



- (51) **International Patent Classification:**
C09D 183/00 (2006.01)
- (21) **International Application Number:**
PCT/EP2012/057242
- (22) **International Filing Date:**
20 April 2012 (20.04.2012)
- (25) **Filing Language:** English
- (26) **Publication Language:** English
- (30) **Priority Data:**
PCT/CN2011/000842 16 May 2011 (16.05.2011) CN
PCT/CN2011/001720
14 October 2011 (14.10.2011) CN
- (71) **Applicant** (for all designated States except AE, AG, AU, BB, BH, 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, SC, SD, SG, SL, SZ, TT, TZ, UG, US, VC, ZA, ZM, ZW): **UNILEVER N.V.** [NL/NL]; Weena 455, NL-3013 AL Rotterdam (NL).
- (71) **Applicant** (for AE, AG, AU, BB, BH, BW, BZ, CA, CY, EG, GB, GD, GH, GM, IE, IL, KE, KN, LC, LK, LS, MT, MW, MY, NA, NG, NZ, OM, PG, QA, RW, SC, SD, SG, SL, SZ, TT, TZ, UG, VC, ZA, ZM, ZW only): **UNILEVER PLC** [GB/GB]; a company registered in England and Wales under company no. 41424 of Unilever House, 100 Victoria Embankment, London Greater London EC4Y 0DY (GB).
- (71) **Applicant** (for IN only): **HINDUSTAN UNILEVER LIMITED** [IN/IN]; Unilever House, B.D. Sawant Marg Chakala Andheri (East), Mumbai, Maharashtra 400 099 (IN).
- (72) **Inventors; and**
- (75) **Inventors/Applicants** (for US only): **LI, Jinyong** [CN/CN]; Unilever (China) Investing Company, Unilever Discover Shanghai 5F, Unilever R&D Centre, 66 Lin Xin Road, Linkong Economic Development Zone Shanghai,

200335 (CN). **TAO, Qingsheng** [CN/CN]; Unilever (China) Investing Company, 66 Linxin Road, Linkong Economic Development Zone, Changning District, Shanghai, 200335 (CN). **RAN, Chunbo** [CN/CN]; Unilever (China) Investing Company, 66 LinXin Road, Linkong Economic Development Zone, Shanghai, 200335 (CN). **WANG, Xiaoliang** [CN/CN]; Unilever (China) Investing Company, 66 LinXin Road, Linkong Economic Development Zone, Shanghai, 200335 (CN).

- (74) **Agent:** **WAHLEY, Christopher**; Unilever Patent Group, Olivier van Noortlaan 120, NL-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, 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, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, 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, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, 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, ML, MR, NE, SN, TD, TG).

Published:

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

(54) **Title:** SUPERHYDROPHOBIC COATING

(57) **Abstract:** Disclosed is a composition capable of yielding a superhydrophobic coating. The composition comprises solvent, silicone and microcluster of silica-based particles. The silicone has a viscosity of at least 30 cSt and the microcluster has a diameter of from 1 nm to 400 nm.



SUPERHYDROPHOBIC COATING**TECHNICAL FIELD OF THE INVENTION**

The present invention is directed to a composition suitable to yield a superhydrophobic coating and a method for making the same. More particularly, the present invention is directed to a superhydrophobic coating comprising silicone having a viscosity of at least 30 cSt and microclusters of silica-based particles wherein the microclusters have diameters from 1 nm to 400 nm.

BACKGROUND TO 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. In fact, the cleaning of surfaces that attempt to mimic the surface of a lotus leaf has been investigated. Taro leaves, for example, have been used as templates for polystyrene structures that can display a lotus leaf effect. Such structures can be used for coatings that possess superhydrophobic properties. Articles with surfaces that are difficult to wet, i.e., articles with superhydrophobic surfaces, are therefore desirable since they possess self-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.

While superhydrophobic surfaces are desirable, compositions that result in such surfaces can be difficult to manufacture and can result in surfaces that display inferior self cleaning, a direct result, for example, of their characteristic contact angles that do not always exceed 140° against water. Moreover, reliable methods for generating superhydrophobic coatings that do not alter the look of treated surfaces are not a given.

- 2 -

There is an increasing interest to develop superhydrophobic coatings that result in surfaces displaying high contact angles against water.

Efforts have been disclosed for preparing hydrophobic surfaces. In *Thin Solid Films* 515 (2006) pp. 1539-1543, Hongli *et al.*; *Applied Surface Science* 253 (2007) pp. 8830-8834, Xu *et al.*; *Journal of Physics D: Applied Physics* 40 (2007) pp. 3485-3489, Zhiqing *et al.*; *Journal of Colloid and Interface Science* 322 (2008) pp. 1-5, Shuaixia *et al.*; and *Langmuir* 24 (2008) pp. 11225-11232, Manoudis *et al.* superhydrophobic surfaces are described.

10 Other efforts have been disclosed for making hydrophobic surfaces. In U.S. patents 6,683,126 and 7,196,043, compositions for producing difficult to wet surfaces and compositions for yielding self-cleaning surfaces, respectively, are described.

15 Still other efforts have been disclosed for making hydrophobic surfaces. In U.S. Patents 7,279,197 and 7,459,197, anti-icing coatings and reversibly adaptive rough micro- and nanostructures, respectively, are described.

Even other efforts have been disclosed for making superhydrophobic surfaces. In International patent application published as WO 2011/020701, ultrahydrophobic coatings
20 made from a multi-solvent system are described.

None of the efforts set forth above describes a composition for making a superhydrophobic coating generated from a composition comprising aggregates or microclusters of silica-based particles, silicone and solvent wherein the aggregates or
25 microclusters have a diameter from 1 nm to 400 nm and the silicone has a viscosity of at least 30 cSt.

The present inventors have recognized that there is a need to generate coatings that do not alter the look of surfaces they are applied on. In addition the present inventors have
30 recognized a need for compositions for generating such a coating and that can be

- 3 -

formulated from readily-available and/or safe materials such that the compositions may be used by consumers in-home. This invention, therefore, is directed to a composition for yielding a superhydrophobic coating comprising silicone and aggregates or microclusters whereby the same comprises silica-based particles and the microclusters have diameters
5 from 1 nm to 400 nm. The coating of this invention is prepared by combining at least aggregates or microclusters of silica-based particle, silicone and solvent to produce a composition that cures to yield the desired coating. Such a composition can be formulated with relatively safe solvents (such as alcohols and/or aqueous solvents) and is typically capable of curing to yield a coating that is at least translucent and often transparent and/or
10 which is durable.

TESTS AND DEFINITIONS

Viscosity

"Viscosity" for the purposes of the present invention means kinematic viscosity at 25 °C
15 and is reported as centiStokes ($1 \text{ cSt} = 1 \text{ mm}^2 \cdot \text{s}^{-1}$). Viscosity of fluids such as silicone oils can be determined, for example, by the relevant international standard, such as ISO 3104.

Microclusters

"Microcluster" as used herein, is meant to mean a bundle of particles, and preferably, a
20 bundle of particles that form an aggregate of the same or varying sizes (i.e., cluster-like appearance). The microcluster may be formed from heterogeneously sized particles or homogeneously sized particles. Heterogeneously sized particles in a microcluster means having particles with different or varying size diameters in the microcluster.

Homogeneously sized particles in a microcluster means having particles with substantially
25 the same size diameters in the microcluster. Substantially the same size means having all particles with diameter sizes within 5% of each other. Diameter is meant to mean the largest measurable distance on a particle or aggregate in the event a well-defined sphere is not generated.

- 4 -

Where the diameter of a microcluster is mentioned this 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).

5 Superhydrophobicity

“Superhydrophobic” as used herein means having a contact angle of at least 140° against water and a sliding angle of less than 20°. Contact angle, as used herein, means the angle at which a water/vapor interface meets a solid surface at a temperature of 25 °C. Such an angle maybe measured with a goniometer or other water droplet shape analysis systems. Sliding angle, as used herein, means the tilt angle of a surface at which a 5 µl droplet of water slides at 25 °C.

10 Refractive Index

Refractive index is quoted at a temperature of 25 °C and a wavelength of 589 nm.

15 Transmittance

Values of transmittance quoted herein are determined at a wavelength of 550 nm and are measured as follows:

- An uncoated glass slide having a transmittance of 89.0% is taken as substrate.
- 20 - Composition is spread on to one side of the slide to give an even coating of about 2.86×10^{-4} mg/mm².
- The coating is cured for 10 minutes or until it forms a cohesive film.
- The coated slide is placed in a UV-vis spectrometer (e.g. Perkin-Elmer Lambda 650S) and the transmittance measured at 25 °C.

25 Transmittance is used herein as a measure of transparency and so should be determined in the absence of any chromophores with appreciable absorbance at 550 nm.

- 5 -

Miscellaneous

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”.

5

All amounts are by weight of the final 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.

10

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. Also for the avoidance of doubt and by way of illustration in this specification, a composition with microclusters comprising silica-based particles yields support for a composition with microclusters consisting essentially of and consisting of silica-based particles.

15

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.

20

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*.

25

SUMMARY OF THE INVENTION

In a first aspect, the present invention is directed to a composition capable of yielding a superhydrophobic coating, the composition comprising

30

- 6 -

- (a) a microcluster of silica-based particles, the microcluster having a diameter from 1 nm to 400 nm;
- (b) silicone having a viscosity of at least 30 cSt; and
- (c) solvent.

5

In a second aspect, the invention is directed to a process for making the composition of the first aspect comprising the step of combining, in no particular order, the silica-based particles, at least a first part of the solvent and the silicone to provide a mixture.

- 10 In a third aspect, the present invention is directed to a method for making a superhydrophobic coating with the composition described in the first aspect of this invention, the method comprising the steps of applying the composition to a surface and allowing the composition to dry.

- 15 In a fourth aspect, the present invention is directed to the superhydrophobic coating obtained and/or obtainable by the method of the third aspect of this invention.

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

20

DETAILED DESCRIPTION

The only limitations with respect to the type of silica-based particle that may be used in this invention is that the same can be used to generate microclusters and can be employed in a composition suitable for use by consumers to generate a superhydrophobic coating.

25

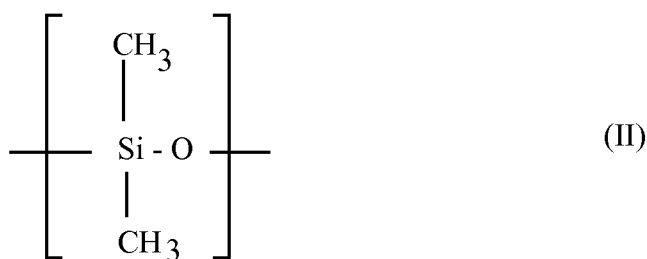
Illustrative silica-based particles suitable for use in this invention comprise at least 25% by weight silicon dioxide (i.e., silica), and preferably, at least 50% by weight silicon dioxide, and most preferably, at least 75% to 100% by weight silicon dioxide, based on total weight of particle and including all ranges subsumed therein. In an often preferred embodiment,
30 the silica-based particle used is silica, especially pyrogenically produced silica (i.e. fumed

- 7 -

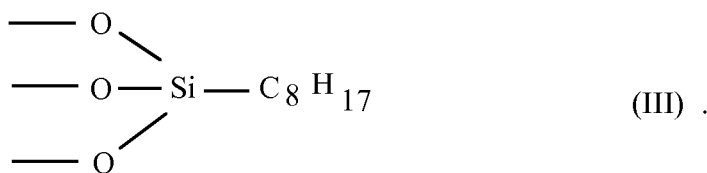
silica) which has been hydrophobically modified. Exemplary hydrophobically modified silicas include those comprising at least one of the following groups:



5



or



10

Such silicas are described, for example, in United States Patent No. 7,282,236 and made commercially available from suppliers like Evonik Degussa GmbH under the names Aerosil[®] R812, R8128, R202, MS202 and R805. Especially preferred are silicas comprising the group represented by formula (I), formula (III) or a combination thereof. Silica of the octylsilane type and comprising the group represented by formula (III) is sold, for example, under the name Aerosil[®] R805 and silica of the hexamethyldisilazane type and comprising the group represented by formula (I) is sold, for example, under the name Aerosil[®] R812S.

20

The size of the silica-based particles used in this invention has no particular limitation save that the particles are necessarily smaller than the size of the micro-cluster. Typically the particles (in an unbundled state) will have a particle size in the range of 0.1 to 100 nm, more preferably 1 to 50 nm and most preferably 3 to 13 nm.

- 8 -

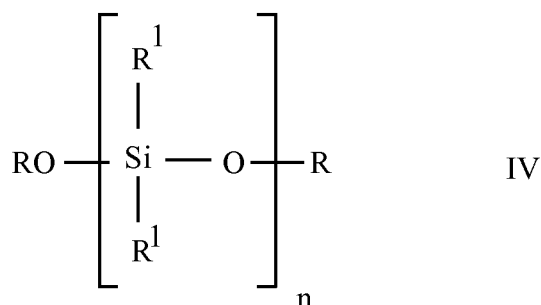
In the composition of the invention, the particles are present as microclusters. Without wishing to be bound by theory, the present inventors believe that the presence of microclusters in the composition provides a rough surface to coatings made from the composition and this roughness is, in part, responsible for superhydrophobicity. The microcluster has a diameter of at least 1 nm and preferably at least 10 nm, more preferably at least 50 nm, more preferably still at least 100 nm and most preferably at least 150 nm.

If the microclusters are too large, however, the structure created in the coating will scatter large amounts of visible light and be opaque. Therefore in compositions of the present invention the microcluster has a diameter of no greater than 400 nm, preferably less than 300 nm, more preferably less than 275 nm, more preferably still less than 250 nm and most preferably less than 225 nm.

The composition preferably comprises the silica-based particles in an amount from 0.25 to 10%, and more preferably from 0.5 to 5%, and most preferably from 1 to 3% by weight based on total weight of composition and including all ranges subsumed therein.

The silicone for use in the present invention is typically liquid in pure form at room temperature (25 °C). Silicone fluids (or oils) are widely commercially available from manufacturers such as Dow Corning or Blue Star Silicones.

Silicones often preferred for use are represented by formula IV:



- 9 -

wherein each R is independently H or a C₁₋₄ alkyl (preferably methyl); each R¹ is independently OR, C₁₋₁₈ alkyl (preferably methyl) or an aryl group (preferably phenyl) where R is as previously defined; and n is an integer from 1 to 1,200.

5

Particularly suitable are dimethicones (polydimethylsiloxane) such as those available under the trade name Xiameter[®].

10

The present inventors have found that by including a silicone having a certain viscosity in the composition of the invention, coatings can be provided which have good durability, especially in terms of peel and/or scratch resistance. Thus the silicone has a viscosity of at least 30 cSt, preferably at least 75 cSt, more preferably at least 100 cSt, more preferably still at least 150 cSt and most preferably least 250 cSt.

15

If the viscosity of the silicone is too high the composition may become difficult to apply to a surface and/or the resulting coating may be less transparent. Thus it is preferred that the silicone has a viscosity of less than 5000 cSt, more preferably less than 1000 cSt, more preferably still less than 750 cSt, even more preferably less than 500 cSt and most preferably less than 300 cSt.

20

A further advantage of silicones employed in the present invention is that they typically have a refractive index which is close to that of silica-based particles. In particular it is preferred that where the silica-based particles have a refractive index n_p , the silicone has a refractive index n_s and the ratio (n_p/n_s) of n_p to n_s is within the range 0.9 to 1.1, more preferably in the range 0.92 to 1.08, even more preferably from 0.93 to 1.07, and most preferably in the range 0.95 to 1.05. Additionally or alternatively the refractive index of the silicone (n_s) is in the range 1.3 to 1.6, more preferably 1.38 to 1.50, even more preferably 1.39 to 1.47 and most preferably 1.40 to 1.45.

25

- 10 -

The present inventors have found that silicone can increase the durability of coatings made from compositions comprising microcluster of silica-based particles even when used in relatively small amounts. For example the weight ratio of amount of silicone to the amount of silica-based particles (silicone:particles) present in the composition may be in
5 the range 1:0.5 to 1:30, more preferably in the range 1:1 to 1:20 and most preferably in the range 1:1.5 to 1:15. Additionally or alternatively the composition may comprise silicone in an amount of from 0.05 to 10% by weight, more preferably from 0.07 to 7%, more preferably still from 0.1 to 5% and most preferably from 0.2 to 3%.

10 Apart from the silica-based particles and silicone, the composition additionally comprises solvent. Often solvent will make up the balance of the composition but optional ingredients such as colourants, preservatives and the like may also be present in the composition. The composition may comprise the solvent in an amount, for example, of from 50 to 99.9% by weight, more preferably from 70 to 99%, more preferably still from 80 to 98% by
15 weight, and most preferably from 90 to 97% by weight.

Most preferred are volatile solvents (i.e. solvents which have a measurable vapour pressure at 25 °C). More preferred are solvents which have a vapour pressure at least equal to that of pure water at 25 °C. Volatile solvents are preferred because of their
20 tendency to evaporate quickly and so leave behind a coating consisting of (or at least consisting essentially of) silica-based particles and silicone.

Occasionally, however, some solvent may remain in the coating and so to prevent unwanted opacity on such occasions, it is preferred to employ a solvent which has a
25 refractive index close to that of the silica particles. Thus it is preferred that the solvent has a refractive index n_a in the range 1.2 to 1.6, more preferably 1.3 to 1.5. Additionally or alternatively, the ratio (n_p/n_a) of n_p to n_a is within the range 0.9 to 1.1, more preferably in the range 0.93 to 1.07.

- 11 -

Particularly preferred solvents, owing to their relative safety and high volatility, are polar organic solvent, more preferably C₁-C₄ alcohol. Most preferably the solvent comprises methanol, ethanol, propanol, isopropanol or a mixture thereof.

- 5 The solvent may additionally or alternatively comprise water, preferably in an amount of at least 5% by weight of the composition, more preferably at least 10%, more preferably still at least 20% and most preferably at least 30%. However water has poor compatibility with silicone and so it is preferred that the amount of water in the composition is less than 80% by weight of the composition, more preferably less than 75% and most preferably less than
10 70%.

- Advantageously polar organic solvent may be used to improve the compatibility of silicone with water. Thus in one embodiment the solvent comprises polar organic solvent (especially C₁-C₄ alcohol) and water. More preferably the solvent comprises polar organic
15 solvent and water in a weight ratio of solvent:water of from 10:1 to 1:10, even more preferably from 5:1 to 1:5, more preferably still from 2:1 to 1:4 and most preferably from 1:1 to 1:3.

- The composition may comprise emulsifier. However emulsifiers may interfere with the
20 clustering and/or surface properties of the silica-based particles and/or may cause the silicone to be emulsified into droplets which scatter light and cause opacity. Thus it is preferred that the composition is essentially free from emulsifier. In particular the composition preferably comprises less than 1% emulsifier by weight of the composition, more preferably less than 0.5%, more preferably still less than 0.1%, even more preferably
25 less than 0.01% and most preferably from 0 to 0.001%.

- The composition of this invention may be useful for preparing long-lasting or even permanent coating. For example the composition may comprise an overprint varnish or may be a premix suitable for combining with an overprint varnish. Suitable compositions
30 and varnishes are described in our co-pending International Patent Application with

- 12 -

application no. PCT/CN2011/000842 filed on 16 May 2011 and which is hereby incorporated by reference in its entirety. In particular, the composition may be a premix suitable for preparing an overprint varnish and comprising:

- 5 (i) 50 parts by weight hexamethyldisilazane-modified silica particles (such as Aerosil R812), 50 parts by weight alkylpolysiloxane oligomer (such as Bluestar BP9400), and 786 parts by weight isopropyl alcohol; or
- (ii) 25 parts by weight hexamethyldisilazane-modified silica particles (such as Aerosil R812), 50 parts by weight alkylpolysiloxane oligomer (such as Bluestar BP9400), and 786 parts by weight isopropyl alcohol; or
- 10 (iii) 50 parts by weight hexamethyldisilazane-modified silica particles (such as Aerosil R812), 10 parts by weight dimethicone (such as Dow Corning D200), and 786 parts by weight isopropyl alcohol; or
- (iv) 50 parts by weight hexamethyldisilazane-modified silica particles (such as Aerosil R812), 50 parts by weight reactive siloxane polymer (such as Dow
- 15 Coming SL-7588), and 786 parts by weight isopropyl alcohol; or
- (v) 50 parts by weight hexamethyldisilazane-modified silica particles (such as Aerosil R812), 50 parts by weight alkylpolysiloxane oligomer (such as Bluestar BP9400), 200 parts by weight octane, 15 parts by weight emulsifier (such as OP-10), and 100 parts by weight water.
- 20 Alternatively the composition may be a composition other than one comprising the specific combinations (i), (ii), (iii), (iv) or (v) of particle, silicone and solvent disclosed above.

In a most preferred embodiment of the invention the composition does not form a permanent coating on application and is preferably free from varnish.

25

The composition of the present invention is preferably used to treat a hard surface, especially to aid cleaning or soil-resistance of the hard surface. "Hard surface" for the purposes of the present invention means any surface comprising a hard material such as glass, glazed ceramics, metal, stone, plastics, lacquer, wood, or combination thereof.

- 13 -

Typically, the hard surface is in a household including window, kitchen, bathroom, toilet, furniture, floor, or the like. Preferably the hard surface comprises, or is, glass.

5 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.

10 The composition of the invention may be made in any convenient way. Suitably, however, the composition is prepared by a process comprising the step of combining, in no particular order, the silica-based particles, at least a first part of the solvent and the silicone to provide a mixture.

15 Where the solvent comprises polar organic solvent it is preferred that the first part of the solvent comprises the polar organic solvent. In this way good mixing of the components is achieved owing to the miscibility of the silicone and polar organic solvent.

20 Following formation of the mixture, a second part of the solvent may be added to the mixture, if desired. In one especially preferred embodiment the second part of the solvent comprises (and most preferably is) water.

The composition of the invention is used to prepare a superhydrophobic coating. The method for making a superhydrophobic coating on a surface preferably comprises the steps of applying the composition to a surface and allowing the composition to dry.

25

Typically, after drying, the coating will comprise less than 30% solvent by weight of the coating, more preferably less than 20%, more preferably still less than 10% and most preferably from 0.001 to 5%.

- 14 -

The coating is superhydrophobic. In some instances, for example, the coating may display a contact angle for water of at least 145 degrees or even from 150 to 160 degrees. Additionally or alternatively the coating may display a sliding angle for water of less than 15 degrees or even from 0.1 to 10 degrees.

5

The coating is typically at least translucent and often transparent. For example, the coating may display a transmittance value of at least 80%, more preferably at least 85% and most preferably from 87 to 95%.

- 10 The surface is preferably a hard surface, especially a hard surface in a household including the window, kitchen, bathroom, toilet, furniture, floor, or the like or any surface in car, ship, or airplane 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
- 15 ceramics, metal, stone, plastics, lacquer, wood, or combination thereof. Especially, the composition according to the invention is applied to coat the hard surface of window, kitchen, bathroom, and/or toilet. Most preferably, the surface is, or comprises, glass.

- In a preferred embodiment the coating is applied to the hard surface; stains and/or soil is
- 20 then allowed to deposit on the coating; and the surface is then cleaned to remove the stains and/or soil. Preferably a composition according to the invention is also applied to the surface during and/or after the step of cleaning to remove the stains and/or soil.

EXAMPLES

25

Materials

- Aerosil®R812S was hexamethyldisilazane-modified silica particles (average primary particle size 7 nm) supplied by Evonic AG.
- Aerosol®R805 was octylsilane-modified silica particles (average primary particle size
- 30 12 nm) supplied by Evonic AG.

- 15 -

- Aerosol[®]R974 was dichlorodimethylsilane-modified silica particles (average primary particle size 12 nm) supplied by Evonic AG.
- Aerosol[®]R972 was dichlorodimethylsilane-modified silica particles (average primary particle size 16 nm) from Evonic AG.
- 5 - RHODORSIL[®] BP9400 was alkylpolysiloxane oligomer from Bluestar Silicones and had a refractive index of 1.42.
- XIAMETER[®] PMX-200 silicones were dimethicones with viscosity of 5 cSt (DC 5), 50 cSt (DC 50), 200 cSt (DC 200) or 350 cSt (DC 350) supplied by Dow Corning and with refractive index of between 1.396 (for DC 5) and 1.403 (for DC 350).

10

All other materials were analytical grade unless otherwise stated.

Characterisation of Films

- Drop shape analysis system 100 (DSA 100, Krüss) was used to measure contact
15 angle and sliding angle. DSA 100 with the tilting table maximum utilization of field of view up to 90 degrees was used for sliding angle test using deionised water drops of around 5 µL applied to five different points of each film and the sliding angle averaged over all 5 drops.
- The visible light transmittance of the superhydrophobic coating was measured by a
20 UV-Vis spectrometer (Perkin-Elmer Lambda 650S).
- Particle size in dispersions (i.e. prior to drying) was measured by Malvern Zetasizer-nano instrument.
- Durability of films was determined using the pull-off test method with Scotch 600 tape (3M) as described in M.H. Blees et al. (*Thin Solid Film*, 359, 1).

25

Example 1

This example demonstrates the effect of composition on the contact angle and sliding angle of films.

Liquid compositions were prepared with various amounts of silica-based particles (Aerosil®R812S), silicone (RHODORSIL® BP9400) and solvent (ethanol or isopropanol). These compositions and the contact angle (CA) and sliding angle (SA) of the films remaining after drying the compositions on a surface are shown in Table 1.

5 TABLE 1

Sample	Composition (wt %)				CA (degrees)	SA (degrees)
	Silicone	Particles	Isopropanol	Ethanol		
1	2.00	---	98.00	---	102	>90
2	5.00	---	95.00	---	106	>90
3	10.00	---	90.00	---	110	>90
4	15.00	---	85.00	---	108	>90
5	---	2.00	98.00	---	153	0.5
6	0.29	2.63	97.08	---	148	<10
7	0.65	5.85	93.50	---	143	<10
8	0.87	1.55	97.58	---	154	<10
9	2.20	3.96	93.84	---	148	<10
10	0.80	2.00	---	97.20	151	<10

The highest contact angle of film prepared without silica-based particles (samples 1 to 4) was about 110 degrees. SEM images of these films showed a smooth and compact surface and so hydrophobicity of the film is mainly attributed to low surface energy of
10 silicone.

The film prepared without silicone (sample 5) was superhydrophobic and SEM images of the film showed the fumed silica particles assembled into a hierarchical structure.

15 When silicone was used as to increase film durability (samples 6 to 10) the hydrophobicity is slightly decreased compared with the film without silicone (sample 5). However, these films remained superhydrophobic and SEM images showed the fumed silica particles

assembled into a hierarchical structure, albeit a more dense structure than was observed for sample 5.

Example 2

- 5 This example demonstrates the effect of silicone on the size of microclusters of silica-based particles dispersed in ethanol.

Dispersions were prepared containing 2 wt% Aerosil®R812S in ethanol either with or without 0.8 wt% RHODORSIL® BP9400. The average size (z-average) of the aggregates
10 in the dispersion containing silicone was 248 nm whilst for the dispersion without silicone the size was 196 nm. Thus the silicone acts to produce larger microclusters but the microclusters are still of a size below the wavelength of visible light.

Example 3

- 15 This example demonstrates the effect of silicone viscosity on appearance and hydrophobicity of films.

Dispersions were prepared containing 2 wt% silica particles in ethanol with 0.8 wt% dimethicone fluid with various viscosities. Particle size was measured in the dispersions
20 whilst transmittance and contact angle were determined on the dried films. The results are shown in Table 2.

TABLE 2

Silicone	Silica	z-average size (nm)	Transmittance (%)	CA (degrees)
DC 5	Aerosil [®] R812S	180	91	151
DC 50	Aerosil [®] R812S	179	89	150
DC 200	Aerosil [®] R812S	217	90	152
DC 350	Aerosil [®] R812S	237	80	149
DC 5	Aerosol [®] R974	257	91	146
DC 50	Aerosol [®] R974	268	87	145
DC 200	Aerosol [®] R974	255	89	143
DC 350	Aerosol [®] R974	278	89	140

All the films show good hydrophobicity (CA > 140 degrees) but the films prepared by R812S/silicone show higher contact angle comparing with films prepared by R974/silicone.

- 5 Film transparency is a direct index of resulting appearance of film on different substrates. Transparency of film was quantitatively reflected by film transmittance at 550 nm wavelength. In general, all the films show good transparency comparing with blank glass (T 89%). From the results a trend is found that size of silica aggregates in dispersion increase as silicone viscosity increases. For silica R812S, the average size of silica
- 10 aggregates changes from 180 nm to 237 nm when silicone changes from DC 5 to DC 350 and the smaller silica aggregates in dispersion lead to higher transparency of film. For silica R974, the average size of silica aggregates increases from 257 nm to 278 nm when silicone changes from DC 5 to DC 350 but there is no clear relationship between the average size of silica clusters and the transparency of film.

15

Example 4

This example demonstrates the effect of silicone viscosity on durability of films.

Films were prepared from dispersions containing 2 wt% Aerosil® R812S in ethanol and 0.8 wt% dimethicone fluid with various viscosities and the durability determined by the pull-off tape test. The results are shown in Table 3.

5 TABLE 3

Silicone	Contact Angle Before Test (degrees)	Contact Angle After Pull- Off (degrees)
DC 5	151	31
DC 50	150	56
DC 200	152	97
DC 350	149	144

It is clear from these results that higher viscosity silicones provide more resistance to peeling and scratching of the film.

10 Example 5

This example demonstrates the effect of the type of surface modification of fumed silica particles on film properties.

15 Dispersions were prepared containing 2 wt% silica particles in ethanol with 0.8 wt% dimethicone fluid (DC 200). Particle size was measured in the dispersions whilst transmittance and contact angle were determined on the dried films. The results are shown in Table 4.

TABLE 4

Aerosil[®] Type	Surface Modification*	Unbundled Size (nm)	z-average size (nm)	Transmittance (%)	CA (degrees)
R812S	HDMS	7	217	90	152
R805	OTS	12	253	88	150
R974	DDS	12	206	90	146
R972	DDS	16	282	85	143

*HDMS = hexamethyldisilazane; OTS = octylsilane; DDS = dichlorodimethylsilane.

- 5 All films were superhydrophobic but the films containing DDS modified fumed silica were less hydrophobic than those made with HDMS or OTS-modified fumed silica.
- Transparency of the films correlated well with size of microclusters in the dispersions from which they were prepared with larger microclusters leading to less transparent films.

10 Example 6

This example demonstrates superhydrophobic films made from dispersions wherein the solvent comprises water.

Dispersions were prepared as follows:

- 15 - Silica-based particles (Aerosil[®]R812S) and silicone (RHODORSIL[®] BP9400) were dispersed in low molecular weight alcohol (ethanol or isopropanol).
- Water was then added to provide the final dispersion.

- 20 The compositions studied and the resulting properties (contact angle and sliding angle) of films made by drying the compositions are given in Table 5.

TABLE 5

Sample	Composition (wt%)					CA (degrees)	SA (degrees)
	Silicone	Particles	Isopropanol	Ethanol	Water		
A	0.80	2.00	48.60	---	48.60	154	<10
B	0.80	2.00	---	48.60	48.60	152	<10
C	0.80	2.00	---	29.16	68.04	151	<10

Example 7

This example demonstrates compositions suitable for use as overprint varnishes.

5

Varnish 7A:

Fifty (50) grams of silica, made commercially available by Evonik Degussa GmbH as Aerosil R812 (particle size about 7 nm), were combined with fifty (50) grams of polydimethylsiloxane made commercially available by Bluestar Silicones under the Bluestar BP9400 name and one (1) litre of isopropyl alcohol. The resulting combination was vigorously mixed to produce a diluted hydrophobic premix wherein mixing was achieved under conditions of standard temperature and pressure. The premix was added to one (1) kilogram of commercially available non-aqueous overprint varnish, GOP-190, made available by Dainippan Ink and Chemicals, Inc. and thoroughly mixed to produce the final varnish.

15

Varnish 7B:

This varnish was made in a manner similar to Varnish 7A except that twenty five (25) grams of silica (Aerosil R812, particle size 7 nm) was used with twenty-five (25) grams of titanium dioxide (particle size 100 nm).

20

Varnish 7C:

This varnish was made in a manner similar to Varnish 7A except that ten (10) grams of D200 silicone, made commercially available by Dow Corning, was used in lieu of the polydimethylsiloxane made available by Bluestar.

25

- 22 -

Varnish 7D:

This varnish was made in a manner similar to Varnish 7A except that fifty (50) grams of silicone (SL-7588 made commercially available by Dow Corning) and two (2) grams of silane-based cross-linking agent was used.

5

Varnish 7E:

Fifty (50) grams of silica (R812S), fifty (50) grams of silicone (Bluestar BP9400), two hundred (200) grams of octane and fifteen (15) grams of OP-10 emulsifier were combined with one hundred (100) grams of water and vigorously mixed under atmospheric conditions and ambient temperature in order to produce an emulsion having particles dispersed therein. The particles dispersed within the emulsion (i.e., oil-in-water emulsion) were then combined with one (1) kilogram of aqueous varnish sold under the Mouben® name as MB-308. The resulting mixture was vigorously stirred in order to produce the final varnish.

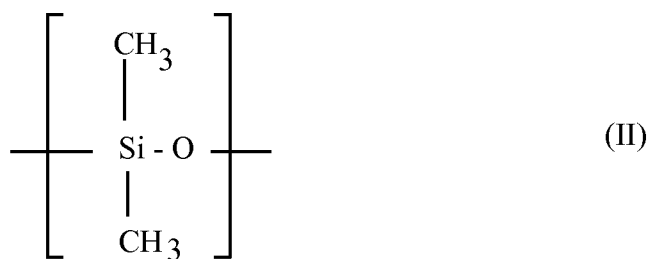
10

15

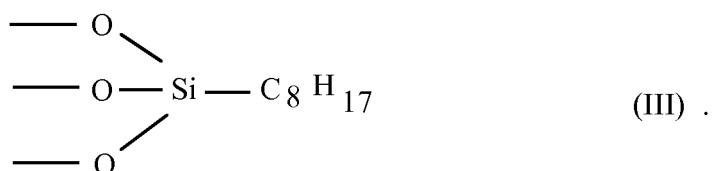
- 23 -

CLAIMS

1. A composition capable of yielding a superhydrophobic coating, the composition comprising
 - (a) microcluster of silica-based particles, the microcluster having a diameter from 1
5 nm to 400 nm;
 - (b) silicone having a viscosity of at least 30 cSt; and
 - (c) solvent.
2. The composition as claimed in claim 1, wherein the microcluster has a diameter of
10 less than 300 nm, preferably in the range 100 to 250 nm.
3. The composition as claimed in claim 1 or claim 2, wherein the silica-based particles are hydrophobically-modified fumed silica particles.
- 15 4. The composition as claimed in claim 3, wherein the silica-based particles comprise at least one of the following groups:



or



- 24 -

5. The composition as claimed in any one of the preceding claims, wherein the silicone has a viscosity of less than 1000 cSt, preferably in the range 100 to 500 cSt.
- 5 6. The composition as claimed in any one of the preceding claims, wherein the silicone is polydimethylsiloxane.
7. The composition as claimed in any one of the preceding claims, wherein the silica-based particles have a refractive index n_p , the silicone has a refractive index n_s and the ratio (n_p/n_s) of n_p to n_s is within the range 0.9 to 1.1, preferably in the range 0.93 to 1.07.
- 10 8. The composition as claimed in any one of the preceding claims, wherein the solvent has a refractive index n_a in the range 1.2 to 1.6, preferably 1.3 to 1.5.
- 15 9. The composition as claimed in any one of the preceding claims wherein the ratio (n_p/n_a) of n_p to n_a is within the range 0.9 to 1.1, preferably in the range 0.93 to 1.07.
- 20 10. The composition as claimed in any one of the preceding claims wherein the solvent comprises a polar organic solvent, preferably a C₁-C₄ alcohol.
11. A process for making the composition of as claimed in any one of the preceding claims, comprising the step of combining, in no particular order, the silica-based particles, at least a first part of the solvent and the silicone to provide a mixture.
- 25 12. The process as claimed in claim 11, wherein the first part of the solvent comprises a polar organic solvent.
- 30 13. The process as claimed in claim 12, wherein a second part of the solvent is added to the mixture.

- 25 -

14. The process as claimed in claim 13, wherein the second part of the solvent comprises water.
- 5 15. A method for making a superhydrophobic coating on a surface, the method comprising the steps of applying the composition as claimed in any one of claims 1 to 10 to a surface and allowing the composition to dry.
16. A superhydrophobic coating obtainable by the method of claim 15.
- 10 17. The superhydrophobic coating as claimed in claim 16, wherein the coating displays a contact angle for water of at least 150 degrees, a sliding angle for water of less than 10 degrees, or both.

15

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2012/057242

A. CLASSIFICATION OF SUBJECT MATTER
INV. C09D183/00
ADD.

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C09D

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.
X,P	WO 2012/003004 A2 (UNIV PITTSBURGH [US]; GAO DI [US]) 5 January 2012 (2012-01-05) paragraph [0003] claims 1,5,9,16,21-23; figures 1-6; example 5	1-17
X	WO 2011/020701 A1 (UNILEVER PLC [GB]; UNILEVER NV [NL]; UNILEVER HINDUSTAN [IN]; LI JIN Y) 24 February 2011 (2011-02-24) cited in the application page 3, line 4 - page 5, line 3 claims 1,8,15-19; examples 1-6 ----- -/-	1-17



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

6 June 2012

Date of mailing of the international search report

13/06/2012

Name and mailing address of the ISA/

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040,
Fax: (+31-70) 340-3016

Authorized officer

Glomm, Bernhard

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2012/057242

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 2004/037944 A1 (JOHNSON & SON INC S C [US]) 6 May 2004 (2004-05-06) cited in the application paragraph [0013] - paragraph [0020] claims 1,5,11-14; figures 1-8; examples 4,6 -----	1-17
X	EP 1 153 987 A2 (BASF AG [DE]) 14 November 2001 (2001-11-14) cited in the application paragraph [0013] - paragraph [0018] claims 1-5,8,13-17; examples 19-22 -----	1-17
X	US 2011/021663 A1 (SACKS ABRAHAM J [CA] ET AL) 27 January 2011 (2011-01-27) paragraph [0015] - paragraph [0021] claims 1-5,9-14,17,19; figures 1-3; example 1 -----	1-17
X	DE 197 54 446 A1 (DYCKERHOFF AG [DE]) 10 June 1999 (1999-06-10) page 3, line 18 - line 67 claims 1,7,11,32 -----	1-17
X	JP 6 057239 A (SHINETSU CHEMICAL CO) 1 March 1994 (1994-03-01) the whole document -----	1-17

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/EP2012/057242

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 2012003004	A2	05-01-2012	NONE
WO 2011020701	A1	24-02-2011	AR 077939 A1 05-10-2011 CA 2767877 A1 24-02-2011 EP 2467417 A1 27-06-2012 WO 2011020701 A1 24-02-2011
WO 2004037944	A1	06-05-2004	AU 2003286586 A1 13-05-2004 CA 2503059 A1 06-05-2004 EP 1556457 A1 27-07-2005 US 2004127393 A1 01-07-2004 WO 2004037944 A1 06-05-2004
EP 1153987	A2	14-11-2001	AT 325166 T 15-06-2006 DE 10022246 A1 15-11-2001 EP 1153987 A2 14-11-2001 ES 2263530 T3 16-12-2006 JP 2002038102 A 06-02-2002 US 2002016433 A1 07-02-2002
US 2011021663	A1	27-01-2011	NONE
DE 19754446	A1	10-06-1999	AT 199143 T 15-02-2001 CZ 9804020 A3 16-06-1999 DE 19754446 A1 10-06-1999 DK 922683 T3 05-06-2001 EP 0922683 A1 16-06-1999 ES 2156640 T3 01-07-2001 HU 9802794 A2 28-10-1999 NO 985438 A 09-06-1999 PL 330167 A1 21-06-1999 SI 9800298 A 30-06-1999 SK 167898 A3 06-08-1999
JP 6057239	A	01-03-1994	NONE