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LIQUID CLEANING COMPOSITION

TECHNICAL FIELD

The present invention relates to liquid compositions for cleaning a variety of inanimate surfaces, including hard surfaces in and around the house, dish surfaces, car and vehicles surfaces, etc. More specifically, the present invention relates to liquid scouring composition comprising suitable particles for cleaning.

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BACKGROUND OF THE INVENTION

Scouring compositions such as particulate compositions or liquid (incl. gel, paste-type) compositions containing abrasive components are well known in the art. Such compositions are used for cleaning a variety of surfaces; especially those surfaces that tend to become soiled with difficult to remove stains and soils.

Amongst the currently known scouring compositions, the most popular ones are based on abrasive particles with shapes varying from spherical to irregular. The most common abrasive particles are either inorganic like carbonate salt, clay, silica, silicate, shale ash, perlite and quartz sand or organic polymeric beads like polypropylene, PVC, melamine, urea, polyacrylate and derivatives, and come in the form of liquid composition having a creamy consistency with the abrasive particles suspended therein.

The surface safety profile of such currently known scouring compositions is inadequate alternatively, poor cleaning performances is shown for compositions with an adequate surface safety profile. Indeed, due to the presence of very hard abrasive particles, these compositions can damage, i.e., scratch, the surfaces onto which they have been applied. Indeed, the formulator needs to choose between good cleaning performance but featuring strong surface damage or compromising on the cleaning performance while featuring acceptable surface safety profile. In addition, such currently known scouring compositions at least in certain fields of application (e.g., hard surface cleaning) are perceived by consumers as outdated, and are often disliked due to unpleasant feel on the hands during usage.

One type of suitable abrasive particles are natural particles such as nut shell particles and vegetable particles. Natural particles have undesired brownish color and a small amount of these

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particles tend to turn the cleaning liquid to brown color which is aesthetically undesired effect. During cleaning, it is observed that residual brown particles left on the surface leave dark residue that compromises the overall cleaning efficiency of the cleaning products. The use of bleached abrasive particles is therefore preferred to improve final cleaning results.

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Additionally brown colored particles are more visible in a cleaning liquid than white colored and therefore white colored abrasive particles are more preferred. This is due white colored particle's ability to improve final cleaning results and their aesthetic features.

It is thus an objective of the present invention to provide a liquid cleaning composition suitable to clean a variety of surfaces, including inanimate surfaces, such hard surfaces in and around the house, dish surfaces, etc., wherein the composition provides good cleaning performance, whilst providing a good surface safety profile. It is another objective of the present invention is to provide aesthetically acceptable cleaning composition comprising abrasive cleaning particles to improve cleaning performance.

It has been found that the above objectives are met by the composition according to the present invention.

It is an advantage of the compositions according to the present invention that they may be used to clean/cleanse inanimate surfaces made of a variety of materials like glazed and non-glazed ceramic tiles, enamel, stainless steel, Inox®, Formica®, vinyl, no-wax vinyl, linoleum, melamine, glass, plastics, Teflon®, painted surfaces and the like.

A further advantage of the present invention is that in the compositions herein, the particles can be formulated at very low levels, whilst still providing the above benefits. Indeed, in general for other technologies, high levels of abrasive particles are needed to reach good cleaning performance, thus leading to high formulation and process cost, difficult rinse and end cleaning profiles, as well as limitation for aesthetics and a pleasant hand feel of the cleaning composition.

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SUMMARY OF THE INVENTION

The present invention relates to a liquid cleaning composition comprising bleached cleaning particles as abrasives, wherein said bleached cleaning particles are selected from the group

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consisting bleached nut shell particles, bleached particles derived from other plant parts, bleached wood particles and mixtures thereof, and wherein bleached abrasive cleaning particles have a degree of whiteness (L*) of greater than 65, measured under D 65 illumination.

The present invention further encompasses a process of cleaning a surface with a liquid, cleaning composition comprising abrasive cleaning particles, wherein said surface is contacted with said composition, preferably wherein said composition is applied onto said surface.

DETAILED DESCRIPTION OF THE INVENTION

The liquid cleaning composition

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The compositions according to the present invention are designed as cleaners for a variety of inanimate surfaces.

In a preferred embodiment, the compositions herein are suitable for cleaning inanimate surfaces selected from the group consisting of household hard surfaces; dish surfaces; surfaces like leather or synthetic leather; and automotive vehicles surfaces.

By "household hard surface", it is meant herein any kind of surface typically found in and around houses like kitchens, bathrooms, e.g., floors, walls, tiles, windows, cupboards, sinks, showers, shower plastified curtains, wash basins, WCs, fixtures and fittings and the like made of different materials like ceramic, vinyl, no-wax vinyl, linoleum, melamine, glass, Inox®, Formica®, vitroceramic, any plastics, plastified wood, metal or any painted or varnished or sealed surface and the like. Household hard surfaces also include household appliances including, but not limited to refrigerators, freezers, washing machines, automatic dryers, ovens, microwave ovens, dishwashers and so on. Such hard surfaces may be found both in private households as well as in commercial, institutional and industrial environments.

By "dish surfaces" it is meant herein any kind of surfaces found in dish cleaning, such as dishes, cutlery, cutting boards, pots, pans, and the like made of different materials like stainless steel, glass, ceramic, china, metal, any plastics, wood, and Teflon. Such dish surfaces may be found both in private households as well as in commercial, institutional and industrial environments.

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The compositions according to the present invention are liquid compositions as opposed to a solid or a gas. Liquid compositions include compositions having a water-like viscosity as well as thickened compositions, such as gels and pastes.

In a preferred embodiment herein, the liquid compositions herein are aqueous compositions. Therefore, they may comprise from 30% to 99.5% by weight of the total composition of water, preferably from 35% to 98% and more preferably from 40% to 95%.

In another preferred embodiment herein, the liquid compositions herein are mostly non-aqueous compositions although they may comprise from 0% to 10% by weight of the total composition of water, preferably from 0% to 5%, more preferably from 0% to 1% and most preferably 0% by weight of the total composition of water.

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In a preferred embodiment herein, the compositions herein are neutral compositions, and thus have a pH, as is measured at 25°C, of 6 - 10, more preferably 6.5 - 9.5, even more preferably 7-9.

In other preferred embodiment compositions have pH preferably above pH 4 and alternatively have pH preferably below pH 9.5.

20 Accordingly, the compositions herein may comprise suitable bases and acids to adjust the pH.

A suitable base to be used herein is an organic and/or inorganic base. Suitable bases for use herein are the caustic alkalis, such as sodium hydroxide, potassium hydroxide and/or lithium hydroxide, and/or the alkali metal oxides such, as sodium and/or potassium oxide or mixtures thereof. A preferred base is a caustic alkali, more preferably sodium hydroxide and/or potassium hydroxide.

Other suitable bases include ammonia, ammonium carbonate, all available carbonate salts such as K₂CO₃, Na₂CO₃, CaCO₃, MgCO₃, etc., alkanolamines (as e.g. monoethanolamine), urea and urea derivatives, polyamine, etc.

Typical levels of such bases, when present, are of from 0.01% to 5.0%, preferably from 0.05% to 3.0% and more preferably from 0.1% to 0.6 % by weight of the total composition.

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The compositions herein may comprise an acid to trim its pH to the required level, despite the presence of an acid, if any, the compositions herein will maintain their neutral to alkaline, preferably alkaline, pH as described herein above. A suitable acid for use herein is an organic and/or an inorganic acid. A preferred organic acid for use herein has a pKa of less than 6. A suitable organic acid is selected from the group consisting of citric acid, lactic acid, glycolic acid, succinic acid, glutaric acid and adipic acid and a mixture thereof. A mixture of said acids may be commercially available from BASF under the trade name Sokalan® DCS. A suitable inorganic acid is selected from the group consisting hydrochloric acid, sulphuric acid, phosphoric acid and a mixture thereof.

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A typical level of such an acid, when present, is of from 0.01% to 5.0%, preferably from 0.04% to 3.0% and more preferably from 0.05% to 1.5 % by weight of the total composition.

In a preferred embodiment according to the present invention the compositions herein are thickened compositions. Preferably, the liquid compositions herein have a viscosity of up to 7500 cps at 20 s⁻¹, more preferably from 5000 cps to 50 cps, yet more preferably from 2000 cps to 50 cps and most preferably from 1500 cps to 300 cps at 20 s⁻¹ and 20°C when measured with a Rheometer, model AR 1000 (Supplied by TA Instruments) with a 4 cm conic spindle in stainless steel, 2° angle (linear increment from 0.1 to 100 sec⁻¹ in max, 8 minutes).

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In another preferred embodiment according to the present invention the compositions herein have a water-like viscosity. By "water-like viscosity" it is meant herein a viscosity that is close to that of water. Preferably the liquid compositions herein have a viscosity of up to 50 cps at 60 rpm, more preferably from 0 cps to 30 cps, yet more preferably from 0 cps to 20 cps and most preferably from 0 cps to 10 cps at 60 rpm and 20°C when measured with a Brookfield digital viscometer model DV II, with spindle 2.

Abrasive cleaning particles

The liquid cleaning composition herein comprise abrasive cleaning particles formed by shearing and/or grinding nut shell, or other plant parts. By other plant parts are meant such as, but not limited to stems, roots, leaves, seeds, roots and mixtures thereof. Wood can also be used to produce the abrasive cleaning particles of the present composition.

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Preferably nut shell is selected from the group consisting of pistachio nut shell, walnut shell, almond shell and mixtures thereof. Preferably nut shell is walnut shell or pistachio nut shell.

When other plant parts are used to produce the cleaning particles of the present invention, they are preferably derived from rice, corn cob, palm biomass, bamboo, kenaf, apple seeds, apricot stone, olive stone and mixtures thereof. When other plant parts are used, preferably cleaning particles are produced from olive stone.

It has surprisingly been found that the abrasive cleaning particles of the present invention show a good cleaning performance even at relatively low levels, such as preferably from 0.1% to 20%, preferably from 0.1% to 10%, more preferably from 0.5% to 5%, even more preferably from 0.5% to 3%, by weight of the total composition of said abrasive cleaning particles.

The abrasive cleaning particles are preferably color stable particles. By "color stable" it is meant herein that color of the particles used in the present invention will substantially not change during storage and use.

The abrasive particles used herein are preferably bleached. A bleaching process for shells of walnuts is described in Research and Industry, Vol. 29, March 1984, pages 10-16. Alternative well-known bleaching processes and chemicals used in bleaching processes are listed below.

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An aqueous bleaching agent is used in the abrasive particle bleaching process. Preferably the aqueous bleaching agent is selected from the group consisting of metal hypochlorite e.g.: calcium or sodium hypochlorite, metal chlorate e.g.: sodium chlorate, hydrogen peroxide, metal perborate e.g.: sodium perborate, metal percarbonate, e.g.: sodium percarbonate, metal peroxide e.g.: calcium, magnesium, acyl or benzoyl peroxide, peracetic acid, ozone, sodium bisulphate, nitrogen dioxide, chlorine, chlorine dioxide, azodicarbonamide, sulphite e.g.: sodium sulphite, sodium metabisulphite, a percarbonate such as sodium percarbonate and tetraacetyleneethylenediamine, metal peroxy monosulfate e.g.: sodium or potassium peroxy monosulfate and mixtures thereof.

Activation via acidification with acetic acid, hydrochloric acid, sulfuric acid or nitric acid is promoting bleaching in some bleaching compositions. Without being bound to the theory, it is

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believed that the bleaching composition is also promoting acetolysis, with incident whitening effect.

The use of hydrogen peroxide, sodium hypochlorite or sodium chlorite with or without acid pretreatment is preferred.

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The bleaching process is also knowingly helping to inhibit bacterial, mold or fungus growth inherently present in nature-derived products.

To reach desired whiteness level in nut and or vegetable particles, additives can be used to boost the bleaching process. Suitable additives are brightening agents such as optical brightening agents, fluorescent brightening agents and fluorescent whitening agents. Suitable optical brighteners include stilbene brighteners. Stilbene brighteners are aromatic compounds with two aryl groups separated by an alkylene chain. Optical brighteners are described in greater detail in U.S. Pat. numbers 4,309,316; 4,298,490; 5,035,825 and 5,776,878. Other useful additives to boost the whitening process are dyes or pigments used as coating agents, especially Titanium dioxide or pearlescent technology described in US 7713921.

The production of whitened abrasive material according to the processes described above are typically achieved before the abrasive is formulated in the cleaning composition, However, in some instance, the whitening process can be achieved also during the process of preparing the cleaning composition and sometime extending during the storage of the finished cleaning composition. In this case bleaching agents of cleaning composition bleaches cleaning particles in situ. The bleached abrasive cleaning particles obtained via this process have a degree of whiteness (L*) of greater than 65, measured under D 65 illumination. Degree of whiteness of greater than 65, measured under D65 illumination is reached in situ bleaching process within 10 days. In situ bleaching compositions comprise bleaching agent at minimum of 3% by weight of the cleaning composition, more preferably minimum of 5% (however maximum quantity of bleaching agent is 20% by weight of the composition), wherein composition comprises maximum of 5% natural abrasive particles by weight of the composition, preferably maximum of 2%. Bleaching agent is selected from sodium hypochlorite or hydrogen peroxide. The bleaching agent is preferably hydrogen peroxide.

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The particles used in the present invention are preferably white having degree of whiteness (L*) of greater than 65, preferably above 75, measured under D 65 illumination.

Additionally suitable color stabilizing agents can be used to stabilize desired color and/or whiteness.

As used herein, the term "degree of whiteness (L*)" means the whiteness value of a tableted sample measured using Gretag machbeathTM 7000 a color-eye instrument or equivalent used in reflectance mode. This instrument provides a choice of light sources; "D65" represents roughly a mid-day sun in western and northern Europe, whilst "illuminant A" is intended to represent typical, domestic, tungsten-filament lighting and "CWF2" represents cool white fluorescent. The instrument thus provides a standard measure of whiteness (L*) that can be determined for daylight, tungsten and fluorescent lighting conditions. Under each set of lightning conditions L* is defined such that 100 is fully white and 0 has no white components. For the purposes of the present invention, the "D65" illuminant is used to measure whiteness.

Whiteness measurement:

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Whiteness (L*) was measured using Gretag Macbeath 7000 a color-eye instrument in reflectance mode with the "D65" light source representing roughly a mid-day sun in western and northern Europe.

Samples were prepared by filling bleached nut shell particles in a holder to ensure good packing of the particle so to make a continuous layer of material. Measurements were made by placing the tabled in the holder of the color-eye instrument. The area if view was 3mm by 8mm with degree observer angle 10°. The specular component was included. Measurements were generally made duplicate and an average was taken.

In a preferred embodiment the abrasive cleaning particles are preferably non-rolling. Alternatively in another preferred embodiment the abrasive cleaning particles are preferably sharp. By non-rolling is meant that the abrasive cleaning particle and the surface are in contact with each other by sliding.

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Indeed the applicant has found that non-rolling and/or sharp abrasive cleaning particles provide good soil removal.

In a preferred embodiment, the abrasive cleaning particles have a mean ECD from 10 μ m to 1000 μ m, preferably from 50 μ m to 500 μ m, more preferably from 100 μ m to 350 μ m and most preferably from 150 to 250 μ m.

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Indeed, the Applicant has found that the abrasive particle size can be critical to achieve efficient cleaning performance whereas excessively abrasive population with small particle sizes e.g.: typically below 10 micrometers feature polishing action vs. cleaning despite featuring a high number of particles per particle load in cleaner inherent to the small particle size. On the other hand, abrasive population with excessively high particle size, e.g.: above 1000 micrometers, do not deliver optimal cleaning efficiency, because the number of particles per particle load in cleaner, decreases significantly inherently to the large particle size. Additionally, excessively small particle size are not desirable in cleaner / for cleaning task since in practice, small and numerous particles are often hard to remove from the various surface topologies which requires excessive effort to remove from the user unless leaving the surface with visible particles residue. On the other hand, excessively large particle are too easily detected visually or provide bad tactile experience while handling or using the cleaner. Therefore, the applicant defines herein an optimal particle size range that delivers both optimal cleaning performance and usage experience.

The abrasive particles have a size defined by their area-equivalent diameter (ISO 9276-6:2008(E) section 7) also called Equivalent Circle Diameter ECD (ASTM F1877-05 Section 11.3.2). Mean ECD of particle population is calculated as the average of respective ECD of each particles of a particle population of at least 10 000 particles, preferably above 50 000 particles, more preferably above 100 000 particles after excluding from the measurement and calculation the data of particles having area-equivalent diameter (ECD) of below 10 micrometers. Mean data are extracted from volume-based vs. number-based measurements.

One suitable way of reducing the nut shell and/or other plant parts to the abrasive cleaning particles herein is to grind or mill said nut shell and/or other plant parts. Other suitable means include the use of eroding tools such as a high speed eroding wheel with dust collector wherein

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the surface of the wheel is engraved with a pattern or is coated with abrasive sandpaper or the like to promote the foam to form the abrasive cleaning particles herein.

Alternatively the bulk nut shell and/or other plant parts can be broken into pieces of a few cm dimensions by manually chopping or cutting, or using a mechanical tool such as a lump breaker, for example the Model 2036 from S Howes, Inc. of Silver Creek, NY. In a second stage, the lumps are agitated using a propeller or saw toothed disc dispersing tool, which causes the nut shell and/or other plant parts to release entrapped water and form liquid slurry of nut shell and/or other plant parts particles dispersed in aqueous phase. In a third stage, a high shear mixer (such as the Ultra Turrax rotor stator mixer from IKA Works, Inc., Wilmington, NC) can be employed to reduce the particle size of the primary slurry to that required for cleaning particles.

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Preferably the abrasive cleaning particles obtained via grinding or milling operation are single particles.

Preferred abrasive cleaning particles in the present invention have hardness from 40 to 90, preferably from 60 to 90, more preferably from 50 to 85 and most preferably from 70 to 80 before being immersed in the liquid cleaning, measured according to Shore D hardness scale. The hardness Shore D is measured with a durometer type D according to a procedure described in ASTM D2240

Alternatively preferred abrasive cleaning particles in the present invention have hardness from 0.2 to 4, preferably from 0.2 to 3 when immersed in the liquid cleaning composition, measured according to MOHS hardness scale. The MOHS hardness scale is an internationally recognized scale for measuring the hardness of a compound versus a compound of known hardness, see Encyclopedia of Chemical Technology, Kirk-Othmer, 4th Edition Vol 1, page 18 or Lide, D.R (ed) CRC Handbook of Chemistry and Physics, 73 rd edition, Boca Raton, Fla.: The Rubber Company, 1992-1993.

The abrasive cleaning particles used in the present invention can be a mixture of bleached nut shell particles or bleached vegetable particles and other suitable abrasive cleaning particles. However all abrasive cleaning particles need to have Shore D hardness scale below or equal to 90 or MOSH hardness equal or below 4. The other abrasive cleaning particles can be selected from the group consisting of plastics, hard waxes, inorganic and organic abrasives, and natural materials. The other abrasive cleaning particle is substantially insoluble or partially soluble in

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water. Most preferably the other abrasive component is calcium carbonate or derived from natural vegetable abrasives.

Optional ingredients

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

Suitable optional ingredients for use herein include suspending aids, chelating agents, surfactants, radical scavengers, perfumes, cleaning and surface-modifying polymers, solvents, builders, buffers, antimicrobial agents, hydrotropes, colorants, stabilizers, bleaches, bleach activators, suds controlling agents both for suds boosting and suds suppression like fatty acids, enzymes, soil suspenders, brighteners, anti dusting agents, dispersants, pigments, dyes, pearlescent agents, rheology modifiers, skin care actives such as emollients, humectants and/or conditioning polymers.

15 Suspending aid

The abrasive cleaning particles present in the composition herein are solid particles in a liquid composition. Said abrasive cleaning particles may be suspended in the liquid composition. However, it is well within the scope of the present invention that such abrasive cleaning particles are not-stably suspended within the composition and either settle or float on top of the composition. In this case, a user may have to temporally suspend the abrasive cleaning particles by agitating (e.g., shaking or stirring) the composition prior to use.

However, it is preferred herein that the abrasive cleaning particles are stably suspended in the liquid compositions herein. Thus the compositions herein comprise a suspending aid.

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The suspending aid herein may either be a compound specifically chosen to provide a suspension of the abrasive cleaning particles in the liquid compositions of the present invention, such as a structurant, or a compound that also provides another function, such as a thickener or a surfactant (as described herein elsewhere).

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Any suitable organic and inorganic suspending aids typically used as gelling, thickening or suspending agents in cleaning compositions and other detergent or cosmetic compositions may be used herein. Indeed, suitable organic suspending aids include polysaccharide polymers. In

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addition or as an alternative, polycarboxylate polymer thickeners may be used herein. Also, in addition or as an alternative of the above, layered silicate platelets e.g.: Hectorite, bentonite or montmorillonites can also be used. Suitable commercially available layered silicates are Laponite RD® or Optigel CL® available from Rockwood Additives. Also, in addition or as an alternative of the above Hydroxyl-containing crystalline structuring agents such as a hydroxyl-containing fatty acid, fatty ester or fatty soap wax-like materials or the like such as the ones described in US patent 6080707 can be used. Said crystalline hydroxyl-containing structuring agent is insoluble in water under ambient to near ambient conditions. Some preferred hydroxyl-containing suspending aids include 12-hydroxystearic acid, 9,10-dihydroxystearic acid, tri-9,10-dihydroxystearin and tri-12-hydroxystearin. Castor wax or hydrogenated castor oil is produced by the hydrogenation (saturation of triglyceride fatty acids) of pure castor oil and is mainly composed of tri-12-hydroxistearin. Commercially available, castor oil-based, crystalline, hydroxyl-containing stabilizers include THIXCIN® from Rheox, Inc. (now Elementis).

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Suitable polycarboxylate polymer thickeners include (preferably lightly) crosslinked polyacrylate. A particularly suitable polycarboxylate polymer thickener is Carbopol commercially available from Lubrizol under the trade name Carbopol 674®.

Suitable polysaccharide polymers for use herein include substituted cellulose materials like carboxymethylcellulose, ethyl cellulose, hydroxyethyl cellulose, hydroxypropyl cellulose, hydroxymethyl cellulose; micro fibril cellulose (MFC) such as described in US 2008/0108714 (CP Kelco) or US2010/0210501 (P&G) succinoglycan and naturally occurring polysaccharide polymers like Xanthan gum, gellan gum, guar gum, locust bean gum, tragacanth gum, succinoglucan gum, or derivatives thereof, or mixtures thereof. Xanthan gum is commercially available from Kelco under the tradename Kelzan T.

More preferred suspending aids are tri-12-hydroxystearin and Xanthan gum. In an alternative embodiment, the suspending aid herein is a polycarboxylate polymer thickeners preferably a (preferably lightly) cross linked polyacrylate. In a highly preferred embodiment herein, the liquid compositions comprise a combination of a polysaccharide polymer or a mixture thereof, preferably Xanthan gum, with a polycarboxylate polymer or a mixture thereof, preferably a cross linked polyacrylate.

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As a preferred example, xanthan gum is preferably present at levels between 0.1% to 5%, more preferably between 0.5% to 2%, even more preferably between 0.8% to 1.2%, by weight of the total composition.

As a preferred example, tri-12-hydroxystearin is present at levels between 0.05% to 5%, more preferably between 0.08% to 3%, even more preferably between 0.1% to 2.5% by weight of the total composition.

Organic Solvent

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As an optional but highly preferred ingredient the composition herein comprises an organic solvents or mixtures thereof.

The compositions herein comprise from 0% to 30%, more preferably about 1.0% to about 20% and most preferably, about 2% to about 15% by weight of the total composition of an organic solvent or a mixture thereof.

Suitable solvents can be selected from the group consisting of: aliphatic alcohols, ethers and diethers having from about 4 to about 14 carbon atoms, preferably from about 6 to about 12 carbon atoms, and more preferably from about 8 to about 10 carbon atoms; glycols or alkoxylated glycols; glycol ethers; alkoxylated aromatic alcohols; aromatic alcohols; terpenes; and mixtures thereof. Aliphatic alcohols and glycol ether solvents are most preferred.

Aliphatic alcohols, of the formula R-OH wherein R is a linear or branched, saturated or unsaturated alkyl group of from about 1 to about 20 carbon atoms, preferably from about 2 to about 15 and more preferably from about 5 to about 12, are suitable solvents. Suitable aliphatic alcohols are methanol, ethanol, propanol, isopropanol or mixtures thereof. Among aliphatic alcohols, ethanol and isopropanol are most preferred because of their high vapor pressure and tendency to leave no residue.

Suitable glycols to be used herein are according to the formula HO-CR₁R₂-OH wherein R1 and R2 are independently H or a C₂-C₁₀ saturated or unsaturated aliphatic hydrocarbon chain and/or cyclic. Suitable glycols to be used herein are dodecaneglycol and/or propanediol.

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In one preferred embodiment, at least one glycol ether solvent is incorporated in the compositions of the present invention. Particularly preferred glycol ethers have a terminal C₃-C₆ hydrocarbon attached to from one to three ethylene glycol or propylene glycol moieties to provide the appropriate degree of hydrophobicity and, preferably, surface activity. Examples of commercially available solvents based on ethylene glycol chemistry include mono-ethylene glycol n-hexyl ether (Hexyl Cellosolve®) available from Dow Chemical. Examples of commercially available solvents based on propylene glycol chemistry include the di-, and tri-propylene glycol derivatives of propyl and butyl alcohol, which are available from Arco under the trade names Arcosolv® and Dowanol®.

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In the context of the present invention, preferred solvents are selected from the group consisting of mono-propylene glycol mono-propyl ether, di-propylene glycol mono-propyl ether, mono-propylene glycol mono-butyl ether, di-propylene glycol mono-butyl ether; tri-propylene glycol mono-butyl ether; ethylene glycol mono-butyl ether; di-ethylene glycol mono-butyl ether, ethylene glycol mono-hexyl ether and di-ethylene glycol mono-hexyl ether, and mixtures thereof. "Butyl" includes normal butyl, isobutyl and tertiary butyl groups. Mono-propylene glycol and mono-propylene glycol mono-butyl ether are the most preferred cleaning solvent and are available under the tradenames Dowanol DPnP® and Dowanol DPnB®. Di-propylene glycol mono-t-butyl ether is commercially available from Arco Chemical under the tradename Arcosoly PTB®.

In a particularly preferred embodiment, the cleaning solvent is purified so as to minimize impurities. Such impurities include aldehydes, dimers, trimers, oligomers and other by-products. These have been found to deleteriously affect product odor, perfume solubility and end result. The inventors have also found that common commercial solvents, which contain low levels of aldehydes, can cause irreversible and irreparable yellowing of certain surfaces. By purifying the cleaning solvents so as to minimize or eliminate such impurities, surface damage is attenuated or eliminated.

Though not preferred, terpenes can be used in the present invention. Suitable terpenes to be used herein monocyclic terpenes, dicyclic terpenes and/or acyclic terpenes. Suitable terpenes are: D-limonene; pinene; pine oil; terpinene; terpene derivatives as menthol, terpineol, geraniol, thymol; and the citronella or citronellol types of ingredients.

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

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 about 1 to about 20 carbon atoms, preferably from about 1 to about 15 and more preferably from about 1 to about 10. For example a suitable aromatic alcohol to be used herein is benzyl alcohol.

Surfactants

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The compositions herein may comprise nonionic, anionic, zwitterionic, amphoteric, cationic surfactants or mixtures thereof. Suitable surfactants are those selected from the group consisting of nonionic, anionic, zwitterionic, cationic and amphoteric surfactants, having hydrophobic chains containing from 8 to 20 carbon atoms. Examples of suitable surfactants are described in McCutcheon's Vol. 1: Emulsifiers and Detergents, North American Ed., McCutcheon Division, MC Publishing Co., 2002.

Preferably, the composition herein comprises from 0.01% to 50%, more preferably from 0.5% to 40%, and most preferably from 1% to 36% by weight of the total composition of a surfactant or a mixture thereof.

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Non-limiting examples of suitable non-ionic surfactants include alcohol alkoxylates, alkyl polysaccharides, amine oxides, block copolymers of ethylene oxide and propylene oxide, fluoro surfactants and silicon based surfactants. Nonionic surfactant, when present as co-surfactant, is comprised in a typical amount of from 0.01% to 15%, preferably 0.1% to 12%, more preferably from 0.5% to 10% by weight of the liquid detergent composition. When present as main surfactant, it is comprised in a typical amount of from 0.8% to 40 %, preferably 1% to 38%, more preferably 2% to 35% by weight of the total composition.

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A preferred class of non-ionic surfactants suitable for the present invention is alkyl ethoxylates. The alkyl ethoxylates of the present invention are either linear or branched, primary or secondary, and contain from 8 carbon atoms to 22 carbon atoms in the hydrophobic tail, and from 1 ethylene oxide units to 25 ethylene oxide units in the hydrophilic head group. Examples of alkyl ethoxylates include Neodol 91-6®, Neodol 91-8® supplied by the Shell Corporation (P.O. Box 2463, 1 Shell Plaza, Houston, Texas), and Alfonic 810-60® supplied by Condea Corporation, (900 Threadneedle P.O. Box 19029, Houston, TX). More preferred alkyl ethoxylates comprise from 9 to 15 carbon atoms in the hydrophobic tail, and from 4 to 12 oxide units in the hydrophilic head group. A most preferred alkyl ethoxylate is C₉₋₁₁ EO₅, available from the Shell Chemical Company under the tradename Neodol 91-5®. Non-ionic ethoxylates can also be derived from branched alcohols. For example, alcohols can be made from branched olefin feedstocks such as propylene or butylene. In a preferred embodiment, the branched alcohol is either a 2-propyl-1-heptyl alcohol or 2-butyl-1-octyl alcohol. A desirable branched alcohol ethoxylate is 2-propyl-1-heptyl EO7/AO7, manufactured and sold by BASF Corporation under the tradename Lutensol XP 79 /XL 79®.

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Another preferred class of non-ionic surfactant suitable for the present invention is amine oxide, especially coco dimethyl amine oxide or coco amido propyl dimethyl amine oxide. Amine oxide may have a linear or mid-branched alkyl moiety. Typical linear amine oxides include watersoluble amine oxides of formula $R^1 - N(R^2)(R^3) \rightarrow O$, wherein R^1 is a C_{8-18} alkyl moiety; R^2 and R^3 are independently selected from the group consisting of C_{1-3} alkyl groups and C_{1-3} hydroxyalkyl groups and preferably include methyl, ethyl, propyl, isopropyl, 2-hydroxethyl, 2-hydroxypropyl and 3-hydroxypropyl. The linear amine oxide surfactants in particular may include linear C₁₀-C₁₈ alkyl dimethyl amine oxides and linear C₈-C₁₂ alkoxy ethyl dihydroxy ethyl amine oxides. Preferred amine oxides include linear C₁₀, linear C₁₀-C₁₂, and linear C₁₂-C₁₄ alkyl dimethyl amine oxides. As used herein "mid-branched" means that the amine oxide has one alkyl moiety having n₁ carbon atoms with one alkyl branch on the alkyl moiety having n₂ carbon atoms. The alkyl branch is located on the α carbon from the nitrogen on the alkyl moiety. This type of branching for the amine oxide is also known in the art as an internal amine oxide. The total sum of n₁ and n₂ is from 10 to 24 carbon atoms, preferably from 12 to 20, and more preferably from 10 to 16. The number of carbon atoms for the one alkyl moiety (n_1) should be approximately the same number of carbon atoms as the one alkyl branch (n_2) such that the one alkyl moiety and the one alkyl branch are symmetric. As used herein "symmetric" means that $| n_1 - n_2 |$ is less than or equal to 5,

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preferably 4, most preferably from 0 to 4 carbon atoms in at least 50 wt%, more preferably at least 75 wt% to 100 wt% of the mid-branched amine oxides for use herein.

The amine oxide further comprises two moieties, independently selected from a C_{1-3} alkyl, a C_{1-3} hydroxyalkyl group, or a polyethylene oxide group containing an average of from about 1 to about 3 ethylene oxide groups. Preferably the two moieties are selected from a C_{1-3} alkyl, more preferably both are selected as a C_1 alkyl.

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Another class of non-ionic surfactant suitable for the present invention is alkyl polysaccharides. Such surfactants are disclosed in U.S. Patent Nos. 4,565,647, 5,776,872, 5,883,062, and 5,906,973. Among alkyl polysaccharides, alkyl polyglycosides comprising five and/or six carbon sugar rings are preferred, those comprising six carbon sugar rings are more preferred, and those wherein the six carbon sugar ring is derived from glucose, i.e., alkyl polyglucosides ("APG"), are most preferred. The alkyl substituent in the APG chain length is preferably a saturated or unsaturated alkyl moiety containing from 8 to 16 carbon atoms, with an average chain length of 10 carbon atoms. C₈-C₁₆ alkyl polyglucosides are commercially available from several suppliers (e.g., Simusol® surfactants from Seppic Corporation, 75 Quai d'Orsay, 75321 Paris, Cedex 7, France, and Glucopon 220®, Glucopon 225®. Glucopon 425®, Plantaren 2000 N®, and Plantaren 2000 N UP®, from Cognis Corporation, Postfach 13 01 64, D 40551, Dusseldorf, Germany). Also suitable are alkylglycerol ethers and sorbitan esters.

Another class of non-ionic surfactant suitable for the present invention is fatty acid amide surfactants comprising an alkyl group containing from 7 to 21, preferably from 9 to 17, carbon atoms. Preferred amides are C_8 - C_{20} ammonia amides, monoethanolamides, diethanolamides, and isopropanolamides.

Other non-ionic surfactants that can be used include those derived from natural sources such as sugars and include C_8 - C_{16} N-alkyl glucose amide surfactants.

Alternative non-ionic detergent surfactants for use herein are alkoxylated alcohols generally comprising from 8 to 16 carbon atoms in the hydrophobic alkyl chain of the alcohol. Typical alkoxylation groups are propoxy groups or ethoxy groups in combination with propoxy groups, yielding alkyl ethoxy propoxylates. Such compounds are commercially available under the

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tradename Antarox[®] available from Rhodia (40 Rue de la Haie-Coq F-93306, Aubervilliers Cédex, France) and under the tradename Nonidet[®] available from Shell Chemical.

The condensation products of ethylene oxide with a hydrophobic base formed by the condensation of propylene oxide with propylene glycol are also suitable for use herein. The hydrophobic portion of these compounds will preferably have a molecular weight of from 1500 to 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 40 moles of ethylene oxide. Examples of compounds of this type include certain of the commercially available Pluronic® surfactants, marketed by BASF. Chemically, such surfactants have the structure (EO)_x(PO)_y(EO)_z or (PO)_x(EO)_y(PO)_z wherein x, y, and z are from 1 to 100, preferably 3 to 50. Pluronic® surfactants known to be good wetting surfactants are more preferred. A description of the Pluronic® surfactants, and properties thereof, including wetting properties, can be found in the brochure entitled "BASF Performance Chemicals Plutonic® & Tetronic® Surfactants", available from BASF.

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Other suitable though not preferred non-ionic surfactants include the polyethylene oxide condensates of alkyl phenols, e.g., the condensation products of alkyl phenols having an alkyl group containing from 6 to 12 carbon atoms in either a straight chain or branched chain configuration, with ethylene oxide, the said ethylene oxide being present in amounts equal to 5 to 25 moles of ethylene oxide per mole of alkyl phenol. The alkyl substituent in such compounds can be derived from oligomerized propylene, diisobutylene, or from other sources of *iso*-octane *n*-octane, *iso*-nonane or *n*-nonane.

Suitable anionic surfactants for use herein are all those commonly known by those skilled in the art. The anionic surfactants for use herein include alkyl sulphonates, alkyl aryl sulphonates, alkyl sulphates, alkyl alkoxylated sulphate surfactants, C₆-C₂₀ alkyl alkoxylated linear or branched diphenyl oxide disulphonates, or mixtures thereof.

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When present in the composition anionic surfactant can be incorporated in the compositions herein in amounts ranging from 0.01% to 50%, preferably 0.5% to 40%, more preferably 2% to 35%.

Suitable sulphate surfactants for use in the compositions herein include water-soluble salts or acids of C₁₀-C₁₄ alkyl or hydroxyalkyl, sulphate and/or ether sulfate. Suitable counterions include hydrogen, alkali metal cation or ammonium or substituted ammonium, but preferably sodium. Where the hydrocarbyl chain is branched, it preferably comprises C₁₋₄ alkyl branching units. The average percentage branching of the sulphate surfactant is preferably greater than 30%, more preferably from 35% to 80% and most preferably from 40% to 60% of the total hydrocarbyl chains.

The sulphate surfactants may be selected from C_8 - C_{20} primary, branched-chain and random alkyl sulphates (AS); C_{10} - C_{18} secondary (2,3) alkyl sulphates; C_{10} - C_{18} alkyl alkoxy sulphates (AE_xS) wherein preferably x is from 1-30; C_{10} - C_{18} alkyl alkoxy carboxylates preferably comprising 1-5 ethoxy units; mid-chain branched alkyl sulphates as discussed in US 6,020,303 and US 6,060,443; mid-chain branched alkyl alkoxy sulphates as discussed in US 6,008,181 and US 6,020,303.

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Suitable alkyl alkoxylated sulphate surfactants for use herein are according to the formula $RO(A)_mSO_3M$ wherein R is an unsubstituted C_6 - C_{20} alkyl or hydroxyalkyl group having a C_6 - C_{20} alkyl component, preferably a C_8 - C_{20} alkyl or hydroxyalkyl, more preferably C_{10} - C_{18} alkyl or hydroxyalkyl, A is an ethoxy or propoxy unit, m is greater than zero, typically between 0.5 and 6, more preferably between 0.5 and 5, and M is H or a cation which can be, for example, a metal cation (e.g., sodium, potassium, lithium, calcium, magnesium, etc.), ammonium or substituted-ammonium cation. Alkyl ethoxylated sulfates as well as alkyl propoxylated sulfates are contemplated herein. Specific examples of substituted ammonium cations include methyl-, dimethyl-, trimethyl-ammonium and quaternary ammonium cations, such as tetramethyl-ammonium, dimethyl piperdinium and cations derived from alkanolamines such as ethylamine, diethylamine, triethylamine, mixtures thereof, and the like. Exemplary surfactants are C_{12} - C_{18} alkyl polyethoxylate (1.0) sulfate (C_{12} - C_{18} E(1.0)SM), C_{12} - C_{18} alkyl polyethoxylate (2.25) sulfate (C_{12} - C_{18} E(2.25)SM), C_{12} - C_{18} alkyl polyethoxylate (3.0) sulfate (C_{12} - C_{18} E(3.0)SM), C_{12} - C_{18} alkyl polyethoxylate (4.0) sulfate (C_{12} - C_{18} E (4.0)SM), wherein M is conveniently selected from sodium and potassium.

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Suitable alkyl sulphonates for use herein include water-soluble salts or acids of the formula RSO₃M wherein R is a C_6 - C_{20} linear or branched, saturated or unsaturated alkyl group, preferably a C_8 - C_{18} alkyl group and more preferably a C_{10} - C_{16} alkyl group, and M is H or a cation, e.g., an alkali metal cation (e.g., sodium, potassium, lithium), or ammonium or substituted ammonium (e.g., methyl-, dimethyl-, and trimethyl ammonium cations and quaternary ammonium cations, such as tetramethyl-ammonium and dimethyl piperdinium cations and quaternary ammonium cations derived from alkylamines such as ethylamine, diethylamine, triethylamine, and mixtures thereof, and the like). Particularly suitable liner alkyl sulphonates include C_{12} - C_{16} paraffin sulphonate like Hostapur® SAS commercially available from Hoechst.

Suitable alkyl aryl sulphonates for use herein include water-soluble salts or acids of the formula RSO₃M wherein R is an aryl, preferably a benzyl, substituted by a C₆-C₂₀ linear or branched saturated or unsaturated alkyl group, preferably a C₈-C₁₈ alkyl group and more preferably a C₁₀-C₁₆ alkyl group, and M is H or a cation, e.g., an alkali metal cation (e.g., sodium, potassium, lithium, calcium, magnesium and the like) or ammonium or substituted ammonium (e.g., methyl-, dimethyl-, and trimethyl ammonium cations and quaternary ammonium cations, such as tetramethyl-ammonium and dimethyl piperdinium cations and quaternary ammonium cations derived from alkylamines such as ethylamine, diethylamine, triethylamine, and mixtures thereof, and the like). An example of commercially available alkyl aryl sulphonate is Lauryl aryl sulphonate from Su.Ma.. Particularly preferred alkyl aryl sulphonates are alkyl benzene sulphonates commercially available under trade name Nansa® available from Albright&Wilson.

Suitable C₆-C₂₀ alkyl alkoxylated linear or branched diphenyl oxide disulphonate surfactants for use herein are according to the following formula:

wherein R is a C_6 - C_{20} linear or branched, saturated or unsaturated alkyl group, preferably a C_{12} - C_{18} alkyl group and more preferably a C_{14} - C_{16} alkyl group, and X+ is H or a cation, e.g., an alkali metal cation (e.g., sodium, potassium, lithium, calcium, magnesium and the like). Particularly

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suitable C_6 - C_{20} alkyl alkoxylated linear or branched diphenyl oxide disulphonate surfactants to be used herein are the C_{12} branched di phenyl oxide disulphonic acid and C_{16} linear di phenyl oxide disulphonate sodium salt respectively commercially available by DOW under the trade name Dowfax 2A1® and Dowfax 8390®.

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Other anionic surfactants useful herein include salts (including, for example, sodium, potassium, ammonium, and substituted ammonium salts such as mono-, di- and triethanolamine salts) of soap, C₈-C₂₄ olefinsulfonates, sulphonated polycarboxylic acids prepared by sulphonation of the pyrolyzed product of alkaline earth metal citrates, e.g., as described in British patent specification No. 1,082,179, C₈-C₂₄ alkylpolyglycolethersulfates (containing up to 10 moles of ethylene oxide); alkyl ester sulfonates such as C₁₄-C₁₆ methyl ester sulfonates; acyl glycerol sulfonates, fatty oleyl glycerol sulfates, alkyl phenol ethylene oxide ether sulfates, alkyl phosphates, isethionates such as the acyl isethionates, N-acyl taurates, alkyl succinamates and sulfosuccinates, monoesters of sulfosuccinate (especially saturated and unsaturated C₁₂-C₁₈ monoesters) diesters of sulfosuccinate (especially saturated and unsaturated C₆-C₁₄ diesters), acyl sarcosinates, sulfates of alkylpolysaccharides such as the sulfates of alkylpolyglucoside (the nonionic nonsulfated compounds being described below), alkyl polyethoxy carboxylates such as those of the formula RO(CH₂CH₂O)_kCH₂COO'M⁺ wherein R is a C₈-C₂₂ alkyl, k is an integer from 0 to 10, and M is a soluble salt-forming cation. Resin acids and hydrogenated resin acids are also suitable, such as rosin, hydrogenated rosin, and resin acids and hydrogenated resin acids present in or derived from tall oil. Further examples are given in "Surface Active Agents and Detergents" (Vol. I and II by Schwartz, Perry and Berch). A variety of such surfactants are also generally disclosed in U.S. Patent 3,929,678, issued December 30, 1975 to Laughlin, et al. at Column 23, line 58 through Column 29, line 23.

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Zwitterionic surfactants represent another class of preferred surfactants within the context of the present invention. When present in the composition, zwitteronic surfactants may be comprised at levels from 0.01% to 20%, preferably from 0.2% to 15%, more preferably 0.5% to 12%.

Zwitterionic surfactants contain both cationic and anionic groups on the same molecule over a wide pH range. The typical cationic group is a quaternary ammonium group, although other positively charged groups like sulfonium and phosphonium groups can also be used. The typical anionic groups are carboxylates and sulfonates, preferably sulfonates, although other groups like

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sulfates, phosphates and the like, can be used. Some common examples of these detergents are described in the patent literature: U.S. Patent Nos. 2,082,275, 2,702,279 and 2,255,082.

Suitable zwitteronic surfactants include betaines such alkyl betaines, alkylamidobetaine, amidazoliniumbetaine, sulfobetaine (INCI Sultaines) as well as the Phosphobetaine and preferably meets formula I:

 R^{1} -[CO-X (CH₂)_n]_x-N⁺(R^{2})(R^{3})-(CH₂)_m-[CH(OH)-CH₂]_v-Y- (I) wherein

 R^1 is a saturated or unsaturated C_{6-22} alkyl residue, preferably C_{8-18} alkyl residue, in particular a saturated C_{10-16} alkyl residue, for example a saturated C_{12-14} alkyl residue;

X is NH, NR^4 with C_{1-4} Alkyl residue R^4 , O or S,

n a number from 1 to 10, preferably 2 to 5, in particular 3,

x 0 or 1, preferably 1,

 R^2 , R^3 are independently a $C_{1\cdot 4}$ alkyl residue, potentially hydroxy substituted such as a hydroxyethyl, preferably a methyl.

m a number from 1 to 4, in particular 1, 2 or 3,

y 0 or 1 and

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Y is COO, SO3, OPO(OR⁵)O or P(O)(OR⁵)O, whereby R⁵ is a hydrogen atom H or a C1-4 alkyl residue.

Preferred betaines are the alkyl betaines of the formula (Ia), the alkyl amido betaine of the formula (Ib), the sulfo betaines of the formula (Ic) and the amido sulfobetaine of the formula (Id);

$$R^1$$
- N^+ (CH₃)₂-CH₂COO⁻ (Ia)

$$R^{1}$$
-CO-NH(CH₂)₃-N⁺(CH₃)₂-CH₂COO⁻ (Ib)

$$R^{1}-N^{+}(CH_{3})_{2}-CH_{2}CH(OH)CH_{2}SO_{3}-$$
 (Ic)

$$R^{1}$$
-CO-NH-(CH₂)₃-N⁺(CH₃)₂-CH₂CH(OH)CH₂SO₃- (Id)

in which R¹ has the same meaning as in formula I. Particularly preferred betaines are the Carbobetaine [wherein Y=COO⁻], in particular the carbobetaine of the formula (Ia) and (Ib), more preferred are the alkylamidobetaine of the formula (Ib).

Examples of suitable betaines and sulfobetaine are the following: almondamidopropyl betaine, Apricotamidopropyl betaine, avocadoamidopropyl betaine, babassuamidopropyl betaine, behen amidopropyl betaine, behenyl betaine, canolamidopropyl betaine, capryl/capramidopropyl betaine, carnitine, cetylbetaine, cocamidoethyl betaine, cocamidopropyl betaine, cocamidopropyl

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hydroxysultaine, cocobetaine, cocohydroxysultaine, coco/oleamidopropyl betaine, coco sultaine, decyl betaine, dihydroxyethyloleylglycinate, dihydroxyethylstearylglycinate, dihydroxyethyl tallow glycinate, dimethicone propyl pg-betaine, erucamidopropyl hydroxysultaine, hydrogenated tallow betaine, isostearamidopropyl betaine, lauramidopropyl betaine, lauryl betaine, lauryl hydroxysultaine, lauryl sultaine, milkamidopropyl betaine, minkamidopropyl betaine, myristyl betaine, oleamidopropyl betaine, oleamidopropyl myristamidopropyl betaine, hydroxysultaine, oleyl betaine, olivamidopropyl betaine, palmamidopropyl betaine, palmitamidopropyl betaine, palmitoyl carnitine, palmkernelamidopropyl betaine, polytetrafluoroethylene acetoxypropyl betaine, ricinoleic amidopropyl betaine, sesamidopropyl betaine, soyamidopropyl betaine, stearamidopropyl betaine, stearyl betaine, tallow amidopropyl betaine, tallow amidopropyl hydroxysultaine, tallow betaine, tallow dihydroxyethyl betaine, undecylenamidopropyl betaine and wheat germ amidopropyl betaine. Prefered betaine is for example cocamidopropyl betaine.

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A specific example of a zwitterionic surfactant is 3-(N-dodecyl-N,N-dimethyl)-2-hydroxypropane-1-sulfonate (Lauryl hydroxyl sultaine) available from the McIntyre Company (24601 Governors Highway, University Park, Illinois 60466, USA) under the tradename Mackam LHS®. Another specific zwitterionic surfactant is C₁₂₋₁₄ acylamidopropylene (hydroxypropylene) sulfobetaine that is available from McIntyre under the tradename Mackam 50-SB®. Other very useful zwitterionic surfactants include hydrocarbyl, e.g., fatty alkylene betaines. A highly preferred zwitterionic surfactant is Empigen BB®, a coco dimethyl betaine produced by Albright & Wilson. Another equally preferred zwitterionic surfactant is Mackam 35HP®, a coco amido propyl betaine produced by McIntyre.

Another class of preferred surfactants comprises the group consisting of amphoteric surfactants. One suitable amphoteric surfactant is a C₈-C₁₆ amido alkylene glycinate surfactant ('ampho glycinate'). Another suitable amphoteric surfactant is a C₈-C₁₆ amido alkylene propionate surfactant ('ampho propionate'). Other suitable, amphoteric surfactants are represented by surfactants such as dodecylbeta-alanine, N-alkyltaurines such as the one prepared by reacting dodecylamine with sodium isethionate according to the teaching of U.S. Patent No. 2,658,072, N-higher alkylaspartic acids such as those produced according to the teaching of U.S. Patent No. 2,438,091, and the products sold under the trade name "Miranol®", and described in U.S. Patent No. 2,528,378.

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Cationic surfactants, when present in the composition, are present in an effective amount, more preferably from 0.1% to 20%, by weight of the liquid detergent composition. Suitable cationic surfactants are quaternary ammonium surfactants. Suitable quaternary ammonium surfactants are selected from the group consisting of mono C_6 - C_{16} , preferably C_6 - C_{10} N-alkyl or alkenyl ammonium surfactants, wherein the remaining N positions are substituted by methyl, hydroxyehthyl or hydroxypropyl groups. Another preferred cationic surfactant is an C_6 - C_{18} alkyl or alkenyl ester of a quaternary ammonium alcohol, such as quaternary chlorine esters.

10 Chelating agents

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One class of optional compounds for use herein includes 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 0.01% to 5.0%.

Suitable phosphonate chelating agents for use 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.

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Ethylenediamine N,N'- disuccinic acids is, for instance, commercially available under the tradename ssEDDS[®] from Palmer Research Laboratories.

Suitable amino carboxylates for use herein include ethylene diamine tetra acetates, diethylene triamine pentaacetates, diethylene triamine pentaacetate (DTPA),N- hydroxyethylethylenediamine triacetates, nitrilotri-acetates, ethylenediamine tetrapropionates, triethylenetetraaminehexaacetates, ethanol-diglycines, 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 diacetic acid (MGDA).

Further carboxylate chelating agents for use herein include salicylic acid, aspartic acid, glutamic acid, glycine, malonic acid or mixtures thereof.

Polymers

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The compositions herein may optionally further comprise one or more alkoxylated polyethyleneimine polymer. The composition may comprise from 0.01% to 10%, preferably from 0.01% to 2%, more preferably from 0.1% to 1.5%, even more preferable from 0.2% to 1.5% by weight of the total composition of an alkoxylated polyethyleneimine polymer as described on page 2, line 33 to page 5, line 5 and exemplified in examples 1 to 4 at pages 5 to 7 of WO2007/135645 The Procter & Gamble Company.

The alkoxylated polyethyleneimine polymer of the present composition has a polyethyleneimine backbone having from 400 to 10000 weight average molecular weight, preferably from 400 to 7000 weight average molecular weight, alternatively from 3000 to 7000 weight average molecular weight.

The alkoxylation of the polyethyleneimine backbone includes: (1) one or two alkoxylation modifications per nitrogen atom, dependent on whether the modification occurs at a internal nitrogen atom or at an terminal nitrogen atom, in the polyethyleneimine backbone, the alkoxylation modification consisting of the replacement of a hydrogen atom by a polyalkoxylene

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chain having an average of about 1 to about 40 alkoxy moieties per modification, wherein the terminal alkoxy moiety of the alkoxylation modification is capped with hydrogen, a C_1 - C_4 alkyl or mixtures thereof; (2) a substitution of one C_1 - C_4 alkyl moiety or benzyl moiety and one or two alkoxylation modifications per nitrogen atom, dependent on whether the substitution occurs at a internal nitrogen atom or at an terminal nitrogen atom, in the polyethyleneimine backbone, the alkoxylation modification consisting of the replacement of a hydrogen atom by a polyalkoxylene chain having an average of about 1 to about 40 alkoxy moieties per modification wherein the terminal alkoxy moiety is capped with hydrogen, a C_1 - C_4 alkyl or mixtures thereof; or (3) a combination thereof.

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The composition may further comprise the amphiphilic graft polymers based on water soluble polyalkylene oxides (A) as a graft base and sides chains formed by polymerization of a vinyl ester component (B), said polymers having an average of ≤ 1 graft site per 50 alkylene oxide units and mean molar mass Mw of from 3,000 to 100,000 described in BASF patent application WO2007/138053 on pages 2 line 14 to page 10, line 34 and exemplified on pages 15-18.

Hydrotrope

The liquid detergent compositions of the invention may optionally comprise a hydrotrope in an effective amount so that the liquid detergent compositions are appropriately compatible in water. Suitable hydrotropes for use herein include anionic-type hydrotropes, particularly sodium, potassium, and ammonium xylene sulfonate, sodium, potassium and ammonium toluene sulfonate, sodium potassium and ammonium cumene sulfonate, and mixtures thereof, and related compounds, as disclosed in U.S. Patent 3,915,903. The liquid detergent compositions of the present invention typically comprise from 0% to 15% by weight of the total liquid detergent composition of a hydrotrope, or mixtures thereof, preferably from 1% to 10%, most preferably from 3% to 10% by weight of the total liquid composition.

Polymeric Suds Stabilizer

These polymeric suds stabilizers provide extended suds volume and suds duration of the liquid detergent compositions. These polymeric suds stabilizers may be selected from homopolymers of (N,N-dialkylamino) alkyl esters and (N,N-dialkylamino) alkyl acrylate esters. The weight average molecular weight of the polymeric suds boosters, determined via conventional gel permeation

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chromatography, is from 1,000 to 2,000,000, preferably from 5,000 to 1,000,000, more preferably from 10,000 to 750,000, more preferably from 20,000 to 500,000, even more preferably from 35,000 to 200,000. The polymeric suds stabilizer can optionally be present in the form of a salt, either an inorganic or organic salt.

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One preferred polymeric suds stabilizer is (N,N-dimethylamino)alkyl acrylate esters. Other preferred suds boosting polymers are copolymers of hydroxypropylacrylate/dimethyl aminoethylmethacrylate (copolymer of HPA/DMAM).

When present in the compositions, the polymeric suds booster/stabilizer may be present from 0.01% to 15%, preferably from 0.05% to 10%, more preferably from 0.1% to 5%, by weight of the liquid detergent composition.

Another preferred class of polymeric suds booster polymers is hydrophobically modified cellulosic polymers having a number average molecular weight (Mw) below 45,000; preferably between 10,000 and 40,000; more preferably between 13,000 and 25,000. The hydrophobically modified cellulosic polymers include water soluble cellulose ether derivatives, such as nonionic and cationic cellulose derivatives. Preferred cellulose derivatives include methylcellulose, hydroxypropyl methylcellulose, hydroxyethyl methylcellulose, and mixtures thereof.

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Enzymes

The composition of the present invention may comprise an enzyme. Enzymes may be incorporated at a level of typically from 0.00001% to 1%, preferably at a level of from 0.0001% to 0.5%, more preferably at a level of from 0.0001% to 0.1% of enzyme protein by weight of the total composition.

The aforementioned enzymes can be provided in the form of a stabilized liquid or as a protected liquid or encapsulated enzyme. Liquid enzyme preparations may, for instance, be stabilized by adding a polyol such as propylene glycol, a sugar or sugar alcohol, lactic acid or boric acid or a protease stabilizer such as 4-formyl phenyl boronic acid according to established methods. Protected liquid enzymes or encapsulated enzymes may be prepared according to the methods disclosed in US 4,906,396, US 6,221,829, US 6,359,031 and US 6,242,405.

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Enzymes suitable for use in the present compositions can be obtained from Genencor International, Palo Alto, California, U.S.A; Novozymes A/S, Bagsvaerd, Denmark; Amersham Pharmacia Biotech., Piscataway, New Jersey, U.S.A; Sigma-Aldrich Company Ltd, Dorset, UK.

5 Radical scavenger

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The compositions of the present invention may further comprise a radical scavenger or a mixture thereof.

Suitable radical scavengers for use herein include the well-known substituted mono and dihydroxy benzenes and their analogs, alkyl and aryl carboxylates and mixtures thereof. Preferred such radical scavengers for use herein include di-tert-butyl-hydroxy toluene (BHT), hydroquinone, di-tert-butyl hydroquinone, mono-tert-butyl hydroquinone, tert-butyl-hydroxy anysole, benzoic acid, toluic acid, catechol, t-butyl catechol, benzylamine, 1,1,3-tris(2-methyl-4-hydroxy-5-t-butylphenyl) butane, n-propyl-gallate or mixtures thereof and highly preferred is di-tert-butyl hydroxy toluene. Such radical scavengers like N-propyl-gallate may be commercially available from Nipa Laboratories under the trade name Nipanox S1®.

Radical scavengers, when used, may be typically present herein in amounts up to 10% by weight of the total composition and preferably from 0.001% to 0.5% by weight. The presence of radical scavengers may contribute to the chemical stability of the compositions of the present invention.

Perfume

Suitable perfume compounds and compositions for use herein are for example those described in EP-A-0 957 156 under the paragraph entitled "Perfume", on page 13. 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%.

<u>Dye</u>

The liquid compositions according to the present invention may be coloured. Accordingly, they may comprise a dye or a mixture thereof.

Preservatives

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The liquid compositions according to present invention may comprise preservatives to prevent bio-growth potentially coming from the natural abrasive.

Delivery form of the compositions

The compositions herein may be packaged in a variety of suitable packaging known to those skilled in the art, such as plastic bottles for pouring liquid compositions, squeeze bottles or bottles equipped with a trigger sprayer for spraying liquid compositions. Alternatively, the paste-like compositions according to the present invention may by packaged in a tube.

In an alternative embodiment herein, the liquid composition herein is impregnated onto a substrate, preferably the substrate is in the form of a flexible, thin sheet or a block of material, such as a sponge.

Suitable substrates are woven or non-woven sheets, cellulosic material based sheets, sponge or foam with open cell structures e.g.: polyurethane foams, cellulosic foam, melamine foam, etc.

The process of cleaning a surface

The present invention encompasses a process of cleaning a surface with a liquid composition according to the present invention. Suitable surfaces herein are described herein above under the heading "The liquid cleaning composition".

In a preferred embodiment said surface is contacted with the composition according to the present invention, preferably wherein said composition is applied onto said surface.

In another preferred embodiment, the process herein comprises the steps of dispensing (e.g., by spraying, pouring, squeezing) the liquid composition according to the present invention from a container containing said liquid composition and thereafter cleaning said surface.

The composition herein may be in its neat form or in its diluted form.

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By "in its neat form", it is to be understood that said liquid composition is applied directly onto the surface to be treated without undergoing any dilution, i.e., the liquid composition herein is applied onto the surface as described herein.

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

The composition herein may be applied using an appropriate implement, such as a mop, paper towel, brush or a cloth, soaked in the diluted or neat composition herein. Furthermore, once applied onto said surface said composition may be agitated over said surface using an appropriate implement. Indeed, said surface may be wiped using a mop, paper towel, brush or a cloth.

The process herein may additionally contain a rinsing step, preferably after the application of said composition. By "rinsing", it is meant herein contacting the surface cleaned/cleansed with the process according to the present invention with substantial quantities of appropriate solvent, typically water, directly after the step of applying the liquid composition herein onto said surface. By "substantial quantities", it is meant herein between 0.01 lt. and 1 lt. of water per m² of surface, more preferably between 0.1 lt. and 1 lt. of water per m² of surface.

Cleaning effectiveness

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20 Cleaning Effectiveness test method:

Ceramic tiles (typically glossy, white, ceramic 24cm x 4cm) are covered with various homecarerelevant soils such as white sauce, vegetable grease, greasy soap scum or neat kitchen dirt. Then
the soiled tiles are cleaned using 4-5ml of the composition of the present invention poured directly
on a Spontex® cellulose sponge pre-wetted with water. The sponge is then mounted on a Wet
Abrasion Scrub Tester Instrument (such as made by Sheen Instruments Ltd. Kingston, England)
with the particle composition coated side facing the tile. The abrasion tester can be configured to
supply pressure (e.g.:600g), and move the sponge over the test surface with a set stroke length
(e.g.:30cm), at set speed (e.g.:37 strokes per minute). The ability of the composition to remove
greasy soap scum is measured through the number of strokes needed to perfectly clean the
surface, as determined by visual assessment. The lower the number of strokes, the higher the
greasy soap scum cleaning ability of the composition.

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Cleaning data below are achieved with 3-10% of abrasive particles in cleaner. Abrasive cleaning particles used to generate the example cleaning data were made from bleached walnut particles.

Product / Soil type	White sauce	Vegetable grease
Dish cleaner	61.2 ± 8.07 strokes to clean	33.8 ± 4.59strokes to clean
Dish cleaner with 5% bleached walnut abrasive particles having Equivalent Circle Diameter 196 µm.	10±1.51 strokes to clean	10.5±1.77 strokes to clean

Product / Soil type	Greasy soap scum
All purpose cleaner	>70 strokes to clean
All purpose cleaner with 3% bleached walnut abrasive particles having Equivalent Circle Diameter 196 µm.	29 strokes to clean
All purpose cleaner with 6% bleached walnut abrasive particles having Equivalent Circle Diameter 196 µm.	23 strokes to clean
All purpose cleaner with 10% bleached walnut abrasive particles having Equivalent Circle Diameter 196 µm.	18 strokes to clean

Product / Soil type	Greasy soap scum
Bathroom cleaner	38.2 strokes to clean
Bathroom cleaner with 3% bleached walnut abrasive particles having Equivalent Circle Diameter 196 µm.	25.1 strokes to clean
Bathroom cleaner with 6% bleached walnut abrasive particles having Equivalent Circle Diameter 196	20 strokes to clean

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μm.	
Bathroom cleaner with 10% bleached walnut abrasive particles having Equivalent Circle Diameter 196 µm.	18.3 strokes to clean

Examples

These following compositions were made comprising the listed ingredients in the listed proportions (weight %). Examples 1-21 are made with bleached walnut particles, alternatively bleached other plant part particles can be used, for example Wood fiber (200-400 microns) or KENAF fiber/pith mix (200-400 microns) would be equally suitable to be used in examples. Examples 1-19 herein are met to exemplify the present invention but are not necessarily used to limit or otherwise define the scope of the present invention.

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Process to bleach abrasive particles:

Cleaned particles are suspended in water and pH is adjusted to >9 with NaHCO3 (solution A). 100 part of solution A is added with 100 part of 30% H2O2 solution. Mix is gently stirred at 50°C for 24hr. Particles are filtered and rinsed with water prior to drying in the oven at 80°C. Operation may be repeated if particle batch is especially dark and incidentally whitening process was incomplete.

Hard surface cleaner Bathroom composition:

% Weight	1	2	3
C9-C11 EO8 (Neodol 91-8®)	3	2.5	3.5
Alkyl Benzene sulfonate		1	
C12-14-dimethyl Aminoxide		1	
n-Butoxy Propoxy Propanol		2	2.5
Hydrogene Peroxide	3		
Hydrophobic ethoxylated polyurethane (Acusol 882®)	1.5	1	0.8
Lactic Acid	3		3.5
Citric Acid		3	0.5

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Polysaccharide (Xanthan Gum, Keltrol CG-SFT® Kelco)	0.25	0.25	0.25
Perfume		0.35	0.35
Bleached walnut shell particles (Equivalent Circle Diameter 196 µm).	1	1	1
Water	Balance	Balance	Balance

Hard surface cleaner Bathroom composition (cont.):

% Weight	4	5	6
Chloridric acid	2		
Linear C10 alkyl sulphate	1.3	2	3
n-Butoxy Propoxy Propanol	2		1.75
Citric Acid		3	3
PolyvinylPyrrolidone (Luviskol K60®)	0.1	0.1	0.1
NaOH		0.2	0.2
Perfume	0.4	0.4	0.4
Polysaccharide (Xanthan Gum Kelzan T®, Kelco)	0.3	0.35	0.35
Bleached walnut shell particles (Equivalent Circle	2	2	2
Diameter 250 μm).			
Water	Balance	Balance	Balance

Hand diswashing detergent composition

% Weight	7	8	9	10	11
Linear Alkylbenzene	-	-		12	-
Sulfonate					
Alkyl Ethoxy Sulfate	23.5	15	9	11	-
Paraffin Sulfonate	-		20	-	-
Coco amido propyl	-		4	-	-
Betaine					
Ethoxylated alkyl alcohol	-		4	0.6	33
Amine Oxide (1)	6.5	5	-	-	2
Alkylpolyglucoside	-	-	-	4	-
Ethanol	-	-	3	2	9
Polypropyleneglycol	1	0.8	-	-	-

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Citrate	-	-	01	0.3	-
NaCl	1.2	1.0%	-	0.2	-
Sodium cumene sulfonate	-	-	0.6	-	3
Bleached Walnut shell	2	3	1.5	1	2
particles (Equivalent					
Circle Diameter 196 µm).					
Hydrogenated castor oil	0.2	0.28	0.18	-	0.2
Minors*	Balance to 100% with water				
рН	9	8.5	7	6	7

^{*}Minors: dyes, opacifier, perfumes, preservatives, hydrotropes, processing aids, stabilizers

General degreaser composition:

% Weight	12	13
C9-C11 EO8 (Neodol 91-8®)	3	3
N-Butoxy Propoxy Propanol	15	15
Ethanol	10	5
Isopropanol		10
Polysaccharide (Xanthan Gum-glyoxal modified Optixan-T)	0.35	0.35
Bleached walnut shell particles (Equivalent Circle	1	1
Diameter 196 μm).		
Water (+ minor e.g.; pH adjusted to alkaline pH)	Balance	Balance

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Scouring composition:

% Weight	14	15	16
Sodium C13-16 prafin sulfonate	2.5	2.5	2.5
C12-14-EO7 (Lutensol AO7®)	0.5	0.5	0.5
Coconut Fatty Acid	0.3	0.3	0.3
Sodium Citrate	3.3	3.3	3.3
Sodium Carbonate	3	3	3
Orange terpenes	2.1	2.1	2.1
Benzyl Alcohol	1.5	1.5	
Polyacrylic acid 1.5Mw	0.75	0.75	0.75

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Diatomaceous earth (Celite 499® median size 10 μm)			
Calcium Carbonate (Merk 2066® median size 10 µm)		25	
Bleached walnut shell particles (Equivalent Circle Diameter 196 µm).	5	5	5
Water	Balance	Balance	Balance

Liquid glass cleaner:

% Weight	17	18
Butoxypropanol	2	4
Ethanol	3	6
C12-14 sodium sulphate	0.24	
NaOH/Citric acid	To pH 10	
Citric Acid		
Bleached walnut shell particles (Equivalent Circle Diameter 100 µm).	0.5	0.5
Water (+ minor)	Balance	Balance

Cleaning wipe (surface cleansing wipe):

% Weight	19	20	21
C10 Amine Oxide	-	0.02	-
C12,14 Amine Oxide	0.4	-	-
Betaine (Rewoteric AM CAS 15 U)	-	-	0.2
C9,11 A5EO (Neodol E 91.5®)	-	0.1	-
C9,11 A8EO (Neodol E 91.8®)	-	-	0.8
C12,14 A5EO	0.125	-	-
2-Ethyl Hexyl Sulphate	-	0.05	0.6
Silicone	0.001	0.003	0.003
EtOH	9.4	8.0	9.5
Propylene Glycol Butyl Ether	0.55	1.2	-
Geraniol	-	-	0.1
Citric acid	1.5	-	-
Lactic acid	-		1.5
Perfume	0.25	0.15	0.15

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Bleached walnut shell particles (Equivalent Circle Diameter	5	3	3
75 μm).			
Nonwoven: Spunlace 100% viscose 50gsm (lotion loading			(x3.5)
fact)			
Nonwoven: Airlaid walkisoft (70% cellulose, 12% Viscose,		(x3.5)	
18% binder) 80gsm (lotion loading factor)			
Carded thermobonded (70% polypropylene, 30% rayon),	(x3.5)		
70gsm (Lotion loading factor)			

The above wipes lotion composition is loaded onto a water-insoluble substrate, being a patterned hydroentangled non-woven substrate having a basis weight of 56 gms comprising 70% polyester and 30% rayon approximately 6.5 inches wide by 7.5 inches long with a caliper of about 0.80 mm. Optionally, the substrate can be pre-coated with dimethicone (Dow Corning 200 Fluid 5cst) using conventional substrate coating techniques. Lotion to wipe weight ratio of about 2:1 using conventional substrate coating techniques.

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The dimensions and values disclosed herein are not to be understood as being strictly limited to the exact numerical values recited. Instead, unless otherwise specified, each such dimension is intended to mean both the recited value and a functionally equivalent range surrounding that value. For example, a dimension disclosed as "40 mm" is intended to mean "about 40 mm".

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CLAIMS

What is claimed is:

1. A liquid cleaning composition comprising bleached cleaning particles as abrasives, wherein said bleached cleaning particles are selected from the group consisting bleached nut shell particles, bleached particles derived from other plant parts, bleached wood particles and mixtures thereof, and wherein bleached abrasive cleaning particles have a degree of whiteness (L*) of greater than 65, measured under D 65 illumination.

- 2. A liquid cleaning composition according to Claim 1, wherein said bleached nut shell particles are selected from the group consisting of pistachio nut shell, walnut shell, almond shell and mixtures thereof, most preferably bleached nut shell particles is walnut shell or pistachio nut shell.
- 3. A liquid cleaning composition according to Claim 1, wherein the bleached particles are derived from plant parts, wherein said plants are selected from the group consisting of rice, corn cob, palm biomass, bamboo, kenaf, apple seeds, apricot stone, olive stone and mixtures thereof, most preferably said plant is olive stone.
- 4. A liquid cleaning composition according to any of the preceding claims further comprising suspending aid, wherein suspending aid is selected from the group consisting of polycarboxylate polymer thickeners; carboxymethylcellulose, ethyl cellulose, hydroxyethyl cellulose, hydroxypropyl cellulose, hydroxymethyl cellulose, succinoglycan and naturally occurring polysaccharide polymers like Xanthan gum, gellan gum, guar gum, locust bean gum, tragacanth gum, succinoglucan gum, or derivatives thereof, or mixtures thereof.
- 5. A liquid cleaning composition according to any of the preceding claims, wherein particles are bleached with aqueous bleaching agent selected from the group consisting of metal hypochlorite, metal chlorate, hydrogen peroxide, metal perborate, metal percarbonate, metal peroxide, acyl or benzoyl peroxide, peracetic acid, ozone, sodium bisulphate, nitrogen dioxide, chlorine, chlorine dioxide, azodicarbonamide, sodium sulphite, sodium metabisulphite, percarbonate tetraacetyleneethylenediamine, metal peroxy monosulfate and mixtures thereof.

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6. A liquid cleaning composition according to any of the preceding claims, wherein liquid composition contains bleaching agents, wherein bleaching of cleaning particles occurs in situ, and wherein bleached abrasive cleaning particles have a degree of whiteness (L*) of greater than 75, measured under D 65 illumination.

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- 7. A liquid cleaning composition according to any of the preceding claims, wherein said composition comprises bleached cleaning particles from 0.1%, to 20%, preferably from 0.3% to 10%, more preferably from 0.5% to 5% and most preferably from 0.5% to 3% by weight of the composition.
- 8. A liquid cleaning composition according to any of the preceding claims, wherein said abrasive particles have a mean particle size as expressed by the Equivalent Circle Diameter from 10 to 1000 μ m, preferably from 50 to 500 μ m and more preferably from 100 to 350 μ m and most preferably from 150 to 250 μ m according to ISO 9276-6.
- 9. A liquid cleaning composition according to any of the preceding claims, wherein water composition exceed 30%, preferably 50%, more preferably 80% and more preferably 90% by weight of total liquid composition
- 10. A liquid cleaning composition according to any of the preceding claims, wherein the cleaning composition is loaded on a cleaning substrate, and wherein the substrate is a paper or nonvowen towel or wipe or a sponge.
- 11. A process of cleaning a surface with a liquid, cleaning composition according to any of the preceding claims, wherein said surface is contacted with said composition, preferably wherein said composition is applied onto said surface.

INTERNATIONAL SEARCH REPORT

International application No PCT/US2011/052258

A. CLASSIFICATION OF SUBJECT MATTER INV. C11D3/14 C11D3/382

C11D3/22

C11D3/37

C11D17/00

C11D17/04

C11D11/00

ADD.

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols) C11D

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

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT			
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.	
X	WO 2004/071483 A1 (STOCKHAUSEN CHEM FAB GMBH [DE]; PETERSEN OLAF [DE]; DANIEL GUENTER [DE) 26 August 2004 (2004-08-26) page 6, line 4 - line 9; claims 1, 9, 12, 15, 16; examples 1, 2 pages 16, 17	1-5,7,8, 11	
X	WO 2007/057134 A1 (STOCKHAUSEN CHEM FAB GMBH [DE]; DANIEL GUENTHER [DE]; FRIEBEL MICHAEL) 24 May 2007 (2007-05-24) pages 14, 15; claims 1, 7-9; examples 1, 2 page 8, lines 14-20 page 5, lines 19-24	1-5,7-9, 11	
X	US 5 830 445 A (BOUILLON GUENTER [DE] ET AL) 3 November 1998 (1998-11-03) claims 1-3, 8-14, 21-23; examples 1-5	1-5,7-9, 11	

Further documents are listed in the continuation of Box C.	See patent family annex.
"A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier document but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art. "&" document member of the same patent family
Date of the actual completion of the international search 25 January 2012	Date of mailing of the international search report $01/02/2012$
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2	Authorized officer

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INTERNATIONAL SEARCH REPORT

International application No PCT/US2011/052258

1	
Category* Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Citation of document, with indication, where appropriate, of the relevant passages US 5 898 026 A (YIANAKOPOULOS GEORGES [BE] ET AL) 27 April 1999 (1999-04-27) column 9, lines 20-49 - column 10, lines 17-37; claims 1-7	Relevant to claim No.

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/US2011/052258

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 2004071483 A1	26-08-2004	AT 430601 T EP 1594458 A1 WO 2004071483 A1	15-05-2009 16-11-2005 26-08-2004
WO 2007057134 A1	24-05-2007	AU 2006314819 A1 BR PI0618740 A2 CA 2629563 A1 CN 101309666 A DE 102005054976 A1 EP 1951195 A1 US 2008248144 A1 WO 2007057134 A1 ZA 200804139 A	24-05-2007 13-09-2011 24-05-2007 19-11-2008 31-05-2007 06-08-2008 09-10-2008 24-05-2007 29-04-2009
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