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(54) **Title**: HARD SURFACE TREATMENT COMPOSITION

(57) **Abstract**: The present invention is in the field of hard surface treatment compositions. The invention particularly relates to hard surface treatment compositions that provide easier cleaning upon the subsequent cleaning. It is an object of the present invention to provide a composition that, upon use, renders a surface hydrophobic and to provide good cleaning. It has been found that poly aluminium chloride and a soap in combination with a poly vinyl alcohol and non-ionic or cationic surfactant provides both good cleaning and good stain/soil repellence.

HARD SURFACE TREATMENT COMPOSITION

Field of the invention

The present invention is in the field of hard surface treatment compositions. The invention particularly relates to hard surface treatment compositions that provide easier cleaning upon the subsequent cleaning.

Background of the invention

Hard surfaces in the home or office are usually cleaned using liquid compositions which comprise one or more surfactants and possibly also pH adjusters like citric acid or sodium salts of citrate. The cleaning compositions can be applied in diluted (in water) or undiluted form, in a spray, or rubbed using a cloth or any other convenient way. Optionally the cleaning composition may be rinsed from the surface after the cleaning. It would be advantageous if the hard surface to be cleaned could be treated with a material which would assist in easier removal of soil and/or stains during subsequent cleaning. This is referred to as the next time cleaning benefit.

Soils on hard surfaces can become more difficult to remove when not cleaned soon after deposition. When not cleaned promptly, soils can become more adherent to surfaces, more viscous and generally tougher, and require more effort to clean. While not being bound by a theory, this more difficult removal of soils can arise from the effects of drying out of soils, from chemical changes in soils, from reactions of soils with environmental agents such as oxygen, etc. Some soils are more susceptible than others to toughening reactions and processes. Soils comprising or containing chemically unsaturated oils and fats can become very tough and difficult to clean over time, especially when exposed to elevated temperatures. Even light can cause such fatty soils to toughen over time. As well as environmental factors, the processes of toughening of soils can be affected by the nature and composition of the surface on which the soil is located.

WO 02/18531 discloses a method for cleaning hard surfaces, wherein the surface is treated with an antioxidant, followed by allowing the surface to become dirty, and subsequently cleaning the surface. The treatment of the surface with the antioxidant prior to the soiling, leads to easier removal of the soil during the subsequent cleaning step. The antioxidant may be present in a cleaning composition, or in a rinse composition that is applied after the cleaning. In addition cleaning compositions comprising antioxidants, preferably at a concentration of 0.1-10 % by weight, are disclosed. Tannic acid was exemplified to be notably efficient.

WO 2006/108475 A1 discloses a method for removing fatty soil from a hard surface, the process comprising the sequential steps of (a) treating the hard surface with a liquid cleaning composition; (b) allowing the fatty soil to deposit; and (c) cleaning the surface to remove the fatty soil.

WO 2010/069731 A1 discloses a method and a composition for treating a fabric substrate to render the substrate repellent to various soils and stains and also hydrophobic. There is disclosed a method of treating the substrate by using a composition of soap and a water soluble trivalent or tetravalent metal and which composition has a pH of less than 6 maintained by the addition of a pH modifying agent.

Self cleaning surfaces are disclosed in WO04037944 A1, wherein a process and a composition are disclosed for producing surfaces that are self-cleaning by water, and in particular, there is disclosed an aqueous system for forming transparent self-cleaning surfaces. In the process of WO04037944 A1, an aqueous mixture comprising nano particles having a particle size of less than 300 nanometers and a surface modifier selected from the group consisting of water-soluble hydrophobic surface modifiers and water-dispersible hydrophobic surface modifiers capable of forming a continuous film from an aqueous solution is provided. The aqueous mixture is applied to a surface, and a self-cleaning transparent coating is formed on the surface upon water evaporation. In one embodiment, the aqueous mixture is essentially free of organic solvents other than coalescing solvents.

In spite of the advantages, the antioxidants as disclosed by the prior art also may suffer from disadvantages. Consumers may regard residues of antioxidants and/or nano particles on the hard surfaces in e.g. kitchen and bathroom to be harmful and undesired.

Microemulsion based cleaners comprising metal soaps and silicon material are disclosed in the art (e.g. US 5,759,983 and US 5,741,760). However, these compositions do not provide the required stain repellence due to lack of hydrophobicity of the surface when the composition is applied.

Thus, a composition which will make a surface both hydrophobic and provides good cleaning remains to be desired.

Without wishing to be bound by a theory, it is though that good cleaning is generally provided by surfactants, however, surfactants render surfaces hydrophilic, which make them more susceptible to aqueous stain deposition, rather than aqueous stain repellence.

Accordingly, it is an object of the present invention to provide a composition that, upon use, renders a surface hydrophobic.

It is another object of the invention to provide a composition that provides good cleaning.

Surprisingly it has been found that poly aluminium chloride and a soap in combination with a poly vinyl alcohol and non-ionic or cationic surfactant provides both good cleaning and good stain/soil repellence.

Summary of the invention

Accordingly, the present invention provides a hard surface treatment composition comprising 0.01-1%w of poly-aluminium-chloride (PAC), 0.01-1%w of soap of C8-C18 fatty acid, 0.05-1%w of a surfactant selected from non-ionic surfactants or quaternary

ammonium cationic surfactants, 0.05-1%w ofpoly vinyl alcohol(PVA), and 0.1-1%w of a quaternary silicon oil, wherein the composition has a pH of between 3 and 5, and the ratio of PAC: soap is between 3:2 and 2:3.

In a second aspect, the invention provides a process for treating a substrate, comprising the steps in sequence of applying the composition according to the invention to a hard surface and leaving the surface to dry wherein the surface is not rinsed between these steps.

In a third aspect, the invention provides a bottled cleaning composition comprising the compositions according to the invention.

These and other aspects, features and advantages will become apparent to those of ordinary skill in the art from a reading of the following detailed description and the appended claims. For the avoidance of doubt, any feature of one aspect of the present invention may be utilised in any other aspect of the invention. The word “comprising” is intended to mean “including” but not necessarily “consisting of” or “composed of.” In other words, the listed steps or options need not be exhaustive. It is noted that the examples given in the description below are intended to clarify the invention and are not intended to limit the invention to those examples per se. Similarly, all percentages are weight/weight percentages unless otherwise indicated. Except in the operating and comparative examples, or where otherwise explicitly indicated, all numbers in this description indicating amounts of material or conditions of reaction, physical properties of materials and/or use are to be understood as modified by the word “about”. Numerical ranges expressed in the format "from x to y" are understood to include x and y. When for a specific feature multiple preferred ranges are described in the format "from x to y", it is understood that all ranges combining the different endpoints are also contemplated.

Detailed description of the invention

The invention comprises Poly-aluminium-chloride (PAC), soap of C8-C18 fatty acid, a surfactant selected from non-ionic surfactants or quaternary ammonium cationic surfactants, PVA (poly vinyl alcohol) and a poly siloxane.

The cleaning compositions according to the invention are preferably for neat application. The pH is between 3 and 5.

Poly aluminium chloride

Poly aluminium chloride is a known polyelectrolyte. The poly aluminium chloride (PAC) may be defined as a non-stoichiometric oligomer of aluminium hydroxychloride having general formula $[Al(OH)_aCl_b]_n$ where the value of *a* is preferably in the range 1.5 to 1.9 and *b* preferably in the range 1.1 to 1.5, wherein *a*+*b*=3. The aluminium content is typically 12-20%.

Commercial PAC may have small amount of impurities including traces of SO_4^{2-}, $CO_3^{2-;}$ NO_3^-, Br^-, HCO_3^-, and HSO_4^-; but such impurities are typically present in a concentration of less than 2%, more preferably less than 1%, still more preferably less than 0.5% or even less than 0.1% by weight of the PAC.

The PAC is present in the composition in a concentration of between 0.01 – 1% by weight, preferably at least 0.1%, more preferably at least 0.25%, or even 0.5% by weight.

Additionally it is considered in the context of the present invention to have a mixed metal system, comprising the Aluminium (from PAC) and 0.01 to 1% by weight of a second metal salt. Said second metal salt is selected from bivalent and trivalent metal salts, preferably selected from calcium, zinc and Iron (III). When the second metal salt is present, it is preferred that the ratio of the PAC to the second metal salt is in the range of 9:1 to 3:2.

Soap

The soap according to the invention is an alkali metal salt of C8-C18 fatty acid. Preferred examples of such fatty acids are saturated fatty acids selected from Lauric acid, Myristic acid, Palmitic acid, Stearic acid, and combinations thereof; and unsaturated fatty acids, such as Myristoleic acid, Palmitoleic acid, Sapienic acid, Oleic acid, Elaidic acid, Vaccenic acid, Linoleic acid, Linoelaidic acid and α-Linolenic acid, and combinations thereof. The alkali metals are sodium, potassium, lithium or their

mixtures. Salts of combinations of saturated and unsaturated fatty acids are also contemplated.

Naturally occurring mixtures predominantly comprising of one or more C8-C18 soap, preferably one or more of the fatty acids as listed above are also included in the scope of the invention. Examples of such mixtures are salts of coconut fatty acid and palm kernel fatty acid.

For the avoidance of doubt by predominantly is meant at least 50%, more preferably at least 60%, still more preferably at least 70%, even more preferably at least 80%, or even at least 90% by weight of the soap.

Soap is present in the composition in a concentration of between 0.01 – 1% by weight, preferably at least 0.1%, more preferably atleast 0.25%, or even 0.5% by weight.

The ratio of PAC to soap is between 3:2 and 2:3, preferably between 4:3 and 3:4, or even between 5:4 and 4:5 for the best results.

In these ratios, it is found that the results for both surface cleaning (gloss) and hydrophobicity are the best.

Surfactant

Suitable surfactants in the context of the present invention are nonionic surfactants and quaternary ammonium cationic surfactants. A combination of both quaternary cationic surfactant and nonionic surfactant is also contemplated.

The skilled person is quite aware of the commonly known surfactants in the art, as described in well known textbooks like "Surface Active Agents" Vol. 1, by Schwartz & Perry, Interscience 1949, Vol. 2 by Schwartz, Perry & Berch, Interscience 1958, and/or the current edition of "McCutcheon's Emulsifiers and Detergents" published by Manufacturing Confectioners Company or in “Tenside-Taschenbuch", H. Stache, 2nd Edn., Carl Hauser Verlag, 1981.

Non-ionic Surfactants

Preferred surfactants are non-ionic surfactants. Non-ionic surfactants are also well-known in the art. They normally consist of a water-solubilising polyalkoxylene (preferably from 3 to10 ethoxy and/or propoxy groups) or a mono- or di-alkanolamide group in chemical combination with an organic hydrophobic group derived from, for example, fatty alcohols with from 9 to 15 carbon atoms (optionally branched, e.g. methyl branched), alkylphenols (preferably from 12 to 20 carbon atoms) in which the alkyl group contains from about 6 to about 12 carbon atoms, dialkylphenols in which each alkyl group contains from 6 to 12 carbon atoms, primary, secondary or tertiary aliphatic alcohols (or alkyl-capped derivatives thereof) monocarboxylic acids having from 10 to about 24 carbon atoms in the alkyl group and polyoxypropylenes.

Fatty acid mono- and dialkanolamides in which the alkyl group of the fatty acid radical contains from 10 to about 20 carbon atoms and the alkyloyl group having from 1 to 3 carbon atoms are also common. In any of the mono- and dialkanolamide derivatives, optionally, there may be a polyoxyalkylene moiety joining the latter groups and the hydrophobic part of the molecule.

In all polyalkoxylene containing surfactants, the polyalkoxylene moiety usually consists of an average of from 2 to 20 groups of ethylene oxide, propylene oxide groups or mixtures thereof. The latter class includes those described in European Patent Specification EP-A-0,225,654, especially for use as all or part of the liquid phase.

Especially preferred are those ethoxylated non-ionics which are condensation products of fatty alcohols with from 9 to 15 carbon atoms condensed with 3 to 12 moles of ethylene oxide (generally understood to be an average value). Examples of those are the condensation products of C_9 to C_{15} alcohols with 3 or 7 moles of ethylene oxide, or mixtures thereof. These may be used as the sole non-ionic surfactant or in combination with those described in EP-A-0 225 654.

Cationic Surfactants

The cationic surfactant according to the invention is a quaternary ammonium salt surfactant, characterised in that the ammonium salt has the general formula: R1R2R3R4N+ X-, wherein R1 to R4 are alkyl or aryl groups, and X^- is an inorganic anion.

Preferably at least one, but typically not more than two, of the alkyl or aryl groups R1-R4 is an alkyl group having a C12-C18 alkyl chain length, or an aryl group, while the remaining alkyl groups are C1-C3 alkyl.

In the quaternary ammonium salts according to the present invention R1 is preferably a C14-C16 straight chain alkyl group, while R2-R4 are preferably methyl groups.

Specifically preferred quaternary ammonium cationic surfactant are benzalkonium chloride (alkyldimethylbenzylammonium chloride) and cetylpyridinium chloride (CPC).

The surfactant, non-ionic or cationic or mixtures thereof, is present in the composition in a concentration of 0.05 – 1% by weight. In order to get the best results on hydrophobicity, the concentration is preferably between 0.1 and 0.8%, more preferably not more than 0.5%, or even at most 0.4% by weight.

Poly vinyl alcolhol

Polyvinyl alcohol (PVOH, PVA, or PVAl) is a water-soluble synthetic polymer. In the context of the invention, both homo polymers of PVA and co-polymers are contemplated, but the homopolymers are the most preferred. Homopolymers or copolymers of vinyl alcohol preferably have a molecular mass of between 10^3 and 10^7 u (u is atomic mass unit (SI), also known as “amu”, or “Dalton”, “D” or “Da”), more preferably from 10^4 to 10^6 u and most preferably from 30,000 to 500,000 u.

The PVA is present in the composition in a concentration of 0.05 – 1% by weight.

The ratio of PVA:surfactant, is preferably at least 1:1, more preferably between 1:1 and 15:1, still more preferably between 2:1 and 15:1.

In these ratios the PVA polymer is found to improve the cleaning effect of the surfactant, without rendering the surface hydrophilic.

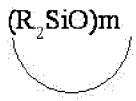
Quaternary silicone oil

To further provide the repellence of oily soils and stains, the composition further comprises a quaternary silicone oil. The preferred quaternary silicon oils are poly siloxanes. Typical examples of such preferred polysiloxanes are siloxanes selected from classes A, B and C below:

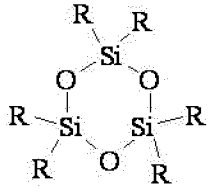
A. Cyclomethicones

Cyclomethicones are defined by the general formula I below, m is an integer of greater or equal to 3, and R is a straight or branched alkyl, cycloalkyl, polycycloalkyl, heterocycloalkyl, alkaryl, alkoxy, aryl, aralkyl, alkenyl or alkynyl moiety.

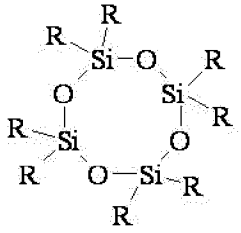
More preferred are cyclomethicones wherein m is 3, 4 or 5 as shown in Formulae IIa, IIb and IIc. Especially preferred are low viscosity Cyclomethicones, including hexamethylcyclotrisiloxanes; octamethylcyclotetrasiloxanes and decamethylcyclopentasiloxanes.



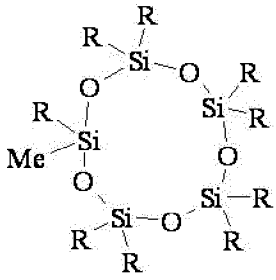
Formula I



Formula IIa



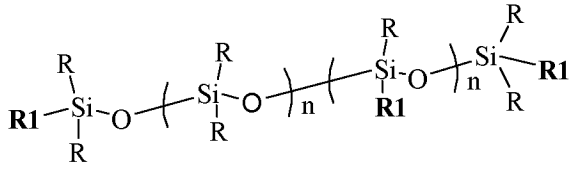
Formula IIb



Formula IIc

B. Dimethicones

Dimethicones are defined by the General formula III below



III

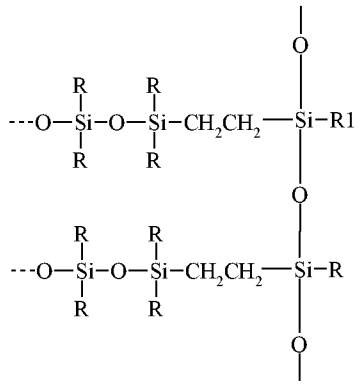
wherein R or R1 is typically selected from a straight or branched alkyl, cycloalkyl, polycycloalkyl, heterocycloalkyl, alkaryl, alkoxy, aryl, aralkyl, alkenyl or alkynyl moiety, –H, –OH. R and R1 may be the same or different.

Dimethicones are commercially available in a wide range of viscosity ranging from $1X10^{-6}$ to $6X10^{-2}$ m^2/sec where n = 1 - 100,000, preferably n= 1 – 1500, most preferably n = 1 - 200. A table exemplifying this is given below.

Viscosity (m^2/sec)	**Approximate molecular weight**	**Approximate "n" value**
0.000005	800	9
0.00005	3780	53
0.0001	6000	85
0.0002	9430	127
0.00035	13650	185
0.0005	17350	230
0.001	28000	375
0.01	67700	910
0.06	116500	1570
0.1	139050	1875

C. Silicone elastomers

Silicone elastomers are defined by the General formula IV below



Formula IV

wherein R or R1 is typically selected from a straight or branched alkyl, cycloalkyl, polycycloalkyl, heterocycloalkyl, alkaryl, alkoxy, aryl, aralkyl, alkenyl or alkynyl moiety, –H, –OH. R and R1 may be the same or different.

The quaternary silicone oil may be present in the compositions in a concentration of less than 1% by weight. The composition preferably comprises less than 0.5% by weight, but preferably more than 0,1% by weight.

Abrasive material

Optionally the composition according to the invention may also comprise an abrasive material.

The abrasive particles are used in an amount of at least 0.1%, preferably 0.5%. In order to retain the transparent character of the total composition the maximum amount of particles is 20%, preferably 10%, more preferably 5%.

The particles may be made of abrasive materials known in the art. Thus, they may consist of granules of one or more of the well known inorganic abrasives such as silica, silicates, calcite and the like. They may consist of polymer granules, such as

polyethylene, polypropylene, polycarbonate and the like. Particularly suitable are granules of a biodegradable polymer, such as the starch-derived plastics known in the art.

Alternatively, the abrasive particles may be made of softer materials such as hard waxes and fats, hard fatty acids, hard fatty acid soaps and the like. Such materials may also be mixed with fine particles of any of the known abrasives or with other materials, preferably solid materials, suitable for improving the cleaning process and thereafter formed into granules of the required size.

In translucent compositions, having a visually appeal to the consumer the particles are preferred to be macroscopic, i.e. clearly visible separately to the naked eye. This is in contrast to most abrasive powder particles which generally have average particle size well below 0.3mm and in the vast majority of cases at most 0.1mm (100µm), or even less than 0.05mm, which are also contemplated in the context of the invention for opaque compositions.

Thus, for translucent composition the particles according to the invention have an average particle size between 0.3 and 2.5mm, preferably more than 0.5 and at most 1.5mm, while for opaque compositions a particles size below 0.3 mm is preferred.

Further, the visual appeal of the compositions is considerably enhanced if the particles are of fairly uniform particle size i.e. they all have a particle size within the range of plus or minus 70% of the average particle size, preferably within a range of plus or minus 50%, more preferably plus or minus 30%.

The visual appeal of the particles, and therefore the total composition, is further enhanced if the particles have a certain minimum sphericity, such that the ratio between the longest and the shortest diameter of a particle in any one direction is at most 3:1, preferably at most 2:1 or even 1.5:1. Particularly preferred are particles with a round, preferably a smooth round shape. Such particles may be made by prilling processes involving making a melt of the particle material, converting it into droplets, which are thereafter cooled in a gas (air) flow. Various processes and suitable

equipment therefore are known in the art and may be applied to the organic abrasives, provided they are sufficiently low melting. High melting powders such as inorganic abrasive powders may be made into suitably shaped particles by various agglomeration processes known in the art, if necessary using an agglomeration binder.

Although the cleaning compositions according to the invention may consist of a colourless liquid and solid particles having their natural colour (in many cases white), the compositions are considerably more attractive to the consumer if the liquid and the particles have clearly different colours. They may have different shades of the same colour, e.g. dark blue particles in a light blue liquid, or preferably, the liquid and the particles have contrasting colours e.g. white particles in a blue, green or yellow liquid or vice versa, or coloured particles in a differently coloured liquid.

Optional ingredients

The composition may further comprise perfumes, bleaches, anti bacterial agents, fluoro-polymers and insect repellent materials.

The perfume may be any commercially available water soluble or miscible perfume composition.

Additionally gloss and cleaning improving aids as known in the are, such as 2-phenoxy ethanol (commercially available as Dowanol ex Dow) may be added in a concentration of 0.05 – 0.5% by weight of the composition.

pH

The pH of the composition according to the invention is between 3 and 5.

Without wishing to be bound by a theory it is thought that when the composition is prepared the PAC and the fatty acid dissociate and partially bind, causing the mixture of the acidic PAC and the alkaline Soap to give an overall pH of between 3 and 5.

It is thought that aluminum salts form different positively charged hydrated species in water in acidic pH eg: $Al_2(OH)_2^{4+}$ and $Al_3(OH)_4^{5+}$. Polyaluminum chloride may also form $Al_{13}O_4(OH)_{24}^{7+}$ in solution, while the fatty acid has a pK_a of 4.5, yielding a pH

range of 3-5 in the mixture. This is thought to cause the precipitation of the hydrophobic compound onto the surface.

Solvents

The composition is preferably an aqueous liquid, however the formulations made in mixed solvents comprising alcohols, including methanol, ethanol and/or isopropanol, where the water to solvent ratio is 20:1 to 99:1 are also contemplated.

Surface treatment process

The invention provides a process for treating a substrate, comprising the steps in sequence of applying the composition according to the invention to a hard surface and leaving the surface to dry wherein the surface is not rinsed between these steps.

Typically the surface is subject to the deposition of dirt after treatment.

The surface is found to be more repellent to aqueous stains when treated with the composition of the invention.

As a further step, the surface may be cleaned again with the treatment composition according to the invention or another composition, preferably with the treatment composition according to the invention.

Product format

The composition may be packaged in the form of any commercially available liquid composition, typically in the form of a bottle containing the liquid.

The composition is preferably applied using a trigger spray applicator. A trigger spray application enables fast and easy use for the consumer and additionally it brings a suitable amount of air into the composition, which aides in the foam formation.

Accordingly, the compositions of the invention may be stored in and dispensed by any suitable means, but spray applicators are particularly preferred. Pump dispensers (whether spray or non-spray pumps) are also possible. Thus, the present invention

provides a container for a liquid hard surface cleaner, the container comprising a reservoir containing the hard surface cleaning composition of the invention, and spray dispenser for dispensing the composition in the form of a spray. The spray dispenser is preferably a trigger spray but may be any mechanical means for ejecting the liquid in spray or aerosol form.

The invention will now be illustrated by means of the following non limiting examples.

Examples

Materials:

PAC:	Polyaluminum chloride (ex Grasim, India)
Soap:	DCFA (Na-salt of distilled coco-fatty acid, ex Godrej Industries Ltd, India)
Silicon:	Polymethylhydrosiloxane (PMHS)(ex Aldrich, USA); Polydimethylsiloxane (PDMS)
Water:	Distilled water (ex Scientific Distillery, Bangalore)
NI	Ethoxylated alcohol non-ionic (EO3, EO7 and EO3:EO7 = 1:1, EO5); EO= Ethylene oxide
Abrasive:	Silica
PVA:	Polyvinyl alcohol (ex Aldrich)
Zn_2NO_3	Zinc nitrate hexahydrate (ex Merck)
$CaCl_2$	Calcium chloride dihydrate (ex Merck)
FeCl3	Ferric chloride (or iron (III) chloride, ex Merck)
Cationic:	Cetylpyridinium chloride (CPC)

Mode of application of oil (test for oil repellence):

25 microlitre of olive oil (Bertolli) was smeared on a glass microscopic slide uniformly. 0.5 mL of the formulation was applied over the glass surface. The layer of liquid was left on the glass surface for ~ 30 seconds. The glass surface was wiped with a tissue paper till it is completely dry.

Test for water repellence (hydrophobicity):

The contact angle of the sessile droplet was measured using a Kruss goniometer by placing a 10 microlitre of distilled water droplet on the glass slide. The angle was analyzed by the image J software using the Drop snake plug-in.

Contact angles above 60 are considered good, above 75 is more preferred.

Test for cleaning (oil removal by gloss measurement):

Gloss of the glass slides after the treatment was measured using a gloss meter at 60 degree reflecting angle against a black background (RGB=0,0,0). Gloss values above 100 are considered acceptable, and above 110 good.

Example 1: Effect on contact angle and oily soil cleaning of glass slides.

In this experiment the effect of the composition according to the invention (Ex1) is compared to different combinations of the same ingredients, where at least one of PAC, Soap, silicon or surfactant (comparative examples A to G).

Set	PAC wt %	soap wt %	PDMS wt %	PVA wt%	EO wt %	contact angle	gloss at 60°
A	0	0	0	0.05	0	26	109
B	0.6	0	0	0.05	0	72	104
C	0	0.6	0	0.05	0	53	115
D	0	0	0.1	0.05	0	62	103
E	0	0	0	0.05	0.1	29	118
F	0.6	0.6	0.1	0.05	0	82	113
G	0.6	0.6	0	0.05	0	74	112
Ex1	0.6	0.6	0.1	0.05	0.1	82	128

The table shows that the composition according to the invention performs better than any of the combinations with one of the ingredients missing

Example 2: Effect of the type of nonionic EO on the stain repellence and cleaning:

In this example the example compositions Ex2a-Ex4 are compared with-different amounts of PAC and Soap, while also demonstrating that different types of nonionics give similar results

Set	PAC wt %	soap wt %	PDMS wt %	PVA wt%	Abrasive wt%	EO3 wt%	EO7 wt%	contact angle	gloss at 60°
Ex2a	0.04	0.04	0.1	0.05	0.1	0.1	0	74	130
Ex2b	0.04	0.04	0.1	0.05	0.1	0	0.1	72	126
Ex2c	0.6	0.6	0.1	0.05	0.1	0.1	0	81	120
Ex3	0.6	0.6	0.1	0.05	0.1	0	0.1	83	123
Ex4	0.6	0.6	0.1	0.05	0.1	0.05	0.05	82	128

The type of EO does not have any effect on the performance, while the table above indicates that different concentrations of PAC and Soap varies the performance on stain repellence (contact angle).

Example 3: Effect of the amount of nonionic EO on stain repellence and cleaning
In this example it is demonstated that the amount of nonionic should be more than 0.05% in examples Ex5-Ex8 compared to comparative example J. An additional comparative example (K) showing the nonionic and PVA inside the claimed range, but without PAC and Soap is also shown to give a poor result on contact angle (hydrophobicity).

Set	PAC wt %	Soap wt %	PDMS wt %	PVA wt%	Abrasive wt%	EO3:EO7 (1:1)wt%	contact angle	gloss at 60°
J	0	0.6	0	0	0	0	24	116
Ex5	0.6	0.6	0.1	0.05	0.1	0.05	78	111
Ex6	0.6	0.6	0.1	0.05	0.1	0.25	80	126
Ex7	0.6	0.6	0.1	0.05	0.1	0.5	64	128
Ex8	0.6	0.6	0.1	0.05	0.1	0.75	50	131
K	0	0	0	0.05	0.1	0.25	26	104

Nonionic surfactant variation shows that the the best cleaning is obtained at at least 0.05% surfactant, while the best stain repellence is obtained between 0.05 - 0.5% surfactant, although acceptable results are still obtained at higher surfactant concentrations.

Higher amounts of surfactant (amphiphilic molecules) are found to be detrimental for hydrophobicity because of their relative orientation on the surface.

Example 4: Effect of surfactant type on the stain repellence and cleaning:

In this examples nonionic (ex 9) and cationic (Ex 10) are compared to anionic surfactant (comparative M).

Set	**PAC wt%**	**Soap wt %**	**PDMS wt %**	**PVA wt%**	**Abrasive wt%**	**Surf**	**Surf wt%**	**contact angle**	**gloss at 60°**
Ex9	0.6	0.6	0.1	0.05	0.1	EO3:EO7 =1:1	0.25	80	126
Ex10	0.6	0.6	0.1	0.05	0.1	CPC	0.25	78	117
M	0.6	0.6	0.1	0.05	0.1	NaLAS	0.25	68	67

The results above show that anionic surfactant does not provide a high enough contact angle or cleaning (gloss).

Example 5: Effect of pH of the treatment formulation on stain repellence and cleaning:

The table below shows compositions with in the pH range according to the invention (Ex 10 and 11), compared to comparative examples N, O and P, outside the claimed range.

Set	PAC wt%	Soap wt %	PDMS wt %	PVA wt%	Abrasive wt%	EO3:EO7 (1:1)wt %	pH	contact angle	Gloss at 60°
N	0.6	0.6	0.1	0.05	0.1	0.1	2	76	101
Ex10	0.6	0.6	0.1	0.05	0.1	0.1	4	80	122
Ex11	0.6	0.6	0.1	0.05	0.1	0.1	5	77	121
O	0.6	0.6	0.1	0.05	0.1	0.1	6	38	122
P	0.6	0.6	0.1	0.05	0.1	0.1	8	29	131

Stain repellence decreases at high pH and so the preferred pH is <6.

Example 6: Effect of PVA and EO combination on stain repellence and cleaning

In this example different ratios of surfactant and PVA are compared.

Set	PAC wt %	Soap wt %	PDMS wt %	PVA wt%	Abrasive wt%	EO3:EO7 (1:1)wt %	contact angle	gloss at 60°
Q	0.6	0.6	0.1	0.80	0.1	0	85	122
Ex12	0.6	0.6	0.1	0.75	0.1	0.05	85	127
Ex13	0.6	0.6	0.1	0.65	0.1	0.15	84	129
Ex14	0.6	0.6	0.1	0.55	0.1	0.25	83	130
Ex15	0.6	0.6	0.1	0.45	0.1	0.35	69	131
Ex16	0.6	0.6	0.1	0.35	0.1	0.45	67	131
Ex17	0.6	0.6	0.1	0.25	0.1	0.55	62	132
Ex18	0.6	0.6	0.1	0.15	0.1	0.65	56	132
Ex19	0.6	0.6	0.1	0.05	0.1	0.75	49	134

The table above shows that for cleaning a minimum amount of nonionic is required for cleaning.

Although acceptable hydrophobicity is achieved at higher surfactant concentrations, the best results are obtained at less than 0.5% surfactant, and a PVA:surfactant ratio of at least 1:1.

Example 7: Ratio of PAC to soap

In this example different ratios of PAC and soap are compared.

Set	PAC wt %	soap wt %	PDMS wt %	PVA wt%	Abrasive wt%	EO3:EO7 (1:1)wt %	contact angle	gloss at 60°
R	0.2	0.6	0.1	0.05	0.1	0.25	35	128
Ex20	0.4	0.6	0.1	0.05	0.1	0.25	72	126
Ex21	0.6	0.6	0.1	0.05	0.1	0.25	79	127
Ex22	0.6	0.4	0.1	0.05	0.1	0.25	76	125
S	0.6	0.2	0.1	0.05	0.1	0.25	52	113

The table above shows that good results for both contact angle (hydrophobicity) and cleaning (gloss) are obtained when the ratio of PAC:Soap is between 3:2 (Ex 22) and 2:3 (Ex20). The best results are obtained at 1:1 (Ex21).

Example 8: Comparison of the silicon oil

In this example the benefit of different silicon oils is demonstrated.

Set	PAC wt %	soap wt %	Silicon oil (0.1%w)	PVA wt%	Abr wt%	EO3:EO7 (1:1, wt%)	contact angle	gloss at 60°
Ex23	0.6	0.6	PMHS	0.05	0.1	0.1	81	128
Ex24	0.6	0.6	decamethylcyclopentasiloxane	0.05	0.1	0.1	80	129
Ex25	0.6	0.6	dimethicone (DC 200)	0.05	0.1	0.1	82	129

The table above shows that good results for both contact angle (hydrophobicity) and cleaning (gloss) are obtained when different siloxanes (silicon oils as defined in the invention) are used.

Example 9: mixed metal example (Calcium)

In this example the effect of mixed metal composition (PAC and calcium chloride) are compared, both inside and outside the indicated pH range.

The compositions are given below. All composition contained 0.55% PVA, 0.1% PDMS, 0.1% of abrasive particles, and 0.25% Nonionic (1:1 EO3:EO7)

Set	PAC wt %	$CaCl_2$ wt %	soap wt %	PAC:Ca	pH	contact angle	gloss at 60°
Ex26	0.6	0	0.6		4	81	129
Ex27	0.54	0.06	0.6	9:1	4	82	126
Ex28	0.3	0.3	0.6	1:1	4	80	123
Ex29	0.36	0.24	0.6	3:2	4	80	122
T	0.24	0.36	0.6	2:3	4	56	123
U	0.06	0.54	0.6	1:9	4	38	112
V	0.54	0.06	0.6	9:1	6	43	121
W	0.3	0.3	0.6	1:1	6	39	118
X	0.36	0.24	0.6	3:2	6	45	116
Y	0.24	0.36	0.6	2:3	6	32	122
Z	0.06	0.54	0.6	1:9	6	36	121

The table above demonstrates that mixed metal systems, within the ratio of 9:1 to 3:2 for PAC:metal salts perform well inside the pH range of 3-5, while other ratios, or a higher pH do not give the required water contact angle (i.e. not the required hydrophobicity).

Example 10: mixed metal example (Zinc)

In this example the effect of mixed metal composition (PAC and zinc nitrate) are compared, both inside and outside the indicated pH range.

The compositions are given below. All composition contained 0.55% PVA, 0.1% PDMS, 0.1% of abrasive particles, and 0.25% Nonionic (1:1 EO3:EO7)

Set	PAC wt %	Zn nitrate wt %	soap wt %	PAC:Zn	pH	contact angle	gloss at 60°
Ex30	0.6	0	0.6		4	81	128
Ex31	0.54	0.06	0.6	9:1	4	83	128
Ex32	0.3	0.3	0.6	1:1	4	80	125
Ex33	0.36	0.24	0.6	3:2	4	81	124
AA	0.24	0.36	0.6	2:3	4	48	121
AB	0.06	0.54	0.6	1:9	4	35	119
AC	0.54	0.06	0.6	9:1	6	45	118
AD	0.3	0.3	0.6	1:1	6	42	122
AE	0.36	0.24	0.6	3:2	6	36	120
AF	0.24	0.36	0.6	2:3	6	30	118
AG	0.06	0.54	0.6	1:9	6	35	123

The table above demonstrates that mixed metal systems, within the ratio of 9:1 to 3:2 for PAC:metal salts perform well inside the pH range of 3-5, while other ratios, or a higher pH do not give the required water contact angle (i.e. not the required hydrophobicity).

Example 11: mixed metal example (Iron)

In this example the effect of mixed metal composition (PAC and ferric chloride) are compared, both inside and outside the indicated pH range.

The compositions are given below. All composition contained 0.55% PVA, 0.1% PDMS, 0.1% of abrasive particles, and 0.25% Nonionic (1:1 EO3:EO7)

Set	PAC wt %	Ferric chloride wt %	soap wt %	PAC:Fe	pH	contact angle	gloss at 60°
Ex34	0.6	0	0.6		4	81	128
Ex35	0.54	0.06	0.6	9:1	4	81	123
Ex36	0.3	0.3	0.6	1:1	4	82	120
Ex37	0.36	0.24	0.6	3:2	4	80	126
AH	0.24	0.36	0.6	2:3	4	39	119
AI	0.06	0.54	0.6	1:9	4	35	114
AJ	0.54	0.06	0.6	9:1	6	46	121
AK	0.3	0.3	0.6	1:1	6	45	128
AL	0.36	0.24	0.6	3:2	6	37	120
AM	0.24	0.36	0.6	2:3	6	35	121
AN	0.06	0.54	0.6	1:9	6	36	124

The table above demonstrates that mixed metal systems, within the ratio of 9:1 to 3:2 for PAC:metal salts perform well inside the pH range of 3-5, while other ratios, or a higher pH do not give the required water contact angle (i.e. not the required hydrophobicity).

Claims

1 A hard surface treatment composition comprising:

a 0.01-1%w of Poly-aluminium-chloride (PAC);

b 0.01-1%w of soap of C8-C18 fatty acid;

c 0.05-1%w of a surfactant selected from non-ionic surfactants or quaternary ammonium cationic surfactants;

d 0.05-1%w of PVA (poly vinyl alcohol); and

e 0.1-1%w of a quaternary silicon oil;

wherein:

a the composition has a pH of between 3 and 5; and

b the ratio of PAC: soap is between 3:2 and 2:3

2 A composition according to claim 1, wherein the PVA:surfactant ratio is at least 1:1, preferably between 1:1 and 15:1

3 A composition according to anyone of the preceding claims wherein the surfactant is an ethoxylated fatty alcohol non-ionic having a alkyl chain of C12-C18 and comprising between 1 and 12 ethylene oxide groups (EO).

4 A composition according to claim 1, wherein the composition further comprises an abrasive material.

5 A composition according to claim 4, wherein the abrasive is selected from inorganic abrasives including silica, silicates, or polymer abrasives, including polyethylene, polypropylene and polycarbonate.

6 A composition according to anyone of the preceding claims further comprising 0.01-1% by weight of a second metal salt, selected from bivalent and trivalent metal salts, wherein the ratio of the PAC to the second metal salt is in the range of 9:1 to 3:2.

7 A process for treating a substrate, comprising the steps in sequence of:

a Applying the composition according to any one of claims 1-5 to a hard surface

b Leaving the surface to dry

wherein the surface is not rinced between steps (a) and (b).

8 A bottled cleaning composition comprising the compositions according to any one of claims 1-6.

9 A bottle according to claim 8, fitted with a trigger spray dispenser.

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2012/056036

A. CLASSIFICATION OF SUBJECT MATTER
INV. C11D3/02 C11D3/37 C11D10/04 C11D3/04
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 practicable, search terms used)
EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 2010/069731 A1 (UNILEVER NV [NL]; UNILEVER PLC [GB]; UNILEVER HINDUSTAN [IN]) 24 June 2010 (2010-06-24) claims; examples	1-9
A	WO 2006/083813 A2 (PROCTER & GAMBLE [US]) 10 August 2006 (2006-08-10) page 10, lines 21-25; claims; examples	1-9
A	WO 2006/108475 A1 (UNILEVER NV [NL]; UNILEVER PLC [GB]; LEVER HINDUSTAN LTD [IN]) 19 October 2006 (2006-10-19) cited in the application page 2, line 24 - page 3, line 12; claims; examples	1-9

☐ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

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Date of the actual completion of the international search	Date of mailing of the international search report
12 June 2012	20/06/2012

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/EP2012/056036

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