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(54) **Liquid cleaning compositions**

(57) Liquid cleaning compositions are disclosed which comprise a nonionic surfactant, a polymer and an amphoteric surfactant according to the formula:



wherein the substituent  $R_1$  is a substituted or unsubstituted, saturated or unsaturated, linear or branched hydrocarbon chain having from 6 to 22 carbon atoms, wherein the substituents  $R_2$  and  $R_3$  each independently are a C1 to C6 alkyl carboxylic acid group, which may be the same or different, and wherein X is hydrogen. These compositions have the advantage to exhibit improved physical stability.

**EP 0 892 039 A1**

**Description**Technical Field

5 The present invention relates to physically stable liquid cleaning compositions comprising a nonionic surfactant, a polymer and a particular amphoteric surfactant. These liquid compositions may be used in various cleaning applications including laundry, softening, carpet cleaning, dishwashing, household cleaning, especially hard-surface cleaning, glass cleaning or toilet bowl cleaning, in oral/dental compositions and beauty care applications.

10 Background of the invention

Various liquid aqueous cleaning compositions have been disclosed in the art. For example much of the focus for liquid cleaning compositions has been on providing outstanding cleaning on a variety of surfaces and soils. Thus, liquid cleaning compositions have been developed based on various cleaning/soil releasing ingredients to improve their overall cleaning performance. For example co-pending European application number 97870018.5 discloses liquid aqueous cleaning compositions particularly suitable for the cleaning of a hard-surface, comprising an antiresoiling polymer (i.e., a copolymer of N-vinylpyrrolidone and alkylenically unsaturated monomer or mixtures thereof) and nonionic surfactants.

However, a drawback associated with the formulation of such liquid aqueous cleaning compositions comprising at least a nonionic surfactant and a polymer like a polyvinylpyrrolidone homopolymer or copolymer is that they tend to be physically unstable. Indeed, the presence of such polymers like a polyvinylpyrrolidone homopolymer or copolymer in a liquid aqueous nonionic surfactant-containing composition can result in a hazy composition upon prolonged periods of storage, typically several days, or even immediately upon their incorporation in the composition, depending on the relative concentration of the nonionic surfactants and the polymers, and more particularly on the concentration of the nonionic surfactants. In other words, the higher the concentration of nonionic surfactants in an aqueous liquid composition, the higher the physical instability of the composition upon addition of such a polymer therein. Thus, this physical instability is especially encountered when concentrated compositions are desired (e.g. total concentration of nonionic surfactants is of 6% or more). More particularly, in those concentrated liquid aqueous compositions the polymers tend to separate from the compositions directly upon their attempted incorporation therein, resulting thereby in two separate clear aqueous layers, one rich in the polymers, the other one rich in the nonionic surfactants. This segregative phase separation phenomenon has been referred to in the scientific literature as "segregation coacervation".

Thus, the object of the present invention is to formulate liquid aqueous cleaning compositions, especially so-called "concentrated" liquid cleaning compositions, comprising at least a nonionic surfactant and a polymer, which exhibit improved physical stability.

35 It has now been found that the physical stability of a liquid aqueous composition comprising at least a nonionic surfactant and a polymer, is improved by adding into this composition a particular amphoteric surfactant as defined herein after. In a preferred embodiment of the present invention, the present invention provides concentrated liquid aqueous compositions, comprising at least a nonionic surfactant at a level of 6% or more by weight of the total composition, a polymer and such an amphoteric surfactant which are physically stable upon prolonged periods of storage.

40 An advantage of the present invention is that this invention is applicable to a wide range of cleaning operations including the cleaning/washing of fabrics or even bleaching of fabrics in the embodiment of the present invention wherein the compositions according to the present invention further comprise a bleaching agent, any household application, dishwashing applications, carpet applications or even dental applications or beauty care applications. Indeed, the compositions herein may be used to clean any surface including animate surfaces (human skin, and/or mouth) and inanimate surfaces including, but not limited to fabrics, clothes, carpets and any hard-surface made of a variety of materials like glazed and non-glazed ceramic tiles, vinyl, no-wax vinyl, linoleum, melamine, glass, plastics, plastified wood, both in neat and diluted conditions, e.g., up to a dilution level of 1:400 (composition:water).

The compositions of the present invention find preferred application in the cleaning of a hard-surface. For example, in a preferred embodiment of the present invention wherein the compositions of the present invention comprising the nonionic surfactant, the amphoteric surfactant and a homopolymer or copolymer of vinylpyrrolidone as the polymer, further comprise an antiresoiling ingredient selected from the group of a polyalkoxyethylene glycol, mono- or di-capped polyalkoxyethylene glycol or a mixture thereof, particularly improved cleaning is provided. Advantageously, these preferred liquid cleaning compositions provide both effective first and next-time cleaning performance when used to clean a hard-surface. More particularly, these cleaning performances, and especially the next-time cleaning performance, are obtained with the compositions according to the present invention on various types of stains/soils including typical greasy stains like kitchen grease and other tough stains such as burnt/sticky food residues typically found in kitchens, while delivering good gloss to said surfaces.

Another advantage associated to the compositions according to the present invention comprising the nonionic sur-

factant, the amphoteric surfactant and a polymer as defined herein, is that they have the ability to provide good shine to the surface they have cleaned. Indeed, less formation of watermarks and/or even limescale deposits are observed on a surface having been cleaned with the compositions of the present invention and later comes in contact with water, for example, during a rinse operation. Advantageously, the shine benefit delivered to the surface even persists after several cycles of rinsing, thus providing long lasting protection against formation of watermarks and/or even limescale deposits on the surface, and hence long lasting shiny surfaces.

#### Background art

The following patent applications are representative of the prior art.

WO 94/26858 discloses a liquid hard-surface composition (pH 2-8) with nonionic surfactants (1-30%) and anionic polymers having an average molecular weight of less than 1 000 000, said polymers being free of quaternary nitrogen groups. Said compositions bring a surprising initial cleaning benefit in addition to the anti-soiling benefit. Indeed, WO 94/26858 discloses that acrylic, methacrylic and maleic anhydride derivatives such as copolymers of styrene with maleic, produce a streak-free finish after drying. No amphoteric surfactants according to the present invention are disclosed. EP-A-635 567 discloses liquid compositions for cleaning solid surfaces comprising a cleaning agent capable of being deposited on the surface during cleaning and of forming a dried layer adhered to the surface, said layer having a cohesive strength such that at least outermost surface portion of the layer is removable by further washing. Polyvinylpyrrolidone is disclosed. However, no nonionic surfactants and amphoteric surfactants according to the present invention are disclosed.

#### Summary of the invention

The present invention encompasses a liquid cleaning composition comprising a nonionic surfactant, a polymer and an amphoteric surfactant according to the formula:



wherein the substituent  $R_1$  is a substituted or unsubstituted, saturated or unsaturated, linear or branched hydrocarbon chain having from 6 to 22 carbon atoms, wherein the substituents  $R_2$  and  $R_3$  each independently are a C1 to C6 alkyl carboxylic acid group, which may be the same or different, and wherein X is hydrogen.

The present invention also encompasses a process of cleaning a surface, preferably a hard-surface wherein a liquid composition as defined herein above, is contacted with said surfaces.

#### Detailed Description of the invention

##### The liquid compositions:

As a first essential ingredient, the compositions according to the present invention comprise a nonionic surfactant or a mixture thereof.

Nonionic surfactants are desired herein as they contribute to the cleaning performance of the compositions of the present invention. Indeed, they contribute to the effective cleaning of the compositions herein regardless of water hardness, thus allowing for compositions low in or free of inorganic or organic builders. Also when the compositions herein are used for the cleaning of a hard-surface said nonionic surfactants also contribute to the gloss benefit of the compositions of the present invention.

Typically, the liquid composition herein comprise from 1% to 50% by weight of the total composition of a nonionic surfactant or a mixture thereof, preferably from 2% to 30% and more preferably from 5% to 30%.

In the preferred embodiment herein wherein the compositions are formulated as so called concentrated compositions, they comprise from 6% to 30% by weight of the total composition of a nonionic surfactant or a mixture thereof, preferably from 7% to 20% and more preferably from 8% to 15%.

Suitable nonionic surfactants for use herein include a class of compounds, which may be broadly defined as compounds produced by the condensation of alkylene oxide groups (hydrophilic in nature) with an organic hydrophobic compound, which may be branched or linear aliphatic (e.g. Guerbet or secondary alcohol) or alkyl aromatic in nature. The length of the hydrophilic or polyoxyalkylene radical which is condensed with any particular hydrophobic group can be readily adjusted to yield a water-soluble compound having the desired degree of balance between hydrophilic and hydrophobic elements.

Accordingly suitable nonionic synthetic detergents include :

(i) The polyethylene oxide condensates of alkyl phenols, e.g., the condensation products of alkyl phenols having an alkyl group containing from 6 to 20 carbon atoms in either a straight chain or branched chain configuration, preferably from 8 to 12 carbon atoms, with ethylene oxide, the said ethylene oxide being present in amounts equal to 10 to 25 moles of ethylene oxide per mole of alkyl phenol. The alkyl substituent in such compounds may be derived from polymerized propylene, diisobutylene, octane, and nonane; Examples of this type of nonionic surfactants include Triton N-57<sup>®</sup> a nonyl phenol ethoxylate (5EO) from Rohm & Haas and Imbentin O200<sup>®</sup> an octyl phenol ethoxylate (20EO) from KOLB.

(ii) Those derived from the condensation of ethylene oxide with the product resulting from the reaction of propylene oxide and ethylene diamine products which may be varied in composition depending upon the balance between the hydrophobic and hydrophilic elements which is desired. Examples are compounds containing from about 40% to about 80% polyoxyethylene by weight and having a molecular weight of from about 5000 to about 11000 resulting from the reaction of ethylene oxide groups with a hydrophobic base constituted of the reaction product of ethylene diamine and excess propylene oxide, said base having a molecular weight of the order of 2500 to 3000. Examples of this type of nonionic surfactants include certain of the commercially available Tetronic<sup>™</sup> compounds, marketed by BASF;

(iii) The condensation product of aliphatic alcohols having from 6 to 22 carbon atoms, in either straight chain or branched chain configuration, preferably from 8 to 18 carbon atoms, with from 2 to 35 moles of ethylene oxide, preferably from 4 to 25 and more preferably from 5 to 18. Example of this type of material are a coconut alcohol ethylene oxide condensate having from 5 to 18 moles of ethylene oxide per mole of coconut alcohol, the coconut alcohol fraction having from 9 to 14 carbon atoms; Other examples of this type of nonionic surfactants include certain of the commercially available Dobanol<sup>®</sup>, Neodol<sup>®</sup> marketed by Shell or Lutensol<sup>®</sup> from BASF. For example Dobanol<sup>®</sup> 23.5 (C12-C13 EO5), Dobanol<sup>®</sup> 91.5 (C9-C11 EO 5) and Lutensol<sup>®</sup> AO30 (C12-C14 EO30);

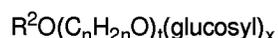
(iv) Trialkyl amine oxides and trialkyl phosphine oxides wherein one alkyl group ranges from 10 to 18 carbon atoms and two alkyl groups range from 1 to 3 carbon atoms; the alkyl groups can contain hydroxy substituents; specific examples are dodecyl di(2-hydroxyethyl)amine oxide and tetradecyl dimethyl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

(v) The condensation products of ethylene oxide with a hydrophobic base formed by the condensation of propylene oxide with propylene glycol; The hydrophobic portion of these compounds will preferably have a molecular weight of from about 1500 to about 1800 and will exhibit water insolubility. The addition of polyoxyethylene moieties to this hydrophobic portion tends to increase the water solubility of the molecule as a whole, and the liquid character of the product is retained up to the point where the polyoxyethylene content is about 50% of the total weight of the condensation product, which corresponds to condensation with up to about 40 moles of ethylene oxide. Examples of compounds of this type include certain of the commercially available Pluronic<sup>™</sup> surfactants, marketed by BASF.

Also useful as a nonionic surfactant are the alkylpolysaccharides disclosed in U.S. Patent 4,565,647, Llenado, issued January 21, 1986, having a hydrophobic group containing from 6 to 30 carbon atoms, preferably from 10 to 16 carbon atoms and polysaccharide, e.g., a polyglycoside, hydrophilic group containing from 1.3 to 10, preferably from 1.3 to 3, most preferably from 1.3 to 2.7 saccharide units. Any reducing saccharide containing 5 or 6 carbon atoms can be used, e.g., glucose, galactose, and galactosyl moieties can be substituted for the glucosyl moieties. (Optionally the hydrophobic group is attached at the 2-, 3-, 4-, etc. positions thus giving a glucose or galactose as opposed to a glucoside or galactoside.) The intersaccharide bonds can be, e.g., between the one position of the additional saccharide units and the 2-, 3-, 4-, and/or 6- positions of the preceding saccharide units.

Optionally, and less desirable, there can be a polyalkyleneoxide chain joining the hydrophobic moiety and the polysaccharide moiety. The preferred alkyleneoxide is ethylene oxide. Typical hydrophobic groups include alkyl groups, either saturated or unsaturated, branched or unbranched containing from 8 to 18, preferably from 10 to 16, carbon atoms. Preferably, the alkyl group can contain up to about 3 hydroxy groups and/or the polyalkyleneoxide chain can contain up to about 10, preferably less than 5, alkyleneoxide moieties. Suitable alkyl polysaccharides are octyl, nonyldecyl, undecyldodecyl, tridecyl, tetradecyl, pentadecyl, hexadecyl, heptadecyl, and octadecyl, di-, tri-, tetra-, penta-, and hexaglycosides, galactosides, lactosides, glucoses, fructosides, fructoses and/or galactoses. Suitable mixtures include coconut alkyl, di-, tri-, tetra-, and pentaglycosides and tallow alkyl tetra-, penta-, and hexaglycosides.

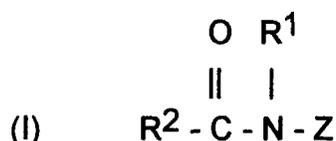
The preferred alkylpolyglycosides have the formula:



wherein R<sup>2</sup> is selected from the group consisting of alkyl, alkylphenyl, hydroxyalkyl, hydroxyalkylphenyl, and mixtures

thereof in which the alkyl groups contain from 10 to 18, preferably from 12 to 14, carbon atoms; n is 2 or 3, preferably 2; t is from 0 to about 10, preferably 0; and x is from 1.3 to 10, preferably from 1.3 to 3, most preferably from 1.3 to 2.7. The glycosyl is preferably derived from glucose. To prepare these compounds, the alcohol or alkylpolyethoxy alcohol is formed first and then reacted with glucose, or a source of glucose, to form the glucoside (attachment at the 1-position).  
 5 The additional glycosyl units can then be attached between their 1-position and the preceding glycosyl units 2-, 3-, 4- and/or 6- position, preferably predominantly the 2-position.

Other suitable nonionic surfactants for use herein include polyhydroxy fatty acid amides of the structural formula:



wherein: R<sup>1</sup> is H, C<sub>1</sub>-C<sub>4</sub> hydrocarbyl, 2-hydroxy ethyl, 2-hydroxypropyl, or a mixture thereof, preferably C<sub>1</sub>-C<sub>4</sub> alkyl, more preferably C<sub>1</sub> or C<sub>2</sub> alkyl, most preferably C<sub>1</sub> alkyl (i.e., methyl); and R<sup>2</sup> is a C<sub>5</sub>-C<sub>31</sub> hydrocarbyl, preferably straight chain C<sub>7</sub>-C<sub>19</sub> alkyl or alkenyl, more preferably straight chain C<sub>9</sub>-C<sub>17</sub> alkyl or alkenyl, most preferably straight chain C<sub>11</sub>-C<sub>17</sub> alkyl or alkenyl, or mixtures thereof; and Z is a polyhydroxyhydrocarbyl having a linear hydrocarbyl chain with at least 3 hydroxyls directly connected to the chain, or an alkoxyated derivative (preferably ethoxylated or propoxylated) thereof. Z preferably will be derived from a reducing sugar in a reductive amination reaction; more preferably Z is a glyceryl. Suitable reducing sugars include glucose, fructose, maltose, lactose, galactose, mannose, and xylose. As raw materials, high dextrose corn syrup can be utilized as well as the individual sugars listed above. These corn syrups may yield a mix of sugar components for Z. It should be understood that it is by no means intended to exclude other suitable raw materials. Z preferably will be selected from the group consisting of -CH<sub>2</sub>-(CHOH)<sub>n</sub>-CH<sub>2</sub>OH, -CH(CH<sub>2</sub>OH)-(CHOH)<sub>n-1</sub>-CH<sub>2</sub>OH, -CH<sub>2</sub>-(CHOH)<sub>2</sub>(CHOR')(CHOH)-CH<sub>2</sub>OH, where n is an integer from 3 to 5, inclusive, and R' is H or a cyclic or aliphatic monosaccharide, and alkoxyated derivatives thereof. Most preferred are glyceryls wherein n is 4, particularly -CH<sub>2</sub>-(CHOH)<sub>4</sub>-CH<sub>2</sub>OH.

In Formula (I), R<sup>1</sup> can be, for example, N-methyl, N-ethyl, N-propyl, N-isopropyl, N-butyl, N-2-hydroxy ethyl, or N-2-hydroxy propyl. R<sup>2</sup>-CO-N< can be, for example, cocamide, stearamide, oleamide, lauramide, myristamide, capricamide, palmitamide, tallowamide, etc. Z can be 1-deoxyglucityl, 2-deoxyfructityl, 1-deoxymaltityl, 1-deoxylactityl, 1-deoxygalactityl, 1-deoxymannityl, 1-deoxymaltotriosityl, etc.

Other suitable nonionic surfactants for use herein include the amine oxides corresponding to the formula:



wherein R is a primary alkyl group containing 6-24 carbons, preferably 10-18 carbons, and wherein R' and R'' are, each, independently, an alkyl group containing 1 to 6 carbon atoms. The arrow in the formula is a conventional representation of a semi-polar bond. The preferred amine oxides are those in which the primary alkyl group has a straight chain in at least most of the molecules, generally at least 70%, preferably at least 90% of the molecules, and the amine oxides which are especially preferred are those in which R contains 10-18 carbons and R' and R'' are both methyl. Exemplary of the preferred amine oxides are the N-hexyldimethylamine oxide, N-octyldimethylamine oxide, N-decyldimethylamine oxide, N-dodecyl dimethylamine oxide, N-tetradecyldimethylamine oxide, N-hexadecyl dimethylamine oxide, N-octadecyldimethylamine oxide, N-eicosyldimethylamine oxide, N-docosyldimethylamine oxide, N-tetracosyl dimethylamine oxide, the corresponding amine oxides in which one or both of the methyl groups are replaced with ethyl or 2-hydroxyethyl groups and mixtures thereof. A most preferred amine oxide for use herein is N-decyldimethylamine oxide.

Other suitable nonionic surfactants for the purpose of the invention are the phosphine or sulfoxide surfactants of formula:



wherein A is phosphorus or sulfur atom, R is a primary alkyl group containing 6-24 carbons, preferably 10-18 carbons, and wherein R' and R'' are, each, independently selected from methyl, ethyl and 2-hydroxyethyl. The arrow in the formula is a conventional representation of a semi-polar bond.

In a preferred embodiment herein suitable nonionic surfactants to be used are polyethylene oxide condensates of alkyl phenols, polyethylene oxide condensates of alkyl alcohols, alkylpolysaccharides, or mixtures thereof. Most preferred are C<sub>8</sub>-C<sub>14</sub> alkyl phenol ethoxylates having from 3 to 15 ethoxy groups and C<sub>8</sub>-C<sub>18</sub> alcohol ethoxylates having from 2 to 35 ethylene oxide units, preferably from 2 to 35, more preferably from 4 to 25 and most preferably from 5 to

18, and mixtures thereof.

As a second essential ingredient, the compositions according to the present invention comprise a polymer or a mixture thereof.

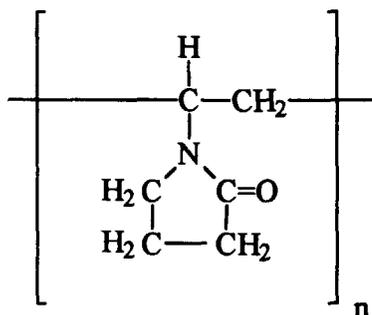
5 The compositions of the present invention comprise from 0.001% to 20% by weight of the total composition of such a polymer or a mixture thereof, preferably from 0.01% to 10%, more preferably from 0.1% to 5% and most preferably from 0.2% to 3%.

In the preferred embodiment herein wherein the compositions are formulated as so called concentrated compositions, they comprise from 0.4% to 3% by weight of the total composition of a polymer or a mixture thereof, preferably from 0.5% to 3% and more preferably from 0.6% to 3%.

10 Particularly suitable polymers for used herein include vinylpyrrolidone homopolymer or copolymer, polysaccharide polymer or a mixture thereof.

Suitable vinylpyrrolidone homopolymers to be used herein is an homopolymer of N-vinylpyrrolidone having the following repeating monomer:

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wherein n (degree of polymerisation) is an integer of from 10 to 1,000,000, preferably from 20 to 100,000, and more preferably from 20 to 10,000.

Accordingly, suitable vinylpyrrolidone homopolymers ("PVP") for use herein have an average molecular weight of from 1,000 to 100,000,000, preferably from 2,000 to 10,000,000, more preferably from 5,000 to 1,000,000, and most preferably from 50,000 to 500,000.

35 Suitable vinylpyrrolidone homopolymers are commercially available from ISP Corporation, New York, NY and Montreal, Canada under the product names PVP K-15<sup>®</sup> (viscosity molecular weight of 10,000), PVP K-30<sup>®</sup> (average molecular weight of 40,000), PVP K-60<sup>®</sup> (average molecular weight of 160,000), and PVP K-90<sup>®</sup> (average molecular weight of 360,000). Other suitable vinylpyrrolidone homopolymers which are commercially available from BASF Cooperation include Sokalan HP 165<sup>®</sup> and Sokalan HP 12<sup>®</sup>; vinylpyrrolidone homopolymers known to persons skilled in the detergent field (see for example EP-A-262,897 and EP-A-256,696).

40 Suitable copolymers of vinylpyrrolidone for use herein include copolymers of N-vinylpyrrolidone and alkylenically unsaturated monomers or mixtures thereof.

The alkylenically unsaturated monomers of the copolymers herein include unsaturated dicarboxylic acids such as maleic acid, chloromaleic acid, fumaric acid, itaconic acid, citraconic acid, phenylmaleic acid, aconitic acid, acrylic acid, N-vinylimidazole and vinyl acetate. Any of the anhydrides of the unsaturated acids may be employed, for example acrylate, methacrylate. Aromatic monomers like styrene, sulphonated styrene, alpha-ethyl styrene, vinyl toluene, t-butyl styrene and similar well known monomers may be used.

The preferred copolymers of N-vinylpyrrolidone and alkylenically unsaturated monomers or mixtures thereof, have a molecular weight of between 1,000 and 1,000,000, preferably between 10,000 and 500,000 and more preferably between 10,000 and 200,000.

50 For example particularly suitable N-vinylimidazole N-vinylpyrrolidone polymers for use herein have an average molecular weight range from 5,000-1,000,000, preferably from 5,000 to 500,000, and more preferably from 10,000 to 200,000. The average molecular weight range was determined by light scattering as described in Barth H.G. and Mays J.W. Chemical Analysis Vol 113, "Modern Methods of Polymer Characterization".

Such copolymers of N-vinylpyrrolidone and alkylenically unsaturated monomers like PVP/vinyl acetate copolymers are commercially available under the trade name Luviskol<sup>®</sup> series from BASF.

Other suitable copolymers of vinylpyrrolidone for use in the compositions of the present invention are quaternized or unquaternized vinylpyrrolidone/dialkylaminoalkyl acrylate or methacrylate copolymers.

Other suitable polymers for used herein are the polysaccharide polymers including substituted cellulose materials

like carboxymethylcellulose, ethyl cellulose, hydroxyethyl cellulose, hydroxypropyl cellulose, hydroxymethyl cellulose, succinoglycan and naturally occurring polysaccharide polymers like xanthan gum, guar gum, locust bean gum, tragacanth gum or derivatives thereof, or mixtures thereof.

Particularly polysaccharide polymers to be used herein are xanthan gum and derivatives thereof. Xanthan gum and derivatives thereof may be commercially available for instance from Kelco under the trade name Keltrol RD<sup>®</sup>, Kelzan S<sup>®</sup> or Kelzan T<sup>®</sup>.

Such polymers are desired in the liquid compositions herein for various reasons depending on the end use envisioned for these compositions. For instance vinylpyrrolidone homopolymers and copolymers have the advantage to act as an antisoiling polymer and/or as a dye transfer inhibiting agent when typically used in a laundry or cleaning application.

More particularly, such vinylpyrrolidone homopolymers and copolymers are desirable in the compositions of the present invention suitable for the cleaning of a hard-surface, as they contribute to the effective next-time cleaning performance associated to the compositions herein, when a hard-surface has been first treated therewith. Although not wishing to be bound by theory, it is speculated that such polymers like vinylpyrrolidone homopolymer or copolymer, have in common the property of adsorbing to a hard-surface being first treated therewith, in such a manner that a hygroscopic layer is left behind. The resulting hygroscopic layer can attract and retain ambient atmospheric water vapor to more effectively reduce adhesion of soils once treated and/or facilitate removal of soils subsequently deposited thereon, i.e. less work (e.g. less scrubbing and/or wiping and/or less chemical action) is required to remove the soils in the next-time cleaning operation, as compared to a similar soiled hard-surface which has been first treated with the same compositions without said polymer.

An advantage of the compositions of the present invention is that the first time cleaning performance is also increased, as compared for example to the same compositions without said vinylpyrrolidone homopolymer or copolymer.

Also such polymers like vinylpyrrolidone homopolymers and/or copolymers, polysaccharide polymers or mixtures thereof as described herein before, when present in a liquid cleaning composition according to the present invention, have been found to reduce or even prevent the formation of limescale deposits and/or watermarks deposition on said surface having first been cleaned with a composition according to the present invention, thereby providing long lasting shine benefit. Furthermore, the presence of such polymers within the compositions of the present invention results in smoother surface, this can be perceived by touching said surfaces.

Also polysaccharide polymers like xanthan gum may act as a thickening agent, accordingly the liquid compositions according to the present invention comprising them may have a viscosity of from 1 cps to 1500 cps at 20 C, preferably from 10 cps to 800 cps and more preferably from 30 cps to 600 cps, when measured with a Carri-med rheometer GLS 100<sup>®</sup> at 5N/m<sup>2</sup>.

As a third essential ingredient, the compositions according to the present invention comprise an amphoteric surfactant or a mixture thereof.

Suitable amphoteric surfactants for use herein are according to the formula:



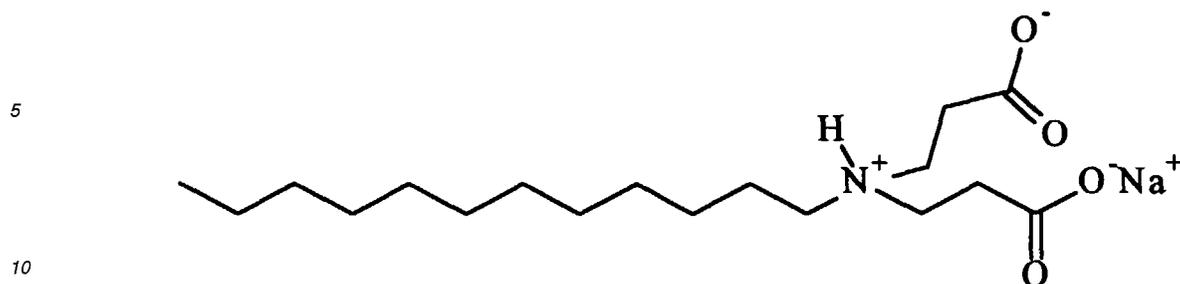
wherein the substituent R<sub>1</sub> is a substituted or unsubstituted, saturated or unsaturated, linear or branched hydrocarbon chain having from 6 to 22 carbon atoms, wherein the substituents R<sub>2</sub> and R<sub>3</sub> each independently are a C1 to C6 alkyl carboxylic acid group, which may be the same or different, and wherein X is hydrogen.

Preferably the substituent R<sub>1</sub> is a substituted or unsubstituted, saturated or unsaturated, linear or branched alkyl group, alkenyl group, or alkyl-aryl group containing from 6 to 22 carbon atoms, more preferably from 8 to 20 carbon atoms and most preferably from 10 to 18 carbon atoms.

Preferably the substituents R<sub>2</sub> and R<sub>3</sub> each independently are a C1 to C4 alkyl carboxylic acid group, which may be the same or different and more preferably are two C2 alkyl carboxylic acid groups. Either one or both of the alkyl carboxylic acid groups may be either associated, i.e. in their acidic form, or dissociated, i.e. in their salt form. In their salt form the carboxylic acid groups may be associated with any common metal counterion such as, for example, sodium or potassium.

Depending on the pH of the compositions of the present invention, these amphoteric surfactants may be present in either their amphoteric form, i.e., R<sub>1</sub>R<sub>2</sub>R<sub>3</sub>N<sup>+</sup>X, typically at neutral or acidic pH (pH 7 or below), e.g., at a pH of 6.5, or in their dianionic form, i.e., R<sub>1</sub>R<sub>2</sub>R<sub>3</sub>N, typically at alcalin pH (pH above 7), e.g., at pH of 11.

A preferred amphoteric surfactant for use herein is cocoiminodipropionate sold by Akzo Nobel as a mono sodium salt under the tradename of Ampholak YCA/P<sup>®</sup>.



Cociminodipropionate may also be commercially available under the trade name Ampholan U203<sup>®</sup> from Akros.

15 Another suitable amphoteric surfactant for use herein is lauryliminodipropionate sold under the trade name Deriphath<sup>®</sup> 160-C from Cospha.

Typically, the compositions of the present invention comprise from 0.001% to 20% by weight of the total composition of such an amphoteric surfactant or a mixture thereof, preferably from 0.01% to 10%, more preferably from 0.1% to 5% and most preferably from 0.2% to 4%.

20 It has now been found that the addition of an amphoteric surfactant as described herein in a liquid aqueous composition comprising a nonionic surfactant and a polymer improves the physical stability of said composition. Thus, in its broadest embodiment the present invention encompasses the use of such an amphoteric surfactant in a composition comprising said nonionic surfactant and polymer to improve the physical stability of said composition.

25 By "improved physical stability" it is meant herein that the time necessary to observe a phase separation upon storage is prolonged in presence of said amphoteric in a given composition comprising a nonionic surfactant and a polymer, as compared to the time necessary to observe a phase separation with the same composition in absence of said amphoteric surfactant as described herein before.

Indeed, the compositions according to the present invention are physically stable, i.e., they do not undergo a phase separation when stored for 4 months at 20 C, and more typically for 6 months at 20 C.

30 Advantageously the present invention allows the formulation of physically stable concentrated aqueous liquid compositions comprising a nonionic surfactant (e.g. at a level of 6% and above) and a polymer (e.g. at a level of 0.4% or above) by adding thereto small amounts of an amphoteric surfactant. Indeed, in the absence of the amphoteric surfactant defined herein, at those concentrations of nonionic surfactant and polymer in an aqueous medium, the polymer tend to separate from the nonionic surfactant to form an aqueous phase which is rich in the polymer and leave a separate aqueous phase which is rich in the nonionic surfactant. This segregative phase separation can be detected visually with or without the aid of microscopy.

#### Optional ingredients:

40 The liquid compositions according to the present invention may comprise a variety of optional ingredients depending on the technical benefit aimed for and the surface treated.

The liquid compositions of the present invention are preferably but not necessarily formulated as aqueous compositions. Aqueous compositions typically comprise from 50% to 99% by weight of the total composition of water, preferably from 60% to 95%, and more preferably from 80% to 95%.

45 Depending on the end used envisioned the liquid compositions herein may be formulated in the full pH range of 0 to 14, preferably 1 to 13. Typically, the compositions particularly suitable for the cleaning of a hard-surface like floors are formulated in a neutral to highly alkaline pH range from 7 to 13, preferably from 9 to 12 and more preferably from 9.5 to 11.5. The pH of the compositions herein can be adjusted by any of the means well-known to those skilled in the art such as acidifying agents like organic or inorganic acids, or alkalinising agents like NaOH, KOH, K<sub>2</sub>CO<sub>3</sub>, Na<sub>2</sub>CO<sub>3</sub> and the like.

50 Where the compositions of the present invention are further designed to remove limescale deposits, they are typically formulated in the acidic pH range, preferably at a pH from 0.1 to 5, more preferably from 0.5 to 4. Preferred organic and inorganic acids for use herein have a first pka of less than 6. Suitable acids for use herein include citric acid, lactic acid, glycolic acid, succinic acid, glutaric acid, sulfamic acid, adipic acid and mixtures thereof.

55 Suitable optional ingredients for use herein include other surfactants, builders, chelants, antiresoiling ingredients, solvents, buffers, bactericides, hydrotropes, colorants, stabilisers, radical scavengers, bleaches, bleach activators, suds controlling agents like fatty acids, enzymes, soil suspenders, soil-release agents, dye transfer agents, brighteners, anti dusting agents, dispersants, dye transfer inhibitors, abrasives, pigments, dyes and/or perfumes.

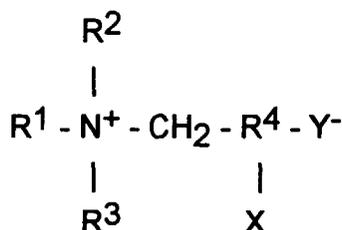
Other Surfactants:

The liquid compositions of the present invention may further comprise other surfactants apart the nonionic and amphoteric ones described hereinbefore, or mixtures thereof. Said surfactant may be present in the compositions according to the present invention in amounts of from 0.1% to 50% by weight of the total composition, preferably of from 0.1% to 20% and more preferably of from 1% to 10%.

Surfactants to be used herein include anionic surfactants, cationic surfactants, other amphoteric surfactants, zwitterionic surfactants, and mixtures thereof.

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

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

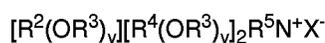


wherein R1 is an alkyl radical containing from 8 to 22 carbon atoms, R2 and R3 contain from 1 to 3 carbon atoms, R4 is an alkylene chain containing from 1 to 3 carbon atoms, X is selected from the group consisting of hydrogen and a hydroxyl radical, Y is selected from the group consisting of carboxyl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

Amphoteric and ampholytic detergents which can be either cationic or anionic depending upon the pH of the system are represented by detergents such as dodecylbeta-alanine, N-alkyltaurines such as the one prepared by reacting dodecylamine with sodium isethionate according to the teaching of U.S. Pat. No. 2,658,072, N-higher alkylaspartic acids such as those produced according to the teaching of U.S. Pat. No. 2,438,091, and the products sold under the trade name "Miranol", and described in U.S. Pat. No. 2,528,378, said patents being incorporated herein by reference.

Additional synthetic detergents and listings of their commercial sources can be found in McCutcheon's Detergents and Emulsifiers, North American Ed. 1980, incorporated herein by reference.

Cationic surfactants suitable for use in compositions of the present invention are those having a long-chain hydrocarbyl group. Examples of such cationic surfactants include the ammonium surfactants such as alkyldimethylammonium halogenides, and those surfactants having the formula:



wherein R<sup>2</sup> is an alkyl or alkyl benzyl group having from 8 to 18 carbon atoms in the alkyl chain, each R<sup>3</sup> is selected from the group consisting of -CH<sub>2</sub>CH<sub>2</sub>-, -CH<sub>2</sub>CH(CH<sub>3</sub>)-, -CH<sub>2</sub>CH(CH<sub>2</sub>OH)-, -CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>-, and mixtures thereof; each R<sup>4</sup> is selected from the group consisting of C<sub>1</sub>-C<sub>4</sub> alkyl, C<sub>1</sub>-C<sub>4</sub> hydroxyalkyl, benzyl ring structures formed by joining the two R<sup>4</sup> groups, -CH<sub>2</sub>CHOH-CHOHCOR<sup>6</sup>CHOHCH<sub>2</sub>OH wherein R<sup>6</sup> is any hexose or hexose polymer having a molecular weight less than about 1000, and hydrogen when y is not 0; R<sup>5</sup> is the same as R<sup>4</sup> or is an alkyl chain wherein the total number of carbon atoms of R<sup>2</sup> plus R<sup>5</sup> is not more than about 18; each y is from 0 to about 10 and the sum of the y values is from 0 to about 15; and X is any compatible anion.

Other cationic surfactants useful herein are also described in U.S. Patent 4,228,044, Cambre, issued October 14, 1980, incorporated herein by reference.

#### Perfumes:

Suitable perfumes to be used herein include materials which provide an olfactory aesthetic benefit and/or cover any "chemical" odor that the product may have. The main function of a small fraction of the highly volatile, low boiling (having low boiling points), perfume components in these perfumes is to improve the fragrance odor of the product itself, rather than impacting on the subsequent odor of the surface being cleaned. However, some of the less volatile, high boiling perfume ingredients provide a fresh and clean impression to the surfaces, and it is desirable that these ingredients be deposited and present on the dry surface. Perfume ingredients can be readily solubilized in the compositions, for instance by the nonionic detergent surfactants.

The perfume ingredients and compositions suitable to be used herein are the conventional ones known in the art. Selection of any perfume component, or amount of perfume, is based solely on aesthetic considerations.

Suitable perfume compounds and compositions can be found in the art including U.S. Pat. Nos. : 4,145,184, Brain and Cummins, issued March 20, 1979; 4,209,417, Whyte, issued June 24, 1980; 4,515,705, Moeddel, issued May 7, 1985; and 4,152,272, Young, issued May 1, 1979, all of said patents being incorporated herein by reference.

In general, the degree of substantivity of a perfume is roughly proportional to the percentages of substantive perfume material used. Relatively substantive perfumes contain at least about 1%, preferably at least about 10%, substantive perfume materials.

Substantive perfume materials are those odorous compounds that deposit on surfaces via the cleaning process and are detectable by people with normal olfactory acuity. Such materials typically have vapor pressures lower than that of the average perfume material. Also, they typically have molecular weights of about 200 and above, and are detectable at levels below those of the average perfume material.

Perfume ingredients useful herein, along with their odor character, and their physical and chemical properties, such as boiling point and molecular weight, are given in "Perfume and Flavor Chemicals (Aroma Chemicals)," Steffen Arctander, published by the author, 1969, incorporated herein by reference.

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

Examples of moderately volatile perfume ingredients are : amyl cinnamic aldehyde, iso-amyl salicylate, beta-caryophyllene, cedrene, cinnamic alcohol, coumarin, dimethyl benzyl carbonyl acetate, ethyl vanillin, eugenol, iso-eugenol, flor acetate, heliotropine, 3-cis-hexenyl salicylate, hexyl salicylate, lilial (para-tertiarybutyl-alpha-methyl hydrocinnamic aldehyde), gamma-methyl ionone, nerolidol, patchouli alcohol, phenyl hexanol, beta-selinene, trichloromethyl phenyl carbonyl acetate, triethyl citrate, vanillin, and veratraldehyde. Cedarwood terpenes are composed mainly of alpha-cedrene, beta-cedrene, and other C<sub>15</sub>H<sub>24</sub> sesquiterpenes.

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

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

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

Chelating agents:

Another class of optional compounds to be used herein include chelating agents or mixtures thereof. Chelating agents can be incorporated in the compositions herein in amounts ranging from 0.0% to 10.0% by weight of the total composition, preferably 0.1% to 5.0%.

Suitable phosphonate chelating agents to be used herein may include alkali metal ethane 1-hydroxy diphosphonates (HEDP), alkylene poly (alkylene phosphonate), as well as amino phosphonate compounds, including amino aminotri(methylene phosphonic acid) (ATMP), nitrilo trimethylene phosphonates (NTP), ethylene diamine tetra methylene phosphonates, and diethylene triamine penta methylene phosphonates (DTPMP). The phosphonate compounds may be present either in their acid form or as salts of different cations on some or all of their acid functionalities. Preferred phosphonate chelating agents to be used herein are diethylene triamine penta methylene phosphonate (DTPMP) and ethane 1-hydroxy diphosphonate (HEDP). Such phosphonate chelating agents are commercially available from Monsanto under the trade name DEQUEST®.

Polyfunctionally-substituted aromatic chelating agents may also be useful in the compositions herein. See U.S. patent 3,812,044, issued May 21, 1974, to Connor et al. Preferred compounds of this type in acid form are dihydroxydisulfobenzenes such as 1,2-dihydroxy -3,5-disulfobenzene.

A preferred biodegradable chelating agent for use herein is ethylene diamine N,N'- disuccinic acid, or alkali metal, or alkaline earth, ammonium or substitutes ammonium salts thereof or mixtures thereof. Ethylenediamine N,N'- disuccinic acids, especially the (S,S) isomer have been extensively described in US patent 4, 704, 233, November 3, 1987, to Hartman and Perkins. Ethylenediamine N,N'- disuccinic acids is, for instance, commercially available under the trade name ssEDDS® from Palmer Research Laboratories.

Suitable amino carboxylates to be used herein include ethylene diamine tetra acetates, diethylene triamine pentaacetates, diethylene triamine pentaacetate (DTPA), N- hydroxyethylethylenediamine triacetates, nitrilotri-acetates, ethylenediamine tetrapropionates, triethylenetetraaminehexa-acetates, ethanoldiglycines, propylene diamine tetracetic acid (PDTA) and methyl glycine diacetic acid (MGDA), both in their acid form, or in their alkali metal, ammonium, and substituted ammonium salt forms. Particularly suitable amino carboxylates to be used herein are diethylene triamine penta acetic acid, propylene diamine tetracetic acid (PDTA) which is, for instance, commercially available from BASF under the trade name Trilon FS® and methyl glycine di-acetic acid (MGDA).

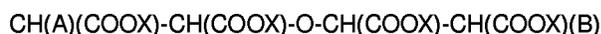
Further carboxylate chelating agents to be used herein include salicylic acid, aspartic acid, glutamic acid, glycine, malonic acid or mixtures thereof.

Builders:

The liquid compositions of the present invention may also comprises a builder or a mixture thereof, as an optional ingredient. Suitable builders for use herein include polycarboxylates and polyphosphates, and salts thereof. Typically, the compositions of the present invention comprise up to 20.0 % by weight of the total composition of a builder or mixtures thereof, preferably from 0.1% to 10.0%, and more preferably from 0.5% to 5.0%.

Suitable and preferred polycarboxylates for use herein are organic polycarboxylates where the highest LogKa, measured at 25°C/0.1M ionic strength is between 3 and 8, wherein the sum of the LogKCa + LogKMg, measured at 25°C/0.1M ionic strength is higher than 4, and wherein LogKCa = LogKMg ± 2 units, measured at 25°C/0.1M ionic strength.

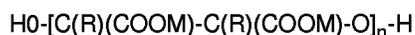
Such suitable and preferred polycarboxylates include citrate and complexes of the formula:



wherein A is H or OH; B is H or -O-CH(COOX)-CH<sub>2</sub>(COOX); and X is H or a salt-forming cation. For example, if in the above general formula A and B are both H, then the compound is oxydissuccinic acid and its water-soluble salts. If A is OH and B is H, then the compound is tartrate monosuccinic acid (TMS) and its water-soluble salts. If A is H and B is -O-CH(COOX)-CH<sub>2</sub>(COOX), then the compound is tartrate disuccinic acid (TDS) and its water-soluble salts. Mixtures of these builders are especially preferred for use herein. Particularly TMS to TDS, these builders are disclosed in U.S. Patent 4,663,071, issued to Bush et al., on May 5, 1987.

Still other ether polycarboxylates suitable for use herein include copolymers of maleic anhydride with ethylene or vinyl methyl ether, 1, 3, 5-trihydroxy benzene-2, 4, 6-trisulfonic acid.

Other useful polycarboxylate builders include the ether hydroxypolycarboxylates represented by the structure :



wherein M is hydrogen or a cation wherein the resultant salt is water-soluble, preferably an alkali metal, ammonium or

substituted ammonium cation, n is from about 2 to about 15 (preferably n is from about 2 to about 10, more preferably n averages from about 2 to about 4) and each R is the same or different and selected from hydrogen, C<sub>1-4</sub> alkyl or C<sub>1-4</sub> substituted alkyl (preferably R is hydrogen).

Suitable ether polycarboxylates also include cyclic compounds, particularly alicyclic compounds, such as those described in U.S. Patents 3,923,679; 3,835,163; 4,158,635; 4,120,874 and 4,102,903, all of which are incorporated herein by reference.

Preferred amongst those cyclic compounds are dipicolinic acid and chelidanic acid.

Also suitable polycarboxylates for use herein are mellitic acid, succinic acid, polymaleic acid, benzene 1,3,5-tricarboxylic acid, benzene pentacarboxylic acid, and carboxymethyloxysuccinic acid, and soluble salts thereof.

Still suitable carboxylate builders herein include the carboxylated carbohydrates disclosed in U.S. Patent 3,723,322, Diehl, issued March 28, 1973, incorporated herein by reference.

Other suitable carboxylates for use herein, but which are less preferred because they do not meet the above criteria are alkali metal, ammonium and substituted ammonium salts of polyacetic acids. Examples of polyacetic acid builder salts are sodium, potassium, lithium, ammonium and substituted ammonium salts of ethylenediamine, tetraacetic acid and nitrotriacetic acid.

Other suitable but less preferred polycarboxylates are those also known as alkyliminoacetic builders such as methyl imino diacetic acid, alanine diacetic acid, methyl glycine diacetic acid, hydroxy propylene imino diacetic acid and other alkyl imino acetic acid builders.

Also suitable in the compositions of the present invention are the 3,3-dicarboxy-4-oxa-1,6-hexanedioates and the related compounds disclosed in U.S. Patent 4,566,984, Bush, issued January 28, 1986, incorporated herein by reference. Useful succinic acid builders include the C<sub>5</sub>-C<sub>20</sub> alkyl succinic acids and salts thereof. A particularly preferred compound of this type is dodecylsuccinic acid. Alkyl succinic acids typically are of the general formula R-CH(COOH)CH<sub>2</sub>(COOH) i.e., derivatives of succinic acid, wherein R is hydrocarbon, e.g., C<sub>10</sub>-C<sub>20</sub> alkyl or alkenyl, preferably C<sub>12</sub>-C<sub>16</sub> or wherein R may be substituted with hydroxyl, sulfo, sulfoxy or sulfone substituents, all as described in the above-mentioned patents.

The succinate builders are preferably used in the form of their water-soluble salts, including the sodium, potassium, ammonium and alkanolammonium salts.

Specific examples of succinate builders include : laurylsuccinate, myristylsuccinate, palmitylsuccinate, 2-dodecylsuccinate (preferred), 2-pentadecylsuccinate, and the like. Laurylsuccinates are the preferred builders of this group, and are described in European Patent Application 86200690.5/0 200 263, published November 5, 1986.

Examples of useful builders also include sodium and potassium carboxymethyloxymalonate, carboxymethyloxysuccinate, cis-cyclohexanehexacarboxylate, cis-cyclopentane-tetracarboxylate, water-soluble polyacrylates and the copolymers of maleic anhydride with vinyl methyl ether or ethylene.

Other suitable polycarboxylates are the polyacetal carboxylates disclosed in U.S. Patent 4,144,226, Crutchfield et al., issued March 13, 1979, incorporated herein by reference. These polyacetal carboxylates can be prepared by bringing together, under polymerization conditions, an ester of glyoxylic acid and a polymerization initiator. The resulting polyacetal carboxylate ester is then attached to chemically stable end groups to stabilize the polyacetal carboxylate against rapid depolymerization in alkaline solution, converted to the corresponding salt, and added to a surfactant.

Polycarboxylate builders are also disclosed in U.S. Patent 3,308,067, Diehl, issued March 7, 1967, incorporated herein by reference. Such materials include the water-soluble salts of homo- and copolymers of aliphatic carboxylic acids such as maleic acid, itaconic acid, mesaconic acid, fumaric acid, aconitic acid, citraconic acid and methylenemalononic acid.

Suitable polyphosphonates for use herein are the alkali metal, ammonium and alkanolammonium salts of polyphosphates (exemplified by the tripolyphosphates, pyrophosphates, and glassy polymeric meta-phosphates), phosphonates. The most preferred builder for use herein is citrate.

#### Divalent ions:

The compositions according to the present invention may further comprise a divalent ion, or mixtures thereof. All divalent ions known to those skilled in the art may be used herein. Preferred divalent ions to be used herein are calcium, zinc, cadmium, nickel, copper, cobalt, zirconium, chromium and/or magnesium and more preferred are calcium, zinc and/or magnesium. Said divalent ions may be added in the form of salts for example as chloride, acetate, sulphate, formate and/or nitrate or as a complex metal salt. For example, calcium may be added in the form of calcium chloride, magnesium as magnesium acetate or magnesium sulphate and zinc as zinc chloride. Typically such ions may be present at a level up to 3 %, preferably from 0.001% to 1% by weight of the total composition.

Antiresoiling ingredients:

The compositions of the present invention particularly suitable for the cleaning of a hard-surface may comprise another antiresoiling ingredient on top of the polymer as described herein before like the N-vinylpyrrolidone homopolymer or copolymer or mixtures thereof. Suitable antiresoiling ingredients to be used herein include those selected from the group consisting of polyalkoxyethylene glycol, mono- and dicapped polyalkoxyethylene glycol and a mixture thereof, as defined herein after. The compositions of the present invention may comprise up to 20% by weight of the total composition of said antiresoiling ingredient or a mixture thereof, preferably from 0.01% to 10%, more preferably from 0.1% to 5% and most preferably from 0.2% to 2%.

Suitable polyalkoxyethylene glycols to be used herein are according to the following formula :  $H-O-(CH_2-CHR_2O)_n-H$ .

Suitable monocapped polyalkoxyethylene glycols to be used herein are according to the following formula :  $R_1-O-(CH_2-CHR_2O)_n-H$ .

Suitable dicapped polyalkoxyethylene glycols to be used herein are according to the formula :  $R_1-O-(CH_2-CHR_2O)_n-R_3$ .

In these formulas the substituents  $R_1$  and  $R_3$  each independently are substituted or unsubstituted, saturated or unsaturated, linear or branched hydrocarbon chains having from 1 to 30 carbon atoms, or amino bearing linear or branched, substituted or unsubstituted hydrocarbon chains having from 1 to 30 carbon atoms,  $R_2$  is hydrogen or a linear or branched hydrocarbon chain having from 1 to 30 carbon atoms, and  $n$  is an integer greater than 0.

Preferably  $R_1$  and  $R_3$  each independently are substituted or unsubstituted, saturated or unsaturated, linear or branched alkyl groups, alkenyl groups or aryl groups having from 1 to 30 carbon atoms, preferably from 1 to 16, more preferably from 1 to 8 and most preferably from 1 to 4, or amino bearing linear or branched, substituted or unsubstituted alkyl groups, alkenyl groups or aryl groups having from 1 to 30 carbon atoms, more preferably from 1 to 16, even more preferably from 1 to 8 and most preferably from 1 to 4. Preferably  $R_2$  is hydrogen, or a linear or branched alkyl group, alkenyl group or aryl group having from 1 to 30 carbon atoms, more preferably from 1 to 16, even more preferably from 1 to 8, and most preferably  $R_2$  is methyl, or hydrogen. Preferably  $n$  is an integer from 5 to 1000, more preferably from 10 to 100, even more preferably from 20 to 60 and most preferably from 30 to 50.

The preferred polyalkoxyethylene glycols, mono and dicapped polyalkoxyethylene glycols to be used herein have a molecular weight of at least 200, more preferably from 400 to 5000 and most preferably from 800 to 3000.

Suitable monocapped polyalkoxyethylene glycols to be used herein include 2-aminopropyl polyethylene glycol (MW 2000), methyl polyethylene glycol (MW 1800) and the like. Such monocapped polyalkoxyethylene glycols may be commercially available from Hoescht under the polyglycol series or Hunstman under the tradename XTJ<sup>®</sup>. Suitable polyalkoxyethylene glycols to be used herein are polyethylene glycols like polyethylene glycol (MW 2000).

Suitable dicapped polyalkoxyethylene glycols to be used herein include O,O'-bis(2-aminopropyl)polyethylene glycol (MW 2000), O,O'-bis(2-aminopropyl)polyethylene glycol (MW 400), O,O'-dimethyl polyethylene glycol (MW 2000), dimethyl polyethylene glycol (MW 2000), or mixtures thereof. A preferred dicapped polyalkoxyethylene glycol for use herein is dimethyl polyethylene glycol (MW 2000). For instance dimethyl polyethylene glycol may be commercially available from Hoescht as the polyglycol series, e.g. PEG DME-2000, or from Huntsman under the name Jeffamine<sup>®</sup> and XTJ<sup>®</sup>.

These polyalkoxyethylene glycols, mono- or dicapped polyalkoxyethylene glycols contribute to the benefit of the liquid hard-surface compositions of the present invention, i.e. they help further improving the next-time cleaning performance of the composition herein.

Dicapped polyalkoxyethylene glycols are highly preferred herein. More particularly, it has surprisingly been found that there is a synergistic effect on next-time cleaning performance associated with the use of a dicapped polyalkoxyethylene glycol on top of the compositions of the present invention comprising as the polymer, a vinylpyrrolidone homopolymer or copolymer, as defined herein.

In a preferred embodiment of the compositions of the present invention the antiresoiling ingredient as defined herein and the vinylpyrrolidone homopolymer or copolymer, as defined herein, as the polymer of the compositions of the present invention are present at a weight ratio of said antiresoiling ingredient to the vinylpyrrolidone homopolymer or copolymer of from 1:100 to 100:1 preferably from 1:10 to 10:1 and more preferably from 1:2 to 2:1.

Suds controlling agents:

The compositions according to the present invention may further comprise a suds controlling agent such as 2-alkyl alkanol, or mixtures thereof, as a preferred optional ingredient. Particularly suitable to be used in the present invention are the 2-alkyl alkanols having an alkyl chain comprising from 6 to 16 carbon atoms, preferably from 8 to 12 and a terminal hydroxy group, said alkyl chain being substituted in the  $\alpha$  position by an alkyl chain comprising from 1 to 10 carbon atoms, preferably from 2 to 8 and more preferably 3 to 6. Such suitable compounds are commercially available, for instance, in the Isofol<sup>®</sup> series such as Isofol<sup>®</sup> 12 (2-butyl octanol) or Isofol<sup>®</sup> 16 (2-hexyl decanol).

Other suds controlling agents may include alkali metal (e.g., sodium or potassium) fatty acids, or soaps thereof, containing from about 8 to about 24, preferably from about 10 to about 20 carbon atoms.

The fatty acids including those used in making the soaps can be obtained from natural sources such as, for instance, plant or animal-derived glycerides (e.g., palm oil, coconut oil, babassu oil, soybean oil, castor oil, tallow, whale oil, fish oil, tallow, grease, lard and mixtures thereof). The fatty acids can also be synthetically prepared (e.g., by oxidation of petroleum stocks or by the Fischer-Tropsch process).

Alkali metal soaps can be made by direct saponification of fats and oils or by the neutralization of the free fatty acids which are prepared in a separate manufacturing process. Particularly useful are the sodium and potassium salts of the mixtures of fatty acids derived from coconut oil and tallow, i.e., sodium and potassium tallow and coconut soaps.

The term "tallow" is used herein in connection with fatty acid mixtures which typically have an approximate carbon chain length distribution of 2.5% C14, 29% C16, 23% C18, 2% palmitoleic, 41.5% oleic and 3% linoleic (the first three fatty acids listed are saturated). Other mixtures with similar distribution, such as the fatty acids derived from various animal tallows and lard, are also included within the term tallow. The tallow can also be hardened (i.e., hydrogenated) to convert part or all of the unsaturated fatty acid moieties to saturated fatty acid moieties.

When the term "coconut" is used herein it refers to fatty acid mixtures which typically have an approximate carbon chain length distribution of about 8% C8, 7% C10, 48% C12, 17% C14, 9% C16, 2% C18, 7% oleic, and 2% linoleic (the first six fatty acids listed being saturated). Other sources having similar carbon chain length distribution such as palm kernel oil and babassu oil are included with the term coconut oil.

Other suitable suds controlling agents are exemplified by silicones, and silica-silicone mixtures. Silicones can be generally represented by alkylated polysiloxane materials while silica is normally used in finely divided forms exemplified by silica aerogels and xerogels and hydrophobic silicas of various types. These materials can be incorporated as particulates in which the suds controlling agent is advantageously releasably incorporated in a water-soluble or water-dispersible, substantially non-surface-active detergent impermeable carrier. Alternatively the suds controlling agent can be dissolved or dispersed in a liquid carrier and applied by spraying on to one or more of the other components.

A preferred silicone suds controlling agent is disclosed in Bartollota et al. U.S. Patent 3 933 672. Other particularly useful suds controlling agents are the self-emulsifying silicone suds controlling agents, described in German Patent Application DTOS 2 646 126 published April 28, 1977. An example of such a compound is DC-544, commercially available from Dow Corning, which is a siloxane-glycol copolymer.

Especially preferred silicone suds controlling agents are described in Copending European Patent application N°92201649.8. Said compositions can comprise a silicone/silica mixture in combination with fumed nonporous silica such as Aerosil<sup>R</sup>.

Especially preferred suds controlling agent are the suds controlling agent system comprising a mixture of silicone oils and the 2-alkyl-alkanols.

Typically, the compositions herein may comprise up to 4% by weight of the total composition of a suds controlling agent, or mixtures thereof, preferably from 0.1% to 1.5% and most preferably from 0.1% to 0.8%.

### Solvents:

The compositions of the present invention may further comprise a solvent or a mixtures thereof. Solvents to be used herein include all those known to the those skilled in the art. Suitable solvents for use herein include ethers and diethers having from 4 to 14 carbon atoms, preferably from 6 to 12 carbon atoms, and more preferably from 8 to 10 carbon atoms, glycols or alkoxyated glycols, alkoxyated aromatic alcohols, aromatic alcohols, aliphatic branched alcohols, alkoxyated aliphatic branched alcohols, alkoxyated linear C1-C5 alcohols, linear C1-C5 alcohols, C8-C14 alkyl and cycloalkyl hydrocarbons and haloalkyl hydrocarbons, C6-C16 glycol ethers and mixtures thereof.

Suitable glycols to be used herein are according to the formula HO-CR<sub>1</sub>R<sub>2</sub>-OH wherein R<sub>1</sub> and R<sub>2</sub> are independently H or a C<sub>2</sub>-C<sub>10</sub> saturated or unsaturated aliphatic hydrocarbon chain and/or cyclic. Suitable glycols to be used herein are dodecaneglycol and/or propanediol.

Suitable alkoxyated glycols to be used herein are according to the formula R-(A)<sub>n</sub>-R<sub>1</sub>-OH wherein R is H, OH, a linear saturated or unsaturated alkyl of from 1 to 20 carbon atoms, preferably from 2 to 15 and more preferably from 2 to 10, wherein R<sub>1</sub> is H or a linear saturated or unsaturated alkyl of from 1 to 20 carbon atoms, preferably from 2 to 15 and more preferably from 2 to 10, and A is an alkoxy group preferably ethoxy, methoxy, and/or propoxy and n is from 1 to 5, preferably 1 to 2. Suitable alkoxyated glycols to be used herein are methoxy octadecanol and/or ethoxyethoxyethanol.

Suitable alkoxyated aromatic alcohols to be used herein are according to the formula R (A)<sub>n</sub>-OH wherein R is an alkyl substituted or non-alkyl substituted aryl group of from 1 to 20 carbon atoms, preferably from 2 to 15 and more preferably from 2 to 10, wherein A is an alkoxy group preferably butoxy, propoxy and/or ethoxy, and n is an integer of from 1 to 5, preferably 1 to 2. Suitable alkoxyated aromatic alcohols are benzyloxyethanol and/or benzyloxypropanol.

Suitable aromatic alcohols to be used herein are according to the formula R-OH wherein R is an alkyl substituted or non-alkyl substituted aryl group of from 1 to 20 carbon atoms, preferably from 1 to 15 and more preferably from 1 to 10. For example a suitable aromatic alcohol to be used herein is benzyl alcohol.

Suitable aliphatic branched alcohols to be used herein are according to the formula R-OH wherein R is a branched saturated or unsaturated alkyl group of from 1 to 20 carbon atoms, preferably from 2 to 15 and more preferably from 5 to 12. Particularly suitable aliphatic branched alcohols to be used herein include 2-ethylbutanol and/or 2-methylbutanol.

Suitable alkoxyated aliphatic branched alcohols to be used herein are according to the formula R (A)<sub>n</sub>-OH wherein R is a branched saturated or unsaturated alkyl group of from 1 to 20 carbon atoms, preferably from 2 to 15 and more preferably from 5 to 12, wherein A is an alkoxy group preferably butoxy, propoxy and/or ethoxy, and n is an integer of from 1 to 5, preferably 1 to 2. Suitable alkoxyated aliphatic branched alcohols include 1-methylpropoxyethanol and/or 2-methylbutoxyethanol.

Suitable alkoxyated linear C1-C5 alcohols to be used herein are according to the formula R (A)<sub>n</sub>-OH wherein R is a linear saturated or unsaturated alkyl group of from 1 to 5 carbon atoms, preferably from 2 to 4, wherein A is an alkoxy group preferably butoxy, propoxy and/or ethoxy, and n is an integer of from 1 to 5, preferably 1 to 2. Suitable alkoxyated aliphatic linear C1-C5 alcohols are butoxy propoxy propanol (n-BPP), butoxyethanol, butoxypropanol, ethoxyethanol or mixtures thereof. Butoxy propoxy propanol is commercially available under the trade name n-BPP<sup>®</sup> from Dow chemical.

Suitable linear C1-C5 alcohols to be used herein are according to the formula R-OH wherein R is a linear saturated or unsaturated alkyl group of from 1 to 5 carbon atoms, preferably from 2 to 4. Suitable linear C1-C5 alcohols are methanol, ethanol, propanol or mixtures thereof.

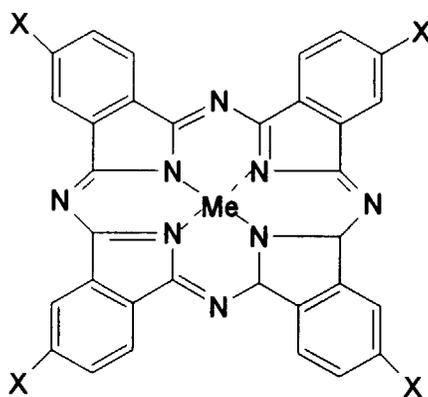
Other suitable solvents include butyl diglycol ether (BDGE), butyltriglycol ether, ter amilic alcohol and the like. Particularly preferred solvents to be used herein are butoxy propoxy propanol, butyl diglycol ether, benzyl alcohol, butoxypropanol, ethanol, methanol, isopropanol and mixtures thereof.

Typically, the compositions of the present invention comprise up to 20% by weight of the total composition of a solvent or mixtures thereof, preferably from 0.5% to 10% by weight and more preferably from 1% to 8%.

### Dyes

The liquid compositions according to the present invention may be colored. Accordingly, they may comprise a dye or a mixture thereof. Suitable dyes to be used herein include  $\alpha$  or  $\beta$  metal phthalocyanines and/or trimethyl methane dyes.

The  $\alpha$  or  $\beta$  metal phthalocyanine dyes suitable to be used in the compositions of the present invention are light-fast organic pigments with four isoindole groups, (C<sub>6</sub>H<sub>4</sub>)C<sub>2</sub>N, linked by four nitrogen atoms to form a conjugated chain. Their general structure is the following:



where the substituent X may be one of the following groups : H, Cl, HSO<sub>3</sub>, COO-M<sup>+</sup>, Br, NO<sub>2</sub>, OCH<sub>3</sub> or a C<sub>1</sub> to C<sub>10</sub> alkyl group and where Me is copper, chromium, vanadium, magnesium, nickel, platinum, aluminium, cobalt, lead, barium or zinc. Preferred  $\alpha$  or  $\beta$  metal phthalocyanine dyes to be used herein are  $\alpha$  or  $\beta$  copper phthalocyanine dyes.

Examples of such  $\alpha$  copper phthalocyanine dyes to be used herein are copper phthalocyanine (X = H, blue colour) commercially available under the name *UNISPERSE Blue B-E*<sup>®</sup> from Ciba-Geigy, or *Cosmenyl blue A2R*<sup>®</sup> from Hoechst, or *Pigmasol blue 6900*<sup>®</sup> from BASF, or chlorinated copper phthalocyanine (X = Cl, green colour) commercially available under the name *Pigmasol Green 8730*<sup>®</sup> from BASF.

Examples of trimethyl methane dyes are commercially available from Hoescht under the name *Vitasyn*<sup>®</sup> or from BASF under the name *Acid Blue*<sup>®</sup>.

Typically, the compositions of the present invention may comprise up to 0.2% by weight of the total composition of a dye or a mixture thereof, preferably from 0.0001% to 0.015% and more preferably from 0.001% to 0.010%.

Bleaching agents:

The liquid compositions herein may also comprise a bleaching component. Any bleach known to those skilled in the art may be suitable to be used herein including any peroxygen bleach as well as a chlorine releasing component.

Suitable peroxygen bleaches for use herein include hydrogen peroxide or sources thereof. As used herein a source of hydrogen peroxide refers to any compound which produces active oxygen when said compound is in contact with water. Suitable water-soluble sources of hydrogen peroxide for use herein include percarbonates, preformed percarboxylic acids, persilicates, persulphates, perborates, organic and inorganic peroxides and/or hydroperoxides.

Suitable chlorine releasing component for use herein is an alkali metal hypochlorite. Advantageously, the composition of the invention are stable in presence of this bleaching component. Although alkali metal hypochlorites are preferred, other hypochlorite compounds may also be used herein and can be selected from calcium and magnesium hypochlorite. A preferred alkali metal hypochlorite for use herein is sodium hypochlorite.

Bleach activators:

The compositions of the present invention that comprise a peroxygen bleach may further comprise a bleach activator or mixtures thereof. By "bleach activator", it is meant herein a compound which reacts with peroxygen bleach like hydrogen peroxide to form a peracid. The peracid thus formed constitutes the activated bleach. Suitable bleach activators to be used herein include those belonging to the class of esters, amides, imides, or anhydrides. Examples of suitable compounds of this type are disclosed in British Patent GB 1 586 769 and GB 2 143 231 and a method for their formation into a prilled form is described in European Published Patent Application EP-A-62 523. Suitable examples of such compounds to be used herein are tetracetyl ethylene diamine (TAED), sodium 3,5,5 trimethyl hexanoyloxybenzene sulphonate, diperoxy dodecanoic acid as described for instance in US 4 818 425 and nonylamide of peroxyadipic acid as described for instance in US 4 259 201 and n-nonanoyloxybenzenesulphonate (NOBS). Also suitable are N-acyl caprolactams selected from the group consisting of substituted or unsubstituted benzoyl caprolactam, octanoyl caprolactam, nonanoyl caprolactam, hexanoyl caprolactam, decanoyl caprolactam, undecenoyl caprolactam, formyl caprolactam, acetyl caprolactam, propanoyl caprolactam, butanoyl caprolactam pentanoyl caprolactam or mixtures thereof. A particular family of bleach activators of interest was disclosed in EP 624 154, and particularly preferred in that family is acetyl triethyl citrate (ATC). Acetyl triethyl citrate has the advantage that it is environmental-friendly as it eventually degrades into citric acid and alcohol. Furthermore, acetyl triethyl citrate has a good hydrolytical stability in the product upon storage and it is an efficient bleach activator. Finally, it provides good building capacity to the composition.

Packaging form of the compositions

The compositions herein may be packaged in a variety of suitable detergent packaging known to those skilled in the art. The liquid compositions are preferably packaged in conventional detergent plastic bottles.

In one embodiment the compositions herein may be packaged in manually operated spray dispensing containers, which are usually made of synthetic organic polymeric plastic materials. Accordingly, the present invention also encompasses liquid cleaning compositions of the invention packaged in a spray dispenser, preferably in a trigger spray dispenser or pump spray dispenser.

Indeed, said spray-type dispensers allow to uniformly apply to a relatively large area of a surface to be cleaned the liquid cleaning compositions suitable for use according to the present invention. Such spray-type dispensers are particularly suitable to clean vertical surfaces.

Suitable spray-type dispensers to be used according to the present invention include manually operated foam trigger-type dispensers sold for example by Specialty Packaging Products, Inc. or Continental Sprayers, Inc. These types of dispensers are disclosed, for instance, in US-4,701,311 to Dunnining et al. and US-4,646,973 and US-4,538,745 both to Focarracci. Particularly preferred to be used herein are spray-type dispensers such as T 8500<sup>®</sup> commercially available from Continental Spray International or T 8100<sup>®</sup> commercially available from Canyon, Northern Ireland. In such a dispenser the liquid composition is divided in fine liquid droplets resulting in a spray that is directed onto the surface to be treated. Indeed, in such a spray-type dispenser the composition contained in the body of said dispenser is directed through the spray-type dispenser head via energy communicated to a pumping mechanism by the user as said user activates said pumping mechanism. More particularly, in said spray-type dispenser head the composition is forced against an obstacle, e.g. a grid or a cone or the like, thereby providing shocks to help atomise the liquid composition, i.e. to help the formation of liquid droplets.

The process of cleaning a surface:

The present invention also encompasses a process of cleaning a surface wherein a liquid composition as

described herein before, is contacted with said surfaces.

By "surface", it is meant herein any surface including animate surface like human skin, mouth, teeth, and inanimate surfaces. Inanimate surfaces include, but are not limited to, hard-surfaces typically found in houses like kitchens, bathrooms, or in car interiors, e.g., tiles, walls, floors, chrome, glass, smooth vinyl, any plastic, plastified wood, table top, sinks, cooker tops, dishes, sanitary fittings such as sinks, showers, shower curtains, wash basins, WCs and the like, as well as fabrics including clothes, curtains, drapes, bed linens, bath linens, table cloths, sleeping bags, tents, upholstered furniture and the like, and carpets. Inanimate surfaces also include household appliances including, but not limited to, refrigerators, freezers, washing machines, automatic dryers, ovens, microwave ovens, dishwashers and so on.

The liquid compositions of the present invention may be contacted to the surface to be cleaned in its neat form or in its diluted form.

By "diluted form", it is meant herein that said liquid composition is diluted by the user typically with water. The composition is diluted prior use to a typical dilution level of 10 to 400 times its weight of water, preferably from 10 to 100. Usual recommended dilution level is a 1.2% dilution of the composition in water.

In the preferred process of cleaning according to the present invention wherein the surface to be cleaned is a hard-surface and where said composition is used in diluted form, there is no need to rinse the surface after application of the composition in order to obtain excellent first and next-time cleaning performance and also excellent end result surface appearance.

#### The process of manufacturing the liquid compositions:

The present invention also encompasses a process of manufacturing the liquid compositions according to the present invention wherein all the ingredients desired, i.e. the nonionic surfactant, the polymer, the amphoteric surfactant and the optional ingredients as desired if any, are brought together with sufficient agitation, typically with a mechanical blade stirrer for 2 to 15 minutes, preferably 10 minutes, at a speed of 50 to 500 revolutions/minute, preferably about 300, so as to obtain the compositions of the present invention. The compositions according to the present invention are clear and transparent compositions.

According to the present invention the different ingredients may be mixed together in any order without affecting the physical stability of the resulting end compositions of the present invention.

#### Test methods:

By "cleaning performance", it is meant herein cleaning on various types of soils including greasy soils, like kitchen grease or burnt/sticky food residues typically found in a kitchen (e.g., burnt milk) and the like.

The first time dilute cleaning performance may be evaluated by the following test method: Tiles of enamel, vinyl or ceramic are prepared by applying to them a representative grease/particulate artificial soil, followed by ageing. The test compositions and the reference composition are diluted (e.g., composition:water 1:50 or 1:100), applied to a sponge, and used to clean the tiles with a Sheen scrub tester. The number of strokes required to clean to 100% clean is recorded. A minimum of 6 replicates can be taken with each result being generated in duplicate against the reference on each soiled tile.

The next-time dilute cleaning performance may be evaluated by the following test method: Following the procedure detailed for first time cleaning the tiles used for this previous test are taken and resoiled directly without first being further washed or rinsed. The cleaning procedure is then repeated using the Sheen scrub tester, taking care that the test compositions are used to clean the same part of the tile as was previously cleaned by them. The number of strokes required to clean to 100% clean is recorded. A minimum of 6 replicates can be taken with each result being generated in duplicate against the reference on each soiled tile. This resoiling and cleaning procedure can be repeated up to 5 times.

The test method for evaluating neat cleaning performance is identical to above except that the test compositions and reference are used undiluted and that after cleaning a rinsing cycle is performed with clean water. This rinsing cycle may be repeated up to 5 times prior to the resoiling step for next time cleaning evaluation.

Obtaining a good shine end result results from a good spreading of a liquid composition over the surface when the surface is treated therewith and from the reduced formation of watermarks and reduced precipitation of poorly water soluble salts when water evaporates. The ability of a composition to provide "shine" to the surface refers to the composition's ability to leave no watermarks after evaporation of water. This can be evaluated by human visual grading.

In a suitable test method two rectangular areas (10 cm x 4 cm) of a sink (made of either stainless steel or ceramic) are treated with a composition according to the present invention and a reference composition, e.g. the same composition but without said polymer. 3 grams of composition is first poured onto each surfaces to be treated and, then wiped (10 strokes) by using a Spontex<sup>®</sup> sponge. Then each treated surface is rinsed with 200 grams of tap water and left to dry. After the surfaces treated with the compositions according to the present invention and those treated with the ref-

erence composition get dried, they are compared side by side and evaluated by visual grading to evaluate shine difference. Evaluation may be generally done by applying the Panel Score Unit (PSU).

In a long lasting shine test method the test method as mentioned above may be carried out, but the rinsing and drying cycle are repeated several times. Each time, after both the surfaces get dried they are compared side by side and evaluated by visual grading to see shine difference. Evaluation is generally done by applying the Panel Score Unit (PSU).

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

Examples

The following compositions were made by mixing the listed ingredients in the listed proportions. All proportions are % by weight of the total composition.

## Compositions (weight%):

	A	B	C	D	E	F	
5							
	<b><u>Nonionic surfactants</u></b>						
	C 11 EO5	-	7.0	6.8	6.0	5.0	6.5
10	C12,14 EO5	3.0	-	-	-	-	-
	C9,11 EO5	3.0	-	-	-	-	-
	AO21	4.0	5.0	3.2	4.0	3.0	3.5
15	<b><u>Anionic surfactants</u></b>						
	NaPS	2.4	-	-	-	-	-
	NaLAS	-	-	-	-	1.0	-
	NaCS	-	-	1.0	-	-	1.0
20	Isalchem® AS	-	-	-	-	-	0.5
	<b><u>Amphoteric surfactant</u></b>						
	Cocoiminodipropionate	2.0	1.8	1.8	2.0	1.5	1.8
25	<b><u>Buffer</u></b>						
	Na <sub>2</sub> CO <sub>3</sub>	1.0	-	1.0	-	1.0	0.1
	K <sub>2</sub> CO <sub>3</sub>	-	2.0	-	1.0	1.0	-
30	Citric acid	0.75	-	1.0	1.0	-	0.5
	Caustic soda	0.6	-	0.9	0.95	-	0.2
	<b><u>Suds control</u></b>						
35	Fatty Acid	0.5	0.8	0.5	0.7	0.6	0.4
	Isofol 12®	0.1	-	-	-	-	0.1
	<b><u>Polymers</u></b>						
40	PVP K90®	1.0	0.8	0.8	0.8	0.8	0.5
	PEG DME -2000 ®	0.5	0.8	0.8	0.8	-	1.0
	Minors and water	-----	-----	up	to	100%	-----
45	pH	11.0	11.0	11.0	11.0	11.0	7.5
50							
55							

## Compositions (weight%):

	<b>A</b>	<b>B</b>	<b>C</b>	<b>D</b>	<b>E</b>	<b>F</b>	
5							
	<b><u>Nonionic surfactants</u></b>						
	C 11 EO5	-	7.0	6.8	6.0	5.0	6.5
10	C12,14 EO5	3.0	-	-	-	-	-
	C9,11 EO5	3.0	-	-	-	-	-
	AO21	4.0	5.0	3.2	4.0	3.0	3.5
15	<b><u>Anionic surfactants</u></b>						
	NaPS	2.4	-	-	-	-	-
	NaLAS	-	-	-	-	1.0	-
	NaCS	-	-	1.0	-	-	1.0
20	Isalchem® AS	-	-	-	-	-	0.5
	<b><u>Amphoteric surfactant</u></b>						
	Lauryliminodipropionate	2.0	1.8	1.8	2.0	1.5	1.8
25	<b><u>Buffer</u></b>						
	Na <sub>2</sub> CO <sub>3</sub>	1.0	-	1.0	-	1.0	0.1
	K <sub>2</sub> CO <sub>3</sub>	-	2.0	-	1.0	1.0	-
30	Citric acid	0.75	-	1.0	1.0	-	0.5
	Caustic soda	0.6	-	0.9	0.95	-	0.2
	<b><u>Suds control</u></b>						
35	Fatty Acid	0.5	0.8	0.5	0.7	0.6	0.4
	Isofol 12®	0.1	-	-	-	-	0.1
	<b><u>Polymers</u></b>						
40	PVP K90®	1.0	0.8	0.8	0.8	0.8	0.5
	PEG DME -2000 ®	0.5	-	-	0.8	-	-
	PEG(2000)	-	0.8	-	-	-	-
	MME PEG (2000)	-	-	0.8	-	-	-
45	Minors and water	-----	-----	up	to	100%	-----
	pH	11.0	11.0	11.0	11.0	11.0	7.5
50							
55							

## Compositions (weight%):

	<b>A</b>	<b>B</b>	<b>C</b>	<b>D</b>	<b>E</b>	<b>F</b>	
5							
	<b><u>Nonionic surfactants</u></b>						
	C 11 EO5	-	7.0	6.8	6.0	6.0	6.5
10	C12,14 EO5	3.0	-	-	-	-	-
	C9,11 EO5	3.0	-	-	-	-	-
	AO21	4.0	5.0	3.2	4.0	4.0	3.5
15	<b><u>Anionic surfactants</u></b>						
	NaPS	2.4	-	-	-	-	-
	NaLAS	-	-	-	-	-	-
	NaCS	-	-	1.0	-	-	1.0
20	Isalchem® AS	-	-	-	-	-	0.5
	<b><u>Amphoteric surfactant</u></b>						
	Cocoiminodipropionate	1.0	1.8	1.8	2.0	2.0	-
25	Lauryliminodipropionate	1.0	-	-	-	-	1.8
	<b><u>Buffer</u></b>						
	Na <sub>2</sub> CO <sub>3</sub>	1.0	-	1.0	-	-	0.1
30	K <sub>2</sub> CO <sub>3</sub>	-	2.0	-	1.0	1.0	-
	Citric acid	0.75	-	1.0	1.0	1.0	0.5
	Caustic soda	0.6	-	0.9	0.95	0.95	0.2
	<b><u>Suds control</u></b>						
35	Fatty Acid	0.5	0.8	0.5	0.7	0.6	0.4
	Isofol 12®	0.1	-	-	-	-	0.1
	<b><u>Polymers</u></b>						
40	PVP K90®	0.5	-	0.8	-	-	-
	PVP K60®	0.5	0.8	0.8	0.8	-	0.5
	Copolymer of PVP:vinyl acetate (7:3)	-	-	-	-	1.0	-
45	PEG DME -2000 ®	-	-	-	0.8	0.8	1.0
	Minors and water	-----	-----	up	to	100%	-----
50	pH	11.0	11.0	11.0	11.0	11.0	7.5
55							

5 PVP K90® is a vinylpyrrolidone homopolymer (average molecular weight of 360,000), commercially available from ISP Corporation, New York, NY and Montreal, Canada.

10 PVP K60® is a vinylpyrrolidone homopolymer (average molecular weight of 160,000), commercially available from ISP Corporation, New York, NY and Montreal, Canada.

PEG DME-2000® is dimethyl polyethylene glycol (MW 2000) commercially available from Hoescht.

15 Isofol 12® is 2-butyl octanol

AO21 is a C12-14 EO21 alcohol ethoxylate.

20 Isalchem® AS is a branched alcohol alkyl sulphate commercially available from Enichem.

NaPS is sodium paraffin sulfonate.

NaLAS is linear alkyl benzene sulfonate.

NACS is cumene sulfonate.

25 Copolymer of PVP:vinyl acetate (7:3) commercially available from BASF under the trade name Luviskol®.

PEG (2000) is polyethylene glycol (MW 2000)

30 MME PEG (2000) is monomethyl ether polyethylene glycol (MW 2000) which is commercially available from Fluka Chemie AG.

35 All the above compositions are physically stable upon storage for prolonged periods of time, e.g., for four weeks at 20°C without undergoing any segregative phase separation. This is not the case for the reference compositions, i.e., the same compositions which do not contain the amphoteric surfactant according to the present invention.

40 Excellent first and next-time cleaning performance and good gloss were delivered to the hard-surfaces cleaned with these compositions both under neat and diluted conditions, e.g. at a dilution level of 50:1 or 200:1 (water:composition).

### Claims

- 45 1. A liquid cleaning composition comprising a nonionic surfactant, a polymer and an amphoteric surfactant according to the formula:



50 wherein the substituent  $R_1$  is a substituted or unsubstituted, saturated or unsaturated, linear or branched hydrocarbon chain having from 6 to 22 carbon atoms, wherein the substituents  $R_2$  and  $R_3$  each independently are a C1 to C6 alkyl carboxylic acid group, which may be the same or different, and wherein X is H.

- 55 2. A composition according to claim 1 which comprises from 1% to 50% by weight of the total composition of said non-ionic surfactant or a mixture thereof, preferably from 5% to 30%, more preferably from 7% to 20% and most preferably from 8% to 15%.

3. A composition according to any of the preceding claims wherein said nonionic surfactant is 10-25 polyethylene

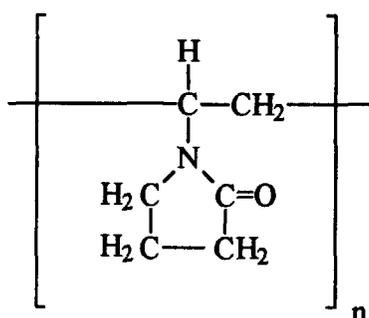
oxide condensate of C6-C20 alkyl phenol, 2-35 polyethylene oxide condensate of C6-C22 alkyl alcohol, alkyl-polysaccharide, or a mixture thereof, preferably a polyethylene oxide condensate of C8-C18 alkyl alcohol with from 4 to 25 moles of ethylene oxide, preferably from 5 to 18 moles of ethylene oxide or a mixture thereof.

- 5 4. A composition according to any of the preceding claims which comprises from 0.001% to 20% by weight of the total composition of a polymer or a mixture thereof, preferably from 0.1% to 5%, more preferably from 0.4% to 5% and most preferably from 0.5% to 3%.
- 10 5. A composition according to any of the preceding claims wherein said polymer is vinylpyrrolidone homopolymer or copolymer, a polysaccharide polymer or a mixture thereof.
6. A composition according to claim 5 wherein said vinylpyrrolidone homopolymer is an homopolymer of N-vinylpyrrolidone having the following repeating monomer:

15

20

25



wherein n is an integer of from 10 to 1,000,000, preferably 20 to 100,000 and more preferably from 20 to 10,000.

- 30 7. A composition according to claims 5 or 6 wherein said vinylpyrrolidone copolymer is a copolymer of N-vinylpyrrolidone and alkylenically unsaturated monomer preferably selected from the group consisting of maleic acid, chloromaleic acid, fumaric acid, itaconic acid, citraconic acid, phenylmaleic acid, aconitic acid, acrylic acid, N-vinylimidazole, vinyl acetate, and anhydrides thereof, styrene, sulphonated styrene, alpha-methyl styrene, vinyl toluene, t-butyl styrene and mixtures thereof and/or a quaternized copolymer of vinylpyrrolidone and dimethylaminoethylmethacrylate.
- 35 8. A composition according to any of the preceding claims 5 to 7, wherein said polysaccharide polymer is carboxymethylcellulose, ethyl cellulose, hydroxyethyl cellulose, hydroxypropyl cellulose, hydroxymethyl cellulose, succinoglycan and naturally occurring polysaccharide polymers like xanthan gum, guar gum, locust bean gum, tragacanth gum or derivatives thereof, or mixtures thereof.
- 40 9. A composition according to any of the preceding claims which comprises from 0.001% to 20% by weight of the total composition of an amphoteric surfactant or a mixture thereof, preferably from 0.01% to 10%, more preferably from 0.1% to 5% and most preferably from 0.2% to 4%.
- 45 10. A composition according to any of the preceding claims wherein in said amphoteric surfactant the substituent R<sub>1</sub> is a substituted or unsubstituted, saturated or unsaturated, linear or branched alkyl group, alkenyl group, or alkyl-aryl group containing from 6 to 22 carbon atoms, more preferably from 8 to 20 carbon atoms and most preferably from 10 to 18 carbon atoms and the substituents R<sub>2</sub> and R<sub>3</sub> each independently are a C1 to C4 alkyl carboxylic acid group, which may be the same or different, and more preferably are two C2 alkyl carboxylic acid groups and wherein more preferably said amphoteric surfactant is cocoiminodipropionate.
- 50 11. A composition according to any of the preceding claims which is an aqueous liquid composition having a pH of from 0 to 14, preferably of from 1 to 13, preferably from 7 to 13 and more preferably from 9 to 12.
- 55 12. A composition according to any of the preceding claims which further comprises an optional ingredient selected from the group consisting of other surfactants apart said nonionic and said amphoteric surfactants, builders, chelants, antiresoiling ingredients, solvents, buffers, bactericides, hydrotropes, colorants, stabilisers, radical scav-

engers, bleaches, bleach activators, fatty acids, enzymes, soil suspenders, soil-release agents, dye transfer agents, brighteners, anti dusting agents, suds controlling agents, dispersants, dye transfer inhibitors, abrasives, pigments, dyes, perfumes and mixtures thereof.

5 13. A composition according to claim 12 which comprise from 0.001% to 20% by weight of the total composition of an antiresoiling ingredient selected from the group consisting of:

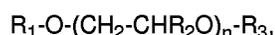
- a polyalkoxyethylene glycol according to the formula:



- a monocapped polyalkoxyethylene glycol of the formula:



- a dicapped polyalkoxyethylene glycol of the formula:



and a mixture thereof, wherein the substituents  $R_1$  and  $R_3$  each independently are substituted or unsubstituted, saturated or unsaturated, linear or branched hydrocarbon chains having from 1 to 30 carbon atoms, or amino bearing linear or branched, substituted or unsubstituted hydrocarbon chains having from 1 to 30 carbon atoms,  $R_2$  is hydrogen or a linear or branched hydrocarbon chain having from 1 to 30 carbon atoms, and wherein  $n$  is an integer greater than 0.

25 14. A process of cleaning a surface, wherein a liquid composition according to any of the preceding claims, is contacted with said surface.

30 15. A process of cleaning a surface according to claim 14 wherein said surface preferably is a hard-surface and wherein said composition is contacted with said surface after having been diluted with water.

16. A process according to claim 15 wherein said surface is not rinsed after said composition has been contacted with said surface.

35 17. The use of an amphoteric surfactant according to the formula:



40 wherein the substituent  $R_1$  is a substituted or unsubstituted, saturated or unsaturated, linear or branched hydrocarbon chain having from 6 to 22 carbon atoms, wherein the substituents  $R_2$  and  $R_3$  each independently are a C1 to C6 alkyl carboxylic acid group, which may be the same or different, and wherein  $X$  is hydrogen, in a liquid composition comprising a nonionic surfactant and a polymer for improving the physical stability of said composition.

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EUROPEAN SEARCH REPORT

Application Number  
EP 97 87 0109

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
X	US 4 416 792 A (BLACKSTONE PAUL C. ) 22 November 1983 * the whole document * ---	1-5, 8-13,17	C11D1/10 C11D1/88 C11D1/94 C11D1/83
A	EP 0 167 382 A (THE PROCTER & GAMBLE CO.) 8 January 1986 * page 2, line 13 - line 30 * * page 7, line 28 - line 36 * * page 8, line 20 - page 9, line 33 * * claims 1,2,6-11,14 * ---	1-5,8,9, 11-13	C11D3/37 C11D3/22 //C11D1:72, C11D1:10, C11D1:88, C11D1:66
A	US 4 264 479 A (FLANAGAN JOHN J. ) 28 April 1981 * column 2, line 6 - line 68 * * column 3, line 42 - column 4, line 45 * * column 6, line 30 - line 64; claims * ---	1-3,9-12	
D,A	WO 94 26858 A (UNILEVER PLC. ) 24 November 1994 * page 5, line 10 - page 11, line 14 * * page 13, line 16 - page 14, line 25 * ---	1-4, 11-16	
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A	EP 0 013 585 A (UNILEVER NV. ) 23 July 1980 * page 5, line 1 - page 8, line 33 * * page 10, line 1 - page 11, line 21 * -----	1-7,12	
The present search report has been drawn up for all claims			
Place of search <b>THE HAGUE</b>		Date of completion of the search <b>10 December 1997</b>	Examiner <b>Serbetsoglou, A</b>
CATEGORY OF CITED DOCUMENTS		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons ----- & : member of the same patent family, corresponding document	
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