(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
11 February 2016 (11.02.2016)

WIPO | PCT

(10) International Publication Number
WO 2016/020141 A1

(51) International Patent Classification:
C09D 183/08 (2006.01) *C11D 3/37* (2006.01)
C11D 1/72 (2006.01)

(21) International Application Number:
PCT/EP2015/065841

(22) International Filing Date:
10 July 2015 (10.07.2015)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
PCT/CN2014/083669 5 August 2014 (05.08.2014) CN
14185767.2 22 September 2014 (22.09.2014) EP

(71) Applicant *(for all designated States except AE, AG, AU, BB, BH, BN, BW, BZ, CA, CY, EG, GB, GD, GH, GM, IE, IL, IN, KE, KN, LC, LK, LS, MT, MW, MY, NA, NG, NZ, OM, PG, QA, RW, SA, SC, SD, SG, SL, SZ, TT, TZ, UG, US, VC, ZA, ZM, ZW)*: **UNILEVER N.V.** [NL/NL]; Weena 455, 3013 AL Rotterdam (NL).

(71) Applicant *(for AE, AG, AU, BB, BH, BN, BW, BZ, CA, CY, EG, GB, GD, GH, GM, IE, IL, IN, KE, KN, LC, LK, LS, MT, MW, MY, NA, NG, NZ, OM, PG, QA, RW, SA, SC, SD, SG, SL, SZ, TT, TZ, UG, VC, ZA, ZM, ZW only)*: **UNILEVER PLC** [GB/GB]; Unilever House, 100 Victoria Embankment, London Greater London EC4Y 0DY (GB).

(71) Applicant *(for US only)*: **CONOPCO, INC., D/B/A UNILEVER** [US/US]; 800 Sylvan Avenue AG West, S. Wing, Englewood Cliffs, New Jersey 07632 (US).

(72) Inventors: **TAO, Qingsheng**; Unilever China (Investing) Company, 66 Linxin Road, Linkong Economic Development Zone, Changning District, Shanghai, 200335 (CN). **ZHOU, Yi**; Unilever (China) Investing Company, 66 Linxin Road, Linkong Economic Development Zone, Changning District, Shanghai, 200335 (CN).

(74) Agent: **CORSTEN, Michael, Allan**; Unilever Patent Group, Olivier van Noortlaan 120, 3133 AT Vlaardingen (NL).

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

(84) Designated States *(unless otherwise indicated, for every kind of regional protection available)*: ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, ST, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

Declarations under Rule 4.17:

— *as to applicant's entitlement to apply for and be granted a patent (Rule 4.17(ii))*

— *as to the applicant's entitlement to claim the priority of the earlier application (Rule 4.17(iii))*

— *of inventorship (Rule 4.17(iv))*

Published:

— *with international search report (Art. 21(3))*

(54) Title: HARD SURFACE TREATMENT COMPOSITION

(57) Abstract: Disclosed is a composition comprising non-ionic surfactant and non-volatile aminosilicone emulsified by emulsifier, wherein the non-volatile aminosilicone accounts for at least 15% by weight of the total non-volatile silicones in the composition, the emulsifier is different from the non-ionic surfactant, the composition has a pH value of no greater than 11.8, and the composition has a pH value of no greater than 8 when the non-volatile aminosilicone comprises aminoethylaminopropyl poly(dimethylsiloxane).

WO 2016/020141 A1

HARD SURFACE TREATMENT COMPOSITION

Field of the invention

The present invention relates to a hard surface treatment composition. In particular, the composition comprises non-ionic surfactant and non-volatile aminosilicone emulsified by emulsifier, wherein the non-volatile aminosilicone accounts for at least 15% by weight of the total non-volatile silicones in the composition, the emulsifier is different from the non-ionic surfactant, the composition has a pH value of no greater than 11.8, and the composition has a pH value of no greater than 8.5 when the non-volatile aminosilicone comprises aminoethylaminopropyl poly(dimethylsiloxane).

Background of the invention

Droughts, poor irrigation and insufficient plumbing systems are just some of the reasons that cause water shortages in certain regions. Shortages of water can create serious social problems, such as health issues, that are a direct result of inadequate cleaning applications in the absence of sufficient amounts of water.

Efforts for cleaning surfaces with limited amounts of water have been made. Articles with surfaces that are difficult to wet, i.e., articles with hydrophobic surfaces, are therefore desirable since they possess easy-cleaning properties when water is present at low volumes. Moreover, such coatings, subsequent to being applied, yield surfaces that make cleaning easier and faster for the consumer.

There is an increasing interest to develop hydrophobic coatings that result in surfaces displaying high contact angles and/or low sliding angles against water.

However, there are still many difficulties when formulating a hard surface treatment composition which can deliver hydrophobic coating to hard surface. Quite a lot of consumer products contain cleansing surfactant and relatively high concentrations of water which may strongly affect their capability to yield a hydrophobic surface onto a hard surface.

Therefore, the present inventers have recognized that there is a need to develop a composition capable of producing hydrophobic coatings on hard surface even in the presence of cleansing surfactant and relatively high concentrations of water. This invention is therefore directed to a hard surface treatment composition comprising non-ionic surfactant and non-volatile aminosilicone emulsified by emulsifier, wherein the non-volatile aminosilicone accounts for at least 15% by weight of the total non-volatile silicones in the composition, and the emulsifier is different from the non-ionic surfactant. It was surprisingly found such a composition can generate hydrophobic coatings on hard surface. Such hydrophobic coating has the benefits of anti-water mark, oil repellence, and/or easy cleaning of aged soil.

Summary of the invention

In a first aspect, the present invention provides a hard surface treatment composition comprising non-ionic surfactant and non-volatile aminosilicone emulsified by emulsifier, wherein the non-volatile aminosilicone accounts for at least 15% by weight of the total non-volatile silicones in the composition, the emulsifier is different from the non-ionic surfactant, the composition has a pH value of no greater than 11.8, and the composition has a pH value of no greater than 8.5 when the non-volatile aminosilicone comprises aminoethylaminopropyl poly(dimethylsiloxane).

In a second aspect, the present invention provides a process for preparing the composition of the present invention, the process comprises the step of emulsifying the non-volatile aminosilicone by emulsifier; and combining the emulsified non-volatile aminosilicone with non-ionic surfactant..

In a third aspect, the present invention provides a method for forming a hydrophobic coating on a surface, the method comprising applying the composition of the present invention to the surface and drying the composition to yield the hydrophobic coating.

All other aspects of the present invention will more readily become apparent upon considering the detailed description and examples which follow.

Detailed description of the invention

Except in the 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 may optionally be understood as modified by the word "about".

All amounts are by weight of the total composition, unless otherwise specified.

It should be noted that in specifying any range of values, any particular upper value can be associated with any particular lower value.

For the avoidance of doubt, 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.

The disclosure of the invention as found herein is to be considered to cover all embodiments as found in the claims as being multiply dependent upon each other irrespective of the fact that claims may be found without multiple dependency or redundancy.

Where a feature is disclosed with respect to a particular aspect of the invention (for example a composition of the invention), such disclosure is also to be considered to apply to any other aspect of the invention (for example a method of the invention) *mutatis mutandis*.

"Hard surface" of present invention generally refers to any surface in household including the window, kitchen, bathroom, toilet, furniture, or floor including windows, mirrors, sinks, basins, toilet bowls, baths/shower trays, wall tiles, floor tiles, cooker tops, oven interiors, cookware, washing machine drums, cooker hoods, extractor fans. These surfaces, for example, may be made of glass, glazed ceramics, metal, stone, plastics, lacquer, wood, or combination thereof.

"Hydrophobic/hydrophobicity" for the purposes of the present invention is used to describe a molecule or portion of a molecule that is attracted to, and tends to be dissolved

by oil (in preference to water), or a surface that has a contact angle against water of greater than 80°, preferably greater than 90°. Such an angle may be measured with a goniometer or other water droplet shape analysis systems, for example by Drop shape analysis system 100 (DSA 100, Krüss) using water droplet of 10 µl at 25 °C.

"Particle size" as used herein refers to particle diameter unless otherwise stated. For polydisperse samples having particulate with diameter no greater than 1 µm, diameter means the z-average particle size measured, for example, using dynamic light scattering (see international standard ISO 13321) with an instrument such as a Zetasizer NanoTM (Malvern Instruments Ltd, UK). For polydisperse samples having particulate with diameter greater than 1 µm, diameter means the apparent volume median diameter (D50, also known as x50 or sometimes d(0.5)) of the particles measurable for example, by laser diffraction using a system (such as a Mastersizer™ 2000 available from Malvern Instruments Ltd) meeting the requirements set out in ISO 13320.

"Non-volatile" as used herein means having vapor pressure from 0 to 0.1 mm Hg (13.3 Pa), preferably from 0 to 0.05 mm Hg, more preferably from 0 to 0.01 mm Hg at 25 °C.

"Viscosity" as used herein means kinematic viscosity at 25°C and is reported as centiStokes (1 cSt = 1 mm2•s-1). Viscosity of fluids such as silicone can be determined, for example, by the relevant international standard, such as ISO 3104.

Non-ionic surfactants suitable for the present invention may comprise:

- compounds produced by the condensation of simple alkylene oxides with an aliphatic or alkyl-aromatic hydrophobic compound having a reactive hydrogen atom;
- tertiary amine oxides of structure $R^1R^2R^3N$-O, where R^1 is an alkyl group of 8 to 20 carbon atoms and R^2 and R^3 are each alkyl or hydroxyalkyl groups of 1 to 3 carbon atoms, e.g. dimethyldodecylamine oxide;
- tertiary phosphine oxides of structure $R^1R^2R^3P$-O, where R^1 is an alkyl group of 8 to 20 carbon atoms and R^2 and R^3 are each alkyl or hydroxyalkyl groups of 1 to 3 carbon atoms, for instance dimethyl-dodecylphosphine oxide;
- dialkyl sulphoxides of structure R^1R^2S=O, where R^1 is an alkyl group of from 10

to 18 carbon atoms and R^2 is methyl or ethyl, for instance methyl-tetradecyl sulphoxide;

- fatty acid alkylolamides, such as the ethanol amides;
- alkylene oxide condensates of fatty acid alkylolamides;
- alkyl mercaptans;
- alkyl polyglucosides (APG), for example C_8-C_{16} alkyl polyglycoside;

or a mixture thereof.

Preferably, the non-ionic surfactant comprises compounds produced by the condensation of simple alkylene oxides with an aliphatic or alkyl-aromatic hydrophobic compound having a reactive hydrogen atom; alkyl polyglucosides; or a mixture thereof.

More preferably, the non-ionic surfactant comprises

- the condensation products of aliphatic alcohols having from 8 to 22 carbon atoms in either straight or branched chain configuration with ethylene oxide, such as a coconut alcohol/ethylene oxide condensates having from 2 to 15 moles of ethylene oxide per mole of coconut alcohol;
- condensates of alkylphenols having C_6-C_{15} alkyl groups with 5 to 25 moles of ethylene oxide per mole of alkylphenol;
- polyoxyethylene sorbitan fatty acid esters, for example polyoxyethylene sorbitan C_{6-24} fatty acid esters;
- alkyl polyglucosides,

or a mixture thereof.

Even more preferably, the non-ionic surfactant comprises ethoxylated alkyl alcohols, alkyl polyglucosides, or a mixture thereof; and still even more preferably ethoxylated C_8–C_{16} alkyl alcohols, C_5–C_{20} alkyl polyglucosides, or a mixture thereof.

Ethoxylated alkyl alcohols are preferably ethoxylated C_8–C_{12} alkyl alcohols, whereby yet more preferably the average degree of ethoxylation is between 5 and 8. An example of particularly effective (and therefore preferred) surfactants are ethoxylated C_9-C_{11} alkyl alcohols with an average degree of ethoxylation of 8, including for instance the commercially surfactant Neodol 91-8.

Preferred alkyl polyglucosides are represented by formula of RO - $(G)_n$, wherein R is a branched or straight chain alkyl group which may be saturated or unsaturated, G is a saccharide group, and the degree of polymerisation, n, may have a value of from 1 to 10; Preferably R has a mean alkyl chain length of from C_5 to C_{20}, G is selected from C_5 or C_6 monosaccharide residues and n has a value of from 1 to 6; more preferably R has a mean alkyl chain length of from C_6 to C_{16}, G is glucose and n has a value of from 1 to 2. Suitable alkyl polyglucosides include those from the Glucopon® range, *e.g.* Glucopon® 425 N from BASF.

The non-ionic surfactant preferably comprises at least 10%, more preferably at least 25% and even more preferably from 40 to 100% of ethoxylated alkyl alcohols by weight of the total non-ionic surfactant.

To have a suitable cleaning capability and/or capability to alter the hard surface to be hydrophobic, the hard surface treatment composition preferably comprises non-ionic surfactant in amount of from 0.01 to 15%, more preferably from 0.1 to 10%, even more preferably from 0.3 to 8% and still even more preferably from 0.8 to 6% and most preferably from 1.2 to 4.8% by weight of the total composition.

By “aminosilicone” is meant a silicone containing at least one primary, secondary or tertiary amine group, or a quaternary ammonium group. Preferably, the aminosilicone is silicone having no quaternary ammonium group. Preferably, the primary, secondary tertiary amine group, and/or quaternary ammonium group is carried by side or pendant group carried by the polymeric backbone. Suitable aminosilicone is described in EP 455,185 (Helene Curtis).

The non-volatile aminosilicone suitable for use in the present invention may be represented by the formula of:

$$R^1_aR_{3-a}Si\text{-}(O\text{-}Si\ R_2)_m\text{-}(O\text{-}Si\ R_bR^1_{2-b})_n\text{-}O\text{-}SiR^1_aR_{3-a} \qquad (I)$$

where:

each R is independently hydrogen, phenyl, OH or a C_1-C_{10} alkyl group, preferably R is OH or a C_1-C_6 alkyl group and more preferably a C_1-C_6 alkyl group, and most preferably a CH_3 group;

each a is independently an integer from 0 to 3, preferably each a is 0;

each b is an integer from 0 to 1, b may be 2 when a is not 0, preferably b is 0 or 1 and most preferably b is 1;

m and n are integers whereby the sum of n+m ranges from 1 to 3,500, preferably from 10 to 2000 and more preferably from 100 to 1200;

each R^1 is independently a monovalent radical of formula $-(CR^2_2)_xL$,

where:

each R^2 is independently H, OH, OCH_3 or C_{1-4} alkyl, preferably each R^2 is independently H, or C_{1-4} alkyl;

x is integer from 1 to 10, preferably from 2 to 6;

and L is an amine or a quaternized amine represented by one of the following groups:

$-NR^3-(CR^2_2)_y-N(R^3)_2$ (1)

$-N(R^3)_2$ (2)

$-[N(R^3)-(CR^2_2)_y]_z-N(R^3)_2$, (3)

$-N^+(R^3)_3A^-$ (4)

$-N(R^3)-(CR^2_2)_y-N^+(R^3)_3A^-$, (5)

$-[N(R^3)-(CR^2_2)_y]_z-N^+(R^3)_3A^-$, (6)

$-[N^+(R^3)_2-(CR^2_2)_y]_z-N(R^3)_2(A^-)^z$, (7)

$-[N^+(R^3)-(CR^2_2)_y]_z-N^+(R^3)_3(A^-)^{z+1}$, (8)

where:

each R^2 is independently H, OH, OCH_3 or C_{1-4} alkyl;

each R^3 is independently hydrogen, phenyl, benzyl or a C_1 to C_{12} alkyl;

each y is independently an integer from 1 to 4;

each z is independently an integer from 1 to 5; and

each A^- is independently anion, preferably fluoride, chloride, bromide or iodide anion.

Preferably, in formula (I), each R is independently OH, or C_1-C_4 alkyl group; each a is 0; b is 1 or 2; m and n are integers wherein the sum of n+m ranges from 30 to 2,000; each R^1 is independently a monovalent radical of formula $–(CR^2_2)_xL$, where each R^2 is independently H, or C_{1-4} alkyl, x is integer from 1 to 4, and L is an amine or a quaternized amine represented by groups (1) to (8), where each R^2 is independently H, or C_{1-4} alkyl; each R^3 is independently hydrogen, or a C_1 to C_4 alkyl; each y is independently an integer from 1 to 4; each z is independently an integer from 1 to 3; and each A^- is independently anion.

More preferably, in formula (I), each R is methyl; each a is 0; b is 1; m and n are integers wherein the sum of n+m ranges from 50 to 1,500; each R^1 is independently a monovalent radical of formula $–(CH_2)_xL$, wherein x is integer from 1 to 4, and L is an amine or a quaternized amine represented by groups (1) to (8), where each R^2 is independently H, or C_{1-4} alkyl; each R^3 is independently hydrogen, or a C_1 to C_4 alkyl; each z is independently an integer from 1 to 3; each y is independently an integer from 1 to 4; and each A^- is independently anion.

Most preferably, in formula (I), each R is methyl; each a is 0; b is 1; m and n are integers wherein the sum of n+m ranges from 80 to 1,000; each R^1 is independently a monovalent radical of formula $–(CH_2)_2L$, wherein L is an amine or a quaternized amine represented by $-NR^3-(CH_2)_2-N(R^3)_2$ or $-N(R^3)-(CH_2)_2-N^+(R^3)_3A^-$, where each R^3 is independently hydrogen, or methyl; and A^- is chloride anion.

The mole % amine functionality of the aminosilicone is preferably at least 0.05%, more preferably in the range of from 0.1 to 8%, even more preferably from 0.3 to 6% and most preferably from 0.5 to 4%.

Preferably, the aminosilicone is amino functional polysiloxanes having the CTFA designation “amodimethicone”.

The weight-average molecular weight of the non-volatile aminosilicone is preferably from 2,000 to 2,000,000, more preferably from 8,000 to 800,000, even more preferably from 20,000 to 400,000, and most preferably from 50,000 to 150,000 Daltons. The weight-

average molecular weight may be measured by following the standard of ASTM D4001-2013.

The non-volatile aminosilicone suitable for use in the compositions of the invention preferably has a $D_{3,2}$ average particle diameter (Sauter mean diameter) in the composition of from 10 nm to 20 micron, more preferably from 20 nm to 5 micron, even more preferably from 30 to 2 micron, still even more preferably from 40 nm to 800 nm, and most preferably from 50 to 200 nm.

Preferably, the non-volatile aminosilicone is emulsified by emulsifier selected from cationic emulsifier, non-ionic emulsifier, anionic emulsifier, or a mixture thereof. More preferably, the emulsifier comprises cationic emulsifier, non-ionic emulsifier, or a mixture thereof. Even more preferably the emulsifier comprises non-ionic emulsifier.

Non-ionic emulsifier is preferably selected from polyoxyethylene alkyl ethers, polyoxyethylene alkyl phenyl ethers, alkylglucosides, polyoxyethylen, fatty acid esters, sorbitan fatty acid esters, polyoxyethylene sorbitan fatty acid esters, poly(oxyethylene)-poly(oxypropylene)-poly(oxyethylene) tri-block copolymer (also referred to as poloxamers), poly(oxyethylene)-poly(oxypropylene) block copolymer derived from the sequential addition of propylene oxide and ethylene oxide to ethylene diamine (also referred to as poloxamines), or mixtures thereof. More preferably the non-ionic emulsifier is selected from polyoxyethylene alkyl ethers, polyoxyethylene alkyl phenyl ethers, alkylglucosides, fatty acid esters, sorbitan fatty acid esters, polyoxyethylene sorbitan fatty acid esters, or mixtures thereof.

Cationic emulsifier is preferably a quaternary ammonium salt. More preferably, the cationic surfactants have the formula $N^+R^4R^5R^6R^7\ X^-$, wherein R^4, R^5, R^6, and R^7 are independently (C_1 to C_{30}) alkyl or benzyl and X is hydroxide or halogen. Preferably, one, two or three of R^4, R^5, R6, and R^7 are independently (C_4 to C_{30}) alkyl and the other R^4, R^5, R6, and R^7 group or groups are (C_1-C_6) alkyl or benzyl and X is hydroxide, chlorine or bromine. Even more preferably, the cationic surfactants has the formula of $N^+(CH_3)_2R^8R^9X^-$, where R^8, and R^9 are independently (C_{12} to C_{30}) alkyl and X is hydroxide,

chlorine or bromine, and most preferably the cationic is C_{12}-C_{30} alkyltrimethylammonium chloride.

The viscosity of the non-volatile aminosilicone itself (not the emulsion or the final hard surface treatment composition) is typically from 20 to 2,000,000 cSt (centi-Stokes) at 25 °C, preferably from 500 cSt to 800,000 cSt, more preferably from 2,400 to 80,000 cSt, even more preferably from 4,000 to 15,000 cSt, and most preferably from 8,000 to 15,000 cSt.

Preferably, the non-volatile aminosilicone is present in the composition in amount from 0.01 to 20% by weight of the composition, more preferably from 0.1 to 15%, even more preferably from 0.2 to 9%, still even more preferably from 0.4 to 6%, most preferably from 0.5 to 3% by weight of the total composition.

Preferably, the non-volatile aminosilicone accounts for at least 25% by weight of the total non-volatile silicone in the composition, more preferably from 40% to 100%, even more preferably from 75% to 100% by weight of the total non-volatile silicone in the composition.

To have a better surface appearance and/or hydrophobicity, the weight ratio of the nonionic surfactant to the non-volatile aminosilicone is preferably from 1:20 to 50:1, more preferably from 1:10 to 20:1, even more preferably from 1:5 to 8:1, and most preferably from 0.4:1 to 4:1.

The hard surface treatment composition of the present invention preferably comprises at least 30% of water by weight of the composition. More preferably, the composition comprises at least 50%, even more preferably from 70 to 99%, still even more preferably from 77 to 97% and most preferably from 84 and 93% of water by weight of the composition.

The composition preferably comprises organic solvents selected from C_{1-8} alcohol, ether having 2 to 16 carbon atoms, ester of C_{2-24} organic acid, C_{6-18} cyclic terpene, and a mixture thereof. More preferably the composition comprises organic solvents selected

from C_{2-8} alcohol, ether having total 2 to 16 carbon atoms, ester having total 2 to 16 carbon atoms, C_{6-16} cyclic terpene, and a mixture thereof. Even more preferably the composition comprises organic solvents selected from C_{2-8} alcohol, ether having total 2 to 12 carbon atoms, ester having total 2 to 12 carbon atoms, C_{6-12} cyclic terpene, and a mixture thereof.

Preferably the composition comprises ethanol, isopropyl alcohol, n-butanol, iso-butanol, n-butoxypropanol, dipropylene glycol, diethylene glycol monobutyl ether, dipropylene glycol monobutyl ether, propylene glycol monomethyl ether, propylene glycol monopropyl ether, methyl ester of caprylic acid, methyl ester of heptylic acid, dimethyl-2-methyl glutarate, esters of polyglycerol, soybean oil methyl ester, limonene or a mixture thereof. More preferably the composition comprises ethanol, isopropyl alcohol, dipropylene glycol, diethylene glycol monobutyl ether, dipropylene glycol monobutyl ether, propylene glycol monomethyl ether, propylene glycol monopropyl ether, methyl ester of caprylic acid, methyl ester of heptylic acid, dimethyl-2-methyl glutarate, esters of polyglycerol and C_{2-8} acid, soybean oil methyl ester, limonene or a mixture thereof. Even more preferably the composition comprises ethanol, isopropyl alcohol, dipropylene glycol, diethylene glycol monobutyl ether, dipropylene glycol monobutyl ether, propylene glycol monomethyl ether, propylene glycol monopropyl ether, methyl ester of caprylic acid, methyl ester of heptylic acid, dimethyl-2-methyl glutarate, limonene or a mixture thereof. Most preferably the composition comprises isopropyl alcohol, dipropylene glycol monobutyl ether, propylene glycol monomethyl ether, propylene glycol monopropyl ether, or a mixture thereof. The organic solvent may be present in the composition in a concentration of 0 to 20%, preferably 0.5-15% by weight of the composition.

The composition preferably comprises abrasive particle, more preferably in amount of 2 to 40%, even more preferably from 5 to 15% by weight of the composition. The abrasive particles can be of any suitable material, both organic and inorganic but preferably comprises inorganic abrasive particles. More preferably the abrasive comprises particles made of zeolites, calcites, dolomites, feldspar, silicas, silicates, other carbonates, aluminas, bicarbonates, borates and sulphates. Even more preferably the composition comprises calcite, silica particles, olive stone fragments, or a mixture thereof. Preferably, the abrasive particles preferably have a volume average median diameter d(0.5) of

150μm or below, more preferably of between 1 to 100 μm, more preferably from 5 to 80 μm and still even more preferably between 10 and 70 μm. Preferably the abrasive particles have sharp edges and an average a particle has at least one edge or surface having concave curvature. More preferably, the particles herein have a multitude of sharp edges and each particle has at least one edge or surface having concave curvature. The sharp edges of the particles are defined by edges having a tip radius below 20 pm, preferably below 8 pm, most preferably below 5 pm. The tip radius is defined by the diameter of an imaginary circle fitting the 15 curvature of the edge extremity.

The composition may comprise from 0.2 to 1.2% of thickener by weight of the composition. This provides the optimum rheological properties of the composition. Suitable thickeners include the modified celluloses for example hydroxyethyl cellulose.

The hard surface cleaning composition according to the invention may further comprise dyes, perfume, and/or preservatives. If present, the amount may be from 0.001 to 5% by weight of the composition.

Preferably, the composition has a pH value of no greater than 8.5 when the non-volatile aminosilicone comprises aminoethylaminopropyl poly(dimethylsiloxane). More preferably the composition has a pH value of no greater than 8.5 when the non-volatile aminosilicone does not comprises quaternary ammonium silicone. The composition preferably has a pH value of no greater than 11.8, more preferably no greater than 8.5, even more preferably between 1 and 8, still even more preferably from 3 to 8. The pH values referred to herein are measured at a temperature of 25 °C.

In general, the hard surface treatment composition of the invention may have any appearance, ranging from opaque to fully transparent. However, the composition is preferably at least partially transparent or translucent, more preferably transparent. By at least partially transparent or translucent is meant that a 1 cm thick sample of the composition transmits at least 20%, preferably at least 50%, of light having wavelength of 460 nm. By transparent is meant that a 1 cm thick sample of the composition transmits at least 70%, preferably at least 90%, of light having wavelength of 460 nm.

The composition of the present invention may be produced by any convenient way. However it is preferred that the process for preparing the composition comprises the steps in sequence of:

a) emulsifying the non-volatile aminosilicone by emulsifier to form an emulsion;
b) combining the emulsified aminosilicone with the non-ionic surfactant; and
c) recovering the hard surface treatment composition,

wherein the non-volatile aminosilicone accounts for at least 15% by weight of the total non-volatile silicones in the composition, and the emulsifier is different from the non-ionic surfactant.

Preferably, the emulsion comprises at least 10% of non-volatile aminosilicone by weight of the emulsion, more preferably from 15 to 90%, even more preferably from 20% to 80% by weight of the emulsion.

Preferably, step (a) is carried out at least half an hour before step (b), more preferably at least 1 day, even more preferably from 1 week to 5 years before step (b).

The composition may be packed in any form, but preferably is packaged as a conventional hard surface treatment or cleaning product. The preferred packaging is a spray applicator. Pump dispersers (whether spray or non-spray pumps) and pouring applications (bottles etc) are also possible. It is also possible to impregnate a wipe with the composition.

When treating a hard surface by the composition, any general way for treating a hard surface is acceptable. Typically, the way for treating a hard surface by the composition is spraying the composition onto the hard surface, or wiping the hard surface by wipe impregnated with the composition, or pouring the composition onto the hard surface, or combination thereof. Preferably, the way for treating a hard surface is spraying the composition onto a hard surface, and/or wiping a hard surface by wipe impregnated with the composition. When spraying is employed for treating a hard surface, there is no limitation how the composition is sprayed. Typically, a spraying bottle for hard surface cleaning product is favourable. When wiping is employed for treating a hard surface, wipe including woven or nonwoven cloth, natural or synthetic sponges or spongy sheets,

"squeegee" materials, paper towel, or the like is suitable. The wipe may be impregnated dry, or more preferably in wet form.

Thus, after treating the surface with the composition, the method for treating a hard surface may optionally further comprises the steps of allowing soil and/or stains to deposit. Thus, the soil or stains will be easily removed when the hard surface is subsequently cleaned according to the method of this invention. Meanwhile, the composition of the invention is also preferably applied to the hard surface during the subsequent cleaning. Optionally, treating of a hard surface with the composition may be followed by a rinsing step, preferably with water.

Therefore a most preferred method for treating a hard surface comprises:

I. forming the hydrophobic coating on the surface;

II. allowing soil and/or stains to deposit on the coating; and then

III. cleaning the surface to remove the soil and/or stains.

The soils and stains of present invention may comprise all kinds of soils and stains generally encountered in the household, either of organic or inorganic origin, whether visible or invisible to the naked eye, including soiling solid debris and/or with bacteria or other pathogens. Specifically the method and compositions according to the invention may be used to treat surface susceptible to fatty or greasy soil and stains.

The present invention may also deliver other benefits such as long last cleaning, less effort for cleaning, less surface corrosion, less noise during cleaning, surface shine, surface smoothness, less damage and/or scratch resistance. Further aspects of the present invention comprise methods for obtaining one or more these other benefits by applying the composition of the present invention to a hard surface and/or use the composition for delivering any one more such benefits mentioned in this invention.

The following examples are provided to facilitate an understanding of the present invention. The examples are not provided to limit the scope of the claims.

Examples

Example 1

This example demonstrates the effect of types of surfactant in samples on the surface wettability of hard surface treated by the samples.

Table 1

Chemical name	Trade name	Samples (active% by weight)			
		1	2	A	B
Primary alcohol ethoxylate	Neodel 91-5 ex Shell	2.00	—	—	—
Alkyl polyglycoside C8-C16	Glucopon® 425 N from BASF	—	2.00	—	—
N,N-Dimethyl-N-dodecylglycine betaine N-(Alkyl C_{10}-C_{16})-N,N-dimethylglycine betaine	Empigen® BB from Sigma-Aldrich	—	—	2.00	—
Sodium Lauryl Ether Sulfate	Texapon N70 from Cognis	—	—	—	2.00
Amodimethicone	Dow Corning 2-8168 microemulsion	1.00	1.00	1.00	1.00
De-ionized water	—	To 100	To 100	To 100	To 100
Contact angle (°)		96.5±2.9	96.4±0.3	76.0±0.8	47.0±3.5

The samples were prepared by mixing the ingredients according to the formulation in Table 1 and stirring for 10 minutes (200 rpm).

Glass slides were chosen as model substrate. Pipette was used to drop the composition on the glass slide (2.5 cm X 7 cm) in a controlled amount of 0.15 ml. After the dispersion was dropped on the target surface, the tip of the pipette was used to spread the composition on the surface to ensure uniform coating. After application of the composition on the substrate, the solvent was allowed to evaporate at room temperature (25 °C).

Drop shape analysis system 100 (DSA 100, Krüss) was used to measure the contact angles at 25°C. 5 µl of water droplets were employed and the average values and

standard derivations of contact angles were obtained from at least 3 droplets. The results for contact angels of glass slides after treatment were shown in last row of Table 1.

The data show that the compositions containing non-ionic surfactant and non-volatile aminosilicone generated hydrophobic coating on hard surface. In contrast, compositions containing non-volatile aminosilicone and anionic surfactant, or containing non-volatile aminosilicone and amphoteric surfactant did not yield hydrophobic coating.

Example 2

This example demonstrates that the types of silicones in compositions on the surface wettability.

Table 2

Chemical name	Trade name	Samples (active% by weight)		
		3	4	C
Primary alcohol ethoxylate	Neodel 91-5 ex Shell	2.00	2.00	2.00
Amodimethicone (and) C12-14 sec-Pareth-7 (and) C12-14 sec-Pareth-5	Dow Corning 2-8168 microemulsion	1.00	—	—
Amodimethicone and Trideceth-12 and Cetrimonium Chloride	Dow Corning 949 cationic emulsion	—	1.00	—
	Dow Corning 5-7134 emulsion	—	—	1.00
De-ionized water	—	To 100	To 100	To 100
Contact angle (°)		96.5±2.9	91.2±0.3	72.4±3.2

The experiments were identical to those of Example 1.

Dow Corning 5-7134 emulsion contains 63% of dimethicone and 7% of amodimethicone.

As can be seen in the results in Table 2, it was unexpectedly found that the compositions containing 100% of aminosilicone by weight of the total non-volatile silicone yielded hydrophobic coating on hard surface. In contrast, the composition containing 10% of

aminosilicone by weight of the total non-volatile silicone did not generate hydrophobic coating on hard surface.

Example 3

This example demonstrates the effect of emulsifier on surface wettability of coating on hard surface by the compositions.

Table 3

Chemical name	Trade name	Samples (active% by weight)	
		5	D
Alkyl polyglycoside C8-C16	Glucopon® 425 N from BASF	2.5	2.5
Amodimethicone (and) C12-14 sec-Pareth-7 (and) C12-14 sec-Pareth-5	Dow Corning 2-8168 microemulsion	1.0	—
amino methoxy functional polydimethylsiloxane	Dow Corning DC 531 Fluid	—	1.0
Propylene Glycol Methyl Ether (PGME)	—	1.0	1.0
De-ionized water	—	To 100	To 100
Contact angle (°)		95.3±0.9	76.6±1.8

The experiments were identical to those of Example 1 except that 15 minutes of homogenization was followed by stirring for the preparation of sample D.

In sample D, the aminosilicone was emulsified by the non-ionic surfactant. The data in Table 3 show that the composition containing aminosilicone which was emulsified by emulsifier different from the non-ionic surfactant yielded a hydrophobic coating.

Example 4

This example demonstrates the benefit of oil repellancy by the present invention

Table 4

Chemical name	Trade name	Samples (active% by weight)
		6
Alkyl polyglycoside C8-C16	Glucopon® 425 N from BASF	2.500

Amodimethicone (and) C12-14 sec-Pareth-7 (and) C12-14 sec-Pareth-5	Dow Corning 2-8168 microemulsion	1.000
Propylene Glycol Methyl Ether (PGME)	—	1.000
polyether modified silicone	—	0.125
Fragrance	—	0.050
De-ionized water	—	To 100

The preparation of the composition in Table 4 and treatment of glass slides, ceramic tile, mirror, and stainless steel was similar as described in Example 1.

Oil contact angle was measured by drop shape analysis system 100 (DSA 100, Krüss) at 25°C. 20 µl of soybean oil droplets were employed and the average value of contact angles was obtained from at least 3 droplets. The contact angles of treated glass and untreated glass were 62.7 ± 4.3° and 16.1 ± 0.6° respectively, manifesting that the oil repellancy had been improved significantly by the coating.

The speed and residue when soybean oil slid off from the hard surface were also measured. The treated and untreated substrates were tilted at a certain angle (5° for ceramic tile and mirror and 10° for stainless steel) and at fixed position. 2 ml of blue dyed soybean oil (0.1% of oil blue dye) was placed into the central area. The mass of the oil collected was monitored and recorded by a computer connected balance. The masses of the collected are shown in Table 5.

Table 5

Substrate	Mass of collected oil After 20 seconds (g)		Mass of collected oil After 3 minutes (g)	
	Coated	Uncoated	Coated	Uncoated
Ceramic tile	1.42	0.43	1.61	1.20
Mirror	1.43	0.61	1.77	1.29
Stainless steel	1.45	0.82	1.57	1.44

It was found that the mass of collected oil generally did not change after 2.5 minutes for all three types of substrates. As can be seen in Table 5, the soybean oil slid off from the untreated substrates much quicker than from the untreated substrates. Furthermore, the oil residue on treated substrates was less than that on the untreated substrates.

Example 5

This example demonstrates the effect of types of silicones on the surface wettability of hard surface treated by the samples.

Table 6

Ingredient	Samples (active% by weight)				
	7	8	9	E	F
Neodel 91-8 from Shell	2.0	2.0	2.0	2.0	2.0
Dow corning® 5-7113 silicone quat microemulsion	2.0	2.0	2.0	—	—
Dow Corning® 2-8168 microemulsion	—	—	—	—	2.0
Citric acid	q.s.	—	—	2.0	—
Sodium hydroxide	—	q.s.	q.s.	q.s.	q.s.
De-ionized Water	To 100	To 100	To 100	To 100	To 100
pH	2.79	7.1	10.98	12.01	10.99
Contact angle (°)	84.1±2.8	88.8±5.0	87.9±4.2	45.2±1.5	61.1±7.3

The samples were prepared according to the formulation in Table 6. Citric acid and sodium hydroxide were employed to adjust the pH value of the composition to the desired value.

The experiments were conducted in a similar manner with those of Example 1.

The pH value of the samples and the contact angle of the generated coatings were listed in the last two rows in Table 6. As can be seen from the results, the composition of the present invention is capable of generating hydrophobic coatings.

Example 6

This example demonstrates the effect of types of surfactants on the surface wettability of hard surface treated by the samples.

The preparation of samples, coating on hard surface and measurement of contact angles were similar with that of Example 1.

Table 7

Ingredient		Samples (active% by weight)		
Chemical name	Product name	4	5	6
Primary alcohol ethoxylate	Neodel 91-8 from Shell	2.0	—	—
Alkyl polyglycoside C8-C16	Glucopon® 425 N from BASF	—	2.0	—
Sodium Lauryl Ether Sulfate	Texapon N70 from Cognis	—	—	2.0
Silicone Quaternium-16	Dow corning® 5-7113 silicone quat microemulsion	1.0	1.0	1.0
De-ionized Water	—	To 100	To 100	To 100
Contact angle (°)		84.0±1.5	86.1±0.4	54.8±6.8

As can be seen from Table 7, the composition containing non-ionic surfactant and aminosilicone can yield a hydrophobic coating on hard surface. In contrast, the composition containing anionic surfactant and aminosilicone did not yield hydrophobic coating.

Claims

1. A hard surface treatment composition comprising:
   a) non-ionic surfactant; and
   b) non-volatile aminosilicone emulsified by emulsifier,
   wherein:
   i. the non-volatile aminosilicone accounts for at least 15% by weight of the total non-volatile silicones in the composition;
   ii. the emulsifier is different from the non-ionic surfactant;
   iii. the composition has a pH value of no greater than 11.8; and
   iv. the composition has a pH value of no greater than 8.5 when the non-volatile aminosilicone comprises aminoethylaminopropyl poly(dimethylsiloxane).

2. The composition according to claim 1 wherein the non-ionic surfactant is present in amount of 0.1 to 10% by weight of the composition, preferably 0.8 to 6% by weight of the composition.

3. The composition according to claim 1 or 2 wherein the non-ionic surfactant comprises ethoxylated alkyl alcohols, alkyl polyglucosides, or a mixture thereof, preferably ethoxylated C_8–C_{16} alkyl alcohols, C_5–C_{20} alkyl polyglucosides, or a mixture thereof.

4. The composition according to any one of the preceding claims wherein the aminosilicone comprising nitrogen in amount of at least 0.05% by weight of aminosilicone, preferably 0.1 to 8% by weight of the aminosilicone.

5. The composition according to any one of the preceding claims wherein the aminosilicone is amodimethicone.

6. The composition according to any one of the preceding claims wherein the aminosilicone has a weight average molecular weight of 2,000 to 2,000,000, preferably from 8,000 to 800,000, more preferably from 20,000 to 400,000, and even more preferably from 50,000 to 150,000 Daltons.

7. The composition according to any one of the preceding claims wherein the aminosilicone has a $D_{3,2}$ average particle diameter of from 10 nm to 20μm, preferably from 30 nm to 2 μm.

8. The composition according to any one of the preceding claims wherein the aminosilicone is present in amount of from 0.01 to 15% by weight of the composition, preferably from 0.5 to 3% by weight of the composition.

9. The composition according to any one of the preceding claims wherein the weight ratio of non-ionic surfactant to the aminosilicone is from 1:10 to 20:1 more preferably from 1:5 to 8:1.

10. The composition according to any one of the preceding claims wherein the emulsifier comprises non-ionic emulsifier, cationic emulsifier, anionic emulsifier, or a mixture thereof, preferably comprise non-ionic emulsifier, cationic emulsifier or a mixture thereof.

11. The composition according to any one of the preceding claims wherein the composition comprises organic solvents selected from C_{2-8} alcohol, ether having total 2 to 16 carbon atoms, ester having total 2 to 16 carbon atoms, C_{6-16} cyclic terpene, and a mixture thereof, preferably the composition comprises ethanol, isopropyl alcohol, dipropylene glycol, diethylene glycol monobutyl ether, dipropylene glycol monobutyl ether, propylene glycol monomethyl ether, propylene glycol monopropyl ether, methyl ester of caprylic acid, methyl ester of heptylic acid, dimethyl-2-methyl glutarate, esters of polyglycerol and C_{2-8} acid, soybean oil methyl ester, limonene, or a mixture thereof.

12. The composition according to any one of the preceding claims wherein the composition has a pH value of no greater than 8.5.

13. A process for preparing the composition of any one of the preceding claims, the process comprises the step of:
    a) emulsifying the non-volatile aminosilicone by emulsifier; and

b) combining the emulsified non-volatile aminosilicone with non-ionic surfactant.

14. A method for forming a hydrophobic coating on a surface, the method comprising applying the composition of any one of the claims 1 to 11 to the surface and drying the composition to yield the hydrophobic coating.

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2015/065841

A. CLASSIFICATION OF SUBJECT MATTER
INV. C09D183/08 C11D1/72 C11D3/37
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)
C09D 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, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 03/035765 A1 (DOW CORNING [US]; JOHNSON BETHANY [US]; KENNAN JOHN [US]; LIN FEIFEI []) 1 May 2003 (2003-05-01) Conditioners B and E to N Shampoos B and D; examples 1,2,3,4,5,6,7,8; tables 2,3,8,11,14,17,20 -----	1-14
X	US 5 866 532 A (JACKSON RONALD C [US] ET AL) 2 February 1999 (1999-02-02) column 2, line 16 - line 18 column 3, line 30 - line 33 column 4, line 37 - column 5, line 40 -----	1-14

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

☒ See patent family annex.

* Special categories of cited documents :

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

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
17 September 2015	30/09/2015

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, Fax: (+31-70) 340-3016	Culmann, J

1

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/EP2015/065841

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 03035765 A1	01-05-2003	AT 408650 T	15-10-2008
		CN 1575320 A	02-02-2005
		EP 1440124 A1	28-07-2004
		JP 2005507022 A	10-03-2005
		US 6607717 B1	19-08-2003
		WO 03035765 A1	01-05-2003
US 5866532 A	02-02-1999	AU 9294498 A	16-03-1999
		EP 1019473 A1	19-07-2000
		US 5866532 A	02-02-1999
		US 6090767 A	18-07-2000
		WO 9910464 A1	04-03-1999