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IS, IT, LT, LU, LV, MC, NL, PL, PT, RO, SE, SI, SK, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:

— with international search report

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: LIQUID HARD SURFACE TREATMENT COMPOSITIONS AND METHODS FOR CLEANING



(57) Abstract: A liquid composition for treating a surface, said composition comprising a hydrophilic polymer and inorganic nanoparticles, wherein the hydrophilic polymer is a nitrogen-containing polymer having surface-modifying properties.

WO 2007/068939 A1

5

**LIQUID HARD SURFACE TREATMENT COMPOSITIONS
AND METHODS FOR CLEANING**

The present invention generally relates to a liquid composition for treating a hard surface. In particular, the present invention relates to a liquid composition for preventing or reducing the formation of deposits, such as hard water, soil, grime or lime scale deposits, on a hard surface, and to improved methods for the cleaning of hard surfaces.

Hard surface cleaning compositions are well known. Such compositions are used to remove grime and lime scale deposits from hard surfaces. Although conventional cleaners are generally effective at removing such deposits from hard surfaces, they are less effective at providing the surface with a long-lasting clean appearance. For example, when the cleaned surface is subsequently wetted with water, the water tends to form a film on the hard surface, which eventually breaks into streaks and droplets. When these streaks and droplets of water dry, they leave unappealing residues on the surface. The problem is particularly acute with bathroom and kitchen surfaces, which routinely come into contact with water. It is therefore desirable to prevent or reduce the formation of these streak- and drop-like residues.

US 2005/0239674 describes a hard surface cleaning composition comprising a colloidal silica sol. The cleaning composition may be used to alter the wetting characteristics of a hard surface, so that it can be wetted uniformly. Accordingly, water tends to form a film on the treated surface, which dries uniformly without the formation of streak or drop residues.

According to a first aspect of the present invention, there is provided a liquid composition for treating a surface, said composition comprising a hydrophilic polymer and inorganic nanoparticles, wherein the hydrophilic polymer is a nitrogen-containing polymer having surface-modifying properties.

The composition of the present invention may be used to clean or coat a surface. In one embodiment, the composition of the present invention may be used to treat a surface, such as a hard surface, after cleaning.

According to a second aspect of the present invention there is provided a process for
5 the cleaning of a hard surface wherein the composition of the first aspect of the invention is applied to a hard surface.

According to a third aspect of the invention there is provided a process for successive cleaning of a hard surface which process contemplates the sequential or intermittent application of a composition according to the first aspect of the invention to a hard surface,
10 whereby an improved cleaning benefit is provided.

It has been found that the composition of the present invention may be used to provide a surface with improved wetting characteristics. In particular, the composition may be used to reduce or prevent the formation of deposits, such as hard water, soil, grime or limescale deposits, on a hard surface. It is believed that the composition of the present
15 invention modifies the surface properties of the treated surface. As a result, water forms a substantially continuous or uniform film on the treated surface, which dries evenly, so as to reduce or avoid the formation of streak or droplet residues known as drying marks on the surface.

Without wishing to be bound by any theory, the hydrophilic polymer and inorganic
20 nanoparticles are believed to work synergistically to provide the improved wetting characteristics. In other words, the combined effect of the hydrophilic polymer and inorganic nanoparticles is greater than would be expected from the effects achieved with each of these components separately. In a preferred embodiment, synergistic amounts of hydrophilic polymer and nanoparticles are employed, so as to ensure that the combined effect of the
25 hydrophilic polymer and inorganic nanoparticles is appreciably greater than would be expected from the effects achieved with each of these components separately.

It has also been found that repeated applications of the cleaning composition of the present invention provides for an improved cleaning benefit when the composition is applied sequentially to a hard surface, or when the composition is applied at intermittent intervals to

a hard surface. It is believed that that following at least an initial application of the inventive composition to a hard surface, that subsequent cleaning of said hard surface is improved, e.g., may be easier to clean and/or, require less of cleaning composition to obtain a satisfactory degree of cleaning than if the composition of the invention had not been previously applied.

5 This is referred to as a “next time cleaning” benefit.

As mentioned above, the composition of the present invention comprises inorganic nanoparticles. The nanoparticles may have a mean particle size of from 1 to 100 nm, preferably 2 to 50 nm, more preferably 4 to 40 nm, even more preferably 5 to 25 nm, for example 6 to 15 nm.

10 The composition may comprise 0.05 to 10 weight % inorganic nanoparticles. Preferably, the composition comprises 0.1 to 5 weight % of the nanoparticles, more preferably 0.25 to 3 weight %, for example about 0.5 weight %.

The nanoparticles may be nanoparticles comprising pure or mixed inorganic oxides. Suitable inorganic oxides include silica, magnesia, alumina and titania. Mixtures of two or
15 more of such oxides may be employed. Mixed oxides, such as aluminasilicates, may also be used. Preferably, the nanoparticles include silica and/or titania. The inorganic oxides may be amorphous.

The nanoparticles may be employed in the form of a colloidal dispersion, for example, as a colloidal sol.

20 Preferably, a colloidal nanoparticulate silica sol is employed. One example of a silica sol which is suitable for use in the context of this invention is the silica sol which is obtainable from Akzo under the trade name Bindzil® CC30 . Further suitable silica sols are for example Bindzil® 15/500, 30/220, 30/360, 40/200 and 257/360 (Akzo); Nyacol®251, 830, 1430 and 2034DI; Nyacol® DP5820, DP5480 and DP5540; Levasil® 100/30, 100F/30,
25 100S/30, 200/30, 200F/30, VP 4038 and VP 4055 (H.C. Starck/Bayer); CAB-O-SPERSE® PG 001 and PG 002 (aqueous dispersions of CAB-O-SIL®, Cabot); Quartron PL-1 and PL-3 (FusoChemical Co.); and Köstrosol 0830, 1030 and 1430 (Chemiewerk Bad Köstritz).

The silica sols used may also be surface-modified silica. For example, the sols may be treated with sodium aluminate (alumina-modified silica).

Nanoparticles that are particularly useful for the present invention are those that are capable of increasing the average micro-roughness of a surface. Microroughness is a parameter known to those skilled in the art and is measurable, for example, by atomic force microscopy (AFM). It refers to the deviation in distance from an ideal smooth surface and is measured in μm or nm . Nanoparticles that are particularly useful for the present invention are those that are capable of increasing the average micro-roughness of a surface by from at least 5 nm to at most 100 nm, preferably from at least 10 nm to at most 30 nm.

Suitable colloidal sols are described in US 2005/0239674, the contents of which are hereby incorporated by reference.

The composition of the present invention includes a nitrogen-containing hydrophilic polymer having surface-modifying properties. Homopolymers and/or copolymers may be employed. The hydrophilic polymer is preferably charged. Preferably, the hydrophilic polymer has a permanent cationic charge or is capable of forming a permanent cationic charge on protonation.

The average molecular weight of the hydrophilic polymer typically ranges from about 5,000 to about 10,000,000. The molecular weight is preferably selected so that the polymer is water soluble or water dispersible to at least 0.01% , preferably up to 1% and even more preferably up to 10% by weight in distilled water at 25°C.

The composition may comprise 0.05 to 10 weight % of the hydrophilic polymer. Preferably, the composition comprises 0.1 to 5 weight % of the hydrophilic polymer, more preferably 0.25 to 3 weight %, for example 1 weight %.

Suitable hydrophilic polymers are described in US 6,926,745, the contents of which are hereby incorporated by reference. Examples of suitable polymers include the polymers and copolymers of N,N dimethyl acrylamide, acrylamide and certain monomers containing quaternary ammonium groups or amphoteric groups that favour substantivity to surfaces, along with co-monomers that favour adsorption of water, such as, for example, acrylic acid and other acrylate salts, sulfonates, betaines and ethylene oxides.

In one embodiment, the hydrophilic polymer is (a) a water soluble or water dispersible polymer formed from:

(i) a first nitrogen-containing monomer that has a permanent cationic charge or that is capable of forming a cationic charge on protonation.

The hydrophilic polymer may be a copolymer that is formed by copolymerising the (i) first nitrogen-containing monomer with (ii) either a second monomer that is acidic and capable of forming an anionic charge, or a (iii) third monomer that has an uncharged hydrophilic group; and (iiii) optionally, a fourth monomer that is hydrophobic.

With respect to the synthesis of the water soluble or water dispersible copolymer, the level of the first monomer, which has a permanent cationic charge or that is capable of forming a cationic charge on protonation, is typically between 3 and 80 mol% and preferably 10 to 60 mol% of the copolymer.

The level of second monomer, which is an acidic monomer that is capable of forming an anionic charge, when present, is typically between 3 and 80 mol% and preferably 10 to 60 mol% of the copolymer.

The level of the third monomer, which has an uncharged hydrophilic group, when present, is typically between 3 and 80 mol% and preferably 10 to 60 mol% of the copolymer.

When present, the level of uncharged hydrophobic monomer is less than about 50 mol% and preferably less than 10 mol% of the copolymer.

The molar ratio of the first monomer to the second monomer typically ranges from 9:1 to 1:6. The molar ratio of the first monomer to the third monomer is typically ranges from 4:1 to 1:4 and preferably ranges from 2:1 to 1:2.

Examples of permanently cationic monomers include, but are not limited to, quaternary ammonium salts of substituted acrylamide, methacrylamide, acrylate and methacrylate, such as trimethylammoniummethacrylate, trimethylammoniumpropylmethacrylamide, trimethylammoniummethacrylate, trimethylammoniumpropylacrylamide, 2-vinyl N-alkyl quaternary pyridinium, 4-vinyl N-alkyl quaternary pyridinium, 4-vinylbenzyltrialkylammonium, 2-vinyl piperidinium, 4-vinyl piperidinium, 3-alkyl 1-vinyl imidazolium, diallyldimethylammonium, and the ionene class of internal cationic monomers as described by D.R. Berger in *Cationic Surfactants, Organic Chemistry*, edited by J.M. Richmond, Marcel Dekker, New York, 1990, ISBN 0-8247-8381-

6. This class includes co-poly ethylene imine, co-poly ethoxylated ethylene imine and co-poly quaternized ethoxylated ethylene imine, co-poly [(dimethylimino) trimethylene (dimethylimino) hexamethylene disalt], co-poly [(diethylimino) trimethylene (dimethylimino) trimethylene disalt], co-poly [(dimethylimino) 2-hydroxypropyl salt], co-polyquaternium-2, co-polyquaternium-17, and co-polyquaternium-18, as described in the International Cosmetic Ingredient Dictionary, 5th Edition, edited by J.A. Wenninger and G.N. McEwan. Other cationic monomers include those containing cationic sulfonium salts such as co-poly-1-[3-methyl-4-(vinyl-benzyloxy)phenyl] tetrahydrothiophenium chloride. Especially preferred monomers are mono- and di-quaternary derivatives of methacrylamide.

10 The counterion of the cationic co-monomer can be selected from, for example, chloride, bromide, iodide, hydroxide, phosphate, sulphate, hydrosulfate, ethyl sulphate, methyl sulphate, formate, and acetate.

Examples of monomers that are cationic on protonation include, but are not limited to, acrylamide N,N-dimethylacrylamide, N,N di-isopropylacrylamide, N-vinylimidazole, N-vinylpyrrolidone, ethyleneimine, dimethylaminohydroxypropyl diethylenetriamine, dimethylaminoethylmethacrylate, dimethylaminopropylmethacrylamide, dimethylaminoethylacrylate, dimethylaminopropylacrylamide, 2-vinyl pyridine, 4-vinyl pyridine, 2-vinyl piperidine, 4-vinylpiperidine, vinyl amine, diallylamine, methylallylamine, vinyl oxazolidone; vinyl methoxazolidone, and vinyl caprolactam.

20 Monomers that are cationic on protonation typically contain a positive charge over a portion of the pH range of 2-11. Such suitable monomers are also presented in *Water-Soluble Synthetic Polymers; Properties and Behaviour*, Volume II, by P. Molyneux, CRC Press, Boca Raton, 1983, ISBN 0-8493-6136. Additional monomers can be found in the *International Cosmetic Ingredient Dictionary*, 5th Edition, edited by J.A. Wenninger and G. N. McEwan, The Cosmetic, Toiletry, and Fragrance Association, Washington D.C., 1993, ISBN 1-882621-06-9. A third source of such monomers can be found in *Encyclopedia of Polymers and Thickeners for Cosmetics*, by R. Y. Lochhead and W. R. Fron, Cosmetics and Toiletries, vol. 108, May 1993, pp 95-135.

Examples of acidic monomers that are capable of forming an anionic charge include, but are not limited to, acrylic acid, methacrylic acid, ethacrylic acid, dimethylacrylic acid, maleic anhydride, succinic anhydride, vinylsulfonate, cyanoacrylic, methylenemalonic acid, vinylacetic acid, allylacetic acid, ethylideneacetic acid, propylideneacetic acid, crotonic acid, fumaric acid, itaconic acid, sorbic acid, angelic acid, cinnamic acid, styrylacrylic acid, citraconic acid, glutaconic acid, aconitic acid, phenylacrylic acid, acryloxypropionic acid, citraconic acid, vinylbenzoic acid, N-vinylsuccinamidic acid, mesaconic acid, methacroylalanine, acryloylhydroxyglycine, sulfoethylmethacrylate, sulfopropyl acrylate, and sulfoethyl acrylate. Preferred acid monomers also include styrenesulfonic acid, 2-methacryloyloxymethane-1-sulfonic acid, 3-methacryloyloxypropane-1-sulfonic acid, 3-(vinylxy)propane-1-sulfonic acid, ethylenesulfonic acid, vinyl sulphuric acid, 4-vinylphenyl sulphuric acid, ethylene phosphonic acid and vinyl phosphoric acid. Most preferred monomers include acrylic acid, methacrylic acid and maleic acid. The copolymers useful in this invention may contain the above acidic monomers and the alkali metal, alkaline earth metal, and ammonium salts thereof.

Examples of monomers having an uncharged hydrophilic group include but are not limited to vinyl alcohol, vinyl acetate, vinyl methyl ether, vinyl ethyl ether, ethylene oxide and propylene oxide. Especially preferred are hydrophilic esters of monomers, such as hydroxyalkyl acrylate esters, alcohol ethoxylate esters, alkylpolyglycoside esters, and polyethylene glycol esters of acrylic and methacrylic acid.

Finally, examples of uncharged hydrophobic monomers include, but are not limited to, C₁-C₄ alkyl esters of acrylic acid and methacrylic acid.

The copolymers are formed by copolymerizing the desired monomers. Conventional polymerization techniques can be employed. Illustrative techniques include, for examples, solution, suspension, dispersion, or emulsion polymerization. A preferred method of preparation is by precipitation or inverse suspension polymerization of the copolymer from a polymerization media in which the monomers are dispersed in a suitable solvent. The monomers employed in preparing the copolymer are preferably water soluble and sufficiently

soluble in the polymerization media to form a homogeneous solution. They readily undergo polymerization to form polymers which are water-dispersible or water-soluble.

The preferred copolymers contain acrylamide, methacrylamide and substituted acrylamides and methacrylamides, acrylic and methacrylic acid and esters thereof. Suitable synthetic methods for these copolymers are described, for example, in Kirk-Othmer, 5 *Encyclopedia of Chemical Technology*, Volume 1, Fourth Ed., John Wiley & Sons.

Suitable hydrophilic polymers are also described in WO 2005/073357, the contents of which are hereby incorporated by reference. Accordingly, the hydrophilic polymer may be obtainable by the reaction of (Aa) polyalkylene polyamines, polyamidoamines, 10 polyamidoamines grafted by ethyleneimine, polyetheramines and mixtures thereof, (Ab) optionally at least bifunctional crosslinkers comprising at least one functional group selected from halogen, halogenhydride, glycidyl, aziridine and isocyanate, and (Ac) monoethylenically unsaturated carboxylic acids, salts, esters, amides or nitriles of monoethylenically unsaturated carboxylic acids, chlorocarboxylic acids and/or glycidyl 15 compounds.

A preferred polymer is sold under the trademark, Sokalan HP 70 (BASF).

Suitable hydrophilic polymers are also described in US-B-6,664,218, the contents of which are hereby incorporated by reference. The polymer is preferably a quaternized ammonium acrylamide/acrylic acid copolymer, such as a diallyl dimethyl ammonium 20 acrylamide/acrylic acid copolymer.

The composition may comprise 0.05 to 10 weight % of the hydrophilic polymer. Preferably, the composition comprises 0.1 to 5 weight % of the hydrophilic polymer, more preferably 0.25 to 3 weight %, for example 1 weight %.

The weight ratio of hydrophilic polymer to nanoparticles may be 0.1 to 20. 25 Preferably, the weight ratio is 0.3 to 5, more preferably 0.5 to 2.

The composition of the present invention may be a cleaning composition, for example, a hard surface cleaning composition. Accordingly, the composition of the present invention may additionally include at least one surfactant. Surfactant(s) may be present in an amount of 0.01 to 10 weight %, preferably 0.01 to 5 weight %, for example, 0.5 to 3 weight

% Of course, the use of two or more surfactants, as well as mixtures of different surfactants may be used.

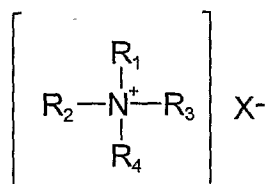
Cationic, anionic, non-ionic and/or amphoteric surfactants may be employed.

However, in certain embodiments, anionic surfactants may be excluded or their amount used reduced from the composition, as their negative charge may interfere with any cationic charges on the hydrophilic polymer. Non-ionic, cationic and/or amphoteric surfactants are preferred. Non-ionic surfactants are particularly preferred.

Examples of cationic surfactants include those of the quaternary ammonium type.

Cationic surfactants may be used in an amount of 0.01 - 5%wt., preferably in amounts from about 0.1 - 3.5%wt., but are most desirably present in reduced weight percentages from about 0.5 - 2.5%wt. based on the total weight of the composition.

Suitable cationic surfactants have the general structural formula:

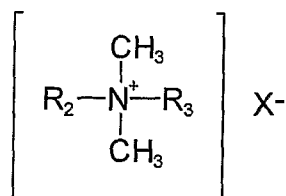


where at least one of R_1 , R_2 , R_3 and R_4 is an alkyl, aryl or alkylaryl substituent of from 6 to 26 carbon atoms, and the entire cation portion of the molecule has a molecular weight of at least 165. The alkyl substituents may be alkyl, alkoxyaryl, alkylaryl, halogen-substituted alkylaryl, alkyphenoxyalkyl, arylalkyl, etc. The remaining substituents on the nitrogen atoms other than the above mentioned alkyl substituents are hydrocarbons usually containing no more than 12 carbon atoms. The substituents R_1 , R_2 , R_3 and R_4 may be straight-chained or may be branched, but are preferably straight-chained, and may include one or more amide, ether or ester linkages. The counterion X may be any salt-forming anion which permits water solubility of the quaternary ammonium complex.

Exemplary quaternary ammonium salts include the alkyl ammonium halides such as cetyl trimethyl ammonium bromide, alkyl aryl ammonium halides such as octadecyl dimethyl benyl ammonium bromide, N-alkyl pyridinium halides such as N-cetyl pyridinium bromide, and the like. Other suitable types of quaternary ammonium salts include those in

which the molecule contains either amide, ether or ester linkages such as octyl phenoxy ethoxy ethyl dimethyl benzyl ammonium chloride, N-(laurylcocoaminoformylmethyl)-pyridinium chloride, and the like. Other very effective types of quaternary ammonium compounds include those in which the hydrophobic radical is characterized by a substituted aromatic nucleus as in the case of lauryloxyphenyltrimethyl ammonium chloride, 5 cetylaminophenyltrimethyl ammonium methosulfate, dodecylphenyltrimethyl ammonium methosulfate, dodecylphenyltrimethyl ammonium chloride, chlorinated dodecylbenzyltrimethyl ammonium chloride, and the like.

Preferred quaternary ammonium compounds include those which have the structural 10 formula:



wherein R₂ and R₃ are the same or different C₈-C₁₂ alkyl, or R₂ is C₁₂₋₁₆ alkyl, C₈₋₁₈ alkylethoxy, C₈₋₁₈ alkylphenoxyethoxy and R is benzyl, and X is a halide, for example chloride, bromide or iodide, or is a methosulfate or saccharinate anion. The alkyl groups 15 recited in R₂ and R₃ may be straight-chained or branched, but are preferably substantially linear.

The cationic surfactant may have antimicrobial or germicidal properties, and in certain preferred embodiments the cationic surfactant includes antimicrobial or germicidal properties.

20 Particularly useful quaternary ammonium compounds include compositions which include a single quaternary compound, as well as mixtures of two or more different quaternary compounds. Such useful quaternary compounds are available under the BARDAC®, BARQUAT®, HYAMINE®, CATIGENE®, LONZABAC®, BTC®, and ONYXIDE® trademarks, which are more fully described in, for example, McCutcheon's 25 Functional Materials, North American and International Editions, 2001, and the respective product literature from the suppliers identified below. For example, BARDAC® 205M is

described to be a liquid containing alkyl dimethyl benzyl ammonium chloride, octyl decyl dimethyl ammonium chloride; didecyl dimethyl ammonium chloride, and dioctyl dimethyl ammonium chloride (50% active) (also available as 60% active (BARDAC® 208M)); described generally in McCutcheon's as a combination of alkyl dimethyl benzyl ammonium chloride and dialkyl dimethyl ammonium chloride); BARDAC® 2050 is described to be a combination of octyl decyl dimethyl ammonium chloride and didecyl dimethyl ammonium chloride, and dioctyl dimethyl ammonium chloride (50% active) (also available as 80% active (BARDAC® 2080)); BARDAC® 2250 is described to be didecyl dimethyl ammonium chloride (50% active); BARDAC® LF (or BARDAC® LF-80), described as being based on dioctyl dimethyl ammonium chloride (BARQUAT® MB-50, MX-50, OJ-50 (each 50% liquid) and MB-80 or MX-80 (each 80% liquid) are each described as an alkyl dimethyl benzyl ammonium chloride; BARDAC® 4250 and BARQUAT® 4260Z (each 50% active) or BARQUAT® 4280 and BARQUAT® 4280Z (each 80% active) are each described as alkyl dimethyl benzyl ammonium chloride/alkyl dimethyl ethyl benzyl ammonium chloride; and BARQUAT® MS-i 00 described as being a mixture of tetradecyl dimethyl benzyl ammonium chloride/dodecyl dimethyl benzyl ammonium chloride/hexadecyl dimethyl benzyl ammonium chloride (100% solid (powder)). Also, HYAMINE® 1622, described as diisobutyl phenoxy ethoxy ethyl dimethyl benzyl ammonium chloride (available either as 100% active or as a 50% active solution); HYAMINE® 3500 (50% active), described as alkyl dimethyl benzyl ammonium chloride (also available as 80% active (HYAMINE® 3500-80)); and HYAMINE® 2389 described as being based on methyl dodecyl benzyl ammonium chloride and/or methyl dodecyl ammonium chloride. (BARDAC®, BARQUAT® and HYAMINE® are presently commercially available from Lonza, Inc., Fairlawn, NJ). BTC® 50 NF (or BIG® 65 NF) is described to be alkyl dimethyl benzyl ammonium chloride (50% active); BIG® 99 is described as didecyl dimethyl ammonium chloride (50% active); BTG® 776 is described to be myristalkonium chloride (50% active); SIC® 818 is described as being octyl decyl dimethyl ammonium chloride, didecyl dimethyl ammonium chloride, and dioctyl dimethyl ammonium chloride (50% active) (available also as 80% active (BTC® 818-80%)); BTC® 824 and BTC® 835 are each described as being of alkyl dimethyl benzyl

ammonium chloride (each 50% active); BTC® 885 is described as a combination of BIG® 835 and BTC® 818 (50% active) (available also as 80% active (BTC® 888)); BIG® 1010 is described as didecyl dimethyl ammonium chloride (50% active) (also available as 80% active (BTC® 1010-80)); BTC® 2125 (or BTC® 2125 M) is described as alkyl dimethyl benzyl ammonium chloride and alkyl dimethyl ethylbenzyl ammonium chloride (each 50% active) (also available as 80% active (BTC® 2125-80 or BIG® 2125 Ni)); BTC® 2565 is described as alkyl dimethyl benzyl ammonium chlorides (50% active) (also available as 80% active (SIC® 2568)); BTC® 8248 (or BTC® 8358) is described as alkyl dimethyl benzyl ammonium chloride (80% active) (also available as 90% active (BIG® 8249)); ONYXIDE® 3300 is described as n 25 alkyl dimethyl benzyl ammonium saccharinate (95% active). GATIGENE series is described as mixtures of alkyl dimethyl benzyl ammonium chlorides/alkyl dimethyl ethyl benzyl ammonium chlorides/dialkyl dimethyl ammonium chlorides. (BTC®, ONYXIDE®, and CATIGENE are presently commercially available from Stepan Company, Northfield, IL (CATIGENE from Stepan Europe)). Polymeric quaternary ammonium salts based on these monomeric structures are also considered desirable for the present invention. One example is POLYQUAT®, described as being a 2- butenyldimethyl ammonium chloride polymer.

Examples of anionic surfactants which may be used in the anionic surfactant constituent include alcohol sulfates and sulfonates, alcohol phosphates and phosphonates, alkyl ester sulfates, alkyl diphenyl ether sulfonates, alkyl sulfates, alkyl ether sulfates, sulfate esters of an alkylphenoxy polyoxyethylene ethanol, alkyl monoglyceride sulfates, alkyl sulfonates, alkyl ether sulfates, alpha-olefin sulfonates, beta-alkoxy alkane sulfonates, alkyl ether sulfates, ethoxylated alkyl sulfonates, alkylaryl sulfonates, alkylaryl sulfates, alkyl monoglyceride sulfonates, alkyl carboxylates, alkyl ether carboxylates, alkyl alkoxy carboxylates having 1 to 5 moles of ethylene oxide, alkylpolyglycoethersulfates (containing up to 10 moles of ethylene oxide), sulfosuccinates, octoxynol or nonoxynol phosphates, taurates, fatty taurides, fatty acid amide polyoxyethylene sulfates, acyl glycerol sulfonates, fatty oleyl glycerol sulfates, alkyl phenol ethylene oxide ether sulfates, paraffin sulfonates, alkyl phosphates, isethionates, N-acyl taurates, alkyl succinamates and sulfosuccinates,

alkylpolysaccharide sulfates, alkylpolyglucoside sulfates, alkyl polyethoxy carboxylates, and sarcosinates or mixtures thereof. These anionic surfactants may be provided as salts with one or more organic counterions, e.g, ammonium, or inorganic counterions, especially as salts of one or more alkaline earth or alkaline earth metals, e.g, sodium.

5 Further examples of anionic surfactants include water soluble salts or acids of the formula $(\text{ROSO}_3)_x\text{M}$ or $(\text{RSO}_3)_x\text{M}$ wherein R is preferably a $\text{C}_6\text{-C}_{24}$ hydrocarbyl, preferably an alkyl or hydroxyalkyl having a $\text{C}_{10}\text{-C}_{20}$ alkyl component, more preferably a $\text{C}_{12}\text{-C}_{18}$ alkyl or hydroxyalkyl, and M is H or a mono-, di- or tri-valent cation, e. g., an alkali metal cation (e. g., sodium, potassium, lithium), or ammonium or substituted ammonium (e. g., methyl-,
10 dimethyl-, and trimethyl ammonium cations and quaternary ammonium cations, such as tetramethyl-ammonium and dimethyl piperdinium cations and quaternary ammonium cations derived from alkylamines such as ethylamine, diethylamine, triethylamine, and mixtures thereof, and the like) and x is an integer, preferably 1 to 3, most preferably 1. Materials sold under the Hostapur and Biosoft trademarks are examples of such anionic surfactants.

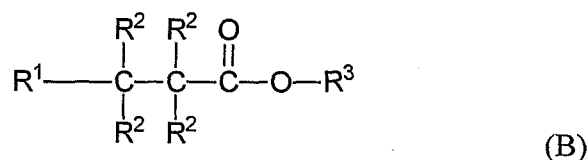
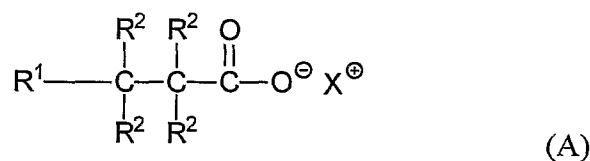
15 Still further examples of anionic surfactants include alkyl-diphenyl-ethersulphonates and alkyl-carboxylates.

Also useful in the anionic surfactant constituent are diphenyl disulfonates, and salt forms thereof, such as a sodium salt of diphenyl disulfonate commercially available as DOWFAX 3B2.

20 Other anionic surfactants can include salts (including, for example, sodium, potassium, ammonium, and substituted ammonium salts such as mono-, di- and triethanolamine salts) of soap, $\text{C}_6\text{-C}_{20}$ linear alkylbenzenesulfonates, $\text{C}_6\text{-C}_{22}$ primary or secondary alkanesulfonates, $\text{C}_6\text{-C}_{24}$ olefinsulfonates, sulfonated polycarboxylic acids prepared by sulfonation of the pyrolyzed product of alkaline earth metal citrates, $\text{C}_6\text{-C}_{24}$
25 alkylpolyglycoethersulfates, alkyl ester sulfates such as C_{14-16} methyl ester sulfates; acyl glycerol sulfonates, fatty oleyl glycerol sulfates, alkyl phenol ethylene oxide ether sulfates, paraffin sulfonates, alkyl phosphates, isethionates such as the acyl isethionates, N-acyl taurates, alkyl succinamates and sulfosuccinates, monoesters of sulfosuccinate (especially saturated and unsaturated $\text{C}_{12}\text{-C}_{18}$ monoesters) diesters of sulfosuccinate (especially saturated

and unsaturated C₆-C₁₄ diesters), acyl sarcosinates, sulfates of alkylpolysaccharides such as the sulfates of alkylpolyglucoside, branched primary alkyl sulfates, alkyl polyethoxy carboxylates such as those of the formula RO(CH₂CH₂O)_kCH₂COO⁻M⁺ wherein R is a C₈-C₂₂ alkyl, k is an integer from 0 to 10, and M is a soluble salt-forming cation. Examples of the foregoing anionic surfactants are available under the following tradenames: RHODAPON, STEPANOL, HOSTAPUR, SURFINE, SANDOPAN, NEODOX, BIOSOFT, and AVANEL.

Preferred anionic surfactant compounds useful in the compositions of the present invention include alphasulpho esters and/or salts thereof. Such anionic surfactants may be represented by the following general structures:



15

wherein, in each of the foregoing:

R¹ represents a C₆ - C₂₂ alkyl or alkenyl group;

each of R² is either hydrogen, or if not hydrogen is a SO₃⁻ having associated with it a cation, X⁺, which renders the compound water soluble or water dispersible, with X preferably being an alkali metal or alkaline earth metal especially sodium or potassium, especially sodium, with the proviso that at least one R², preferably at least two R² is a (SO₃⁻) having an associated cation X⁺, and,

R³ represents a C₁-C₆, preferably C₁-C₄ lower alkyl or alkenyl group, especially methyl.

The one or more anionic surfactants, when present, may be present in amounts of from about 0.01 - 5%wt., preferably in amounts from about 0.1 - 3.5%wt., but are most

desirably present in reduced weight percentages from about 0.2 – 1%wt. based on the total weight of the composition of which they form a part.

One class of exemplary useful nonionic surfactants are polyethylene oxide condensates of alkyl phenols. These compounds include the condensation products of alkyl phenols having an alkyl group containing from about 6 to 12 carbon atoms in either a straight chain or branched chain configuration with ethylene oxide, the ethylene oxide being present in an amount equal to 5 to 25 moles of ethylene oxide per mole of alkyl phenol. The alkyl substituent in such compounds can be derived, for example, from polymerized propylene, diisobutylene and the like. Examples of compounds of this type include nonyl phenol condensed with about 9.5 moles of ethylene oxide per mole of nonyl phenol; dodecylphenol condensed with about 12 moles of ethylene oxide per mole of phenol; dinonyl phenol condensed with about 15 moles of ethylene oxide per mole of phenol and diisooctyl phenol condensed with about 15 moles of ethylene oxide per mole of phenol.

Further useful nonionic surfactants include the condensation products of aliphatic alcohols with from about 1 to about 60 moles of ethylene oxide. The alkyl chain of the aliphatic alcohol can either be straight or branched, primary or secondary, and generally contains from about 8 to about 22 carbon atoms. Examples of such ethoxylated alcohols include the condensation product of myristyl alcohol condensed with about 10 moles of ethylene oxide per mole of alcohol and the condensation product of about 9 moles of ethylene oxide with coconut alcohol (a mixture of fatty alcohols with alkyl chains varying in length from about 10 to 14 carbon atoms). Other examples are those C₆-C₁₁ straight-chain alcohols which are ethoxylated with from about 3 to about 6 moles of ethylene oxide. Their derivation is well known in the art. Examples include Alfonic® 810-4.5 (also available as Teric G9A5), which is described in product literature from Sasol as a C₈₋₁₀ having an average molecular weight of 356, an ethylene oxide content of about 4.85 moles (about 60 wt.%), and an HLB of about 12; Alfonic® 810-2, which is described in product literature from Sasol as a C₈₋₁₀ having an average molecular weight of 242, an ethylene oxide content of about 2.1 moles (about 40 wt.%), and an HLB of about 12; and Alfonic® 610-3.5, which is described in product literature from Sasol as having an average molecular weight of 276, an ethylene

oxide content of about 3.1 moles (about 50 wt.%), and an HLB of 10. Product literature from Sasol also identifies that the numbers in the alcohol ethoxylate name designate the carbon chain length (numbers before the hyphen) and the average moles of ethylene oxide (numbers after the hyphen) in the product.

5 Further exemplary useful nonionic surfactants include alcohol ethoxylates including C₁₀ oxo -alcohol ethoxylates available from BASF under the Lutensol ON tradename. They are available in grades containing from about 3 to about 11 moles of ethylene oxide (available under the names Lutensol ON 30; Lutensol ON 50; Lutensol ON 60; Lutensol ON 65; Lutensol ON 66; Lutensol ON 70; Lutensol ON 80; and Lutensol ON 110). Yet further
10 examples of ethoxylated alcohols include the Neodol® 91 series non-ionic surfactants available from Shell Chemical Company which are described as C₉-C₁₁ ethoxylated alcohols. The Neodol® 91 series non-ionic surfactants of interest include Neodol 91-2.5, Neodol 91-6, and Neodol 91-8. Neodol 91-2.5 has been described as having about 2.5 ethoxy groups per molecule; Neodol 91-6 has been described as having about 6 ethoxy groups per molecule;
15 and Neodol 91-8 has been described as having about 8 ethoxy groups per molecule. Still further examples of ethoxylated alcohols include the Rhodasurf® DA series non-ionic surfactants available from Rhodia which are described to be branched isodecyl alcohol ethoxylates. Rhodasurf DA-530 has been described as having 4 moles of ethoxylation and an HLB of 10.5; Rhodasurf DA-630 has been described as having 6 moles of ethoxylation with
20 an HLB of 12.5; and Rhodasurf DA-639 is a 90% solution of DA-630.

Further examples of ethoxylated alcohols include those from Tomah Products (Milton, WI) under the Tomadol tradename with the formula RO(CH₂CH₂O)_nH where R is the primary linear alcohol and n is the total number of moles of ethylene oxide. The ethoxylated alcohol series from Tomah include 91-2.5; 91-6; 91-8 - where R is linear
25 C₉/C₁₀/C₁₁ and n is 2.5, 6, or 8; 1-3; 1-5; 1-7; 1-73B; 1-9; - where R is linear C₁₁ and n is 3, 5, 7 or 9; 23-1; 23-3; 23-5; 23-6.5 - where R is linear C₁₂/C₁₃ and n is 1, 3, 5, or 6.5; 25-3; 25-7; 25-9; 25-12 - where R is linear C₁₂/C₁₃ C₁₄/ C₁₅ and n is 3, 7, 9, or 12; and 45-7; 45-13 - where R is linear C₁₄/ C₁₅ and n is 7 or 13.

Other examples of nonionic surfactants include primary and secondary linear and branched alcohol ethoxylates, such as those based on C₆-C₁₈ alcohols which further include an average of from 2 to 80 moles of ethoxylation per mol of alcohol. These examples include the Genapol UD series from Clariant, described as tradenames Genapol UD 030, C₁₁-Oxo-alcohol polyglycol ether with 3 EO; Genapol UD, 050 C₁₁-Oxo-alcohol polyglycol ether with 5 EO; Genapol UD 070, C₁₁-Oxo-alcohol polyglycol ether with 7 EO; Genapol UD 080, C₁₁-Oxo-alcohol polyglycol ether with 8 EO; Genapol UD 088, C₁₁-Oxo-alcohol polyglycol ether with 8 EO; and Genapol UD 110, C₁₁-Oxo-alcohol polyglycol ether with 11 EO.

Other examples of useful nonionic surfactants include those having a formula RO(CH₂CH₂O)_nH wherein R is a mixture of linear, even carbon-number hydrocarbon chains ranging from C₁₂H₂₅ to C₁₆H₃₃ and n represents the number of repeating units and is a number of from about 1 to about 12. Surfactants of this formula are presently marketed under the Genapol® tradename. available from Clariant, Charlotte, N.C., include the 26-L series of the general formula RO(CH₂CH₂O)_nH wherein R is a mixture of linear, even carbon-number hydrocarbon chains ranging from C₁₂H₂₅ to C₁₆H₃₃ and n represents the number of repeating units and is a number of from 1 to about 12, such as 26-L-1, 26-L-1.6, 26-L-2, 26-L-3, 26-L-5, 26-L-45, 26-L-50, 26-L-60, 26-L-60N, 26-L-75, 26-L-80, 26-L-98N, and the 24-L series, derived from synthetic sources and typically contain about 55% C₁₂ and 45% C₁₄ alcohols, such as 24-L-3, 24-L-45, 24-L-50, 24-L-60, 24-L-60N, 24-L-75, 24-L-92, and 24-L-98N. From product literature, the single number following the "L" corresponds to the average degree of ethoxylation (numbers between 1 and 5) and the two digit number following the letter "L" corresponds to the cloud point in °C of a 1.0 wt.% solution in water.

A further class of nonionic surfactants which are contemplated to be useful include those based on alkoxy block copolymers, and in particular, compounds based on ethoxy/propoxy block copolymers. Polymeric alkylene oxide block copolymers include nonionic surfactants in which the major portion of the molecule is made up of block polymeric C₂-C₄ alkylene oxides. Such nonionic surfactants, while preferably built up from an alkylene oxide chain starting group, and can have as a starting nucleus almost any active

hydrogen containing group including, without limitation, amides, phenols, thiols and secondary alcohols.

One group of such useful nonionic surfactants containing the characteristic alkylene oxide blocks are those which may be generally represented by the formula (A):

5



where EO represents ethylene oxide,

PO represents propylene oxide,

10

y equals at least 15,

(EO)_{x+y} equals 20 to 50% of the total weight of said compounds, and, the total molecular weight is preferably in the range of about 2000 to 15,000. These surfactants are available under the PLURONIC tradename from BASF or Emulgen from Kao.

15

Another group of nonionic surfactants appropriate for use in the new compositions can be represented by the formula (B):



20

wherein R is an alkyl, aryl or aralkyl group, where the R group contains 1 to 20 carbon atoms, the weight percent of EO is within the range of 0 to 45% in one of the blocks a, b, and within the range of 60 to 100% in the other of the blocks a, b, and the total number of moles of combined EO and PO is in the range of 6 to 125 moles, with 1 to 50 moles in the PO rich block and 5 to 100 moles in the EO rich block.

25

Further nonionic surfactants which in general are encompassed by Formula B include butoxy derivatives of propylene oxide/ethylene oxide block polymers having molecular weights within the range of about 2000-5000.

Still further useful nonionic surfactants containing polymeric butoxy (BO) groups can be represented by formula (C) as follows:



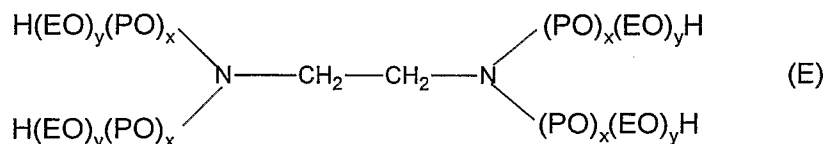
wherein R is an alkyl group containing 1 to 20 carbon atoms,
n is about 5-15 and x is about 5-15.

5 Also useful as the nonionic block copolymer surfactants, which also include polymeric butoxy groups, are those which may be represented by the following formula (D):



10 wherein n is about 5-15, preferably about 15,
x is about 5-15, preferably about 15, and
y is about 5-15, preferably about 15.

Still further useful nonionic block copolymer surfactants include ethoxylated derivatives of propoxylated ethylene diamine, which may be represented by the following
15 formula:



where (EO) represents ethoxy,

(PO) represents propoxy,

20 the amount of (PO)_x is such as to provide a molecular weight prior to ethoxylation of about 300 to 7500, and the amount of (EO)_y is such as to provide about 20% to 90% of the total weight of said compound.

The inventive compositions may also include a nonionic amine oxide constituent.

Exemplary amine oxides include:

25 (A) Alkyl di (lower alkyl) amine oxides in which the alkyl group has about 10-20, and preferably 12-16 carbon atoms, and can be straight or branched chain, saturated or

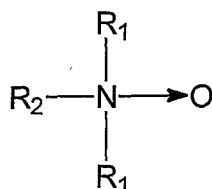
unsaturated. The lower alkyl groups include between 1 and 7 carbon atoms. Examples include lauryl dimethyl amine oxide, myristyl dimethyl amine oxide, and those in which the alkyl group is a mixture of different amine oxide, dimethyl cocoamine oxide, dimethyl (hydrogenated tallow) amine oxide, and myristyl/palmityl dimethyl amine oxide;

5 (B) Alkyl di (hydroxy lower alkyl) amine oxides in which the alkyl group has about 10-20, and preferably 12-16 carbon atoms, and can be straight or branched chain, saturated or unsaturated. Examples are bis(2-hydroxyethyl) cocoamine oxide, bis(2-hydroxyethyl) tallowamine oxide; and bis(2-hydroxyethyl) stearylamine oxide;

10 (C) Alkylamidopropyl di(lower alkyl) amine oxides in which the alkyl group has about 10-20, and preferably 12-16 carbon atoms, and can be straight or branched chain, saturated or unsaturated. Examples are cocoamidopropyl dimethyl amine oxide and tallowamidopropyl dimethyl amine oxide; and

15 (D) Alkylmorpholine oxides in which the alkyl group has about 10-20, and preferably 12-16 carbon atoms, and can be straight or branched chain, saturated or unsaturated.

Preferably the amine oxide constituent is an alkyl di (lower alkyl) amine oxide as denoted above and which may be represented by the following structure:



wherein each:

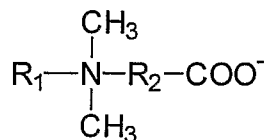
20 R_1 is a straight chained C_1 - C_4 alkyl group, preferably both R_1 are methyl groups; and, R_2 is a straight chained C_8 - C_{18} alkyl group, preferably is C_{10} - C_{14} alkyl group, most preferably is a C_{12} alkyl group.

Each of the alkyl groups may be linear or branched, but most preferably are linear. Technical grade mixtures of two or more amine oxides may be used, wherein amine oxides of varying chains of the R_2 group are present. Further and preferred exemplary amine oxides
25 include: alkyl di(C_1 - C_7) amine oxides in which the alkyl group has about 10-20, and

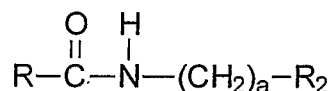
preferably 12-16 carbon atoms, and can be straight or branched chain, saturated or unsaturated. Examples of such compounds include lauryl dimethyl amine oxide, myristyl dimethyl amine oxide, and those in which the alkyl group is a mixture of different amine oxide, dimethyl cocoamine oxide, dimethyl (hydrogenated tallow) amine oxide, and myristyl/palmityl dimethyl amine oxide; alkyl di(hydroxy C₁-C₇) amine oxides in which the alkyl group has about 10-20, and preferably 12-16 carbon atoms, and can be straight or branched chain, saturated or unsaturated. Examples of such compounds include bis(2-hydroxyethyl) cocoamine oxide, bis(2-hydroxyethyl) tallowamine oxide; and bis(2-hydroxyethyl) stearylamine oxide; alkylamidopropyl di(C₁-C₇) amine oxides in which the alkyl group has about 10-20, and preferably 12-16 carbon atoms, and can be straight or branched chain, saturated or unsaturated. Examples of such compounds include cocoamidopropyl dimethyl amine oxide and tallowamidopropyl dimethyl amine oxide; and alkylmorpholine oxides in which the alkyl group has about 10-20, and preferably 12-16 carbon atoms, and can be straight or branched chain, saturated or unsaturated.

The one or more nonionic surfactants, when present, may be present in amounts of from about 0.01 - 5%wt., preferably in amounts from about 0.1 - 3.5%wt., but are most desirably present in reduced weight percentages from about 0.2 - 1%wt. based on the total weight of the composition of which they form a part.

Betaine surfactants may also be used as amphoteric surfactants. The betaine surfactant may be represented by the general formula:



wherein R₁ is an alkyl group containing from 8 to 18 carbon atoms, or the amido radical which may be represented by the following general formula:

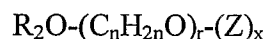


wherein R is an alkyl group having from 8 to 18 carbon atoms, a is an integer having a value of from 1 to 4 inclusive, and R₂ is a C₁-C₄ alkylene group. Examples of such water-soluble betaine surfactants include dodecyl dimethyl betaine, as well as cocoamidopropylbetaine.

The one or more amphoteric surfactants, when present, may be present in amounts of
 5 from about 0.01 - 5%wt., preferably in amounts from about 0.1 – 3.5%wt., but are most desirably present in reduced weight percentages from about 0.5 – 2.5%wt. based on the total weight of the composition of which they form a part.

Further classes of surfactants which are contemplated as being useful include
 10 alkylmonoglycosides and alkylpolyglycosides which include known nonionic surfactants which are alkaline and electrolyte stable. Alkylmonoglycosides and alkylpolyglycosides are prepared generally by reacting a monosaccharide, or a compound hydrolyzable to a monosaccharide with an alcohol such as a fatty alcohol in an acid medium. Various glycoside and polyglycoside compounds including alkoxyated glycosides and processes for making
 15 3,772,269; 3,839,318; 3,974,138; 4,223,129 and 4,528,106 the contents of each which are incorporated by reference.

One exemplary group of such useful alkylpolyglycosides include those according to the formula:



20 wherein:

R₂ is a hydrophobic group selected from alkyl groups, alkylphenyl groups, hydroxyalkylphenyl groups as well as mixtures thereof, wherein the alkyl groups may be straight chained or branched, and which contain from about 8 to about 18 carbon atoms, n has a value of 2 – 8, especially a value of 2 or 3; r is an integer from 0 to 10, but is
 25 preferably 0, Z is derived from glucose; and, x is a value from about 1 to 8, preferably from about 1.5 to 5. Preferably the alkylpolyglycosides are nonionic fatty alkylpolyglucosides which contain a straight chain or branched chain C₈-C₁₅ alkyl group, and have an average of from about 1 to 5 glucose units per fatty alkylpolyglucoside molecule. More preferably, the nonionic fatty alkylpolyglucosides which contain straight chain or branched C₈-C₁₅ alkyl

group, and have an average of from about 1 to about 2 glucose units per fatty alkylpolyglucoside molecule. Exemplary useful include, for example APG 325 CS Glycoside® which is described as being a 50% C₉-C₁₁ alkyl polyglycoside, also commonly referred to as D-glucopyranoside, (commercially available from Henkel KGaA) and
5 Glucopon® 625 CS which is described as being a 50% C₁₀-C₁₆ alkyl polyglycoside, also commonly referred to as a D-glucopyranoside, (ex. Henkel).

The one or more surfactants based on alkylmonoglycosides and alkylpolyglycosides, when present, may be present in amounts of from about 0.01 - 5%wt., preferably in amounts from about 0.1 - 3.5%wt., but are most desirably present in reduced weight percentages from
10 about 0.5 - 2.5%wt. based on the total weight of the composition of which they form a part.

Preferably the total amount of surfactants which may be present in the compositions of the invention does not exceed 20%wt, and in increasing order of preference, does not exceed; 19%wt., 18%wt., 17%wt., 16%wt., 15%wt., 14%wt., 13%wt., 12%wt., 11%wt., 10%wt., 9%wt., 8%wt., 7.5%wt., 7%wt., 6.5%wt., 6%wt., 5.5%wt., 5%wt., 4.5%wt., 4%wt.,
15 3.5%wt., 3%wt., and 2.5%wt. based on the total weight of the compositions of which they form a part. Preferably, if present in the compositions, the total weight of the surfactants in the composition is at least 0.01%wt., and in increasing order of preference; 0.02%wt., 0.05%wt., 0.075%wt., 0.1%wt., 0.15%wt., 0.2%wt. and 0.25%wt. based on the total weight of the compositions of which they form a part.

20 The compositions may optionally contain one or more organic solvents. Exemplary useful organic solvents which may be present in the inventive compositions include those which are at least partially water-miscible such as alcohols (e.g., low molecular weight alcohols, such as, for example, ethanol, propanol, isopropanol, and the like), glycols (such as, for example, ethylene glycol, propylene glycol, hexylene glycol, and the like), water-miscible
25 ethers (e.g. diethylene glycol diethylether, diethylene glycol dimethylether, propylene glycol dimethylether), water-miscible glycol ether (e.g. propylene glycol monomethylether, propylene glycol mono ethylether, propylene glycol monopropylether, propylene glycol monobutylether, ethylene glycol monobutylether, dipropylene glycol monomethylether, diethyleneglycol monobutylether), lower esters of monoalkylethers of ethylene glycol or

propylene glycol (e.g. propylene glycol monomethyl ether acetate), and mixtures thereof. Glycol ethers having the general structure Ra-Rb-OH, wherein Ra is an alkoxy of 1 to 20 carbon atoms, or aryloxy of at least 6 carbon atoms, and Rb is an ether condensate of propylene glycol and/or ethylene glycol having from one to ten glycol monomer units.

5 Mixtures of two or more specific organic solvents may be used, or alternately a single organic solvent may be provided as the organic solvent constituent. When present, of the foregoing classes of organic solvents, one or more glycol ethers or monohydric alcohols, especially C₁-C₄ alcohols are preferably used. When present, such organic solvent(s) may be present in amounts of up to about 10%wt, more preferably in amounts to about 5%wt., more
10 preferably are present amount of up to about 3%wt., still more preferably in amounts of at least 0.001%wt. to about 2%wt., and yet more preferably are present in amounts of from about 0.01 – 1.2%wt. When present, the organic solvents are preferably present in amounts of at 0.05%wt., more preferably at least 0.075%wt., and still more preferably in amounts of at least 0.1%wt, based on the total weight of the composition of which it forms a part.

15 The compositions of the invention may include an alkanolamine, preferably selected from monoalkanolamines, dialkanolamines, trialkanolamines of 1 to 7 carbons in length, preferably is a single monoalkanolamine selected from linear monoethanolamine, monopropanolamine or monobutanolamine, and when present, the alkanolamine is especially preferably is monoethanolamine. Mixtures of two or more alkanolamines may also be used.
20 When present, such alkanolamines may provide or impart alkalinity to the compositions of which they form a part, and they may be present in any effective amount in order to achieve a desired pH level in the inventive compositions. Advantageously the alkanolamine, when present is included in amounts of up to about 3%wt, still more preferably in amounts of at least 0.001%wt. to about 2%wt., and yet more preferably are present in amounts of from
25 about 0.01 – 1.2%wt. When present, the alkanolamine is are preferably present in amounts of at 0.05%wt., more preferably at least 0.1%wt., yet more preferably in amounts of at least 0.2%wt., and still more preferably in amounts of at least 0.25%wt, based on the total weight of the composition of which it forms a part.

The compositions of the invention may include a bleach constituent or an oxidizing constituent.

When present, the bleach constituent include those selected from alkali metal and alkaline earth salts of hypohalite, haloamines, haloimines, haloimides and haloamides. All of these are believed to produce hypohalous bleaching species in situ. Hypochlorite and compounds producing hypochlorite in aqueous solution are preferred, although hypobromite is also suitable. Representative hypochlorite-producing compounds include sodium, potassium, lithium and calcium hypochlorite, chlorinated trisodium phosphate dodecahydrate, potassium and sodium dichloroisocyanurate and trichlorocyanuric acid.

Organic bleach sources suitable for use include heterocyclic N-bromo and N-chloro imides such as trichlorocyanuric and tribromocyanuric acid, dibromo- and dichlorocyanuric acid, and potassium and sodium salts thereof, N-brominated and N-chlorinated succinimide, malonimide, phthalimide and naphthalimide. Also suitable are hydantoins, such as dibromo- and dichloro dimethylhydantoin, chlorobromodimethyl hydantoin, N-chlorosulfamide (haloamide) and chloramine (haloamine). Particularly preferred for use is sodium hypochlorite having the chemical formula NaOCl . The oxidizing constituent is preferably a peroxyhydrate or other agent which releases hydrogen peroxide in aqueous solution. Such materials are per se, known to the art. Such peroxyhydrates are to be understood as to encompass hydrogen peroxide as well as any material or compound which in an aqueous composition yields hydrogen peroxide. Examples of such materials and compounds include without limitation: alkali metal peroxides including sodium peroxide and potassium peroxide, alkali perborate monohydrates, alkali metal perborate tetrahydrates, alkali metal persulfate, alkali metal percarbonates, alkali metal peroxyhydrate, alkali metal peroxydihydrates, and alkali metal carbonates especially where such alkali metals are sodium or potassium. Further useful are various peroxydihydrate, and organic peroxyhydrates such as urea peroxide. When an oxidizing agent is present, especially where such is hydrogen peroxide, it may be advantageous to include a peroxide stabilizer which may be useful in improving the high temperature stability of the peroxide constituent, and of the compositions as well. Such a peroxide stabilizer may be one or more known art peroxide stabilizers

including, inter alia, one or more organic phosphonates, stannates, pyrophosphates. . Further known art peroxide stabilizers include 1-hydroxy-1,1-ethylidene diphosphonate commercially available as DEQUEST 2010 as well as further similar phosphonate compounds. By way of non-limiting example further useful peroxide stabilizers include:

5 amino tri (methylene-phosphonic acid) available as DEQUEST 2000 and DEQUEST 2000LC; amino tri (methylene-phosphonic acid) pentasodium salt available as DEQUEST 2006; 1-hydroxyethylene-1,1,-diphosphonic acid commercially available as DEQUEST 2010; 1-hydroxyethylene-1,1,-diphosphonic acid tetrasodium salt available as DEQUEST 2016 and DEQUEST 2016D; ethylene diamine tetra(methylene phosphonic acid) available as

10 DEQUEST 2041; ethylene diamine tetra(methylene phosphonic acid) pentasodium salt available as DEQUEST 2046; hexamethylenediamine tetra(methylene phosphonic acid) potassium salt available as DEQUEST 2054; diethylenetriamine penta(methylene phosphonic acid) available as DEQUEST 2060S; diethylenetriamine penta (methylenephosphonic acid) trisodium salt available as DEQUEST 2066A; diethylenetriamine penta

15 (methylenephosphonic acid) pentasodium salt available as DEQUEST 2066; diethylenetriamine penta(methylene phosphonic acid) pentasodium salt commercially available as DEQUEST 2066C2; bis-hexamethylene triaminepenta(methylenephosphonic acid) chloride salt commercially available as DEQUEST 2090A 2-phosphonobutane-1,2,4-tricarboxylic acid commercially available as DEQUEST 7000, tetrasodium salt of 1-hydroxy

20 ethylen (1, 1-diphosphonic acid) commercially available as DEQUEST SPE 9528, as well as other materials sold under the DEQUEST tradename, particularly DEQUEST 2086, DEQUEST 3000S, as well as DEQUEST 6004. Other known art compositions or compounds which provide a similar peroxide stabilizing effect may also be used.

When present, the oxidizing constituent, namely a bleach constituent or an oxidizing

25 constituent, is advantageously present in the inventive compositions in an amount of from about 0.01%wt. to about 10%wt., preferably from about 0.01 - 8%wt., more preferably present in an amount of 0.1 – 5%wt. and most preferably is present in an amount of about 0.5 - 5%wt. based on the total weight of the composition of which it forms a part.

When present concurrently with an oxidizing constituent, the peroxide stabilizer may be included in any effective amount. Generally amounts of from about 0.001 – 1.2%wt., preferably 0.01 – 0.5%wt. may be included in the inventive composition. Such amounts are to be considered in addition to the amount of the oxidizing constituent which is necessarily
5 concurrently present.

The compositions may optionally include one or more one or more further constituents useful in improving one or more aesthetic and/or technical characteristics of the compositions. Exemplary further optional constituents include colouring agents, fragrances and fragrance solubilizers, viscosity modifying agents including one or more thickeners, pH
10 adjusting agents and pH buffers including organic and inorganic salts, optical brighteners, opacifying agents, hydrotropes, abrasives, and preservatives, as well as other optional constituents providing improved technical or aesthetic characteristics known to the relevant art.

When present, the total amount of such one or more optional constituents present in the inventive compositions do not exceed about 10%wt., preferably do not exceed 5%wt.,
15 more preferably to not exceed 7.5%wt., yet more preferably do not exceed 5%wt., still more preferably do not exceed 2.5%wt., and yet more preferably do not exceed 2%wt, still more preferably do not exceed 1.5%wt., and most preferably do not exceed 1%wt., based on the total weight of the composition of which they form a part.

By way of non-limiting example pH adjusting agents include phosphorus containing compounds, monovalent and polyvalent salts such as of silicates, carbonates, and borates, certain acids and bases, tartrates and certain acetates. Further exemplary pH adjusting agents include mineral acids, basic compositions, and organic acids, which are typically required in only minor amounts. By way of further non-limiting example pH buffering compositions
25 include the alkali metal phosphates, polyphosphates, pyrophosphates, triphosphates, tetraphosphates, silicates, metasilicates, polysilicates, carbonates, hydroxides, and mixtures of the same. Certain salts, such as the alkaline earth phosphates, carbonates, hydroxides, can also function as buffers. It may also be suitable to use as buffers such materials as aluminosilicates (zeolites), borates, aluminates and certain organic materials such as

gluconates, succinates, maleates, and their alkali metal salts. When present, the pH adjusting agent, especially the pH buffers are present in an amount effective in order to maintain the pH of the inventive composition within a target pH range.

The compositions of the invention optionally but in certain cases desirably include a
5 fragrance constituent. Fragrance raw materials may be divided into three main groups: (1) the essential oils and products isolated from these oils; (2) products of animal origin; and (3) synthetic chemicals.

The essential oils consist of complex mixtures of volatile liquid and solid chemicals found in various parts of plants. Mention may be made of oils found in flowers, e.g., jasmine,
10 rose, mimosa, and orange blossom; flowers and leaves, e.g., lavender and rosemary; leaves and stems, e.g., geranium, patchouli, and petitgrain; barks, e.g., cinnamon; woods, e.g., sandalwood and rosewood; roots, e.g., angelica; rhizomes, e.g., ginger; fruits, e.g., orange, lemon, and bergamot; seeds, e.g., aniseed and nutmeg; and resinous exudations, e.g., myrrh. These essential oils consist of a complex mixture of chemicals, the major portion thereof
15 being terpenes, including hydrocarbons of the formula $(C_5H_8)_n$ and their oxygenated derivatives. Hydrocarbons such as these give rise to a large number of oxygenated derivatives, e.g., alcohols and their esters, aldehydes and ketones. Some of the more important of these are geraniol, citronellol and terpineol, citral and citronellal, and camphor. Other constituents include aliphatic aldehydes and also aromatic compounds including
20 phenols such as eugenol. In some instances, specific compounds may be isolated from the essential oils, usually by distillation in a commercially pure state, for example, geraniol and citronellal from citronella oil; citral from lemon-grass oil; eugenol from clove oil; linalool from rosewood oil; and safrole from sassafras oil. The natural isolates may also be chemically modified as in the case of citronellal to hydroxy citronellal, citral to ionone,
25 eugenol to vanillin, linalool to linalyl acetate, and safrol to heliotropin.

Animal products used in perfumes include musk, ambergris, civet and castoreum, and are generally provided as alcoholic tinctures.

The synthetic chemicals include not only the synthetically made, also naturally occurring isolates mentioned above, but also include their derivatives and compounds

unknown in nature, e.g., isoamylsalicylate, amylcinnamic aldehyde, cyclamen aldehyde, heliotropin, ionone, phenylethyl alcohol, terpineol, undecalactone, and gamma nonyl lactone.

Fragrance compositions as received from a supplier may be provided as an aqueous or organically solvated composition, and may include as a hydrotrope or emulsifier a surface-active agent, typically a surfactant, in minor amount. Such fragrance compositions are quite
5 usually proprietary blends of many different specific fragrance compounds. However, one of ordinary skill in the art, by routine experimentation, may easily determine whether such a proprietary fragrance composition is compatible in the compositions of the present invention.

One or more colouring agents may also be used in the inventive compositions in order
10 to impart a desired coloured appearance or coloured tint to the compositions. Known art water soluble or water dispersible pigments and dyes may be added in effective amounts.

The compositions may include a hydrotrope constituent comprising one or more compounds which exhibit a hydrotropic functionality in the inventive compositions. Exemplary hydrotropes include, *inter alia*, benzene sulfonates, naphthalene sulfonates, C₁-
15 C₁₁ alkyl benzene sulfonates, naphthalene sulfonates, C₅-C₁₁ alkyl sulfonates, C₆-C₁₁ alkyl sulfates, alkyl diphenyloxide disulfonates, and phosphate ester hydrotropes. The hydrotropic compounds of the invention are often provided in a salt form with a suitable counterion, such as one or more alkali, or alkali earth metals, such as sodium or potassium, especially sodium. However, other water soluble cations such as ammonium, mono-, di- and tri- lower
20 alkyl, i.e., C₁₋₄ alkanol ammonium groups can be used in the place of the alkali metal cations. Exemplary alkyl benzene sulfonates include, for example, isopropylbenzene sulfonates, xylene sulfonates, toluene sulfonates, cumene sulfonates, as well as mixtures thereof. Exemplary C₅-C₁₁ alkyl sulfonates include hexyl sulfonates, octyl sulfonates, and hexyl/octyl sulfonates, and mixtures thereof. Particularly useful hydrotrope compounds include benzene
25 sulfonates, o-toluene sulfonates, m-toluene sulfonates, and p-toluene sulfonates; 2,3-xylene sulfonates, 2,4-xylene sulfonates, and 4,6-xylene sulfonates; cumene sulfonates, wherein such exemplary hydrotropes are generally in a salt form thereof, including sodium and potassium salt forms. When present the hydrotrope constituent may be present in any

effective amounts, or they may be omitted. Advantageously, when present, the hydrotrope constituent comprises 0.001 – 1.5%wt. of the composition of which it forms a part.

A further optional constituent are one or more preservatives. Such preservatives are primarily included to reduce the growth of undesired microorganisms within the composition during storage prior to use. Exemplary useful preservatives include compositions which include parabens, including methyl parabens and ethyl parabens, glutaraldehyde, formaldehyde, 2-bromo-2-nitropropoane-1,3-diol, 5-chloro-2-methyl-4-isothiazolin-3-one, 2-methyl-4-isothiazoline-3-one, and mixtures thereof. One exemplary composition is a combination 5-chloro-2-methyl-4-isothiazolin-3-one and 2-methyl-4-isothiazolin-3-one where the amount of either component may be present in the mixture anywhere from 0.001 to 99.99 weight percent, based on the total amount of the preservative. Further exemplary useful preservatives include those which are commercially including a mixture of 5-chloro-2-methyl-4-isothiazolin-3-one and 2-methyl-4-isothiazolin-3-one marketed under the trademark KATHON® CG/ICP as a preservative composition presently commercially available from Rohm and Haas (Philadelphia, PA). Further useful and commercially available preservative compositions include KATHON® CG/ICP II, a further preservative composition presently commercially available from Rohm and Haas (Philadelphia, PA), PROXEL® which is presently commercially available from Zeneca Biocides (Wilmington, DE), SUTTOCID® A which is presently commercially available from Sutton Laboratories (Chatam, NJ) as well as TEXTAMER® 38AD which is presently commercially available from Calgon Corp. (Pittsburgh, PA). Certain cationic surfactants may also have anti-microbial properties. Examples of cationic surfactants are those of the quaternary ammonium type. (may be include specifics after consultation with Bob Hyde on quaternary surfactants/biocides)

Optionally one or more abrasives may be included in the inventive compositions. Exemplary abrasives include: oxides, e.g., calcined aluminum oxides and the like, carbonates, e.g., calcium carbonate and the like, quartzes, siliceous chalk, diatomaceous earth, colloidal silicon dioxide, alkali metasilicates, e.g., sodium metasilicate and the like, perlite, pumice, feldspar, calcium phosphate, organic abrasive materials based on comminuted or particulate polymers especially one or more of polyolefins, polyethylenes,

polypropylenes, polyesters, polystyrenes, acetonitrile-butadiene-styrene resins, melamines, polycarbonates, phenolic resins, epoxies and polyurethanes, natural materials such as, for example, rice hulls, corn cobs, and the like, or talc and mixtures thereof. The particle size of the abrasive agent typically may range from about 1 μm to about 1000 μm , preferably
5 between about 10 μm to about 200 μm , and more preferably between about 10 μm and about 100 μm . It is preferred to use those abrasive agents that will not scratch most hard surfaces. Such abrasive agents include calcium carbonate, siliceous chalk, diatomaceous earth, colloidal silicon dioxide, sodium metasilicate, talc, and organic abrasive materials. Calcium carbonate is preferred as being effective and available at a generally low cost. A single type
10 of abrasive, or a mixture of two or more differing abrasive materials may be used.

Optionally the compositions may include an effective amount of at least one inorganic chloride salt, which are believed to improve the metal cleaning characteristics of the inventive compositions. The inorganic chloride salt is desirably present in an amount effective to provide improved cleaning of metal surfaces which are immersed or contacted
15 with the inventive compositions. The inorganic chloride salt(s) used in the compositions of the present invention can be any water-soluble inorganic chloride salt or mixtures of such salts. For purposes of the present invention, "water-soluble" means having a solubility in water of at least 10 grams per hundred grams of water at 20° C. Examples of suitable salts include various alkali metal and/or alkaline earth metal chlorides including sodium chloride,
20 calcium chloride, magnesium chloride and zinc chloride. Particularly preferred are sodium chloride and calcium chloride which have been surprisingly observed to provide excellent metal cleaning efficacy particularly of aged copper surfaces. The inorganic chloride salt(s) is present in the compositions of the present invention in an amount which will provide an improved cleaning of metal surfaces, particularly copper surfaces, compared to an identical
25 composition which excludes the inorganic chloride salts(s). Preferably the inorganic chloride salt(s) are present in amounts of from about 0.00001 to about 2.5% by weight, desirably in amounts of 0.001 to about 2% by weight, yet more desirably from about 0.01 to about 1.5% by weight and most desirably from about 0.2 to about 1.5% weight. Particularly preferred inorganic chloride salt(s) and weight percentages thereof are described with reference to one

or more of the Examples. In certain preferred embodiments the sole inorganic salts present are one or more inorganic chloride salts.

The compositions may include a thickener constituent which may be added in any effective amount in order to increase the viscosity of the compositions. Exemplary thickeners useful in the thickener constituent include one or more of polysaccharide polymers selected from cellulose, alkyl celluloses, alkoxy celluloses, hydroxy alkyl celluloses, alkyl hydroxy alkyl celluloses, carboxy alkyl celluloses, carboxy alkyl hydroxy alkyl celluloses, naturally occurring polysaccharide polymers such as xanthan gum, guar gum, locust bean gum, tragacanth gum, or derivatives thereof, polycarboxylate polymers, polyacrylamides, clays, and mixtures thereof.

Examples of the cellulose derivatives include methyl cellulose ethyl cellulose, hydroxymethyl cellulose hydroxy ethyl cellulose, hydroxy propyl cellulose, carboxy methyl cellulose, carboxy methyl hydroxyethyl cellulose, hydroxypropyl cellulose, hydroxy propyl methyl cellulose, ethylhydroxymethyl cellulose and ethyl hydroxy ethyl cellulose.

Exemplary polycarboxylate polymers thickeners have a molecular weight from about 500,000 to about 4,000,000, preferably from about 1,000,000 to about 4,000,000, with, preferably, from about 0.5% to about 4% crosslinking. Preferred polycarboxylate polymers include polyacrylate polymers including those sold under trade names Carbopol®, Acrysol® ICS-1 and Sokalan®. The preferred polymers are polyacrylates. Other monomers besides acrylic acid can be used to form these polymers including such monomers as ethylene and propylene which act as diluents, and maleic anhydride which acts as a source of additional carboxylic groups.

Exemplary clay thickeners comprise, for example, colloid-forming clays, for example, such as smectite and attapulgite types of clay thickeners. The clay materials can be described as expandable layered clays, i.e., aluminosilicates and magnesium silicates. The term "expandable" as used to describe the instant clays relates to the ability of the layered clay structure to be swollen, or expanded, on contact with water. The expandable clays used herein are those materials classified geologically as smectites (or montmorillonite) and attapulgites (or polygorskites).

Preferred thickeners are those which provide a useful viscosity increasing benefit at the ultimate pH of the compositions, particularly thickeners which are useful at pH's of about 3 or less.

Wetting agents may optionally be included in the composition. Suitable wetting agents are characterized by an HLB value of 6-10, preferably 7-9. The one or more wetting agents are present in amounts of from about 0.01 - 5%wt., preferably in amounts from about 0.1 - 3.5%wt., but are most desirably present in reduced weight percentages from about 0.2 - 1%wt. based on the total weight of the composition of which they form a part.

As is noted above, the compositions according to the invention are largely aqueous in nature. Water is added to order to provide to 100% by weight of the compositions of the invention. The water may be tap water, but is preferably distilled and is most preferably deionized water. If the water is tap water, it is preferably substantially free of any undesirable impurities such as organics or inorganics, especially minerals salts which are present in hard water which may thus undesirably interfere with the operation of the constituents present in the aqueous compositions according to the invention. Preferably at least 70%wt, more preferably at least 75%wt of the compositions are water and in increasing order of preference: 73%wt., 74%wt., 75%wt., 76%wt., 77%wt., 78%wt., 79%wt., 80%wt., 81%wt., 82%wt., 83%wt., 84%wt., 85%wt., 86%wt., 87%wt., 88%wt., 89%wt., 90%wt., 91%wt., 92%wt., 93%wt., 94%wt., and 95%wt. are water.

While in certain embodiments the compositions may comprise a thicker constituent, it is generally preferred the compositions exhibit viscosities similar to that of water. The compositions preferably have a viscosity of not more than about 200 cps at room temperature; more preferably have a viscosity of not more than about 50 cps at room temperature.

The compositions according to the invention are advantageously provided as a ready to use product which may be directly applied to a hard surface. The compositions may be used as a cleaning composition or as a composition for treating hard surfaces, for example, after cleaning.

The composition may have a pH of from 1 to 14, preferably pH 1 to 6 or 8 to 12 and even more preferably pH 2 to 5 or 9 to 11.

Hard surfaces which are to be particularly denoted are lavatory fixtures, lavatory appliances (toilets, bidets, shower stalls, bathtubs and bathing appliances), wall and flooring surfaces especially those which include refractory materials and the like. Further hard surfaces which are particularly denoted are those associated with dishwashers, kitchen environments and other environments associated with food preparation. Hard surfaces which are those associated with hospital environments, medical laboratories and medical treatment environments. Such hard surfaces described above are to be understood as being recited by way of illustration and not by way of limitation.

The compositions may be packaged in any suitable container particularly flasks or bottles, including squeeze-type bottles, as well as bottles provided with a spray apparatus (e.g. trigger spray) which is used to dispense the composition by spraying. The compositions are readily pourable and readily pumpable cleaning compositions which features the benefits described above. Accordingly the compositions are desirably provided as a ready to use product in a manually operated spray dispensing container, or may be supplied in aerosolized product wherein it is discharged from a pressurized aerosol container. Propellants which may be used are well known and conventional in the art and include, for example, a hydrocarbon, of from 1 to 10 carbon atoms, such as n-propane, n-butane, isobutane, n-pentane, isopentane, and mixtures thereof; dimethyl ether and blends thereof as well as individual or mixtures of chloro-, chlorofluoro- and/or fluorohydrocarbons- and/or hydrochlorofluorocarbons (HCFCs). Useful commercially available compositions include A-70 (Aerosol compositions with a vapor pressure of 70 psig available from companies such as Diversified and Aeropress) and Dymel® 152a (1,1-difluoroethane from DuPont). Compressed gases such as carbon dioxide, compressed air, nitrogen, and possibly dense or supercritical fluids may also be used. In such an application, the composition is dispensed by activating the release nozzle of said aerosol type container onto the area in need of treatment, and in accordance with a manner as above-described the area is treated (e.g., cleaned and/or sanitized and/or disinfected). If a propellant is used, it will generally be in an amount of from about 1% to

about 50% of the aerosol formulation with preferred amounts being from about 2% to about 25%, more preferably from about 5% to about 15%. Generally speaking, the amount of a particular propellant employed should provide an internal pressure of from about 20 to about 150 psig at 70°F.

5 Preferably, the composition is adapted for being dispensed using a trigger spray. Alternately, preferably, the composition is adapted for being dispensed using a squeeze bottle through a nozzle.

The compositions according to the invention can also be suited for use in a consumer “spray and wipe” application as a cleaning composition. In such an application, the consumer
10 generally applies an effective amount of the composition using the pump and within a few moments thereafter, wipes off the treated area with a cloth, towel, or sponge, usually a disposable paper towel or sponge. In certain applications, however, especially where undesirable stain deposits are heavy, the cleaning composition according to the invention may be left on the stained area until it has effectively loosened the stain deposits after which
15 it may then be wiped off, rinsed off, or otherwise removed. For particularly heavy deposits of such undesired stains, multiple applications may also be used. Optionally, after the composition has remained on the surface for a period of time, it could be rinsed or wiped from the surface.

Whereas the compositions of the present invention are intended to be used in the
20 types of liquid forms described, nothing in this specification shall be understood as to limit the use of the composition according to the invention with a further amount of water to form a cleaning solution there from. In such a proposed diluted cleaning solution, the greater the proportion of water added to form said cleaning dilution will, the greater may be the reduction of the rate and/or efficacy of the thus formed cleaning solution. Accordingly,
25 longer residence times upon the stain to effect their loosening and/or the usage of greater amounts may be necessitated. Conversely, nothing in the specification shall be also understood to limit the forming of a “super-concentrated” cleaning composition based upon the composition described above. Such a super-concentrated ingredient composition is

essentially the same as the cleaning compositions described above except in that they include a lesser amount of water.

The composition of the present invention, whether as described herein or in a concentrate or super concentrate form, can also be applied to a hard surface by the use of a carrier substrate. One example of a useful carrier substrate is a wet wipe. The wipe can be of a woven or non-woven nature. Fabric substrates can include non-woven or woven pouches, sponges including both closed cell and open celled sponges, including sponges formed from celluloses as well as other polymeric material, as well as in the form of abrasive or non-abrasive cleaning pads. Such fabrics are known commercially in this field and are often referred to as wipes. Such substrates can be resin bonded, hydroentangled, thermally bonded, meltblown, needlepunched, or any combination of the former. The carrier substrate useful with the present inventive compositions may also be a wipe which includes a film forming substrate such as a water soluble polymer. Such self-supporting film substrates may be sandwiched between layers of fabric substrates and heat sealed to form a useful substrate.

The compositions of the present invention are advantageously absorbed onto the carrier substrate, i.e., a wipe to form a saturated wipe. The wipe can then be sealed individually in a pouch which can then be opened when needed or a multitude of wipes can be placed in a container for use on an as needed basis. The container, when closed, sufficiently sealed to prevent evaporation of any components from the compositions. In use, a wipe is removed from the container and then wiped across an area in need of treatment; in case of difficult to treat stains the wipe may be re-wiped across the area in need of treatment, or a plurality of saturated wipes may also be used.

Certain embodiments of the invention, including certain particularly preferred embodiments of the invention are disclosed in the following examples.

Examples

A number of formulations were produced by mixing the constituents outlined in Table 1 by adding the individual constituents into a beaker of deionized water at room temperature which was stirred with a conventional magnetic stirring rod. Stirring continued

until the formulation was homogenous in appearance. It is to be noted that the constituents might be added in any order. The exact compositions of the example formulations are listed on Table 1, below, and are identified by one or more digits preceded by the letter "E".

Certain comparative compositions are also disclosed on Table 1, and are identified by one or
5 more digits preceded by the letter "C".

	C1	C2	E1
Bindzil CC30	0.6	--	0.6
Sokalan HP 70	--	0.5	0.5
deionized water	q.s.	q.s.	q.s.

All of the formulations on the foregoing Table 1 are indicated in weight percent, and each composition comprised 100%wt. The individual constituents were used, "as-supplied"
10 from their respective source and unless otherwise indicated, each of the constituents are to be understood as being "100%wt. actives". Deionized water was added in quantum sufficient, "q.s.", to provide the balance to 100%wt. of each of the example compositions. The sources of the constituents used in the formulations of Tables 1 are described on the following Table
2.

15

Bindzil CC30	commercial silica sol preparation supplied as a liquid at a pH of 7 – 9 comprising modified amorphous colloidal silica (ex. Akzo)
Sokalan HP 70	commercial polymer preparation supplied as a liquid at pH of 5 comprising 40%wt. modified polyamine and 1-2 %wt. acrylic acid.polymer (ex. BASF)
deionized water	deionized water

Several of the foregoing compositions were tested and evaluated according to one or
20 more of the following test protocols.

Preparation of test tiles:

A series of glass mirror tiles, each measuring 15 by 15 cm were first cleaned with a suitable cleaner, rinsed with water, and then again rinsed with a volatile organic solvent,

isopropanol and then allowed to fully dry permitting the organic solvent to evaporate before being used in any test. Thereafter to the surface of each tile was applied 1 gram of one of the tested formulations according to Table 1, and the sample was allowed to dry. Subsequently the treated tiles were placed in a dishwasher (BOSCH LogiXX) and subjected to a specified number of wash/rinse cycle at 45°C for 30 minutes in the absence of any rinse aids or cleaning compositions. This was repeated 5 and 10 times. The purpose of this was to mimic the effect of sprayed water in a humid environment on the treated mirror tile surfaces.

Evaluation of sheeting ability:

The tiles were then fully submerged in a large beaker of deionised water and raised vertically. The sheeting/run off patterns on the tiles were assessed by five panellists. Scores were awarded based on a scale of from “0” to “5” depending on the appearance of the tile. Maximum scores, viz., “5” were assigned when the deionised water flowed off the tiles as a uniform sheet, with minimum or no observable streaking on the test tile, while minimum scores, viz., “0”, were assigned when beads or droplets of water appeared on the tested tile.

The averaged scores of the panelists for each of the tested tiles is reported on the following Table A:

Table A – visual assessment of treated tiles (sheeting/beading)			
	C1	C2	E1
5 wash wash/rinse cycles	2.3	2.8	5
10 wash wash/rinse cycles	3	2.2	4.8

The results of the scores of Table A are also shown on Figure 1. It can be seen that the test composition E1 illustrating a formulation of the invention demonstrates a surprising and significant improvement the compositions of comparative examples C1 and C2, indicating excellent sheeting action of the tiles treated with composition E1 according to the invention, notwithstanding that the tested tiles had been subjected to had been subjected to 0, 5 and 10 wash/rinse cycle which also suggests superior durability of the surface treatment imparted to the test tiles by composition E1.

Evaluation of surface durability:

The following formulations were produced in the manner described above and were applied to two different hard surfaces, tempered glass and ceramic hard surfaces. The tempered glass were 20 cm by 20 cm tempered glass tiles, while the ceramic were 15 cm by 15 cm black ceramic wall tiles.

Table 3			
	C3	C4	E2
Bindzil CC30	--	2	2
Sokalan HP 70	1.75	--	1.75
deionized water	q.s.	q.s.	q.s.

The individual constituents are as identified on Table 2, supra. Prior to testing, sample tiles of tempered glass and ceramic surfaces were first cleaned with a suitable commercial hard surface cleaner, rinsed with large amounts of deionized water to ensure full removal of the said hard surface cleaner, and then again rinsed with a volatile organic solvent, isopropanol or ethanol, and again rinsed with deionized water to ensure removal of the organic solvent. The cleaned tiles were placed into a rack where they were held in a vertical position and then allowed to fully dry permitting the organic solvent to evaporate before being used in any test. Thereafter to the surface of each sample tile was applied 1.5 grams of a sample formulation according to Table 3 when applied to a ceramic tile, and 3 grams of a sample formulation according to Table 3 when applied to a glass tile. After the application of said sample formulation, the surface of the sample tile was then wiped with an absorbent disposable paper towel in order to spread the applied sample formulation into a film lamina on the tile. Thereafter the formulation was allowed to dry. Subsequently the treated tiles were placed in a dishwasher (BOSCH LogiXX) and subjected to a specified number of wash/rinse cycle at 45°C for 30 minutes in the absence of any rinse aids or cleaning compositions. This was repeated 0, 5 and 10 times. The purpose of this was to mimic the effect of sprayed water in a humid environment on the treated surfaces of the test tile, and to later evaluate the relative durability of the applied compositions to the tile surfaces. After allowing the tiles to dry following the above wash/rinse treatment the tiles were tested to determine the decrease in the film thickness of the applied test composition

prior to the above wash/rinse treatment of the test tiles. The thickness was determined utilizing a Philips SD Ellipsometer which measured the change in polarization of light passing through the film layer and reflected off the substrate, the results were analyzed and the McCracken method was used to calculate film thickness. The foregoing is a conventional quantitative analysis method, and other quantitative analytical techniques for measuring the film thickness may have been used as well.

The averaged scores of the evaluated film thickness on the tested tempered glass tile surfaces is reported on the following Table B:

	C3	C4	E2
0 wash wash/rinse cycles	176	113	188
5 wash wash/rinse cycles	82	87	120
10 wash wash/rinse cycles	58	86	104

The averaged scores of the evaluated film thickness on the ceramic tile surfaces is reported on the following Table C:

	C3	E2
0 wash wash/rinse cycles	229	219
5 wash wash/rinse cycles	95	216
10 wash wash/rinse cycles	60	209

It can be seen that the test composition E2 illustrating a formulation of the invention demonstrates an improvement over the compositions of comparative examples C3 and C4, as evidenced by a strong resistance to the degradation of the applied composition to the surface of the test tiles. This was particularly noted on the surface of the ceramic tiles treated with E2 which had been subjected to 5 and 10 wash/rinse cycle indicating both good durability of the compositions following repeated washings, and when considered in conjunction with the results reported on prior Table B suggests improved resistance to subsequent buildup of limescale on hard surfaces, which in turn indicates that a real “next time cleaning” benefit is provided. Such treated surfaces, exhibiting both durability of the applied composition and

concurrently reduced tendency for limescale buildup, as well as improved water sheeting benefits directly provides for reduced cleaning which will be required at a future time. Thus, hard surfaces treated with a composition of the invention are expected to be easier to clean and/or, require less of cleaning composition to obtain a satisfactory degree of cleaning than if the composition of the invention had not been previously applied. Alternately such hard surfaces treated with a composition of the invention may be cleaned more infrequently by a consumer, as the durability of the applied composition and concurrently reduced tendency for limescale buildup between cleaning operations. Such a benefit is believed to be more evident when hard surfaces are cleaned several successive times with compositions according to the present invention.

Evaluation of resistance to soap scum buildup:

The benefit of the inclusion of a hydrophilic nitrogen-containing polymer having surface-modifying properties and inorganic nanoparticles with further constituents in a representative hard surface cleaning composition was demonstrated by producing the following test formulations identified in the following Table 4. The test formulations were formed by simple mixing of the individual constituents in the general manner described above; in the following table the amounts of the individual constituents used are to be considered as '100%wt. actives' unless otherwise indicated.

Table 4	C5	E3
C ₉ -C ₁₁ alcohol ethoxylate, 6 EO	1.0	1.0
sulfamic acid	5	5
phosphoric acid (75%wt. active)	5	5
fragrance	0.15	0.15
colorant	0.0005	0.0005
Bindzil CC30 (30%wt. active)	--	2.0
Sokalan HP 70 (40%wt. active)	--	1.25
deionized water	q.s.	q.s.

As is seen from the foregoing, the formulation according to the invention, E3, included the Bindzil CC30 and Sokalan HP 70 identified on Table 2, supra. A similar comparative

formulation, C5 omitted these two constituents. A further comparative composition, C6, namely pure deionized water was also used in the test. The remaining constituents identified on Table 4 were obtained from commercial sources.

Prior to testing, sample tiles of tempered glass and ceramic surfaces were first cleaned
5 with a suitable commercial hard surface cleaner, rinsed with large amounts of deionized water to ensure full removal of the said hard surface cleaner, and then again rinsed with a volatile organic solvent, isopropanol or ethanol, and again rinsed with deionized water to ensure removal of the organic solvent. The cleaned tiles were placed into a rack where they were held in a vertical position and then allowed to fully dry permitting the organic solvent to
10 evaporate before being used in any test.

A standardized 0.5%wt. soap scum solution was first prepared. Each of the sample tiles used in the test was supplied with a standardized layer of soap scum in accordance with the following process.

A standardized hard water solution was also prepared for use to provide limescale
15 deposition on the tile surfaces. The standardized hard water solution was made by mixing two aqueous premixtures, a first comprising water and calcium chloride, and a second comprising sodium bicarbonate, such that the resulting mixture was a standardized hard water solution comprising 430 mg/liter of calcium carbonate. This standardized hard water solution was sprayed (squirted) onto the test tiles as described in more detail hereinafter.

Each cleaned tile was retained vertically, and then each tile was squirted (sprayed)
20 (single squirt) with tap water from a first trigger spray bottle containing the same. Then using a second trigger spray bottle identical to the first said trigger spray bottle, and positioned relative to the tile surface in the same manner as the first trigger spray bottle, a squirt (single squirt) of the standardized 0.5%wt. soap scum solution was applied to the
25 surface of the tile, after which the tile was allowed to partially dry for 5 minutes. Thereafter a second squirt (single squirt) of the standardized 0.5%wt. soap scum solution was applied to the surface of the tile, after which the tile was allowed to partially dry for 5 minutes. Finally, for a third time a squirt (single squirt) of the standardized 0.5%wt. soap scum solution was applied to the surface of the tile, after which the tile was allowed to completely dry.

The sequence outlined in the foregoing paragraph was then repeated three more times, thus providing a total of 4 treatments per said foregoing paragraph of the application of tap water interspersed by three treatments of the standardized 0.5%wt. soap scum solution, and drying. The tile was then allowed to dry in the vertical position. In this matter the test
5 tiles bearing the standardized soap scum stains were prepared for further testing.

Subsequently the formulations of Table 4 were applied to the surface of each test tile using a further trigger spray bottles identical to the first said trigger spray bottle, and positioned relative to the tile surface in the same manner as the first trigger spray bottle. The test tiles were again retained vertically and the measured amounts of the formulations of
10 Table 4 were applied (supplying a calculated amount of 1.5 grams of a test formulation per 200 cm² of the tile surface), and thereafter wiped with a folded absorbent paper towel in order to wipe and spread the applied formulation across the surface of the test tile, and subsequently the test tile was placed into a vertical rack and allowed to dry.

Subsequently the treated tiles were placed in a dishwasher (BOSCH LogiXX) and
15 subjected to a specified number of wash/rinse cycle at 45°C for 30 minutes in the absence of any rinse aids or cleaning compositions. This was repeated 0, 5 and 10 times. The purpose of this was to mimic the effect of sprayed water in a humid environment on the treated tile surfaces.

Thereafter each of the ceramic tiles was treated in accordance with the following
20 treatment cycle. Each ceramic tile was retained vertically, and squirted three times (three squirts) with the standardized hard water solution from a trigger spray bottle identical to the first trigger spray bottle used above and then the tile was allowed to dry. This cycle was repeated nineteen more times, thus providing twenty hard water, wetting and drying cycles to the surface. The tile was then allowed to dry in the vertical position.

25 Thereafter each of the tempered glass tiles was treated as in accordance with the following cycle. Each tempered glass tile was retained vertically, and squirted six times (six squirts) with the standardized hard water solution from a trigger spray bottle identical to the first trigger spray bottle used above and then the tile was allowed to dry. This sequence was

repeated nineteen more times, thus providing thirty squirts of hard water to the tile surface. The tile was then allowed to dry in the vertical position.

Subsequently the tiles were assessed by ten panelists on a scale from “1” to “9” depending on the visible lime scale on the tile apparent to an observer (test panelist). The lowest scores, “1”, were assigned for high levels of lime scale residue. Maximum scores of “9” were assigned when no lime scale residue was present on the tiles. The averaged scores of the ten panelists for each of the tested tiles is reported on the following Table E:

	C5	C6	E3
0 wash wash/rinse cycles	5.4	3.3	6.1
5 wash wash/rinse cycles	4.4	2.9	6.2
10 wash wash/rinse cycles	4.7	5.9	6.3

The results of the scores of Table D are also shown on Figure 2. As can be seen from the reported test results, the compositions of the invention provided an improved “next time cleaning” benefit to the treated tile surfaces, as is evident from the reduced amount of limescale buildup on the tiles, particularly following the initial cleaning of the tiles with compositions according to the invention followed by the successive rinse/clean cycles in the dishwasher simulating a weathering effect on the tiles. Notwithstanding these harsh conditions, the compositions of the invention showed good initial cleaning of soap scum and the later test results suggest that the compositions of the invention form a continuous or semicontinuous film which is both durable and retards the subsequent buildup of limescale on the tile surfaces treated with said compositions, even subsequent to the simulated weathering of the tiles. Such results demonstrate reduced need for cleaning or reduced frequency of cleaning operations of the treated tiles in order to remove limescale deposits from the tile surfaces, following sequential or intermittent application of a composition according to the invention. Such also demonstrates the “next time cleaning” benefit provided by the compositions according to the invention.

Although this invention has been shown and described with respect to the detailed embodiments thereof, it will be understood by those of skill in the art that various changes

may be made and equivalents may be substituted for elements thereof without departing from the scope of the invention. In addition, modifications may be made to adapt a particular situation or material to the teachings of the invention without departing from the essential scope thereof. Therefore, it is intended that the invention not be limited to the particular
5 embodiments disclosed in the above detailed description, but that the invention will include all embodiments falling within the scope of the appended claims.

10

Claims

1. A liquid composition for treating a surface, said composition comprising a hydrophilic polymer and inorganic nanoparticles, wherein the hydrophilic polymer is a nitrogen-containing polymer having surface-modifying properties.
2. A composition as claimed in claim 1, wherein the nanoparticles are nanoparticles comprising silica, magnesia, alumina and/or titania or mixed metal oxides thereof.
3. A composition as claimed in claim 1 or 2, wherein the nanoparticles are charged.
4. A composition as claimed in any one of the preceding claims, wherein the nanoparticles are from 2 to 100 nm in size.
5. A composition as claimed in any one of the preceding claims, which comprises a colloidal dispersion of said nanoparticles.
6. A composition as claimed in any one of the preceding claims, wherein the hydrophilic polymer is a homopolymer or a copolymer.
7. A composition as claimed in any one of the preceding claims, wherein the hydrophilic polymer is charged.
8. A composition as claimed in claim 7, wherein the hydrophilic polymer is a quaternized ammonium acrylamide/acrylic acid copolymer.
9. A composition as claimed in claim 8, wherein the hydrophilic polymer is a diallyl dimethyl ammonium acrylamide/acrylic acid copolymer.

10. A composition as claimed in any one of the preceding claims, wherein the weight ratio of hydrophilic polymer to nanoparticles is 0.1 to 20.
- 5 11. A composition as claimed in any one of the preceding claims, which comprises 0.05 to 10 weight % of hydrophilic polymer.
12. A composition as claimed in any one of the preceding claims, which comprises 0.05 to 10 weight % inorganic nanoparticles.
- 10 13. A composition as claimed in any one of the preceding claims, which additionally comprises a surfactant.
14. A composition as claimed in claim 13, wherein the surfactant is a non-ionic
15 surfactant.
15. A composition as claimed in any one of the preceding claims, which additionally comprises an organic solvent.
- 20 16. A composition as claimed in any one of the preceding claims, which additionally comprises a bleach constituent or an oxidizing constituent.
17. A composition as claimed in any one of the preceding claims, which has a pH of 2-5 or 9-11.
- 25 18. Use of a composition as claimed in any one of the preceding claims, to reduce or prevent the formation of deposits on a surface.

- 19. Use as claimed in claim 18, wherein the deposits are lime scale, soap scum and other organically encrusted or flocculated deposits.

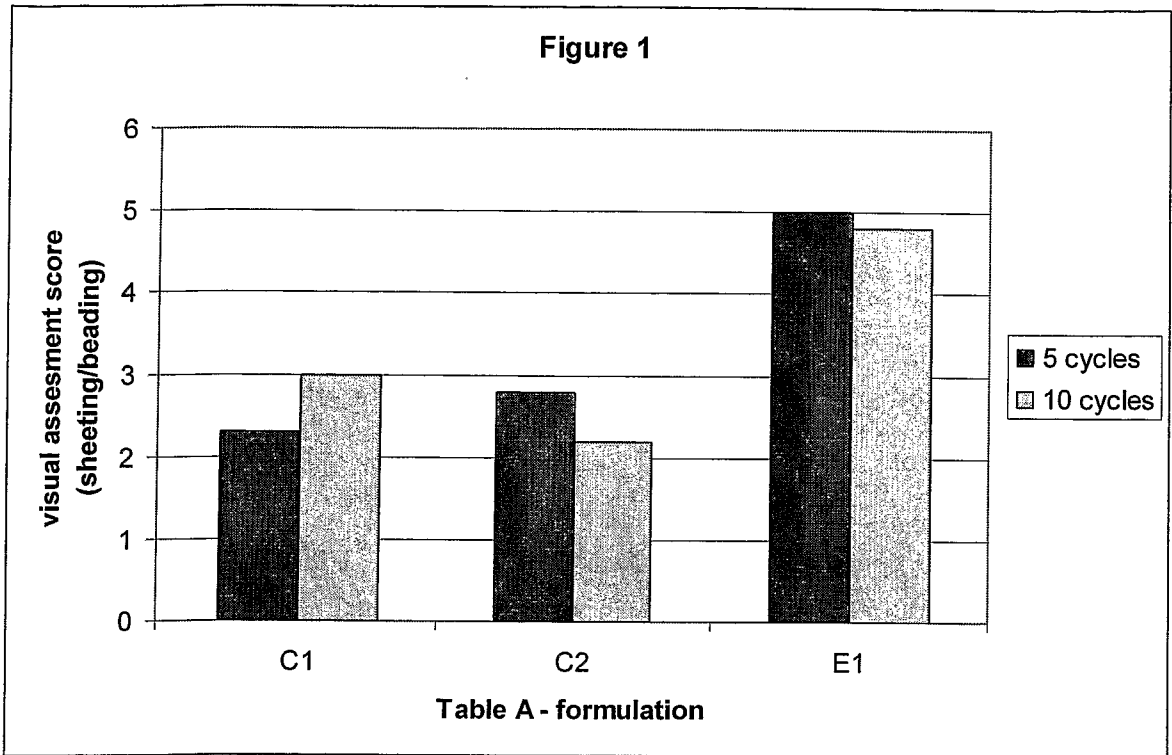
- 5 20. Use of a hydrophilic polymer and inorganic nanoparticles in the manufacture of a composition for treating a surface, as an agent for reducing or preventing the formation of deposits on a surface, wherein the hydrophilic polymer is a nitrogen-containing polymer having surface-modifying properties.

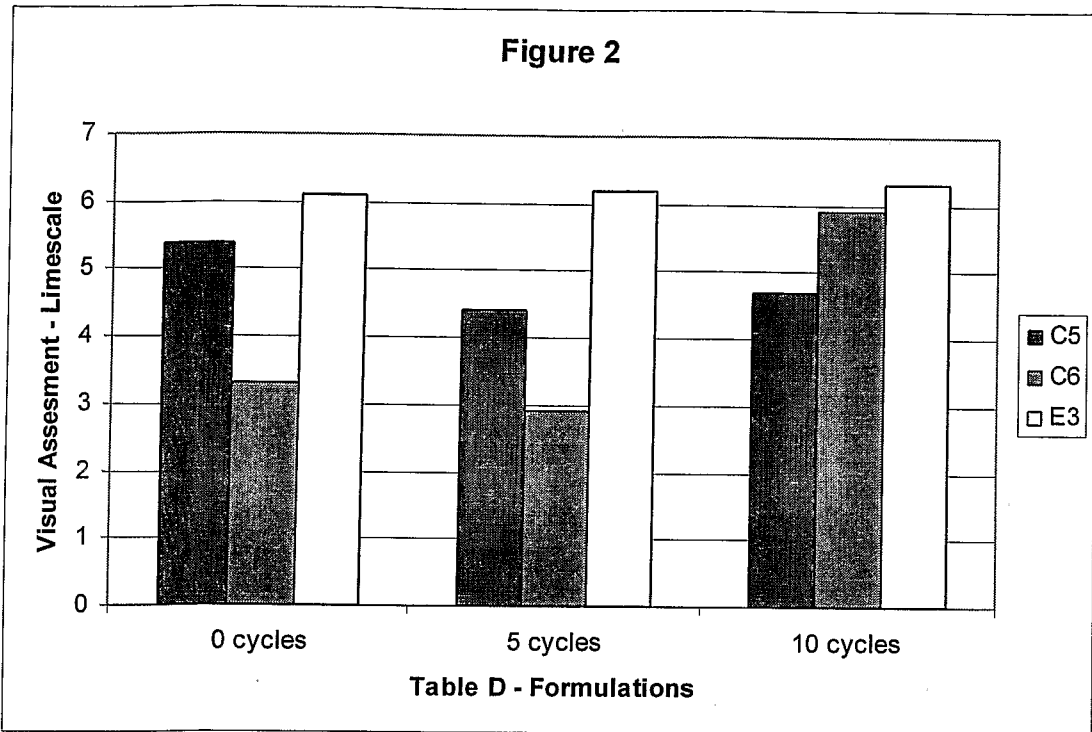
- 10 21. Use as claimed in claim 20, wherein the deposits are lime scale, soap scum and other organically encrusted or flocculated deposits.

- 22. Use as claimed in claim 20 or 21, wherein the surface is a hard surface, preferably siliceous surface, more preferably a glass or ceramic surface.

- 15 23. A method of treating a hard surface, said method comprising applying a composition as claimed in any one of claims 1 to 17 to the hard surface.

20





INTERNATIONAL SEARCH REPORT

International application No
PCT/GB2006/004692

A. CLASSIFICATION OF SUBJECT MATTER
 INV. C11D17/00 C11D7/20 C11D3/12 C11D3/37 B82B3/00
 B05D5/08 B08B17/06

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED
 Minimum documentation searched (classification system followed by classification symbols)
 C11D B05D B08B B82B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the International search (name of data base and, where practical, search terms used)
 EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 952 119 A (NALCO CHEMICAL CO) 27 October 1999 (1999-10-27) claims; examples -----	1-23
X	US 2002/108640 A1 (BARGER BRUCE ET AL) 15 August 2002 (2002-08-15) paragraph [0100]; claims; examples XI-XV -----	1-23
X	US 2002/054862 A1 (PERRON BEATRICE ET AL) 9 May 2002 (2002-05-09) claims; example -----	1-23
X	US 2003/134761 A1 (SEBILLOTTE-ARNAUD LAURENCE ET AL) 17 July 2003 (2003-07-17) examples 7-10 -----	1-23
	-/--	

Further documents are listed in the continuation of Box C.

See patent family annex.

* Special categories of cited documents :

A document defining the general state of the art which is not considered to be of particular relevance	*T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
E earlier document but published on or after the international filing date	*X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
L document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	*Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
O document referring to an oral disclosure, use, exhibition or other means	*Z* document member of the same patent family
P document published prior to the international filing date but later than the priority date claimed	

Date of the actual completion of the international search 13 February 2007	Date of mailing of the international search report 06/03/2007
---	--

Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Authorized officer Hillebrecht, Dieter
---	---

INTERNATIONAL SEARCH REPORT

International application No

PCT/GB2006/004692

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	FR 2 789 591 A1 (RHONE POULENC CHIMIE) 18 August 2000 (2000-08-18) claims; example 5 -----	1-23
X	WO 01/96511 A2 (PROCTER & GAMBLE) 20 December 2001 (2001-12-20) page 6, line 13 - line 32; claims; example 27 page 24, line 25 - page 26, line 12 page 44, line 16 - page 45, line 28 -----	1-23

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/GB2006/004692

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
EP 0952119	A	27-10-1999	EP 0952118 A1	27-10-1999
US 2002108640	A1	15-08-2002	ZA 200308359 A	13-08-2004
US 2002054862	A1	09-05-2002	EP 1190698 A1 FR 2814064 A1 JP 2002193759 A	27-03-2002 22-03-2002 10-07-2002
US 2003134761	A1	17-07-2003	CN 1398581 A EP 1277463 A1 FR 2827515 A1 JP 2003113073 A KR 20030009213 A	26-02-2003 22-01-2003 24-01-2003 18-04-2003 29-01-2003
FR 2789591	A1	18-08-2000	AU 2677300 A EP 1151068 A1 WO 0049119 A1 US 6905814 B1	04-09-2000 07-11-2001 24-08-2000 14-06-2005
WO 0196511	A2	20-12-2001	AU 6840301 A CA 2410600 A1 CN 1439041 A EP 1299481 A2 JP 2004503662 T MX PA02012433 A	24-12-2001 20-12-2001 27-08-2003 09-04-2003 05-02-2004 25-04-2003