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(54) **Title**: GLASS CLEANER

(57) **Abstract**: Disclosed is a glass cleaning composition comprising silanized colloidal silica particles and surfactant. The glass cleaning composition has a pH less than 8, a turbidity of less than 100 NTU and is capable of providing a ultrahydrophilic coating on a glass surface.

GLASS CLEANER

FIELD OF THE INVENTION

The present invention relates to a composition for cleaning glass. In particular, the present invention relates to a composition which comprises silanized colloidal silica particles and surfactant and which is capable of cleaning glass to leave a coating which provides resistance to staining and/or soiling.

BACKGROUND OF THE INVENTION

With increasing global urbanization and improvement of living conditions, especially in developing countries, more and more people inhabit spaces with more household surface to clean. Also people are increasingly seeking relief from housework to have more time for other activities. Therefore, the requirement of consumers for household cleaning products is continually increasing. Other than the basic cleaning function, benefits including less cleaning effort, less time to clean, and a better cleaning result are desired of such cleaning products.

Cleaning of surfaces which are transparent and/or required to be reflective can be particularly demanding. This is because the optical properties of such surfaces can be compromised by even a tiny amount of dirt or residue of product. In this respect, forming a water-sheeting layer during cleaning and after cleaning may be desirable. Water which forms sheets on the surface (rather than discreet droplets) tends to dry easily due to the water spreading area being lager upon sheeting. Also drying will be more uniform such that unappealing water marks will not be formed onto the hard surfaces, giving the consumer an appealing appearance, even when the hardness of water is high. Moreover, for subsequent cleaning, the soil particulates will be distributed uniformly on the hard surface instead of aggregated within the water marks, due to the uniform water film. Thus the period between cleaning can be prolonged, so saving time and effort for consumers.

Efforts have been made to provide hard surface cleaning composition for water spreading benefit. US patent published as US7699941 (The Clorox Company) discloses cleaning composition comprising a water-soluble or water-dispersible copolymer. The cleaning compositions are said to enhance hard surfaces to exhibit excellent water-spreading and oil-repellency and therefore provide a next time easier cleaning consumer benefit.

US patent published as US7745383 (Henkel AG & Co. KGaA) discloses cleaner for hard surfaces, especially glass. Application of the cleaner containing a colloidal silica sol results in a modification of the steaming potential of the surface by -5 to -50 mV. The cleaner is said to be used to hydrophilize and clean hard surfaces.

International patent application published as WO 2009/121682 (Unilever) discloses use of citric acid and/or a salt of citric acid in cleaning composition for cleaning hard surfaces. The use of citric acid and/or a salt of citric acid will facilitate the removal of soil and obtain a next time cleaning benefit.

International patent application published as WO 2005/097961 (AKZO NOBEL N.V.) discloses a method of preparing an aqueous detergent dispersion comprising mixing at least one silane compound, colloidal silica particles, and a detergent to form an aqueous detergent dispersion comprising silanized colloidal silica particles. The detergent dispersions are said to be useful in the treatment of hard surfaces as well as of fibre and textile surfaces. In one embodiment the dispersion is a glass cleaner.

However, the robustness of any layer deposited during cleaning with known compositions is not always good. Often after rinsing, the layer may deteriorate and visible residue may become apparent. We have recognized a need to develop a composition for cleaning glass which can deposit a robust hydrophilic layer onto the glass. The present invention, therefore, is directed to a glass cleaning composition. More particularly, the invention involves the use of non-basic compositions comprising silanized colloidal silica particles

and surfactant to treat surfaces comprising glass. The treated glass surface surprisingly has good resistance to soil and stains even after repeated rinsing.

DEFINITIONS

Hydrophilic

"Hydrophilic" 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 water (in preference to oil), or a surface that has a contact angle against water of less than 90º. "Ultrahydrophilic" as used herein means having a contact angle of less than 30° against water. "Superhydrophilic" as used herein means having a contact angle of less than 10° against water. Contact angle, as used herein, means the angle at which a water/vapour interface meets a solid surface at a temperature of 25 °C. Such an angle may be measured with a goniometer or other water droplet shape analysis systems.

pH

pH values referred to herein are measured at a temperature of 25 °C.

Turbidity

Turbidity values referred to herein are in Nephelometric Turbidity Units (NTU) unless otherwise stated. Nephelometric Turbidity Units are also referred to in the art variously as Formazin Turbidity Units (FTU) or Formazin Nephelometric Units (FNU). Determination of turbidity can be made using a nephelometer complying with ISO 7027 or EPA 180.1. Preferably turbidity is determined at a temperature of 25 °C.

Particle Size

Particle size as used herein refers to particle diameter unless otherwise stated. Diameter is meant to mean the largest measurable distance on a particle or aggregate in the event a well-defined sphere is not generated. For polydisperse samples, 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 Nano™ (Malvern Instruments Ltd, UK).

"Primary particle size" refers to the diameter of particles in an unaggregated state.

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".

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.

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*.

SUMMARY OF THE INVENTION

In a first aspect, the present invention provides a glass cleaning composition comprising:

(a) silanized colloidal silica particles; and

(b) surfactant;

wherein the glass cleaning composition has a pH less than 8, a turbidity of less than 100 NTU and is capable of providing a ultrahydrophilic coating on a glass surface

In a second aspect the present invention provides a method of cleaning a surface comprising glass, the method comprising a step of treating the surface with the composition of the first aspect.

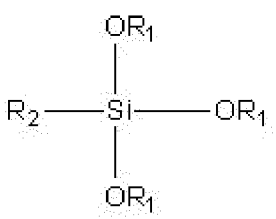
In a third aspect the present invention provides a process for manufacturing the composition of the first aspect, the process comprising combing the silanized colloidal silica particles and surfactant to provide a mixture and adjusting or controlling the pH of the mixture to a value less than 8.

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

DETAILED DESCRIPTION

There is no limit to the silanized colloidal silica particles that may be employed in the present invention, save that they must be compatible with surfactant such that the final composition is capable of providing an ultrahydrophilic coating on a glass surface.

Typically the colloidal silica particles are silanized (or at least obtainable by silanization) with hydrophilic silane, more preferably with hydrophilic silane having general formula (I):



(I)

wherein
each R_1 is independently selected from H and hydrolysable alkyl group having 1 to 6 carbon atoms (for example, each R_1 may be independently selected from H, methyl, ethyl and propyl); and
R_2 is a hydrophilic group.

Especially preferred are colloidal silica particles silanized with hydrophilic silane having general formula (I) and wherein R_2 comprises hydroxyalkyl, aminoalkyl, alkoxy, halogen, glycidoxyalkyl, gluconamidealkyl, polyethylene glycol, polyethylene imine or combinations thereof. Even more preferably, R_2 is selected from glycidoxyalkyl, gluconamidealkyl, polyethylene glycol, polyethylene imine or combinations thereof. Most preferably R_2 is glycidoxypropyl or gluconamidepropyl.

Examples of suitable silanized colloidal silica particles include those described in WO 2005/097961 (hereby incorporated by reference in its entirety).

The silanized colloidal silica particles may be derived from e. g. precipitated silica, micro silica (silica fume), pyrogenic silica (fumed silica) or silica gels with sufficient purity, and mixtures thereof.

The silica particles may be modified and can contain other elements such as amines, aluminium and/or boron, however preferably the silanized colloidal silica particles comprise at least 90% by weight silica, more preferably at least 93%, even more preferably 95%, even more preferably still at least 97% and most preferably from 98 to 100% by weight of the particles including all ranges subsumed therein.

The colloidal silica particles suitably have a primary particle size ranging from 2 to 150 nm, preferably from 3 to 50 nm, and most preferably from 5 to 40 nm. Suitably, the colloidal

silica particles have a specific surface area from 20 to 1500, preferably from 50 to 900, and most preferably from 70 to 600 m^2/g.

The composition may contain besides silanized colloidal silica particles also, at least to some extent, non-silanized colloidal silica particles depending on the size of the silica particles, weight ratio of silane to silica, type of silane compound, reaction conditions etc. Suitably, at least 40% of the total amount of colloidal silica particles are silanized, preferably at least 65%, more preferably at least 90%, and most preferably from 99 to 100 wt%.

The composition may comprise besides silane in the form of silane groups or silane derivatives bound or linked to the surface of the silanized colloidal silica particles also at least to some extent freely dispersed unbound silane compounds. Suitably, at least 40%, preferably at least 60%, more preferably at least 75%, even more preferably at least 90%, and most preferably from 95 to 100 wt% of the total amount of silane groups are bound or linked to the surface of the silica particles.

Suitably, at least 1% by number of the silanol surface groups on the colloidal silica particles are bound or linked to a silane group, preferably at least about 5%, more preferably at least about 10%, even more preferably at least about 30%, and most preferably from 50 to 100% bind or link to a silane group.

Preferably, the weight ratio of the total silane content to the total silica content in the composition is from about 0.01 to about 1.5, more preferably from about 0.05 to about 1, and most preferably from about 0.05 to about 0.5.

Particularly preferred are silanized colloidal silica particles made commercially available by AkzoNobel under the trade name Bindzil™ and especially Bindzil™ CC301.
The composition preferably comprises the silanized colloidal silica particles in an amount of from 0.001 to 4% by weight, more preferably from 0.01 to 2% by weight, even more

preferably from 0.02 to 1% by weight and most preferably from 0.04 to 0.5% by weight of the composition including all ranges subsumed therein.

Surprisingly the present inventors have found that the robustness of a hydrophilic layer formed on glass by silanized colloidal silica particles is significantly enhanced at pH values lower than those typically used in glass cleaning compositions. Thus the glass cleaning composition of the present invention has a pH less than 8, preferably the pH is in the range 1 to 7, more preferably in the range 2 to 6, more preferably still 2 to 5, and most preferably 3 to 4.

Glass cleaning compositions of the present invention are typically transparent or at least translucent so that any residue formed during cleaning has minimum visibility. Thus the composition of the present invention has a turbidity of less than 100 NTU, preferably less than 50 NTU, more preferably less than 30 NTU, more preferably still less than 20 NTU and most preferably in the range 0.01 to 10 NTU.

The composition of the present invention is suitable for cleaning and therefore comprises surfactant. The surfactant may be anionic, non-ionic, cationic, amphoteric, zwitterionic or a mixture thereof. However we have found that anionic surfactants in particular can be employed in the composition of the invention without interfering with the ability of the silanized colloidal silica particles to form a hydrophilic layer on glass. Thus preferably the surfactant comprises anionic surfactant, more preferably at least 50% by total weight of surfactant in the composition is anionic surfactant, more preferably still at least 75% by weight, most preferably from 80 to 100%.

The anionic surfactant preferably comprises alkyl ether sulphate, alkyl benzene sulphonate, secondary alkane sulphonate, primary alkyl sulphate, alpha olefin sulphonate, alkyl carboxylates, or a mixture thereof.

Examples of such anionic surfactants are salts of

- Alkyl benzene sulphonate, such as those in which the alkyl group contains of 6 to 20 carbon atoms, typically 10 to 20 carbon atoms;
- Secondary alkane sulphonate, especially those in which the alkane group have 15 to 17 carbon atoms;
- Primary alkyl sulphate, especially those wherein the alkyl contains 12 to 14 carbon atoms;
- Alkyl ether sulphate having 12 to 15 carbon atoms and with 1 to 3 ethoxy groups;
- Alpha olefin sulphonate wherein the alpha olefin contains 14 to 16 carbon atoms;
- Alkyl carboxylates wherein the alkyl group contain 10 to 18 carbon atoms;

or a mixture thereof.

The preferred anionic surfactants are the alkali metal (such as sodium and potassium) and/or alkaline earth metal (such as calcium and magnesium) salt of alkyl ether sulphate having 10 to 20 carbon atoms and 1 to 5 ethoxy groups, and/or alkyl benzene sulphonate wherein the alkyl contains 10 to 14 carbon atoms. More preferably, the anionic surfactants comprise sodium lauryl ether sulphate, linear alkyl benzene sulphonate sodium, mixtures thereof, or the like.

Typically, the composition comprises the surfactant in an amount of from 0.01 to 4% by weight, more preferably 0.02 to 1%, more preferably still 0.03 to 0.7%, even more preferably 0.04 to 0.5%, most preferably 0.05 to 0.3%. Additionally or alternatively the composition preferably comprises the silanized colloidal silica particles and surfactant in a weight ratio of from 10:1 to 1:10, more preferably from 5:1 to 1:5 and most preferably from 2:1 to 1:2.

The glass cleaning composition is found to be highly compatible with water which may be important from an environmental and/or safety perspective. In particular the composition may comprise water in an amount of at least 90% by weight, more preferably from 95 to 99% by total weight of the composition.

It may be advantageous to include organic compounds (such as solvents) in the composition as such compounds and/or solvents may assist in removal of certain soil and stains. Suitable organic compounds include, for example, ethylene glycol methyl ether, ethylene glycol ethyl ether, ethylene glycol propyl ether, ethylene glycol mono-n-butyl ether, diethylene glycol methyl ether, diethylene glycol ethyl ether, propylene glycol methyl, ethyl or propyl ether, dipropylene glycol monomethyl or monoethyl ether, diisopropylene glycol monomethyl or monoethyl ether, methoxy, ethoxy or butoxytriglycol, 1-butoxyethoxy-2- propanol, 3-methyl-3- methoxybutanol, propylene glycol t-butyl ether, alcohols, more particularly C_{1-4} alkanols, glycols, polyethylene glycols, preferably with a molecular weight of 100 to 100,000 and more particularly in the range from 200 to 10,000 and polyols, such as sorbitol and mannitol, and polyethylene glycol liquid at room temperature, carboxylic acid esters, polyvinyl alcohols, ethylene oxide/propylene oxide block copolymers and mixtures of the above. Amounts of such organic compounds preferably range from 0.01 to 10 wt% by total weight of the composition, more preferably from 0.1 to 7% and most preferably 1 to 5% by total weight of the composition including all ranges subsumed therein. The most preferred organic compound is the solvent PnP (1-propoxy-2-propanol).

The composition may further comprise a component to improve water sheeting effect and/or increase the robustness of water sheeting effect. Such component may comprise an organic acid. Exemplary acids include, without limitation, citric acid, glycolic acid, lactic acid, acetic acid, gluconic acid, malonic acid, maleic acid, benzoic acid, acrylic acid, polyacrylic acid, acrylic acid/maleic acid copolymer, methyl vinyl ether/maleic acid copolymer and mixtures thereof. The most preferred acid being lactic acid. The preferred amount is in the range of 0.01% to 4% organic acid by weight of the composition, more preferably from 0.05 to 2 wt% and most preferably from 0.1 to 1% by total weight of the composition including all ranges subsumed therein.

The composition may also comprise colourants, whiteners, optical brightness, soil suspending agents, detersive enzymes, bleaching agent, gel-control agents, freeze-thaw stabilisers, bactericides, abrasives, preservatives, and/or perfumes, provided that the presence of such components does not cause undue turbidity and/or interfere with the ability of the colloidal silica particles to form a hydrophilic layer on glass.

Occasionally glass cleaning compositions contain polyvinyl alcohol. We have found however that presence of polyvinyl alcohol in the compositions of the present invention is not required to achieve good cleaning results. Therefore it is preferred that compositions according to the present invention comprise less than 0.1% polyvinyl alcohol by weight of the composition, more preferably less than 0.05%, more preferably still less than 0.01% and most preferably from 0 to 0.001% by weight of the total composition including all ranges subsumed therein.

When cleaning glass with the composition, any general way for cleaning glass is acceptable. Typically, the way for treating a hard surface comprising glass by the composition is by spraying the composition onto the hard surface, or wiping the hard surface by wipe impregnated with the composition, or dripping 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.

Whilst not being bound by any particular theory or explanation, we believe that the composition exerts it effect by depositing silanized colloidal silica particles onto glass, forming a layer attached to the glass. The layer is hydrophilic and so can enhance water

spreading behaviour. Water will be easily spread along the hard surface, resulting in a better visual appearance. In addition the layer is robust and resists soiling or staining even after multiple rinses.

Thus the composition of the invention is capable of providing an ultrahydrophilic coating on a glass surface. More preferably the composition is capable of providing a coating on glass, wherein the coating has a contact angle of less than 20 degrees. More preferably still the composition of the invention is capable of providing a superhydrophilic coating on a glass surface, most preferably the composition is capable of providing a coating on glass, wherein the coating has a contact angle in the range 1 to 8 degrees.

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

A preferred method for cleaning a surface comprising glass, comprises the steps in sequence of:

(i) treating the surface with composition according to the invention;
(ii) allowing the soil or stains to deposit on the surface; and
(iii) cleaning the surface (preferably with the composition of the invention) to remove the soil or 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, and/or scratch resistance. Further aspects of the present invention comprise methods for obtaining one or more these other benefits in a glass cleaning operation and/or use the composition in methods

for the manufacture of products for delivering any one more such benefits mentioned in this invention.

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 glass in windows.

There is no limitation as to how the glass cleaning composition may be made. However, in a preferred aspect, the process for manufacturing the composition comprises combing the silanized colloidal silica particles and surfactant to provide a mixture and adjusting or controlling the pH of the mixture to a value less than 8. When recovering the hard surface cleaning composition from the mixture, any other necessary or optional components may be combined with the mixture.

The composition could be packed in any form of conventional hard surface cleaning product. The preferred packaging is spray applicators. Pump dispensers (weather spray or non-spray pumps) and pouring applicators (bottles etc) are also possible. It is also possible to impregnate a wipe with the composition.

EXAMPLES

Example 1

This example demonstrates the effect of pH on the hydrophilicity and cleanliness of glass surfaces treated with a formulation comprising silanized colloidal silica particles and sufactant.

Materials

Materials used in this example include:

SLES was sodium lauryl ether sulphate (1 EO) from Cognis (Germany);

Bindzil™ CC301 was epoxy-silane (glycidoxypropyl) surface modified colloidal silica having a particle size of 7 nm and supplied by AkzoNobel (USA) as a 30 wt% aqueous dispersion;

PnP was1-propoxy-2-propanol supplied by Dow Chemical with a trade name Dowanol* PnP glycol ether;

Lactic acid was 2-hydroxypropanoic acid and obtained from Sinopharm Chemical Reagent Co. Ltd. as an 85 wt% aqueous solution;

Ammonium hydroxide was obtained from Sinopharm Chemical Reagent Co. Ltd as a 25% aqueous solution;

Deionized water was produced by Milli-Q system (Millipore, USA); and

Hard water was tap water with a French Hardness of 24-26°.

Formulations

Formulations were prepared by mixing the materials at room temperature. The final compositions are given in Table 1. The composition according to the invention (Sample 1) had a pH of about 3 while the comparative composition (Sample 2) had a basic pH above 8. Both formulations were optically clear and had absorption at 750 nm of much less than 0.02, corresponding to a turbidity of much less than about 20 NTU (see K. L. Goodner, "Estimating Turbidity (NTU) From Absorption Data", Sensus Technical Note SEN-TN-0010, available from SENSUS LLC, Hamilton, OH, USA – www.sensusflavors.com).

TABLE 1

Material (wt%)	Sample 1	Sample 2
SLES	0.2	0.2
PnP	2.9	2.9
Lactic Acid	0.2	----
Ammonium Hydroxide	----	0.2
Bindzil™ CC301	0.3*	0.3*
Deionised Water	To 100	To 100

*Amount given is amount of colloidal silica. Actual amount of commercial dispersion added was 1.0 wt%.

Tests

Sample (2 ml) was applied to clean mirrored glass (pre cleaned with Calcite) with a damp Ballerina™ cloth (2.5 w/w hard water) using a film applicator (Model 1133N from Sheen Instruments, UK). Any residue was allowed to dry and buffed out using dry Ballerina™ cloth to a perfect end result. Contact angle of the surface was then measured by placing 5 drops (5 µl each drop) of deionised water at well-spaced locations on the treated glass and averaging the angle over the 5 drops.

Rinsing was then performed with hard water (2 g) which was sprayed onto the glass and allowed to drain and dry. Samples were visually assessed and ranked for cleanliness by trained assessors using a 0-5 scale where 0 indicates no visual residue and 5 indicates severe staining by water marks. The contact angle of the rinsed surface was then measured. The rinsing and drying cycle was performed a total of 5 times. No contact angle measurements were made after the final rinse.

Results

The results of the contact angle measurements are given in Table 2 (errors quoted represent 95% confidence interval).

TABLE 2

Rinse Cycle	Sample 1 Contact Angle (degrees)	Sample 2 Contact Angle (degrees)
Initial Application	6.7±0.3	8.0±0.2
1st	7.1±0.2	18.2±0.8
2nd	31±1	40±2
3rd	40±5	45±7
4th	43±3	42±7

These results show that both samples create a superhydrophilic layer on glass. In fact both samples produced a coating with a contact angle below 10°. However the layer produced by the sample according to the invention (Sample 1) was more robust with the surface remaining significantly more hydrophilic than that produce by Sample 2 even after the second rinse. After the 3rd rinse there was no significant difference in the contact angle for the surfaces produced by the two samples.

The results of the cleanliness assessment are given in Table 3.

TABLE 3

Rinse Cycle	Sample 1 Residue Score	Sample 2 Residue Score
1st	0.5	1.0
2nd	0.5	1.5
3rd	1.0	2.5
4th	2.5	3.0
5th	3.0	4.0

These results show that the sample according to the invention (Sample 1) produced a surface on the glass which was more resistant to staining by hard water than that produced by Sample 2, even after repeated rinsing.

Example 2

This example demonstrates the effect of pH on the hydrophilicity and cleanliness of glass surfaces treated with another formulation comprising silanized colloidal silica particles and sufactant.

Materials and conditions were similar to those described in Example 1. The formulations tested are given in Table 4. The composition according to the invention (Sample 3) had a pH of about 3 while the comparative composition (Sample 4) had a basic pH above 8.

TABLE 4

Material (wt%)	Sample 3	Sample 4
SLES	0.2	0.2
PnP	2.9	2.9
Lactic Acid	0.2	----
Ammonium Hydroxide	----	0.2
Bindzil™ CC301	0.1*	0.1*
Deionised Water	To 100	To 100

*Amount given is amount of colloidal silica. Actual amount of commercial dispersion added was 0.33 wt%.

The results of the contact angle measurements are given in Table 5.

TABLE 5

Rinse Cycle	Sample 3 Contact Angle (degrees)	Sample 4 Contact Angle (degrees)
Initial Application	4±1	3.6±0.6
1st	7±1	10.3±0.3
2nd	19±1	22±1
3rd	22±5	37±1
4th	34±2	37±3

Again these results demonstrate the increased robustness of the hydrophilic surface generated by the composition of the invention (Sample 3) over that of an equivalent composition but having a basic pH (Sample 4).

The results of the cleanliness assessment are given in Table 6.

TABLE 6

Rinse Cycle	Sample 3 Residue Score	Sample 4 Residue Score
1st	0.5	1.0
2nd	0.5	1.0
3rd	2.0	3.0
4th	2.0	3.0
5th	3.0	4.0

These results show that the sample according to the invention (Sample 3) produced a surface on the glass which was more resistant to staining by hard water than that produced by Sample 4, even after repeated rinsing.

Example 3

This example demonstrates the effect of pH on the cleanliness of glass surfaces treated with another formulation comprising silanized colloidal silica particles and sufactant.

Materials and conditions were similar to those described in Example 2 except that colloidal silica silanized with a gluconamidealkyl silane was used in place of the Bindzil™ CC301.

The gluconamidealkyl-silane modified silica was produced as follows: 5 ml of a commercial colloidal silica dispersion (Bindzil™ 2040 – a 40 wt% aqueous dispersion of 20 nm unmodified colloidal silica particles) was diluted with 15 ml deionised water. The diluted dispersion (10 wt%) was thoroughly mixed under magnetic stirring at room temperature.

pH value of the mixture was maintained from 10 to 11. Then 0.1 g GLU-S (50 wt% ethanolic solution of N-(3-triethoxysilylpropyl)gluconamide made commercially available by Gelest Inc) was added over 30 min using a syringe pump. After that, the reaction was further allowed to proceed overnight at room temperature. The as-prepared gluconamidealkyl silane modified silica was stored for formulation afterwards.

The formulations tested are given in Table 7. The composition according to the invention (Sample 5) had a pH of about 3 while the comparative composition (Sample 6) had a basic pH above 8.

TABLE 7

Material (wt%)	Sample 5	Sample 6
SLES	0.2	0.2
PnP	2.9	2.9
Lactic Acid	0.2	----
Ammonium Hydroxide	----	0.2
Silanized Silica	0.2*	0.2*
Deionised Water	To 100	To 100

*Amount given is amount of colloidal silica.

The results of the cleanliness assessment are given in Table 8.

TABLE 8

Rinse Cycle	Sample 5 Residue Score	Sample 6 Residue Score
1st	1.0	1.5
2nd	2.0	2.5
3rd	2.5	3.0
4th	2.5	3.5
5th	3.0	4.0

These results show that the sample according to the invention (Sample 5) produced a surface on the glass which was more resistant to staining by hard water than that produced by Sample 6 even after repeated rinsing.

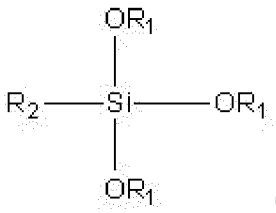
CLAIMS

1. A glass cleaning composition comprising:
   (a) silanized colloidal silica particles; and
   (b) surfactant;
   wherein the glass cleaning composition has a pH less than 8, a turbidity of less than 100 NTU and is capable of providing an ultrahydrophilic coating on a glass surface.

2. The glass cleaning composition as claimed in claim 1, wherein the composition has a pH in the range 1 to 7, preferably in the range 2 to 6.

3. The glass cleaning composition as claimed in claim 1 or claim 2, wherein the composition has a turbidity of less than 50 NTU, preferably in the range 0.01 to 20 NTU.

4. The glass cleaning composition as claimed in any one of the preceding claims, wherein the colloidal silica particles are silanized with hydrophilic silane having general formula (I):



(I)

wherein
each R_1 is independently selected from H and hydrolysable alkyl group having 1 to 6 carbon atoms; and
R_2 is a hydrophilic group.

5. The glass cleaning composition as claimed in claim 4, wherein R_2 comprises hydroxyalkyl, aminoalkyl, alkoxy, halogen, glycidoxyalkyl, gluconamidealkyl, polyethylene glycol, polyethylene imine or combinations thereof.

6. The glass cleaning composition as claimed in claim 5, wherein R_2 is selected from glycidoxyalkyl, gluconamidealkyl, polyethylene glycol, polyethylene imine or combinations thereof.

7. The glass cleaning composition as claimed in claim 6, wherein R_2 is glycidoxypropyl.

8. The glass cleaning composition as claimed in any one of the preceding claims, wherein the surfactant comprises anionic surfactant.

9. The glass cleaning composition as claimed in claim 8, wherein the surfactant comprises alkyl ether sulphate, primary alkyl sulphate, alkyl benzene sulphonate, secondary alkane sulphonate, alpha olefin sulphonate, alkyl carboxylates, or a mixture thereof.

10. The glass cleaning composition as claimed in any one of the preceding claims, wherein the composition comprises the surfactant in an amount of from 0.01 to 4% by weight.

11. The glass cleaning composition as claimed in any one of the preceding claims, wherein the composition comprises the silanized colloidal silica particles in an amount of from 0.01 to 4% by weight.

12. The glass cleaning composition as claimed in any one of the preceding claims, wherein the composition comprises the silanized colloidal silica particles and surfactant in a weight ratio of from 10:1 to 1:10, preferably from 5:1 to 1:5.

13. The glass cleaning composition as claimed in any one of the preceding claims, wherein the composition comprises from 0.01 to 4 wt% organic acid, preferably lactic acid.

14. The glass cleaning composition as claimed in any one of the preceding claims, wherein the composition comprises from 0.01 to 10 wt% organic solvent, preferably PnP (1-propoxy-2-propanol).

15. The glass cleaning composition as claimed in any one of the preceding claims, wherein the composition comprises water in an amount of at least 90% by weight, preferably from 95 to 99%.

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2012/070363

A. CLASSIFICATION OF SUBJECT MATTER
INV. C11D3/12 C11D3/16
ADD.

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

B. FIELDS SEARCHED

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

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

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
EPO-Internal, 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 2005/097961 A1 (AKZO NOBEL NV [NL]; EKA CHEMICALS AB [SE]) 20 October 2005 (2005-10-20) pages 5,10; claims; example 1	1-15
X	US 2010/006006 A1 (BOHLANDER RALF [DE] ET AL) 14 January 2010 (2010-01-14) paragraphs [0018] - [0019], [0045] - [0046]; claims	1-15
X	WO 2007/068939 A1 (RECKITT BENCKISER UK LTD [GB]) 21 June 2007 (2007-06-21) pages 41-44,34; claims pages 9,12-14,	1-15

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

☒ See patent family annex.

* Special categories of cited documents :

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"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
31 January 2013	14/02/2013

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/EP2012/070363

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