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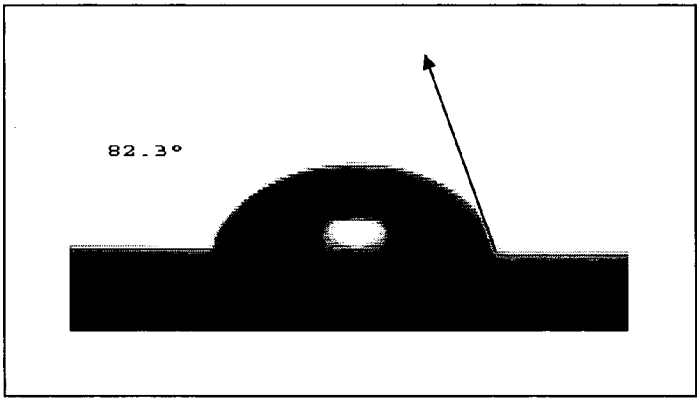
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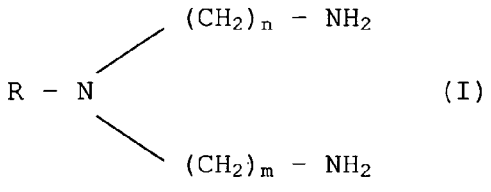
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(54) Title: LIQUID COMPOSITION FOR CLEANING SUFACES AND FOR PROVIDING HYDROPHOBIC COATING FILM THEREON

Fig. 2





(I)

(57) Abstract: The invention relates to a liquid composition for cleaning hard surfaces comprising: a carrier, at least some of which is aqueous; one or more surfactants; and an effective amount of a compound of formula (I) wherein m and n, equal or different, are integers from 2 to 8 and R is an optionally substituted alkyl chain having from 8 to 18 carbon atoms, for providing a hydrophobic coating film on said hard surfaces. The invention also relates to a liquid composition for coating a substrate and for providing a hydrophobic coating film thereon comprising: a liquid carrier and an effective amount of a compound of formula (I). The liquid composition of the invention is effective for rendering self-cleaning said hard surface and for reducing the presence of water marks on said hard surface, even after said hard surface has been later subjected to aqueous contacts. Another aspect of the invention includes a hydrophobic coating film for at least partially covering a substrate, said hydrophobic coating film comprising a compound of formula (I).

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Liquid composition for cleaning surfaces and for providing hydrophobic coating film thereon

DESCRIPTION

Field of the invention

The present invention relates to liquid compositions which are suited for cleaning hard surfaces and for imparting hydrophobic properties to said surfaces.

More specifically, the present invention relates to liquid compositions suited to the cleaning and the imparting of hydrophobic properties to hard surfaces such as ceramic, steel, plastic, glass and/or painted surfaces.

According to another aspect, the invention relates to liquid compositions suited for coating a substrate and for providing a hydrophobic coating film thereon.

Still according to another aspect, the invention relates to hydrophobic coating film for at least partially covering a substrate and to a method for providing said hydrophobic coating film on said substrate.

Still according to another aspect, the invention relates to a method for cleaning hard surfaces and for imparting hydrophobic properties to said surfaces.

Furthermore, according to another aspect, the invention relates to the use of said cleaning compositions for rendering hydrophobic said hard surfaces.

Background of the invention

Products for cleaning hard surfaces are widely available on the market. These products are used for cleaning soil from the surface and for leaving said surface with an aesthetically pleasing finish e.g. spot-free or shiny.

Products for cleaning hard surfaces available on the market often require rinsing with water after use. Typically when the water dries from the surface water-marks, smears or spots are left behind. These water-marks, it is believed may be due to the evaporation of water from the surface leaving behind deposits of minerals which were present as dissolved solids in the water, for example calcium, magnesium and sodium ions and salts thereof or may be deposits of water-carried soils, or even remnants from a cleaning product, for example soap scum.

This problem is often exacerbated by some cleaning compositions which modify the surface during the cleaning process in such a way that, after rinsing, water forms discrete droplets or beads on the surface instead of draining off. These droplets or beads dry to leave consumer noticeable spots or marks known as water-marks. This problem is particularly apparent when cleaning ceramic, steel, plastic, glass or painted surfaces.

It is desirable to leave these surfaces with a clean finish that lasts for a maximum period of time between two cleaning operations without the surface appearing dirty to the observer. Even though such surfaces are left with a spotfree finish, when the surfaces are contacted with water, such as rainwater, in the case of surfaces exposed to outside elements, or tap water, for interior surfaces such as shower walls, these surfaces quickly lose their spot-free finish (frequently named as the resoiling tendency of clean surfaces) due to the same factors that cause spotting (dirt, deposits of minerals which were present as dissolved solids in the water, and the like) when the surfaces are originally cleaned.

In order to satisfy all of these requirements, the cleaning compositions should modify the surface to be cleaned in such a way that the wetting behavior changes compared to an

untreated surface, so that it is soiled less rapidly and dries rapidly without the formation of water-marks.

Compositions which are capable of solving some of the addressed problems are known in the art.

For example, U.S. Patent no. 5,759,980 discloses a composition for cleaning cars which is described to eliminate the problem of water-marks. The composition therein described comprises a surfactant package comprising a silicone-based surfactant and a polymer which is capable of bonding to a surface to make it hydrophilic. However, it is believed that the polymers described in this document may tend to be removed from the surface during rinsing of the product from the surface. Hence since the surface hydrophilicity is allegedly provided by the composition as described in the patent and the composition may be removed from the surface after the first rinse, the alleged hydrophilicity is also removed. The wetting/sheeting effect is short-lived, with spotting/residue negatives returning within 1-2 rinses or when subjected to exposures to the rainwater or to tap water in a shower. The result is that the benefit provided by the composition is lost when the surface is rinsed.

Elevating the levels of polymers is not the solution to this problem. This is especially evident on automobile surfaces, residential windows, building exteriors, shower units and dishware where elevated levels of polymers result in unacceptable residue problem.

U.S. Patent Application Publication No. 2002/0048679 discloses a process for providing a long-term hydrophobic coatings on polymeric substrates by initially reacting the polymeric substrate with a specific silane derivative, thereby structuring the surfaces of the polymeric substrates, and then with a hydrophobic compound.

U.S. Patent No. 5,324,566 discloses the use of hydrophobic fluorinated siloxane polymers for producing water repellent surfaces. It is disclosed in this patent that the water repelling properties of the fluorinated siloxane polymer surface film can be improved by forming surface irregularities in the surface and/or the surface film. In one form, the surface is provided with irregularities of a height from about 0.1 micrometers up to the wavelength of visible light.

The International Patent Application WO 01/96512 discloses the use of non-photoactive nanoparticles, which is said to allow for the creation of coatings, compositions, methods and articles of manufacture that create multi-use benefits to modified hard surfaces. These surface modifications are said to produce durable, long lasting or semi-permanent multiuse benefits such as quick and uniform drying, soil removal, self-cleaning, anti-spotting, anti-soil deposition, clean appearance.

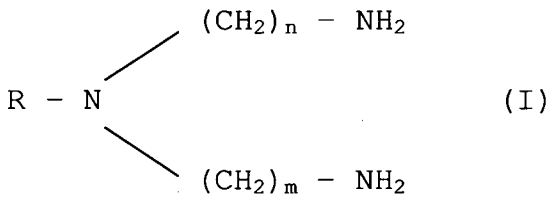
The International Patent Application WO 04/37944 discloses a composition comprising a aqueous mixture of nanoparticles having size of less than 300 nm, and a hydrophobic surface modifier which is water-soluble or water-dispersible and forms a continuous film from an aqueous solution. The composition is said to produce a transparent and stain resistant self-cleaning coating without significant loss of gloss when the water evaporates from the mixture.

The use of compositions comprising nanoparticles for cleaning and treating a hard surface has been also disclosed in International Patent Applications published as WO 01/27236, WO 01/32820, WO 01/83662, WO 01/96511, WO 01/96516, WO 02/70612 and WO 02/103105.

However, there is the continuous need to provide still more effective alternatives to the known in the art solutions to reduce the presence of water marks on hard surfaces.

Summary of the invention

The present inventors have surprisingly discovered that a compound of formula:



(I)

wherein m and n, equal or different, are integers from 2 to 8 and R is an optionally substituted alkyl chain having from 8 to 18 carbon atoms,

known as disinfectant, is capable of imparting hydrophobic properties to a substrate if properly formulated in a cleaning or coating composition.

According to a first aspect, the present invention provides a liquid composition which attains a satisfactory cleaning action of hard surfaces, allowing at the same time said hard surfaces to appear clean and free of water-marks to the observer for a maximum period of time between two cleaning operations.

More specifically, the liquid composition for cleaning hard surfaces of the present invention comprises:

- a carrier, at least some of which is aqueous;

- one or more surfactants; and

- an effective amount of the compound of formula (I) for providing a hydrophobic coating film on said hard surfaces.

The inventors have observed that the aforementioned liquid composition is effective for rendering self-cleaning said hard surface and for reducing the presence of water marks on said hard surface, even after said hard surface has been later subjected to aqueous contacts.

For the purposes of the present description and of the claims which follow, the term "liquid composition" is used to indicate compositions in the form of liquids, aqueous gels, phase-separated liquid compositions (such as suspensions) and/or colored liquid compositions.

For the purposes of the present description and of the claims which follow, the term "hard surface" is used to indicate any kind of rigid surfaces typically found in houses like kitchens, bathrooms, or the exterior surfaces of a vehicle, e. g., floors, walls, tiles, windows, sinks, showers, shower plastified curtains, wash basins, WCs, dishes, fixtures and fittings and the like made of different materials like ceramic, vinyl, nowax vinyl, linoleum, melamine, glass, any plastics, plastified wood, metal, especially steel and chrome metal or any painted or varnished or sealed surface and the like. Surfaces also include household appliances including, but not limited to, refrigerators, freezers, washing machines, automatic dryers, ovens, microwave ovens, dishwashers and so on. The present composition is especially efficacious in the cleaning of ceramic, enamel, steel, plastic, glass surfaces found in kitchens, bathrooms and the like.

For the purposes of the present description, the expression "aqueous contacts" is used to indicate any situation in which said hard surfaces may come in contact with a certain amount of an aqueous mean, such as water. Typical aqueous contacts are, for example, rainwater, tap water, shower water, rinses, drips and any kind of situation in which an aqueous mean may voluntary or occasionally enter in contact with said hard surface, leaving it wet.

For the purposes of the present description and of the claims which follow, the expression "lower than", as used before any numerical value, is meant to exclude such a numerical value and used to encompass only a range of lower values.

For the purposes of the present description and of the claims which follow, except where otherwise indicated, all numerical values expressing parameters such as amounts, weights, temperatures, percentages, and so forth, are to be understood as being modified in all instances by the term "about". Also, all ranges include any combination of the maximum and minimum points disclosed and include any intermediate ranges therein, which may or may not be specifically enumerated herein.

According to a second aspect, the present invention provides a liquid composition for coating a substrate as defined in attached claim 2.

More specifically, the liquid composition of the present invention for coating a substrate and providing a hydrophobic coating film thereon comprises:

- a liquid carrier; and

- an effective amount of a compound of formula (I), as above described.

By the term "hydrophobic" it is meant that the surface has a low affinity for water. On the other side, by the term "hydrophilic" it is meant that the surface has a high affinity for water.

By the term "substrate" it is meant any kind of hard surface as previously disclosed or any kind of soft and/or flexible surface, such as fabric, textiles, fibers, woven materials, non-woven materials, and carpets.

The inventors have observed that the aforementioned liquid composition is effective for rendering hydrophobic said substrates; thus, after said substrates have been subjected to an aqueous contact, the aqueous drops slip away from said substrates. The presence of water marks due to the prolonged permanence staying of water drops onto said

substrates is thus reduced, even if the substrates are subjected to several aqueous contacts in the period of time between two cleaning operations.

Preferably said substrate is a hard surface, more preferably is a ceramic, enamel, glass, plastics, plastified wood, metal, varnished or sealed surfaces.

The carrier medium can form part of the liquid composition, or it can comprise the medium in which the compound of Formula (I) is carried (or transported) for application to the hard surface.

For the purposes of the present invention, the carrier medium is contained in the liquid composition in an amount suitable to transport and/or solubilize the various ingredients described herein.

Such amount is readily ascertained by one of ordinary skill in the art and is based on many factors, such as the physical and chemical nature of the ingredients, the application technique of the liquid composition, and the like.

Several non-limiting examples of types of carrier mediums are provided hereinbelow by way of explanation, and not by way of limitation.

In one example, the liquid composition can be provided in the form of an aqueous liquid in a container, and the liquid can be pored, applied by means of a cloth or sponge or sprayed onto a hard surface. In such a case, the aqueous liquid carrier in the container holding the coating composition may be referred to herein as the "static carrier". When this coating composition is sprayed onto the hard surface, the liquid droplets in the spray may be referred to herein as the "dynamic carrier" (the medium that transports the ingredients to the surface in order to contact the surface).

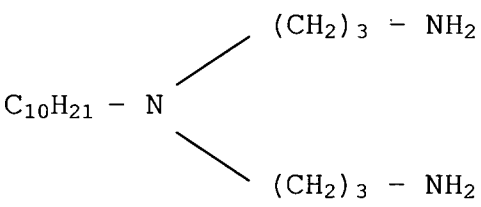
The term "carrier", as used herein, includes both static and dynamic carriers.

Suitable carrier mediums include liquids, at least some of which is aqueous. One suitable carrier medium is water, which can be distilled, deionized, or tap water. Water is valuable due to its low cost, availability, safety, and compatibility. In certain embodiments in which the carrier medium is aqueous, it may be preferred that at least some of the aqueous carrier is purified beyond the treatment it received to convert it to tap water (that is, the tap water is post-treated, e. g., deionized or distilled). The purified water could comprise: all or part of the static carrier for the composition; all or part of the dynamic carrier; or, all or part of both.

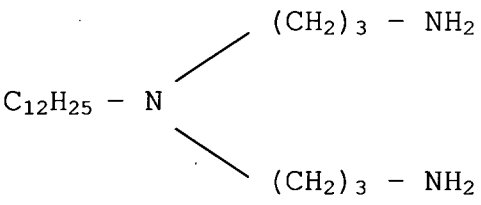
Other carrier mediums which may be used in combination with water are those containing a low molecular weight organic solvent that is highly soluble in water, e.g., ethanol, methanol, propanol, isopropanol and the like, and mixtures thereof. Low molecular weight alcohols can allow the treated hard surface to dry faster. The optional water soluble low molecular weight solvent can be used at a level of up to about 50%, typically from about 0.1% to about 25%, alternatively from about 2% to about 15%, alternatively from about 5% to about 10%, by weight of the suitable carrier medium.

Preferably, in the previous Formula (I), m and n are integers from 3 to 5; also preferably, R is an alkyl chain having from 10 to 14 carbon atoms.

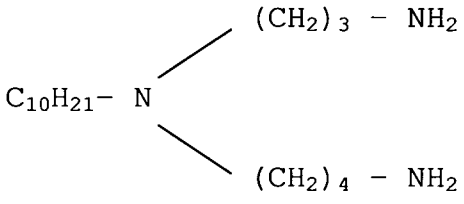
Not limiting examples of compounds of Formula (I) useful in the present invention are:



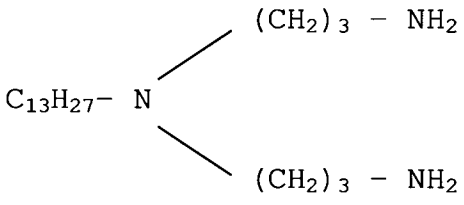
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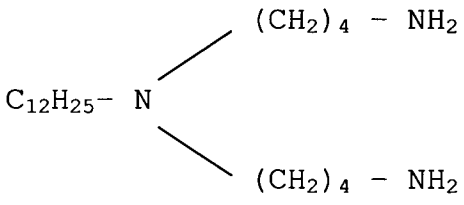
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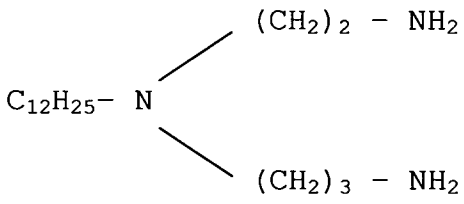
(I.3)



(I.4)



(I.5)



(I.6)

The preparation methods for obtaining compounds of Formula (I) are know in the art (see, for example, US Patent No. 4,416,808 or Denton TT , et al. in *Journal of Organic Chemistry,* Vol. 72 (13), pp. 4997-5000, 2007).

Preferably, the liquid composition of the present invention comprises 0.01% to 10.0%, more preferably 0.05% to 5.0%, by weight of said compound of formula (I).

Preferably, the liquid composition of the present invention further comprises a surfactant; in fact, it has been found that the presence of surfactants not only improves the cleaning performance, but also facilitates the dispersion of the compound of Formula (I).

Suitable surfactant useful in the present invention is surfactant selected from the group consisting of anionic surfactants, cationic surfactants, nonionic surfactants, amphoteric surfactants, zwitterionic surfactants and mixtures thereof.

For the purposes of the present invention, the surfactant is contained in the liquid composition in an effective amount to provide one, or more of the benefits described herein.

As used herein, "effective amount of the surfactant" refers to the quantity of surfactant described herein necessary to achieve at least one of the desired cleaning action, ability of dispersing the compound of Formula (I) and of other optional adjunct ingredients. Such effective amount may be readily ascertained by one of ordinary skill in the art and is based on many factors, such as the specific composition of the liquid composition, the application technique of the liquid composition, and the like.

The concentration of surfactant in the liquid compositions described herein is preferably comprised between 0.1 and

40% by weight as a function of the application technique of the liquid composition.

Thus, for example, a liquid composition that is to be applied to the hard surface to be cleaned by pouring or by means of a sponge or cloth may comprise from 0.3 to 20% by weight, more preferably from 1.5 to 10% by weight, of surfactant, whereas a liquid composition that is to be applied to the hard surface to be cleaned by spraying may comprise from 0.5 to 10% by weight, more preferably from 1.0 to 6.0% by weight, of surfactant in order to reduce the formation of foam, enhance the rinsability characteristics and reduce the costs.

Suitable anionic surfactants for use in the compositions herein include water-soluble salts or acids of the formula $ROSO_3M$, wherein R preferably is a C_7-C_{24} hydrocarbyl, preferably an alkyl or hydroxyalkyl having a C_7-C_{24} alkyl component, more preferably a C_{12}-C_{18} alkyl or hydroxyalkyl, 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).

Other suitable anionic surfactants for use herein are water-soluble salts or acids of the formula $RO(A)mSO_3M$, wherein R is an unsubstituted C_{10}-C_{24} alkyl or hydroxyalkyl group having a C_{10}-C_{24} alkyl component, preferably a C_{12}-C_{20} alkyl or hydroxyalkyl, more preferably C_{12}-C_{18} alkyl or hydroxyalkyl, A is an ethoxy or propoxy unit, m is greater than zero, typically between about 0.5 and about 6, more preferably between about 0.5 and about 3, 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)M), C_{12}-C_{18} alkyl polyethoxylate (2.25) sulfate, C_{12}-C_{18}E(2.25)M), C_{12}-C_{18} alkyl polyethoxylate (3.0) sulphate, C_{12}-C_{18}E(3.0), and C_{12}-C_{18} alkyl polyethoxylate (4.0) sulfate C_{12}-C_{18}E(4.0)M), wherein M is conveniently selected from sodium and potassium.

Other particularly suitable anionic surfactants for use herein are alkyl sulphonates including water-soluble salts or acids of the formula RSO_3M, wherein R is a C_6-C_{22} linear or branched, saturated or unsaturated alkyl group, preferably a C_{10}-C_{16} alkyl group and more preferably a C_{12}-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 trimethylammonium cations and quaternary ammonium *cations,* such *as* tetramethylammonium and dimethyl piperdinium cations and quaternary ammonium cations derived from alkylamines such as ethylamine, diethylamine, triethylamine, and mixtures thereof, and the like).

Suitable alkyl aryl sulphonates for use herein include water-soluble salts or acids of the formula RSO_3M, wherein R is an aryl, preferably a benzyl, substituted by a C_6-C_{22} linear or branched saturated or unsaturated alkyl group, preferably a C_{10}-C_{18} alkyl group and more preferably a C_{12}-C_{16} alkyl group, and M is H or a cation, e.g., an alkali metal cation (e.g., sodium, potassium, lithium, calcium, magnesium etc*)* *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).

The alkylsulfonates and alkyl aryl sulphonates for use herein include primary and secondary alkylsulfonates and primary and secondary alkyl aryl sulphonates. By "secondary C_6-C_{22} alkyl or C_6-C_{22} alkyl aryl sulphonates", it is meant herein that in the formula as defined above, the SO_3M or aryl-SO_3M group is linked to a carbon atom of the alkyl chain being placed between two other carbons of the said alkyl chain (secondary carbon atom).

Other anionic surfactants useful for detersive purposes can also be used herein. These can include salts (including, for example, sodium, potassium, ammonium, and substituted ammonium salts such as mono-, di- and triethanolamine salts) of soap, C_8-C_{24} olefinsulfonates, sulfonated polycarboxylic acids prepared by sulfonation of the pyrolyzed product of aikaline earth meta) citrates, C_8-C_{24} alkylpolyglycolethersulfates (containing up to 10 moles of ethylene oxide); alkyl ester sulfonates such as C_{14}-C_{16} methyl ester sulfonates; acyl glycerol sulfonates, fatty oleyl glycerol sulfates, alkyl phenol ethylene oxide ether sulfates, paraffin sulfonates, alkyl phosphates, isethionates such as the acyl isethionates, N-acyl taurates, alkyl succinamates and sulfosuccinates, monoesters of sulfosuccinate (especially saturated and unsaturated C_{12}-C_{18} monoesters) diesters of sulfosuccinate (especially saturated and unsaturated C_6-C_{14} diesters), ethoxylated sulphosuccinates, sulfates of alkylpolysaccharides such as the sulfates of alkylpolyglucoside (the nonionic nonsulfated compounds being described below), branched primary alkyl sulfates,

alkyl polyethoxy carboxylates such as those of the formula $RO(CH_2CH_2O)_kCH_2OOO\text{-}M^+$ wherein R is a C_8-C_{22} alkyl, k is an integer from 0 to 10, and M is a soluble salt-forming cation.

Other particularly suitable anionic surfactants for use herein are alkyl carboxylates and alkyl alkoxycarboxylates having from 4 to 24 carbon atoms in the alkyl chain, preferably from 8 to 18 and more preferably from 8 to 16, wherein the alkoxy is propoxy and/or ethoxy and preferably is ethoxy at an alkoxylation degree of from 0.5 to 20, preferably from 5 to 15.

Preferred alkylalkoxycarboxylate for use herein is sodium laureth 11 carboxylate (i.e., $RO(C_2\text{-}H_{40})_{10}\text{-}CH_2COONa$, with R= C_{12}-C_{14}).

Suitable amphoteric surfactants for use herein include amine oxides having the following formula $R_1R_2R_3NO$ wherein each of R_1, R_2 and R_3 is independently a saturated substituted or unsubstituted, linear or branched hydrocarbon chain of from 1 to 30 carbon atoms. Preferred amine oxide surfactants to be used according to the present invention are amine oxides having the following formula $R_1R_2R_3NO$ wherein R_1 is a hydrocarbon chain comprising from 1 to 30 carbon atoms, preferably from 6 to 20, more preferably from 8 to 16, most preferably from 8 to 12, and wherein R_2 and R_3 are independently substituted or unsubstituted, linear or branched hydrocarbon chains comprising from 1 to 4 carbon atoms, preferably from 1 to 3 carbon atoms, and more preferably are methyl groups. R_1 may be a saturated, substituted or unsubstituted linear or branched hydrocarbon chain. Suitable amine oxides for use herein are for instance natural blend C_8-C_{10} amine oxides as well as C_{12}-C_{16} amine oxides commercially available from Hoechst.

Suitable zwitterionic surfactants for use herein contain both a cationic hydrophilic group, i.e., a quaternary ammonium group, and anionic hydrophilic group on the same molecule at a relatively wide range of pH's. The typical anionic hydrophilic groups are carboxylates and sulfonates, although other groups like sulfates, phosphonates, and the like can be used. A generic formula for the zwitterionic surfactants to be used herein is :

$$R_1-N^+(R_2)(R_3)R_4X^-$$

wherein R_1 is a hydrophobic group; R_2 is hydrogen, C_1-C_6 alkyl, hydroxy alkyl or other substituted C_1-C_6 alkyl group; R_3 is C_1-C_6 alkyl, hydroxy alkyl or other substituted C_1-C_6 alkyl group which can also be joined to R_2 to form ring structures with the N, or a C_1-C_6 carboxylic acid group or a C_1-C_6 sulfonate group; R_4 is a moiety joining the cationic nitrogen atom to the hydrophilic group and is typically an alkylene, hydroxy alkylene, or polyalkoxy group containing from 1 to 10 carbon atoms; and X is the hydrophilic group which is a carboxylate or sulfonate group.

Preferred hydrophobic groups R_1 are aliphatic or aromatic, saturated or unsaturated, substituted or unsubstituted hydrocarbon chains that can contain linking groups such as amido groups, ester groups. More preferred R_1 is an alkyl group containing from 1 to 24 carbon atoms, preferably from 8 to 18, and more 20 preferably from 10 to 16. These simple alkyl groups are preferred for cost and stability reasons. However, the hydrophobic group R1 can also be an amido radical of the formula R_a-C(O)-NH-$(C(R_b)_2)_m$, wherein R_a is an aliphatic or aromatic, saturated or unsaturated, substituted or unsubstituted hydrocarbon chain, preferably an alkyl group containing from 8 up to 20 carbon atoms, 25 preferably up to 18, more preferably up to 16, R_b is selected from the group consisting of hydrogen and hydroxy groups, and m is from 1 to 4, preferably from 2 to 3, more

preferably 3, with no more than one hydroxy group in any ($C(R_b)2$) moiety. Preferred R_2 is hydrogen, or a C_1-C_3 alkyl and more preferably methyl. Preferred R_3 is a C_1-C_4 carboxylic acid group or C_1-C_4 sulfonate group, or a C_1-C_3 alkyl and more preferably methyl. Preferred R_4 is $(CH_2)_n$ wherein n is an integer from 1 to 10, preferably from 1 to 6, more preferably is from 1 to 3.

Examples of particularly suitable alkyldimethyl betaines include coconut-dimethyl 1o betaine, lauryl dimethyl betaine, decyl dimethyl betaine, 2-(N-decyl-N, N-dimethyl-ammonia)acetate, 2-(N-coco N, N-dimethylammonio) acetate, myristyl dimethyl betaine, palmityl dimethyl betaine, cetyl dimethyl betaine, stearyl dimethyl betaine. For example Coconut dimethyl betaine is commercially available from Seppic under the trade name of Amonyl 265®. Lauryl betaine is commercially available from Albright & Wilson under the trade name Empigen BB/L®.

Examples of amidobetaines include cocoamidoethylbetaine, cocoamidopropyl betaine or C_{10}-C_{14} fatty acylamidopropylene(hydropropylene)sulfobetaine. For example C_{10}-C_{14} fatty acylamidopropylene(hydropropylene)sulfobetaine is commercially available from Sherex Company under the trade name "Varion CAS® sulfobetaine".

A further example of betaine is Lauryl-imino-dipropionate commercially available from Rhone-Poulenc under the trade name Mirataine H2C-HA ®.

Suitable cationic surfactants for use herein include derivatives of quaternary ammonium, phosphonium, imidazolium and sulfonium compounds. Preferred cationic surfactants for use herein are quaternary ammonium compounds wherein one or two of the hydrocarbon groups linked to nitrogen are a saturated, linear or branched alkyl group of 6 to 30 carbon atoms, preferably of 10 to 25 carbon atoms, and more preferably of 12 to 20 carbon atoms,

and wherein the other hydrocarbon groups (Le. three when one hydrocarbon group is a long chain hydrocarbon group as mentioned hereinbefore or two when two hydrocarbon groups are long chain hydrocarbon groups as mentioned hereinbefore) Linked to the nitrogen are independently substituted or unsubstituted, linear or branched, alkyl chain of from 1 to 4 carbon atoms, preferably of from 1 to 3 carbon atoms, and more preferably are methyl groups.

Amongst the nonionic surfactants, alkoxylated nonionic surfactants are suitable for use herein. Such alkoxylated nonionic are preferably alkoxylated alcohols having a carbon chain containing from 8 to 20 carbon atoms, more preferably from 10 to 18 carbon atoms and most preferably from 10 to 15 carbon atoms. The alkoxylation may be provided by ethoxylate, propoxylate or butoxylate groups, preferably ethoxylate groups. In a preferred aspect the ethoxylated alcohol comprises from 0.5 to 20, more preferably from 2 to 10, most preferably from 4 to 6 ethoxy groups.

Suitable capped alkoxylated nonionic surfactants for use herein are according to the formula:

$$R_1(O\text{-}CH_2\text{-}CH_2)_n\text{-}(OR_2)_m\text{-}O\text{-}R_3$$

wherein R_1 is a C_8-C_{24} linear or branched alkyl or alkenyl group, aryl group, alkaryl group, preferably R_1 is a C_8-C_{18} alkyl or alkenyl group, more preferably a C_{10}-C_{15} alkyl or alkenyl group, even more preferably a C_{10}-C_{15} alkyl group; wherein R_2 is a C_1-C_{10} linear or branched alkyl group, preferably a C_2-C_{10} linear or branched alkyl group, wherein R_3 is a C_1-C_{10} alkyl or alkenyl group, preferably a C_1-C_5 alkyl group, more preferably methyl; and wherein n and m are integers independently ranging in the range of from 1 to 20, preferably from 1 to 10, more preferably from 1 to 5; or mixtures thereof.

These surfactants are commercially available from BASF under the trade name Plurafac®, from HOECHST under the trade name Genapol® or from ICI under the trade name Symperonic®. Preferred capped nonionic alkoxylated surfactants of the above formula are those commercially available under the tradename Genapol® L 2.5 NR from Hoechst, and Plurafac® from BASF.

In another preferred alternative embodiment suitable surfactants include the alkyl polysaccharide surfactants. The alkyl polysaccharide surfactants, have a hydrophobic group containing from 8 to 20 caron atoms, preferably from 10 to 18 carbon atoms, and a polysaccharide hydrophilic group containing from 1.5 to 10, preferably from 1.5 to 4 saccharide units. Suitable saccharide units include galactoside, glucoside, fructoside, glycosyl, fructosyl and/or galactosyl. Mixtures of saccharide units may be used in the alkyl polysaccharide. Typical hydrophobic groups include alkyl groups, either saturated or nonsaturated, branched or unbranched containing from 6 to 20, preferably from 8 to 18 carbon atoms. Preferably the alkyl group is a linear, saturated alkyl group. The alkyl group can contain up to 3 hydroxy groups and/or the polyalkoxide chain can contain up to 30, preferably less than 10 alkoxide groups. Suitable alkyl polysaccharides are octyl, decyl, dodecyl, tetradcyl, pentadecyl, hexadecyl and actadecyl, di-, tri-, tetra-, penta- and hexa-glucosides, lactosides, fructosides, fructosyls, lactosyis, glucosyls, galactosyls and mixtures thereof.

Other suitable surfactants include silicone surfactants such as organsilane or organosiloxane. Preferably the silicone surfactants have molecular weight of from 600 to 10,000, more preferably from 900 to 6000, most preferably about 3000.

Such compounds are well known in the art, examples of which can be found in for example US 3299112, US 4311695, US

4782095 the disclosures of which are incorporated herein by reference. Suitable siloxane oligomers are described in US 4005028. Suitable silicone surfactants include polysiloxane polyethylene glycol copolymers, polyalkylene oxide-modified polydimethylsiloxane copolymers.

Other suitable surfactants include the fluorosurfactants which comprise a hydrophilic and a hydrophobic section. The hydrophilic section comprises an alkyl group having from 2 to 12 carbons and an ester, sulfonate or carboxylate moiety. The hydrophobic section is fluorinated. Preferred fluorosurfactants include alkyl fluorocarboxylates for example ammonium perfluroalkyl carboxylate and potassium fluroalkyl carboxylate. A particularly suitable fluorosurfactants is an aqueous mixture of potassium fluoroalkyl carboxylate and has from 40-44% fluoroalkyl carboxylate having 8 carbon atoms in the alkyl chain, from 1-5% fluoroalkyl carboxylates having 6 carbon atoms in the alkyl chain, from 1-5% fluoroalkyl carboxylates having 4 carbon atoms in the alkyl chain, from 1-3% fluoroalkyl carboxylates having 7 carbon atoms in the alkyl chain and from 0.1-1% fluoroalkyl carboxylates having 5 carbon atoms in the alkyl chain.

In a preferred aspect of the present invention the surfactant is a system comprising at least one anionic surfactant in combination with a non ionic surfactant. Particularly preferred anionic surfactants are the alkyl sulfates and the salts of natural fatty acids surfactants. Particularly preferred non ionic surfactants are the alkoxylated hydrocarbons, such as alkoxylated terpene.

In another preferred aspect of the present invention the surfactant is a system comprising at least one non ionic surfactant. Particularly preferred non ionic surfactants are alkoxylated hydrocarbons, such as alkoxylated terpene, and alkoxylated alcohols such as Laureth-4 (ethoxylated dodecyl alcohol).

In a preferred embodiment, the liquid composition for cleaning hard surfaces further comprises inorganic particles having a particle size of from 0.5 to 5 μm, preferably from 0.5 to 1.5 μm.

In this way, the ability of the inorganic particles of reaching dirt and soil located in the tiniest scratches of the surface to be cleaned and the ability of the liquid composition of exerting its cleaning action without affecting the surface integrity and its gloss are advantageously enhanced.

For the purposes of the invention, the particle size of the inorganic particles can be measured according to known methods, such as, for example, by using transmission electron microscopy (TEM).

For the purposes of the invention, suitable inorganic particles are selected from phosphates, oxides, silicates, carbonates, hydroxides and mixtures thereof.

In a preferred embodiment, the inorganic particles are selected from acid phosphates, calcium phosphates, hydroxyapatite, modified hydroxyapatite, alkaline earth metal phosphates, ammonium phosphates, brushite, monetite, feldspar, quartz, topaz, calcite, alumina, limonite, kimenite, ceramic, leucite, glass, taconite, silica sand, flint, vermiculite, fire clay, diaspore, bauxite, limestone, magnetite, hematite, and mixtures thereof.

In a particularly preferred embodiment, the solid inorganic particles are particles of a carbonate-substituted non-stoichiometric hydroxyapatite having the formula:

$$Ca_{10}(PO_4)_{6-y}(CO_3)_{y+z}(OH)_{2-z}$$

wherein y is a number comprised between 0.065 and 0.9 and z is a number comprised between 0 and 0.32.

In additional embodiments of the invention, inorganic particles suitable for the purposes of the present invention are layered clay minerals and inorganic metal oxides.

The layered clay minerals suitable for use in the present invention include those in the geological classes of the smectites, the kaolins, the illites, the chlorites, the attapulgites and the mixed layer clays. Typical examples of specific clays belonging to these classes are the smectites, kaolins, illites, chlorites, attapulgites and mixed layer clays. Smectites, for example, include montmorillonite, bentonite, pyrophyllite, hectorite, saponite, sauconite, nontronite, talc, beidellite, volchonskoite and vermiculite. Kaolins include kaolinite, dickite, nacrite, antigorite, anauxite, halloysite, indellite and chrysotile. Illites include bravaisite, muscovite, paragonite, phlogopite and biotite. Chlorites include corrensite, penninite, donbassite, sudoite, pennine and clinochlore. Attapulgites include sepiolite and polygorskyte. Mixed layer clays include allevardite and vermiculitebiotite. Variants and isomorphic substitutions of these layered clay minerals offer unique applications.

The layered clay minerals of the present invention may be either naturally occurring or synthetic. An example of one embodiment of the present invention uses natural or synthetic hectorites, montmorillonites and bentonites. Another embodiment uses the hectorites clays commercially available.

The inorganic metal oxides of the present invention may be silica-or alumina-based microparticles that are naturally occurring or synthetic. Aluminum can be found in many naturally occurring sources, such as kaolinite and bauxite. The naturally occurring sources of alumina are processed by the Hall process or the Bayer process to yield the desired alumina type required.

Various forms of alumina are commercially available in the form of Gibbsite, Diaspore, and Boehmite.

Natural clay minerals typically exist as layered silicate minerals and less frequently as amorphous minerals. A layered silicate mineral has SiO_4 tetrahedral sheets arranged into a two-dimensional network structure. A 2:1 type layered silicate mineral has a laminated structure of several to several tens of silicate sheets having a three layered structure in which a magnesium octahedral sheet or an aluminum octahedral sheet is sandwiched between two sheets of silica tetrahedral sheets.

A sheet of an expandable layer silicate has a negative electric charge, and the electric charge is neutralized by the existence of alkali metal cations and/or alkaline earth metal cations.

For the purposes of the present invention, the inorganic particles are contained in the liquid composition in an effective amount to provide one, or more of the benefits described herein.

As used herein, "effective amount of the inorganic particles" refers to the quantity of inorganic particles of the present invention described herein necessary to allow the hard surface to maintain its hydrophobic characteristics. Such effective amounts are readily ascertained by one of ordinary skill in the art and is based on many factors, such as the particular inorganic particles used, their particle dimensions, the application technique of the liquid composition, the specific composition of the liquid composition, and the like.

Thus, for example, a liquid composition that is to be applied to the hard surface by pouring or by means of a sponge or cloth may comprise from 5 to 50% by weight, more preferably from 10 to 40% by weight, of inorganic

particles, whereas a liquid composition that is to be applied to the hard surface by spraying may comprise from 0.1 to 15% by weight, more preferably from 0.5 to 5% by weight, of inorganic particles in order not to clog the spraying device.

The liquid compositions described herein may comprise a variety of optional ingredients depending on the technical benefit required and the surface treated.

Suitable optional ingredients for use herein can be selected from anti-resoiling ingredients, solvents, pH adjusting agents, rheology regulators, perfumes and minor ingredients such as colorants, preservatives and/or disinfectants.

Suitable amounts of these optional ingredients may be easily selectable by those skilled in the art as a function of the specific characteristics to be imparted to the liquid composition.

In one preferred embodiment the composition comprises an anti-resoiling ingredient.

For the purposes of the present invention, the anti-resoiling ingredients are contained in the liquid composition in an effective amount to provide one, or more of the benefits described herein.

As used herein, "effective amount of the anti-resoiling ingredient" refers to the quantity of this ingredient necessary to impart anti-resoling properties to the cleaned surface thanks to the film-foaming action of this ingredient.

Such effective amounts are readily ascertained by one of ordinary skill in the art and is based on many factors, such as the particular anti-resoiling ingredient used, the application technique of the liquid composition, the

specific composition of the liquid composition, and the like.

The concentration of the anti-resoiling ingredients in the liquid compositions described herein is preferably comprised between 0.1 and 2% by weight, more preferably between 0.25% and 1.5% by weight, as a function of the application technique of the liquid composition.

Suitable anti-resoiling ingredients include those well known to those skilled in the art, amongst which include polyalkoxylene glycol diester, vinylpyrrolidone homopolymer or copolymer, polysaccharide polymer, polyalkoxylene glycol, mono- or di-capped polyalkoxylene glycol, as defined herein after, or a mixture thereof.

Suitable vinylpyrrolidone homopolymers for use herein is an homopolymer of N-vinylpyrrolidone ("PVP") having 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.

Suitable copolymers of vinylpyrrolidone for use herein include copolymers of N-15 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, 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-methyl styrene, vinyl toluene, t-butyl styrene and similar well known monomers may be used.

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 preferred polysaccharide polymers *to* be used in the liquid composition are xanthan gum and derivatives thereof.

Suitable additional anti-resoiling ingredients for use herein further include alkyl ether glycols, polyalkoxylene glycol, mono- and dicapped polyalkoxylene glycol or a mixture thereof, as defined herein after.

Suitable alkyl ether glycols for use herein are according to the following formula: $R_1-(CH_2-CHR_2O)_n-H$.

Suitable polyalkoxylene glycols for use herein are according to the following formula: $H-O-(CH_2-CHR^2O)_n-H$.

Suitable monocapped polyalkoxylene glycols for use herein are according to the following formula: $R^1-O-(CH_2-CHR^2O)_n-H$.

Suitable dicapped polyalkoxylene glycols for use 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.

Particularly preferred alkyl ether glycol to be used in the liquid composition disclosed herein is butyl glycol.

The liquid compositions described herein may further optionally comprise one or more solvents.

For the purposes of the present invention, the solvents are contained in the liquid composition in an effective amount to provide one, or more of the benefits described herein.

As used herein, "effective amount of the solvents" refers to the quantity of this ingredient necessary to solubilize the soil or dirt removed from the surface preventing its redeposition on the cleaned surface.

Such effective amounts are readily ascertained by one of ordinary skill in the art and is based on many factors, such as the particular solvents used, the application technique of the liquid composition, the specific composition of the liquid composition, and the like.

The concentration of the solvents in the liquid compositions described herein is preferably comprised between 0.1 and 5% by weight as a function of the application technique of the liquid composition.

Thus, for example, a liquid composition that is to be applied to the hard surface by pouring or by means of a sponge or cloth may comprise from 1.0 to 5% by weight, more preferably from 1.5 to 2.5% by weight, of one or more solvents, whereas a liquid composition that is to be applied to the hard surface by spraying may comprise from 0.75 to 5% by weight, more preferably from 1.0 to 2.5% by weight, of one or more solvents.

Solvents for use herein include all those known to 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 alkoxylated glycols, alkoxylated aromatic alcohols, aromatic alcohols, aliphatic branched alcohols, alkoxylated

aliphatic branched alcohols, alkoxylated linear C1-C5 alcohols, linear C1-C5 alcohols, C8-C14 alkyl and cycloalkyl hydrocarbons and halohydrocarbons, C6-C16 glycol ethers and mixtures thereof.

Preferred solvents among the above-identified ones are: dodecaneglycol and/or propanediol, methoxy octadecanol and/or ethoxyethoxyethanol, benzoxyethanol and/or benzoxypropanol, benzyl alcohol, 2-ethylbutanol and/or 2-methylbutanol, 1-methylpropoxyethanol and/or 2-methyl butoxyethanol, butoxy propoxy propanol (n-BPP), butoxyethanoi, butoxypropanol, ethoxyethanol, methanol, ethanol, propanol, butyl díglycol ether (BDGE), butyltriglycol ether, ter amilic alcohol, or mixtures thereof.

In the embodiment of the present invention the liquid compositions are preferably formulated at basic pH range, typically from 10 to 12, in order to enhance the degreasing action of the liquid composition.

To this end, the liquid compositions may further comprise an effective amount of a suitable compound or a combination of compounds adapted to regulate the pH of the composition to such range of values.

As used herein, "effective amount of the pH adjusting agent" refers to the quantity of this ingredient necessary to achieve the desired pH value of the liquid composition.

Such effective amounts are readily ascertained by one of ordinary skill in the art and is based on many factors, such as the particular pH adjusting agents used, the application technique of the liquid composition, the specific composition of the liquid composition, and the like.

The concentration of the pH adjusting agents in the liquid compositions described herein is preferably comprised

between 2 and 5% by weight, more preferably between 2.5 and 3.5% by weight, as a function of the application technique of the cleaning composition.

pH adjusting agents for use herein include all those known to those skilled in the art. Suitable pH adjusting agents for use herein include inorganic bases, such as sodium hydroxide, potassium hydroxide, phosphates, such as potassium diphosphates, carbonates, such as sodium carbonate, or any other compound or mixture compounds known to those skilled in the art and suitable to achieve the desired pH value of the liquid composition.

The compositions described herein may further optionally comprise one or more rheology regulators.

For the purposes of the present invention, the rheology regulators are contained in the liquid composition in an effective amount to provide one, or more of the benefits described herein.

As used herein, "effective amount of the rheology regulators" refers to the quantity of this ingredient necessary to regulate the rheology characteristics of the liquid composition, such as for example viscosity and thixotropicity, as a function of the application techniques.

Such effective amounts are readily ascertained by one of ordinary skill in the art and is based on many factors, such as the particular rheology regulators used, the application technique of the liquid composition, the specific composition of the liquid composition, and the like.

In the embodiment of the present invention the liquid compositions are preferably formulated at a viscosity comprised between 2000 and 30000 cps at 20°C, and more preferably, between 6000 and 10000 cps at 20°C as a

function of the application technique of the liquid composition.

The concentration of the rheology regulators in the liquid compositions described herein is preferably comprised between 0.1 and 2% by weight as a function of the application technique of the liquid composition.

Thus, for example, a liquid composition that is to be applied to the hard surface by pouring or by means of a sponge or cloth may comprise from 0.25 to 1.50 % by weight, more preferably from 0.30 to 0.80 % by weight, of one or more rheology regulators, whereas a liquid composition that is to be applied to the hard surface by spraying may comprise from 0.10 to 3.0 % by weight, more preferably from 0.25 to 1.50 % by weight, of one or more rheology regulators.

Rheology regulators for use herein include all those known to those skilled in the art. Suitable rheology regulators for use herein include thickeners, adapted to adjust the viscosity of the composition, as well as thixotroping agents, adapted to impart suitable thixotropic properties to the composition.

Suitable thickening agents are those known in the art. Examples of thickening agents include gum-type polymers (e.g. xanthan gum), polyvinyl alcohol and derivatives thereof, cellulose and derivatives thereof and polycarboxylate polymers.

In a particularly preferred embodiment of the present invention the thickening agent comprises a polymeric sulfonic acid, gum-type polymer or a polycarboxylate polymer.

The gum-type polymer may be selected from the group consisting of polysaccharide hydrocolloids, xanthan gum, guar gum, succinoglucan gum, Cellulose, derivatives of any

of the above and mixtures thereof. In a preferred aspect of the present invention the gum-type polymer is a xanthan gum or derivative thereof.

The polycarboxylate polymer can be a homo or copolymer of monomer units selected from acrylic acid, methacrylic acid, maleic acid, malic acid, maleic anhydride. Suitable polymers have molecular weight in the range of from 10000 to 100 000 000 most preferably 1000000 to 10 000 000.

Particularly preferred examples of these thickening agents are polymeric sulfonic acid, xanthan gum and cross-linked polycarboxylate polymers.

Suitable thixotroping agents are those known in the art. Examples of thixotroping agents include vinylpyrrolidone homopolymer or copolymers, xantan gum, acrylic homo polymers or copolymers, or mixture thereof.

Suitable vinylpyrrolidone homopolymers for use herein is an homopolymer of N-vinylpyrrolidone ("PVP") having 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.

Suitable vinylpyrrolidone copolymers for use herein is an ammonium acryloyldimethylaurate/VP Copolymer.

The compositions described herein may further optionally comprise one or more perfumes.

For the purposes of the present invention, the perfumes are contained in the liquid composition in an effective amount to provide the benefits disclosed herein.

As used herein, "effective amount of the perfumes" refers to the quantity of this ingredient necessary to attain the aforementioned effect as a function of the application techniques.

Such effective amounts are readily ascertained by one of ordinary skill in the art and is based on many factors, such as the particular perfumes used, the application technique of the liquid composition, the specific composition of the liquid composition, and the like.

The concentration of the perfumes in the liquid compositions described herein is preferably comprised between 0.01 and 5% by weight.

Suitable perfumes for use 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 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.

The compositions described herein may further optionally comprise one or more minor ingredients selected among colorants, preservatives and disinfectants.

For the purposes of the present invention, these minor ingredients are contained in the liquid composition in an effective amount to provide the benefits disclosed herein.

As used herein, "effective amount of the minor ingredients" refers to the quantity of these ingredients necessary to

attain the desired effect as a function of the application techniques.

Such effective amounts are readily ascertained by one of ordinary skill in the art and is based on many factors, such as the particular ingredient used, the application technique of the liquid composition, the specific composition of the liquid composition, and the like.

The concentration of the minor ingredients in the liquid compositions described herein is preferably comprised between 0.01 and 2% by weight.

Suitable colorants are those known in the art. Examples of colorants include well known water soluble dyes and pigments both of natural and of synthetic origin.

Suitable preservatives are those known in the art. Examples of preservatives are any compound that can be stably added to the composition that kills or at least inactivates microbes, for example bacteria and fungi. Particularly preferred preservatives are 5-choloro-2-methyl-4-isothiazolin-3-one and 2-methyl-4-isothiazolin-3-one available from Rohm & Haas under the trade name KATHON® CG, 1,2-benzisothiazolin-3-one available from Avecia under the trade name Proxel GXL, phenoxyethanol available from BASF under the trade name Protectol PP or gluteraldehyde available from BASF under the trade name Protectol GDA.

Suitable disinfectants are those known in the art. Examples of disinfectants are any compound that can be stably added to the composition that kills or at least inactivates microbes, for example bacteria, thereby exerting sanitizing effect on the cleaned surface. Particularly preferred disinfectants are quaternary ammonium salts, such as benzalkonium chloride.

For the purposes of the invention, one or more of the ingredients illustrated hereinabove may exert more than one

function at the same time thereby advantageously reducing the number of total ingredients and the production costs.

Thus, for example, preferred embodiments of the liquid compositions may include xantham gum which may act both as an anti-resoiling agent and as a thickener adjusting the viscosity characteristics of the composition. As mentioned above, furthermore, the surfactants may act both as cleaning agents and as suspending agents of the inorganic particles and/or of other ingredients such as the perfumes.

For the purposes of the invention, the liquid compositions described herein may be prepared using mixing procedures of the ingredients well known to those skilled in the art.

According to a third aspect thereof, the present invention relates to a hydrophobic coating film for at least partially covering a substrate, as defined in attached claim 17.

More specifically, the present invention refers to a hydrophobic coating film for at least partially covering a substrate, said hydrophobic coating film comprising a compound of formula (I) as above.

The inventors have observed that the aforementioned hydrophobic coating film is effective for rendering hydrophobic said substrate at least partially covered by said hydrophobic coating film, allowing the substrate to be self-cleaning and allowing the reduction of water marks on said substrate, even after that said substrate has been subjected to aqueous contacts.

Preferably said substrate is a hard surface.

Hydropobicity can be determined by measuring the contact angle between the surface and a droplet of water on the surface. Contact angle is measured according to procedures known in the art for measuring contact angle, for example

using the apparatus commercially sold under the trade name DigiDrop, Model DS by GBX, Romans-sur-Isère, France and the software WINDROP++ also commercially available from GBX, Romans-sur-Isère, France.

In a preferred embodiment of the present invention, the hydrophobic coating film applied to the substrate is capable of modifying the substrate to render it hydrophobic, providing a contact angle between water and the substrate higher than 40°, more preferably higher than 60°, most preferably higher than 75°.

According to a fourth aspect thereof, the present invention relates to a method for providing said hydrophobic coating film on a substrate, as defined in attached claim 18.

More specifically, the present invention refers to a method for providing said hydrophobic coating film on a substrate, comprising the steps of:

- applying to said substrate a liquid composition comprising:

  - a liquid carrier; and

  - an effective amount of a compound of formula (I), as previously described, and

- allowing the water to evaporate thereby forming the hydrophobic coating film on the substrate.

Preferably said substrate is a hard surface.

The inventors have observed that the aforementioned method for providing said hydrophobic coating film on a substrate is very simple and allows said substrate to maintain its hydrophobic properties even after that it has later been subjected to aqueous contacts.

According to a fifth aspect thereof, the present invention relates to a method of cleaning a hard surface and of imparting hydrophobic properties to said hard surface, as defined in attached claim 19.

More specifically, the present invention refers to a method of cleaning a hard surface and of imparting hydrophobic properties to said surface comprising the steps of:

- applying to said hard surface a liquid composition comprising:

  - a carrier, at least some of which is aqueous;

  - one or more surfactants;

  - an effective amount of a compound of formula (I), as disclosed above, and

- rinsing the composition applied to the surface.

By this way, the hard surfaces remain clean and free of watermarks to the observer, by thus reducing the number of cleaning operations needed to maintain clean said hard surfaces for a prolonged period of time.

Furthermore, the above benefit provided by the process of the present invention is durable, meaning that the benefit can still be perceived after successive water contacts.

In a preferred embodiment of the present invention, the liquid composition may be applied to the hard surface by pouring the composition over the surface, by applying the composition on the surface by means of a cloth or sponge or by spraying the composition on the surface.

Preferably said hard surface is a ceramic, enamel, glass, plastics, plastified wood, metal, varnished or sealed surfaces.

In a preferred embodiment of said method, said composition is capable of modifying the cleaned surface to render it hydrophobic, providing a contact angle between water and the cleaned surface higher than 40°, more preferably higher than 60°, most preferably higher than 75°.

In a preferred embodiment of said method, said liquid composition is applied to the surface of an article by pouring the composition over the surface, by applying the composition on the surface by means of a cloth or sponge or by spraying the composition on the surface.

In a preferred embodiment, said method further comprises the step of letting the surface dry naturally.

In a alternative preferred embodiment, said method further comprises the step of drying the surface with cloth or chamois.

According to a sixth aspect thereof, the present invention relates to the use of liquid compositions for rendering hydrophobic a hard surface, as defined in attached claim 25.

More specifically, the present invention refers to the use of liquid compositions comprising:

- a liquid carrier; and

- an effective amount of a compound of formula (I), as disclosed above,

for rendering hydrophobic a hard surface.

The inventors have observed that the use of said aforementioned liquid composition is effective for rendering hydrophobic said hard surface; thus, after said hard surfaces have been subjected to aqueous contacts, the aqueous drops slip away from said hard surfaces. The presence of water marks due to the prolonged permanence

staying of water drops onto said hard surfaces is thus reduced.

In a preferred embodiment of this aspect of the present invention, the liquid composition may further comprises one or more surfactants in order to improve the cleaning performance of the liquid composition.

Typical surfactants useful to this aspect of the invention are selected from the group consisting of anionic surfactants, cationic surfactants, nonionic surfactants, amphoteric surfactants, zwitterionic surfactants and mixtures thereof, as previously described.

According to a seventh aspect thereof, the present invention relates to the use of a diamine compound for rendering hydrophobic a hard surface, as defined in attached claim 26.

More specifically, the present invention refers to the use of a compound of formula (I), as disclosed above, for rendering hydrophobic a hard surface.

In a preferred embodiment of this aspect of the present invention, in the previous Formula (I) m and n are integers from 3 to 5; also preferably, R is an alkyl chain having from 10 to 14 carbon atoms to enhance the hydrophobic properties of the hard surfaces.

Furthermore, the above benefit provided by the process of the present invention is durable, meaning that the benefit can still be perceived after successive rinses, including after intentional rinsing by the user or by rain water. By intentional rinsing it is meant rinsing the surface using a suitable rinsing device such as a hose, shower, bucket, cloth, sponge.

Additional features and advantages of the present invention will be more readily apparent by the following Examples of

some preferred embodiments of the present invention given hereinbelow by way of illustration and not of limitation.

In these drawings:

- Fig. 1 shows an image of a drop placed on a hard surface not being surface treated with any liquid composition and of the contact angle formed between the drop and the surface;

- Fig. 2 shows an image of a drop placed on a hard surface and of the contact angle formed between the drop and the cleaned surface after that the hard surface has been sprayed with a liquid composition according to the invention.

In the following Examples, percentages and parts are by weight unless otherwise indicated.

EXAMPLES

Liquid compositions adapted to be applied to a surface were prepared. The ingredients of the compositions are reported in the following Table 1.

Composition L1 (Invention).

The composition was prepared by first slowly adding 1 g of ammonium acrylodimethyltaurate vinyl pyrrolidone copolymer to 94 g of demineralized water until a homogeneous solution was obtained. Then, 1.75 g of terpene ethoxylated propoxylated and 1 g of butoxyrethanol were first added, under agitation, to the obtained solution and, later, a previously prepared solution comprising 1 g of ethoxylated dodecyl alcohol (commercially available as Laureth 4) and 1 g of perfume was also added. Finally, 0.05 g of methylchloroisothiazolinone-methylisothiazolinone, known as Kathon CG, and 0.20 g of the compound of Formula (I.2) previously disclosed were added to obtain the final liquid

composition L1. All the dissolving and stirring steps were carried out taking care that aeration is avoided.

Composition L2 (Invention).

5 g of carbonate hydroxyapatite having a particle size of 2 μm, were added to 89 g of demineralized water to obtain a solution thereof. Then, 1 g of ammonium acrylodimethyl-taurate vinyl pyrrolidone copolymer was slowly added to the obtained solution till a homogeneous mixture has been obtained. Then, 1,75 g of terpene ethoxylated propoxylated and 1 g of butoxyrethanol were first added, under shearing, to the obtained mixture and later a previously prepared solution comprising 1 g of ethoxylated dodecyl alcohol (commercially available as Laureth 4) and 1 g of perfume was also added. Finally, 0,05 g of methylchloro isothiazolinone-methylisothiazolinone, known as Kathon CG, and 0,2 g of the compound of Formula (I.2) previously disclosed were added to obtain the final liquid composition L2.

Composition L3 (comparison).

Liquid composition L3 was prepared as liquid composition L1, with the only difference that the compound of Formula (I.2) was replaced by the same amount of demineralized water.

Composition L4 (inventon).

Liquid composition L4 was prepared as liquid composition L1, with the only difference that the terpene ethoxylated propoxylated and butoxyrethanol compounds were replaced by the same amount of demineralized water.

Table 1

Ingredients	L1 (inv.) (w/w%)	L2 (inv.) (w/w%)	L3 (comp.) (w/w%)	L4 (inv.) (w/w%)
Aqueous carrier (Aqua)	94.00	91.50	94.20	96.75
Inorganic abrasive (Carbonate hydroxyapatite)	-	2.50	-	-
Thixotroping agent/thickener (Ammonium acrylodimethyltaurate VP copolymer)	1.00	1.00	1.00	1.00
Non ionic surfactant (Terpene Ethoxylated Propoxylated)	1.75	1.75	1.75	-
Solvent (Butoxyethanol)	1.00	1.00	1.00	1.00
Non ionic surfactant (Ethoxylated dodecyl alcohol)	1.00	1.00	1.00	-
Perfume	1.00	1.00	1.00	1.00
Preservative (Methylchloroisothiazolinone-Methylisothiazolinone)	0.05	0.05	0.05	0.05
Compound of Formula (I.2)	0.20	0.20	-	0.20

Evaluation test.

In order to evaluate the ability of the liquid compositions of the invention to clean and to render hydrophobic a hard surface the following tests were carried out.

Hydropobicity of a hard surface was determined by measuring the contact angle between the surface and a droplet of water placed onto said surface.

Test 1 (reference).

A water drop was placed onto a glass slide not being surface treated with any liquid composition. A photographic picture of the water drop was taken through the apparatus

commercially sold under the trade name DigiDrop, Model DS by GBX, Romans-sur-Isère, France (see figure 1). The contact angle between the horizontal flat surface of the drop placed onto the not-treated surface and the tangent to the drop itself was calculate utilizing the software WINDROP++ also commercially available from GBX, Romans-sur-Isère, France. A value of 33.3° was obtained.

Test 2 (comparison).

The same a glass slide was then cleaned with the liquid composition L3 (comparison) by pouring a small amount of the composition L3 on a cloth, wiping the surface with a cloth, rinsing and letting the surface dry naturally.

Then a water drop was placed onto the dry cleaned surface and a photographic picture of the water drop was taken (see figure 2). The contact angle was measured in the same way of test 1 and the obtained value of the contact angle was of 32.8°.

Test 3 (invention).

As in test 2, with the only difference that the liquid composition L3 (comparison) was replaced by the liquid composition L1 (invention). The value of the obtained contact angle was of 82.3°.

Test 4 (invention).

As in test 2, with the only difference that the liquid composition L3 (comparison) was replaced by the liquid composition L2 (invention). The value of the obtained contact angle was of 46.6°.

Test 5 (invention).

As in test 2, with the only difference that the liquid composition L3 (comparison) was replaced by the liquid

composition L4 (invention). The value of the obtained contact angle was of 82.3°.

The results are summarized in the following Table 2.

TABLE 2

	Hard surface treatment	Contact Angle
Test 1	NO	33.3°
Test 2	Composition L3 (comparison)	32.8°
Test 3	Composition L1 (invention)	82.3°
Test 4	Composition L2 (invention)	46.6°
Test 5	Composition L4 (invention)	82.3°

Table 2 shows that, when the hard surface onto which the liquid compositions of the invention L1, L2 or L4, (respectively, Tests 3, 4 and 5) have been poured, the water drop placed onto said hard surface presents a very high contact angle value (higher than 40°). That means that the hard surface has a very high hydrophobic feature, allowing the water drop to run away from the surface. Water marks are thus greatly reduced.

On the contrary, Table 2 also shows that, when the hard surface has not been treated with any kind of liquid composition (Test 1) or when the comparison liquid compositions L3 (Test 2) has been poured onto said hard surface, the water drop placed onto said hard surface presents a very low contact angle value (lower than 40°). That means that, in said cases, the hard surface has a low hydrophobic feature, allowing the water drop to stay for a prolonged period of time onto the surface. Water marks are thus greatly visible.

In addition, liquid compositions L1, L2 and L4 also showed good cleaning performances.

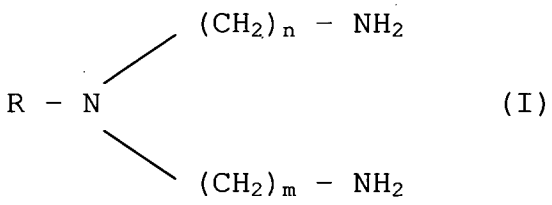
Claims.

1. Liquid composition for cleaning hard surfaces comprising:

- a carrier, at least some of which is aqueous;

- one or more surfactants;

- an effective amount of a compound of formula:



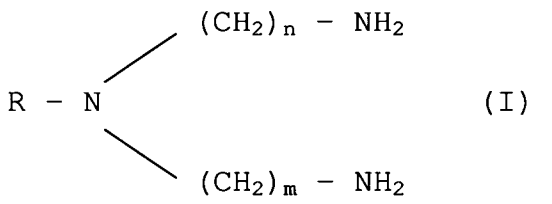
(I)

wherein m and n, equal or different, are integers from 2 to 8 and R is an optionally substituted alkyl chain having from 8 to 18 carbon atoms, for providing a hydrophobic coating film on said hard surfaces.

2. Liquid composition for coating a substrate and providing a hydrophobic coating film thereon comprising:

- a liquid carrier, and

- an effective amount of a compound of formula:



(I)

wherein m and n, equal or different, are integers from 2 to 8 and R is an optionally substituted alkyl chain having from 8 to 18 carbon atoms.

3. Liquid composition according to claim 1 or 2, wherein m and n are integers from 3 to 5.

4. Liquid composition according to any one of the preceding claims, wherein R is an alkyl chain having from 10 to 14 carbon atoms.

5. Liquid composition according to any one of the preceding claims, wherein said composition comprises 0.01% to 10.0% by weight of said compound of formula (I).

6. Liquid composition according to claim 5, wherein said composition comprises 0.05% to 5.0% by weight of said compound of formula (I).

7. Liquid composition according to claim 1, further comprising inorganic particles having a particle size of from 0.5 to 5 μm.

8. Liquid composition according to claim 7, wherein said inorganic particles are selected from phosphates, oxides, silicates, carbonates, hydroxides, and mixture thereof.

9. Liquid composition according to claim 7 or 8, wherein said inorganic particles are selected from acid phosphates, calcium phosphates, hydroxyapatite, modified hydroxyapatite, alkaline earth metal phosphates, ammonium phosphates, brushite, monetite, feldspar, quartz, topaz, calcite, alumina, limonite, kimenite, ceramic, leucite, glass, taconite, silica sand, flint, vermiculite, fire clay, diaspore, bauxite, limestone, magnetite, hematite, and mixtures thereof.

10. Liquid composition according to claim 7, wherein said inorganic particles are selected from:

a) inorganic metal oxides, natural clays, synthetic clays, and mixtures thereof;

b) synthetic clays selected from the group consisting of kaolinite, montmorillinite/smectite, illite, variants and isomorphous substitutions of said synthetic clay groups, and mixtures thereof;

c) synthetic clays selected from the group consisting of layered hydrous silicate, layered hydrous aluminum silicate, fluorosilicate, mica-montmorillonite, hydrotalcite, lithium magnesium silicate, lithium magnesium fluorosilicate, and mixtures thereof.

11. Liquid composition according to claim 7, wherein said inorganic particles are particles of a carbonate-substituted non-stoichiometric hydroxyapatite having the formula:

$$Ca_{10}(PO_4)_{6-y}(CO_3)_{y+z}(OH)_{2-z}$$

wherein y is a number comprised between 0.065 and 0.9 and z is a number comprised between 0 and 0.32.

12. Liquid composition according to any one of claims 7 to 11, comprising 0.1 to 60% by weight of said inorganic particles.

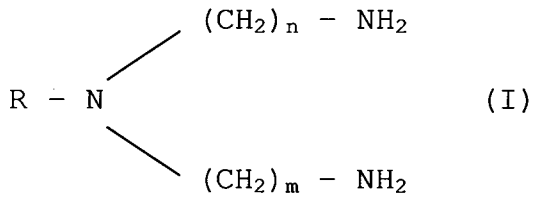
13. Liquid composition according to claim 1, having a pH comprised between 10 and 12.

14. Liquid composition according to claim 1, having a viscosity comprised between 2000 and 30000 cps at 20°C.

15. Liquid composition according to claim 1 and claims 3 to 14, wherein said surfactant is selected from anionic, non-ionic, cationic, amphoteric, zwitterionic surfactants, and mixture thereof.

16. Liquid composition according to claim 1 and claims 3 to 15, wherein said liquid composition comprises 0.1 to 40% by weight of one or more of said surfactants.

17. Hydrophobic coating film for at least partially covering a substrate, said hydrophobic coating film comprising a compound of formula:



(I)

wherein m and n, equal or different, are integers from 2 to 8 and R is an optionally substituted alkyl chain having from 8 to 18 carbon atoms.

18. A method for providing a hydrophobic coating film on a substrate comprising the steps of:

- applying the liquid composition according to any one of claims 2 to 14 to said substrate, and

- allowing the water to evaporate thereby forming the hydrophobic coating film on the substrate.

19. A method of cleaning a hard surface and of imparting hydrophobic properties to said surface comprising the steps of:

- applying to said hard surface a liquid composition according to any one of claims 1 and 3 to 16, and

- rinsing the composition applied to the surface.

20. A method according to claim 19, wherein said surface is ceramic, enamel, glass, plastics, plastified wood, metal, varnished or sealed surfaces.

21. A method according to claim 19, wherein said composition is capable of modifying the cleaned surface to render it hydrophobic, providing a contact angle between water and the cleaned surface higher than 40°.

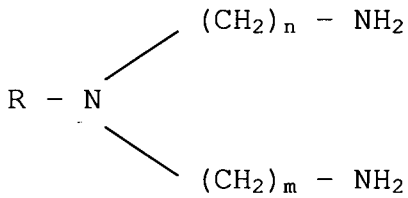
22. A method according to claim 19, wherein said liquid composition is applied to the surface of an article by pouring the composition over the surface, by applying the composition on the surface by means of a cloth or sponge or by spraying the composition on the surface.

23. A method according to claim 19, further comprising the step of letting the surface dry naturally.

24. A method according to claim 19, further comprising the step of drying the surface may with cloth or chamois.

25. Use of the liquid composition according to any one of the claims 1 to 16, for rendering hydrophobic a substrate.

26. Use of a compound of formula:



Formula (I)

wherein m and n, equal or different, are integers from 2 to 8 and R is an optionally substituted alkyl chain having from 8 to 18 carbon atoms, for imparting hydrophobic properties to a substrate.

27. Use according to claim 26, wherein m and n are integers from 3 to 5 and R is an alkyl chain having from 10 to 14 carbon atoms.

28. Use according to claim 26, wherein said substrate is a hard surface.

Fig. 1

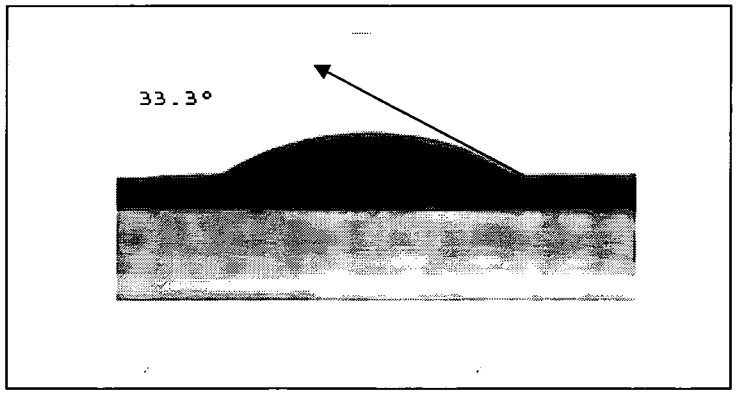
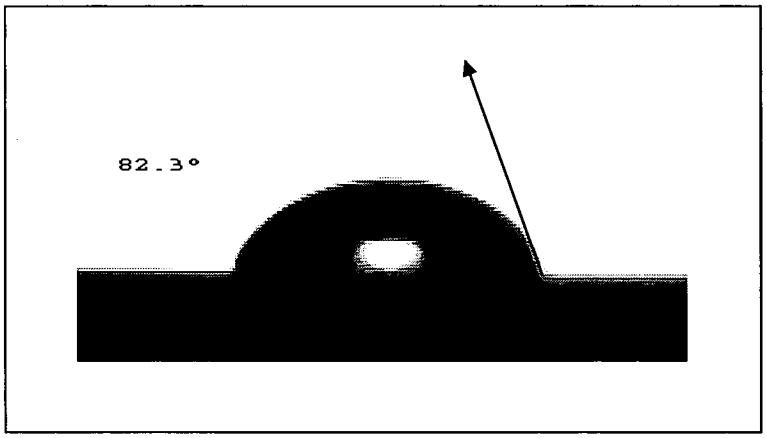


Fig. 2



INTERNATIONAL SEARCH REPORT

International application No
PCT/IB2007/002859

A. CLASSIFICATION OF SUBJECT MATTER
INV. C11D3/30 C11D11/00

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, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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X	DE 197 49 964 A1 (ULRICH GRAJECKI GMBH & CO DIPL [DE]) 6 May 1999 (1999-05-06) claims 1-5,8-10,12-14 example 1	1-6,13, 15-17
X	WO 2006/093249 A (WAKO PURE CHEM IND LTD [JP]; SAN AI OIL CO LTD [JP]) 8 September 2006 (2006-09-08) the whole document	1-6,13, 15-17
E	-& EP 1 865 049 A (WAKO PURE CHEM IND LTD [JP]; SAN AI OIL CO LTD [JP]) 12 December 2007 (2007-12-12) claims 1-3,8,9 examples page 8, paragraph 52 - paragraph 53	1-6,13, 15-17

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[X] Further documents are listed in the continuation of Box C.

[X] See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

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"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

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"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

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"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
9 June 2008	16/06/2008

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

INTERNATIONAL SEARCH REPORT

International application No
PCT/IB2007/002859

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 6 191 092 B1 (BRAGULLA SIEGFRIED [DE] ET AL) 20 February 2001 (2001-02-20) example 2 claims 1,4,5,8-12 column 2, line 10 - line 36	1-6,13, 15-17
X	EP 1 818 389 A (AIR LIQUIDE SANTE INT [FR]) 15 August 2007 (2007-08-15) claims 1,4,7 examples page 3, paragraph 16 - paragraph 17	1-6, 15-17
A	US 2004/170822 A1 (ROHRBAUGH ROBERT HENRY [US] ET AL) 2 September 2004 (2004-09-02) the whole document	1-28

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
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