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(54) Title: COATING COMPOSITION AND PROCESS FOR THE PREPARATION THEREOF

(57) Abstract: The invention relates to coating compositions and processes for the preparation thereof. The coating composition is used for the formation of hydrophobic coatings on a substrate. The coating composition may be used for the formation of hydrophobic particulate coatings.

COATING COMPOSITION AND PROCESS FOR THE PREPARATION THEREOF

FIELD OF THE INVENTION

The present invention relates to a coating composition for providing a hydrophobic coating and to a process for the preparation thereof.

BACKGROUND

Hydrophobic and superhydrophobic materials have many applications where non-wettable or contamination resistant surfaces are required. The term “hydrophobic” is typically used to describe surfaces with a water contact angle of 90 degrees or higher. The term “superhydrophobic” is usually used to describe surfaces with a water contact angle greater than 150 degrees and a low water droplet roll-off (sliding) angle.

In nature some plant leaves, such as “lotus leaf”, show water-repellent and self-cleaning behaviour because of their superhydrophobic surface characteristics. There is a great deal of practical interest in daily life, industry and in the medical fields for making materials hydrophobic and in particular, superhydrophobic, on demand, thereby enabling materials to be water repellent, anti-sticking, anti-contamination and/or self-cleaning.

In the production of hydrophobic and superhydrophobic materials it is desirable to make the surface of the substrate material very rough and with a surface free energy that is as low as possible. To date, research on superhydrophobic surfaces has used physical or chemical methods of preparation.

One route for the preparation of superhydrophobic surfaces involves the physical roughening of the surface of a material via etching. The roughened surface shows superhydrophobic properties when the material itself is hydrophobic. In another route, a rough surface is physically introduced onto a substrate, which is then followed by lowering the surface free energy via a surface coating treatment.

In addition to physical processes, the preparation of superhydrophobic surfaces by chemical processes that introduce a nano-structured surface on a substrate, followed by a separate surface hydrophobic treatment has also been described.

The majority of techniques used to prepare superhydrophobic surfaces however involve complex multiple-step procedures which make them difficult and expensive to implement on a large scale.

It would be desirable to address some or all of these problems of the prior art and to provide a coating composition which is able to form a hydrophobic coating on the surface of a substrate and which can be prepared in a convenient manner.

A reference herein to a patent document or other matter which is given as prior art is not to be taken as an admission that that document or matter was known or that the information it contains was part of the common general knowledge as at the priority date of any of the claims.

SUMMARY

In a first aspect, the present invention provides a coating composition for forming a hydrophobic coating on a substrate, the composition including:

a plurality of silica particles, and

a hydrolysis product obtained from the hydrolysis of one or more hydrolysable silane compounds, wherein at least one of the hydrolysable silane compounds includes at least one organofunctional substituent,

and wherein at least a portion of the hydrolysis product covers at least a portion of the surface of the silica particles.

In a second aspect, the present invention provides a coating composition for forming a hydrophobic coating on a substrate, the composition including:

a plurality of silica particles, and

a silica resin including a plurality of organofunctional substituents,

wherein at least a portion of the silica resin covers at least a portion of the surface of the silica particles.

In one embodiment, at least a portion of the hydrolysis product (in the first aspect) or the silica resin (in the second aspect) substantially covers the surface of the silica particles. Preferably, the silica particles and either the hydrolysis product (in the first aspect) or the silica resin (in the second aspect) covering the silica particles form core-shell particles. Each core-shell particle has a core including a silica particle and a shell surrounding the core, wherein the shell includes either the hydrolysis product (in the first aspect) or the silica resin (in the second aspect).

In a third aspect, the present invention provides a process for the preparation of a coating composition for forming a hydrophobic coating on a substrate, the process including the step of mixing a first hydrolysable silane compound with a second hydrolysable silane compound, wherein the second hydrolysable silane compound includes at least one organofunctional substituent, under conditions allowing hydrolysis of the first and second hydrolysable silane compounds to form a coating composition including a plurality of silica particles and a hydrolysis product which is at least partly derived from the second hydrolysable silane compound, wherein at least a portion of the hydrolysis product covers at least a portion of the surface of the silica particles.

In a fourth aspect, the present invention provides a process for the preparation of a coating composition for forming a hydrophobic coating on a substrate, the process including the step of mixing a first hydrolysable silane compound with a second hydrolysable silane compound, wherein the second hydrolysable silane compound includes at least one organofunctional substituent, under conditions allowing hydrolysis of the first and second hydrolysable silane compounds to form a coating composition including a plurality of silica particles and a silica resin including a plurality of organofunctional substituents, wherein at least a portion of the silica resin covers at least a portion of the surface of the silica particles.

In one embodiment, the first and second hydrolysable silane compounds undergo co-hydrolysis to produce the hydrolysis product (in the third aspect) or the silica resin (in the fourth aspect).

In one embodiment, at least a portion of the hydrolysis product (in the third aspect) or the silica resin (in the fourth aspect) substantially covers the surface of the silica particles. Preferably, the silica particles and either the hydrolysis product (in the third aspect) or the silica resin (in the fourth aspect) covering the silica particles form core-shell particles. Each core-shell particle has a core including a silica particle and a shell surrounding the core, wherein the shell includes either the hydrolysis product (in the third aspect) or the silica resin (in the fourth aspect).

The present invention also provides in a fifth aspect a method for forming a hydrophobic coating on a substrate including the steps of:

(i) applying to the surface of the substrate a coating composition including:

  (a) a plurality of silica particles, and

  (b) a hydrolysis product obtained from the hydrolysis of one or more hydrolysable silane compounds, wherein at least one of the hydrolysable silane compounds includes at least one organofunctional substituent, and wherein at least a portion of the hydrolysis product covers at least a portion of the surface of the silica particles; and

(ii) drying the coated substrate.

Still further, the present invention provides in a sixth aspect a method for forming a hydrophobic coating on a substrate including the steps of:

(i) applying to the surface of the substrate a coating composition including:

  (a) a plurality of silica particles, and

(b) a silica resin including a plurality of organofunctional substituents, wherein at least a portion of the silica resin covers at least a portion of the surface of the silica particles; and

(ii) drying the coated substrate.

In one embodiment, at least a portion of the hydrolysis product (in the fifth aspect) or the silica resin (in the sixth aspect) substantially covers the surface of the silica particles. Preferably, the silica particles and either the hydrolysis product (in the fifth aspect) or the silica resin (in the sixth aspect) covering the silica particles form core-shell particles. Each core-shell particle has a core including a silica particle and a shell surrounding the core, wherein the shell includes either the hydrolysis product (in the fifth aspect) or the silica resin (in the sixth aspect).

BRIEF DESCRIPTION OF THE FIGURES

Figure 1 shows SEM images of a polyester fabric coated by the coating composition of Example 1 and a photographic image of a water droplet on the surface of the coated polyester fabric.

Figure 2 shows FTIR spectra of a polyester fabric before and after coating with the coating composition of Example 1.

Figure 3 shows (a) XPS survey spectra and (b) XPS high resolution spectra of elements C_{1s} and Si_{2p} on the surface of a polyester fabric coated with the coating composition of Example 1.

Figure 4 shows photographic images of water droplets on various substrate surfaces coated with the coating composition of Example 1.

Figure 5 shows a TEM image of core-shell particles prepared in accordance with one embodiment of the invention.

Figure 6 shows a graph illustrating the effect of FAS/TEOS ratio and treatment times on the water contact angles of a polyester fabric coated with a coating composition in accordance with Example 2.

DETAILED DESCRIPTION

While the following detailed discussion of the invention will be largely focussed on its application to providing a superhydrophobic coating, it is to be understood that the invention is not so limited and is also applicable to producing hydrophobic coatings.

Coating Composition

In accordance with a first aspect, the present invention provides a coating composition for forming a hydrophobic coating on a substrate, the composition including:

a plurality of silica particles, and

a hydrolysis product obtained from the hydrolysis of one or more hydrolysable silane compounds, wherein the at least one of the hydrolysable silane compounds includes at least one organofunctional substituent,

and wherein at least a portion of the hydrolysis product covers at least a portion of the surface of the silica particles.

In accordance with a second aspect, the present invention provides a coating composition for forming a hydrophobic coating on a substrate, the composition including:

a plurality of silica particles, and

a silica resin including a plurality of organofunctional substituent,

wherein at least a portion of the silica resin covers at least a portion of the surface of the silica particles.

In both the first and second aspects of the invention the coating composition includes a plurality of silica particles. In one embodiment, the silica particles are formed in-situ during preparation of the coating composition. The in-situ formation of the silica particles preferably occurs by hydrolysis of a suitable silane compound under appropriate conditions. Any suitable hydrolysable silane compound may be used for the in-situ formation of silica particles. Preferably, the suitable hydrolysable silane compound is one that is fully hydrolysable. A fully hydrolysable silane compound typically includes substituent groups that are each able to undergo hydrolysis under hydrolysis conditions. Examples of fully hydrolysable silane compounds include tetraethyl orthosilicate (TEOS) and silicon tetrachloride ($SiCl_4$). The person skilled in the art would understand that under appropriate conditions, such compounds can form silicon dioxide (silica).

The formation of the silica particles may occur under any suitable hydrolysis conditions. Examples of suitable conditions include those employed in sol-gel techniques. In a preferred embodiment, the silica particles are formed in-situ in the composition under alkaline hydrolysis conditions. The use of alkali is preferred as it enables silica particles of greater size to be formed compared to when acid catalysed conditions are used. Such alkaline hydrolysis conditions are described below.

The silica particles are used to impart a sufficient degree of roughness to a substrate to which the coating composition is applied. It is believed that the roughness assists to provide hydrophobic, preferably superhydrophobic properties to the resultant coating. Where alkaline hydrolysis conditions are used to form the silica particles, the silica particles may have a particle size in the range of from about 10 to 900nm, preferably in the range of from about 30 to 500nm, more preferably in the range of from about 50 to 300nm.

A coating composition in accordance with the first aspect of the invention also includes a hydrolysis product. The hydrolysis product is obtained from the hydrolysis of one or more hydrolysable silane compounds. In accordance with the invention, at least one of the one or more hydrolysable silane compounds includes at least one organofunctional substituent. Consequently, the hydrolysis product will typically contain at least one organofunctional substituent, which is derived from the hydrolysable silane compound including at least one organofunctional substituent. Preferably, the hydrolysis product includes a plurality of organofunctional substituents.

The term "organofunctional" is used herein to refer to functional groups that are not based on silicon. The organofunctional substituent is generally a non-hydrolysable substituent group. That is, the organofunctional substituent is not reactive under the hydrolysis conditions used to prepare the coating composition of the invention.

The hydrolysable silane compound that contains the organofunctional substituent also includes at least one hydrolysable substituent. The presence of the hydrolysable substituent enables the silane compound to react under hydrolysis conditions. A person skilled in the relevant art would understand that the ratio of organofunctional substituent groups to hydrolysable substituent groups can vary from 1:3 to 3:1, according to the valency of the silicon atom. Preferably, a silane compound including at least one organofunctional substituent and at least two hydrolysable substituents is used,

The hydrolysis product that results from the hydrolysis of the one or more hydrolysable silane compounds preferably has a low surface free energy.

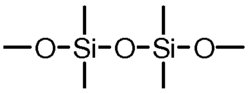
In one embodiment, the hydrolysis product is obtained from the hydrolysis of two or more hydrolysable silane compounds. The hydrolysis product may be obtained from the co-hydrolysis and co-condensation of a first hydrolysable silane compound and a second hydrolysable silane compound, wherein the second hydrolysable silane compound includes at least one organofunctional substituent. Preferably, the first hydrolysable silane is a fully hydrolysable silane compound including a plurality of hydrolysable substituents that are each able to react under hydrolysis conditions. Examples of fully hydrolysable silane compounds include tetraethyl orthosilicate (TEOS) and silicon tetrachloride ($SiCl_4$). The first hydrolysable silane compound is preferably the compound that is used to form silica particles in situ in the coating composition.

In accordance with the invention, at least a portion of the hydrolysis product covers at least a portion of the surface of the silica particles. In one embodiment, at least a portion of the hydrolysis product substantially covers the surface of one or more silica particles. In one embodiment, the hydrolysis product may coat the surface of each silica particle. The silica particles together with the hydrolysis product that covers the surface thereof may form core-shell particles. Generally, such core-shell particles each have a core including a silica particle and a shell substantially surrounding the core, wherein the shell includes the hydrolysis product. In some cases, the core-shell structure may also include a co-condensed interlayer in-between the core and the shell region, where the interlayer is formed from the co-hydrolysis of the silanes.

Any portion of the hydrolysis product which does not cover the silica particles may function as a binder or resin to immobilise the silica particles when the coating composition is applied to the surface of a substrate material.

In one embodiment of the first aspect of the invention, the hydrolysis product is a silicone polymer including a plurality of organofunctional substituents. The silicone polymer described herein is also known as a silica resin. The silica resin is formed when one or more hydrolysable silane compounds hydrolyse and condense under appropriate conditions to give rise to a silica sol. At least one of the one or more hydrolysable silane compounds used to form the silica resin includes at least one organofunctional substituent. Thus in one embodiment, the hydrolysis product of the invention is a silica resin having a plurality of organofunctional substituents.

A person skilled in the art would understand that the silica resin is a silicone polymer having a backbone of the following structure:



$$—O-\underset{|}{\overset{|}{Si}}-O-\underset{|}{\overset{|}{Si}}-O—$$

The backbone structure is formed when two or more functional groups in a silane compound react under selected conditions, such as under hydrolysis conditions, to provide the Si-O bond. Hydrolysis products which are not silica resin may also be formed in addition to, or instead of, the silica resin under the hydrolysis conditions. Where a silica resin having a plurality of organofunctional substituents is formed, the organofunctional substituent groups of the silica resin are each derived from a hydrolysable silane compound. The silica resin may be of any suitable molecular weight and may include any number of organofunctional substituent groups.

The second aspect of the coating composition of the invention includes a silica resin including a plurality of organofunctional substituents. The silica resin may be formed by any suitable means but is typically produced by a hydrolysis reaction.

In one embodiment the silica resin is obtained from the hydrolysis of two or more hydrolysable silane compounds. The silica resin may be obtained from the co-hydrolysis and co-condensation of a first hydrolysable silane compound and a second hydrolysable silane compound, wherein the second hydrolysable silane compound includes at least one organofunctional substituent. Preferably, the first hydrolysable silane is a fully hydrolysable silane compound including a plurality of hydrolysable substituents that are each able to react under hydrolysis conditions. Examples of fully hydrolysable silane compounds include tetraethyl orthosilicate (TEOS) and silicon tetrachloride ($SiCl_4$). The first hydrolysable silane compound is preferably the compound that is used to form silica particles in situ in the coating composition.

In either the first or second aspect of the coating composition of the invention, the organofunctional substituent at each occurrence includes a suitable non-hydrolysable organic functional moiety. In one preferred embodiment, each organofunctional substituent includes a moiety independently selected from the group consisting of alkyl, alkenyl, alkynyl, alkyl ethers, alkyl esters, aryl, cycloalkyl, haloalkyl, haloether, cyano, epoxy, amino, aminoalkyl, aminoalkenyl, aminoalkynyl, aminoaryl, and aminocycloalkyl and mixtures thereof. The terms “alkyl”, “alkenyl and alkynyl” as used herein refers to both linear (straight chain) and branched hydrocarbon structures.

Preferably, each organofunctional substituent includes a moiety independently selected from the group consisting of C_1 to C_{20} alkyl, C_2 to C_{30} alkenyl, C_3 to C_{10} alkyl epoxy, C_2 to C_{20} aminoalkyl, C_5 to C_{10} aminocycloalkyl, C_5 to C_{10} aryl, C_1 to C_{20} haloalkyl, C_3 to C_{10} cycloalkyl and C_2 to C_{20} cyanoalkyl. More preferably, each organofunctional substituent includes a moiety independently selected from the group consisting of C_1 to C_{20} alkyl, C_3 to C_{10} alkyl epoxy, C_5 to C_{10} aryl and C_1 to C_{20} haloalkyl (such as C_1 to C_{20} perfluoroalkyl moiety).

In either the first or second aspect of the coating composition of the invention, the organofunctional substituents may, at each occurrence, have the same type of organic functional moiety or alternatively, they may have different types of organic functional moieties. A person skilled in the relevant art would understand that the types of organic functional moieties and the types of organofunctional substituents would depend on the nature of hydrolysable silane compounds used in the preparation of the hydrolysis product or silica resin.

In one embodiment, each organofunctional substituent includes a long chain alkyl. Long chain alkyl may be C_8-C_{20} alkyl. Long chain alkyl may help to provide a coating composition having greater hydrophobicity than coatings formed with silane compounds having shorter alkyl substituents. Some examples of long chain alkyl are octyl and hexadecyl alkyl.

In another embodiment, each organofunctional substituent includes a haloalkyl moiety. A preferred haloalkyl is fluoroalkyl. In one embodiment, each organofunctional substituent includes a C_1 to C_{20} perfluoroalkyl moiety. A preferred perfluoroalkyl moiety is $-(CH_2)_2-(CF_2)_5-CF_3$. Without wishing to be limited by theory, it is believed that fluorinated alkyl chains may be advantageous in assisting to impart a low surface free energy to the coating that results after application of the coating composition to the surface of a substrate.

In one embodiment the hydrolysable silane compound including at least one organofunctional substituent is a trialkoxysilane. Trialkoxysilanes include three hydrolysable substituents and one non-hydrolysable organofunctional substituent. The organofunctional substituent preferably includes an organic moiety as described in the preceding paragraph. Examples of suitable trialkoxysilanes including an organofunctional substituent that may be used in accordance with the invention are as follows:

Alkyl

Methyl-tripropoxysilane, Trimethoxymethylsilane, Methyltris(tri-*sec*-butoxysilyloxy)silane, 1-(Triethoxysilyl)-2-pentene, Ethyltrimethoxysilane, Propyltriethoxysilane, Trimethoxy(propyl)silane, Triethoxy(isobutyl)silane, Isobutyl(trimethoxy)silane, Triethoxy(octyl)silane, Trimethoxy(octyl)silane, Dodecyltriethoxysilane, Hexadecyltrimethoxysilane, Trimethoxy(octadecyl)silane

Alkenyl

Trimethoxy(vinyl)silane, Trimethoxy(7-octen-1-yl)silane, Amyltriethoxysilane, 3-(Trimethoxysilyl)propyl methacrylate, Allyltriethoxysilane, 3-(Trimethoxysilyl)propyl acrylate

Cycloalkyl

Cyclopentyltriethoxysilane, (Triethoxysilyl)cyclohexane, [2-(Cyclohexenyl)ethyl]triethoxysilane

Amino

3-amino-propyl trimethoxysilane, *N*-[3-(Trimethoxysilyl)propyl]aniline, (*N*,*N*-Dimethylaminopropyl)trimethoxysilane, 3-[2-(2-Aminoethylamino)ethylamino]propyl-trimethoxysilane

Cyano

3-Cyanopropyltriethoxysilane, 3-(Triethoxysilyl)propionitrile

Halo

(4-Chlorophenyl)triethoxysilane, (3-Chloropropyl)tris(trimethylsiloxy)silane, (3-Bromopropyl)trimethoxysilane, (3-Chloropropyl)trimethoxysilane, (3-Chloropropyl)triethoxysilane, (Pentafluorophenyl)triethoxysilane, Triethoxy(4-(trifluoromethyl)phenyl)silane, 1*H*,1*H*,2*H*,2*H*-Perfluorooctyltriethoxysilane, Trimethoxy(3,3,3-trifluoropropyl)silane, Tridecafluorooctyl triethoxysilane

Alkyl epoxy

[2-(3,4-Epoxycyclohexyl)ethyl]trimethoxysilane, (3-Glycidyloxypropyl)trimethoxysilane

Aryl

Triethoxyphenylsilane, Triethoxy-*p*-tolylsilane, Triethoxy(4-methoxyphenyl)silane, Trimethoxy(2-phenylethyl)silane , Triethoxy(1-phenylethenyl)silane

One or more of the above trialkyoxysilanes may be used to prepare a coating composition in accordance with the invention.

The hydrolysis product (in the first aspect) or the silica resin (in the second aspect) of the coating composition may also include at least one functional group adapted to participate in covalent bonding reactions. The presence of the functional group may be advantageous to introduce functionality to the hydrolysis product or silica resin and to enable the properties of the coating formed from the coating composition to be adjusted or to improve stability.

In one embodiment, the hydrolysis product or the silica resin includes at least one functional group selected from the group consisting of halo, amino, epoxy, hydroxy, thiol, carboxy and anhydride functional groups. Preferably, the functional group is selected from the group consisting of epoxy, carboxy and anhydride functional groups. Functional groups adapted to participate in covalent bonding reactions may be introduced into the hydrolysis product or silica resin by employing an appropriately functionalised hydrolysable silane compound in the formation of the coating composition. Examples of hydrolysable silane compounds having a functional group adapted to participate in covalent bonding reactions include the halo, amino and epoxy trialkoxysilanes described above.

When the hydrolysis product or silica resin includes a functional group adapted to participate in covalent bonding reactions, the coating composition and the coating formed from the composition may exhibit improved adhesion to a substrate material. In this regard, it would be appreciated by one skilled in the relevant art that substrates including polymeric materials (for example polyesters), wool, cotton and the like may have functional groups (for example amino, hydroxy or carboxy groups) that are able to participate in covalent bonding reactions. As such, the functional group of the hydrolysis product or silica resin may react with functional groups present on the surface of a substrate to thereby form a covalent bond between the resulting coating and the substrate.

In addition, a hydrolysis product or silica resin including a functional group adapted to participate in covalent bonding reactions may provide a coating with improved stability. In this respect, the functional group may participate in crosslinking reactions to result in the formation of a crosslinked coating on the surface of a substrate. A crosslinked coating may exhibit greater stability than non-crosslinked coatings.

Furthermore, the presence a functional group adapted to participate in covalent bonding reactions in the hydrolysis product or silica resin may be useful to enable the properties of the coating composition to be adjusted. In this regard, the functional groups may be capable of reacting with an appropriate agent to impart additional properties to the resultant coating. In one embodiment, an agent may be grafted to the hydrolysis product or silica resin via reaction of the functional group of the hydrolysis product or silica resin with a complementary functional group in the agent. For example, if the hydrolysis product includes a functional group such as epoxy, carboxy or anhydride, such functional groups may covalently react with an agent having a complementary functional group such an amino or hydroxy group. A person skilled in the art would understand that a range of different functional groups are capable of reacting together to form a covalent bond there between and therefore the invention is not limited in this respect.

The coating composition of the invention may further include a solvent. In one embodiment, the silica particles and the hydrolysis product (in the first aspect) or the silica resin (in the second aspect) are dispersed in the solvent. Any suitable solvent may be used. Preferably the solvent is a volatile solvent. In a preferred embodiment the solvent is an alcohol. A preferred alcohol is ethanol. The solvent is typically that remaining after the process for forming the coating composition of the invention. The solvent also typically solubilises the components of the coating composition.

In use, the coating composition is applied to the surface of a substrate. The inventors have found that the composition may be applied to a wide range of different substrates, including but not limited to synthetic substrates such polymeric materials (such as polyesters), natural substrates such as wool, cotton, wood and paper, metals, silicon, glass and ceramics. In this sense, the coating composition is a “universal” coating composition as it is not constrained to use on one particular type of substrate as many prior art coatings are. Furthermore, the coating composition may be applied to the substrate using any suitable technique. Examples of application techniques include padding, dipping, brushing, spraying or spin coating. It is preferred that a substantially uniform layer of the coating composition be applied to the surface of the substrate. The coating composition may also be applied to one surface, or to two or more surfaces, of the substrate. In one embodiment, the substrate is a fabric having two surfaces. The coating composition may be applied to one surface, or to both surfaces, of the fabric.

Once applied to the surface of a substrate and dried and/or cured, the coating composition of the invention provides a coating that exhibits a high water contact angle. The contact angle is often determined by surface interactions across a given interface. The skilled addressee would appreciate that high water contact angles (usually greater than 90 degrees) is typical of hydrophobic surfaces. Preferably, the composition provides a coating that exhibits a water contact angle of at least about 120 degrees, more preferably at least about 150 degrees, even more preferably at least about 160 degrees, and most preferably at least about 170 degrees. Observed water contact angles of greater than 150 degrees is indicative of superhydrophobic surfaces.

As shown in Figure 1 and Figure 4, the high water contact angle exhibited by coatings prepared using the compositions of the invention allows water droplets to form a nearly spherical shape on the treated substrate surface. Such a droplet was observed by the inventors to be capable of maintaining this shape for a long period of time.

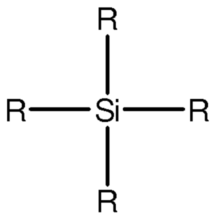
When the coating composition of the invention is applied to the surface of a substrate, the composition may also provide a coating that exhibits a low sliding angle. A person skilled in the art would understand that the sliding angle is a measure of the critical angle at which a droplet of water will slide down an inclined plane. The sliding angle may be indicative of the relative hydrophobicity of the coating. In one embodiment, the coating composition of the invention may provide a coating that exhibits a sliding angle of no more than about 35 degrees once the coating has been applied to the surface of a substrate. Preferably, the coating exhibits a sliding angle of no more than about 20 degrees, more preferably no more than about 15 degrees and most preferably no more than about 10 degrees.

Process for preparation of coating composition

In a third aspect, the present invention also provides a process for the preparation of a coating composition for forming a hydrophobic coating on a substrate, the process including the step of mixing a first hydrolysable silane compound with a second hydrolysable silane compound, wherein the second hydrolysable silane compound includes at least one organofunctional substituent, under conditions allowing hydrolysis of the first and second hydrolysable silane compounds to form a coating composition including a plurality of silica particles and a hydrolysis product which is at least partly derived from the hydrolysis of the second hydrolysable silane compound, wherein at least a portion of the hydrolysis product covers at least a portion of the surface of the silica particles.

In a fourth aspect, the present invention further provides a process for the preparation of a coating composition for forming a hydrophobic coating on a substrate, the process including the step of mixing a first hydrolysable silane compound with a second hydrolysable silane compound, wherein the second hydrolysable silane compound includes at least one organofunctional substituent, under conditions allowing hydrolysis of the first and second hydrolysable silane compounds to form a coating composition including a plurality of silica particles and a silica resin including a plurality of organofunctional substituents, wherein at least a portion of the silica resin covers at least a portion of the silica particles.

In the third and fourth aspects of the invention, the first hydrolysable silane compound is preferably a fully hydrolysable silane compound. Thus the first hydrolysable silane compound typically includes a plurality of hydrolysable substituents that can each react under appropriate hydrolysis conditions. In one preferred embodiment, the first hydrolysable silane compound is of general formula (I)



$$R-\overset{\displaystyle R}{\underset{\displaystyle R}{Si}}-R$$

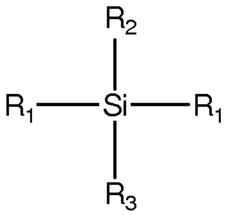
(I)

where

R is a hydrolysable group and at each occurrence is independently selected from the group consisting of alkoxy, alkenyloxy and halo.

Preferred alkoxy is C_1 to C_4 alkoxy and preferred halo is chloro. In one preferred embodiment, R is the same at each occurrence. Examples of preferred compounds as the first hydrolysable silane compound are tetraalkyl orthosilicates, where R at each occurrence is C_1 to C_4 alkoxy. An example of a preferred tetraalkyl orthosilicate is tetraethyl orthosilicate (TEOS). Other compounds may also be used as the first hydrolysable silane compound. An example of such a compound is silicon tetrachloride ($SiCl_4$).

In the third and fourth aspects of the invention, the second hydrolysable silane compound may be any suitable silane compound that includes at least one organofunctional substituent. Preferably, the organofunctional substituent includes an organic functional moiety as described herein. In one embodiment, the second hydrolysable silane compound is a compound of general formula (II):



$$\begin{array}{c} R_2 \\ | \\ R_1 - \mathrm{Si} - R_1 \\ | \\ R_3 \end{array}$$

(II)

where

R_1 is a hydrolysable group and at each occurrence is independently selected from the group consisting of alkoxy, alkenyloxy and halo,

R_2 is a hydrolysable group selected from the group consisting of alkoxy, alkenyloxy and halo, or

R_2 is a non-hydrolysable organofunctional substituent including a moiety selected from the group consisting of alkyl, alkenyl, alkynyl, alkyl ethers, alkyl esters, aryl, cycloalkyl, haloalkyl, haloether, cyano, cyanoalkyl, alkylepoxy, amino, aminoalkyl, aminoalkenyl, aminoalkynyl, aminoaryl, aminocycloalkyl and mixtures thereof, and

R_3 is a non-hydrolysable organofunctional substituent including a moiety selected from the group consisting of alkyl, alkenyl, alkynyl, alkyl ethers, alkyl esters, aryl, cycloalkyl, haloalkyl, haloether, cyano, cyanoalkyl, alkylepoxy, amino, aminoalkyl, aminoalkenyl, aminoalkynyl, aminoaryl, aminocycloalkyl and mixtures thereof.

The terms “alkyl”, “alkenyl” and “alkynyl” as used herein refers to both linear (straight chain) and branched hydrocarbon structures.

In one embodiment, each organofunctional substituent includes a moiety independently selected from the group consisting of C_1 to C_{20} alkyl, C_2 to C_{30} alkenyl, C_3 to C_{10} alkyl epoxy, C_2 to C_{20} aminoalkyl, C_5 to C_{10} aminocycloalkyl, C_5 to C_{10} aryl, C_1 to C_{20} haloalkyl, C_3 to C_{10} cycloalkyl and C_2 to C_{20} cyanoalkyl. More preferably, each organofunctional substituent includes a moiety independently selected from the group consisting of C_1 to C_{20} alkyl (preferably C_8-C_{20} alkyl), C_3 to C_{10} alkyl epoxy, C_5 to C_{10} aryl and C_1 to C_{20} haloalkyl (preferably C_1 to C_{20} fluoroalkyl).

In either the third or fourth aspects of the process of the invention, the organofunctional substituents may, at each occurrence, have the same type of organic functional moiety or alternatively, they may have different types of organic functional moieties. The organic functional moieties may be selected to impart desired properties to the hydrolysis product or silica resin prepared in accordance with the processes of the invention. A person skilled in the relevant art would understand that the types of organic functional moieties and consequently, the types of organofunctional substituents, would depend on the nature of hydrolysable silane compounds used.

In one embodiment, each organofunctional substituent includes a long chain alkyl. Long chain alkyl may be C_8-C_{20} alkyl. Long chain alkyl may help to provide a coating composition having greater hydrophobicity than coatings formed with silane compounds having shorter alkyl substituents. Some examples of long chain alkyl are octyl and hexadecyl alkyl.

In another embodiment, each organofunctional substituent includes a haloalkyl moiety. A preferred haloalkyl is fluoroalkyl. In one embodiment, each organofunctional substituent includes a C_1 to C_{20} perfluoroalkyl moiety such as $-(CH_2)_2-(CF_2)_5-CF_3$. Without wishing to be limited by theory, it is believed that fluorinated alkyl chains may be advantageous in assisting to impart a low surface free energy to the coating that results after application of the coating composition to the surface of a substrate.

In one preferred embodiment the second hydrolysable silane compound is a trialkoxysilane. In this regard, the substituent groups R_1 and R_2 in compounds of general formula (II) are each alkoxy. Preferred alkoxy are C_1 to C_4 alkoxy. The organofunctional substituent group R_3 in the trialkoxysilane may include a moiety as described in the paragraph above. One preferred moiety is a C_1 to C_{20} fluoroalkyl moiety, more preferably a C_1 to C_{20} perfluoroalkyl moiety such as $-(CH_2)_2-(CF_2)_5-CF_3$. Examples of other suitable trialkoxysilanes including organofunctional substituents are given below:

Alkyl

Methyl-tripropoxysilane, Trimethoxymethylsilane, Methyltris(tri-*sec*-butoxysilyloxy)silane, 1-(Triethoxysilyl)-2-pentene, Ethyltrimethoxysilane, Propyltriethoxysilane, Trimethoxy(propyl)silane, Triethoxy(isobutyl)silane, Isobutyl(trimethoxy)silane, Triethoxy(octyl)silane, Trimethoxy(octyl)silane, Dodecyltriethoxysilane, Hexadecyltrimethoxysilane, Trimethoxy(octadecyl)silane

Alkenyl

Trimethoxy(vinyl)silane, Trimethoxy(7-octen-1-yl)silane, Amyltriethoxysilane, 3-(Trimethoxysilyl)propyl methacrylate, Allyltriethoxysilane, 3-(Trimethoxysilyl)propyl acrylate

Cycloalkyl

Cyclopentyltriethoxysilane, (Triethoxysilyl)cyclohexane, [2-(Cyclohexenyl)ethyl]triethoxysilane

Amino

3-amino-propyl trimethoxysilane, *N*-[3-(Trimethoxysilyl)propyl]aniline, (*N*,*N*-Dimethylaminopropyl)trimethoxysilane, 3-[2-(2-Aminoethylamino)ethylamino]propyl-trimethoxysilane

Cyanoalkyl

3-Cyanopropyltriethoxysilane, 3-(Triethoxysilyl)propionitrile

Halo

(4-Chlorophenyl)triethoxysilane, (3-Chloropropyl)tris(trimethylsiloxy)silane, (3-Bromopropyl)trimethoxysilane, (3-Chloropropyl)trimethoxysilane, (3-Chloropropyl)triethoxysilane, (Pentafluorophenyl)triethoxysilane, Triethoxy(4-(trifluoromethyl)phenyl)silane, 1*H*,1*H*,2*H*,2*H*-Perfluorooctyltriethoxysilane, Trimethoxy(3,3,3-trifluoropropyl)silane, Tridecafluorooctyl triethoxysilane

Alkyl epoxy

[2-(3,4-Epoxycyclohexyl)ethyl]trimethoxysilane, (3-Glycidyloxypropyl)trimethoxysilane

Aryl

Triethoxyphenylsilane, Triethoxy-*p*-tolylsilane, Triethoxy(4-methoxyphenyl)silane, Trimethoxy(2-phenylethyl)silane , Triethoxy(1-phenylethenyl)silane

The first and second hydrolysable silane compounds may be used in any proportion and in any amount that achieves the advantages of the invention. In one embodiment, the ratio of the first hydrolysable silane compound to the second hydrolysable silane compound is the range of from about 200:1 to 1:50 (mol/mol). Preferably, the ratio is in the range of from about 100:1 to 1:10, more preferably in the range of from about 50:1 to 5:1. In some instances, higher amounts of the second hydrolysable silane compound may be desirable to provide a coating with greater hydrophobicity. However, the skilled addressee would understand that the relative quantities of each silane compound used will depend on nature of the silane compounds and the desired properties of the coating composition and any coating formed from the coating composition. Consequently, it would be appreciated that ratios that may be useful for one combination of silane compounds may not always be useful for other combinations of silane compounds.

If desired, one or more further hydrolysable silane compounds may be mixed with the first and second hydrolysable silane compounds to introduce further functionality or properties to the coating composition and any coating formed from the composition. Accordingly, in one embodiment, the process of the invention may further include the step of mixing a further hydrolysable silane compound with the first and second hydrolysable silane compounds. The further hydrolysable silane compound may be added to the first and second silane compounds before or during the hydrolysis reaction. Preferably, the further hydrolysable silane compound is mixed with the first and second silane compounds before commencement of any hydrolysis reactions. The further hydrolysable silane compound may also be any suitable silane compound. Preferably, the further hydrolysable silane compound includes an organofunctional substituent. Thus, the coating composition may include a mixture of two or more hydrolysable silane compounds having an organofunctional substituent. Examples of hydrolysable silane compounds including an organofunctional substituent include those described above.

When used, the further hydrolysable silane compound may be present in any desired amount. It may be convenient to define the desired amount of the further hydrolysable silane compound by reference to an amount of the second hydrolysable silane compound. In one embodiment, the further hydrolysable silane compound may be present in an amount that provides a mole ratio of the further hydrolysable silane compound to the second hydrolysable silane compound in the range of from about 10:1 to 1:10, preferably in the range of from about 5:1: to 1:5, more preferably in the range of from about 2:1 to 1:2.

In one embodiment, the further hydrolysable silane compound includes an organofunctional substituent adapted to participate in covalent bonding reactions. Such organofunctional substituents would contain at least one functional group that is capable of participating in covalent bonding reactions. Consequently, in one embodiment the process of the invention may further include the step of mixing a further hydrolysable silane compound including an organofunctional group adapted to participate in covalent bonding reactions with the first and second hydrolysable silane compounds. The further hydrolysable silane compound reacts with at least the second hydrolysable silane compound to introduce at least one functional group adapted to participate in covalent bonding reactions in the hydrolysis product (in the third aspect) or the silica resin (in the fourth aspect). In one embodiment, the further hydrolysable silane compound includes an organofunctional substituent including a functional group selected from the group consisting of halo, amino, epoxy, hydroxy, thiol, carboxy and anhydride functional groups. Accordingly, the resulting hydrolysis product or silica resin may therefore contain a functional group selected from the group consisting of halo, amino, epoxy, hydroxy, thiol, carboxy and anhydride functional groups. In one preferred embodiment, the further hydrolysable silane compound includes an organofunctional substituent including a functional group selected from the group consisting of epoxy, carboxy and anhydride functional groups. Examples of hydrolysable silane compounds having organofunctional substituents including functional groups adapted to participate in covalent bonding reactions are described above.

When a hydrolysable silane compound including an organofunctional substituent adapted to participate in covalent bonding reactions is used in the preparation of the coating composition of the invention, the coating formed from the composition may exhibit improved adhesion to the substrate material, improved stability or be capable of being derivatised by covalent reaction with an agent, as described above.

Under hydrolysis conditions, at least the first and second hydrolysable silane compounds can form a coating composition in accordance with the invention.

The hydrolysis of the first and second silane compounds may occur under any suitable conditions that achieve the advantages of the invention. The hydrolysis is preferably performed under alkali catalysed conditions. More preferably, the hydrolysis is performed under alkaline conditions in a solution including an alkali and a solvent.

Where the hydrolysis is performed in the presence of an alkali, any suitable alkali may be used. The alkali may be an organic alkali or an inorganic alkali. Preferably, the alkali is selected from the group consisting of ammonium hydroxide, amines, imidazole, pyridines and metal hydroxides. More preferably, the alkali is ammonium hydroxide.

In addition, where a solvent is present, any suitable solvent may be used. In one embodiment, the solvent is a volatile solvent. Preferably, the solvent is an alcohol. A preferred alcohol is ethanol.

The hydrolysis may also be performed at any temperature and for any length of time suitable to give the desired coating composition. Preferably, the hydrolysis is performed for a period of time in the range of 8-14 hours, more preferably for about 12 hours. The temperature for hydrolysis may be any suitable temperature. In one embodiment, the hydrolysis is carried at a temperature of up to about 50°C, and more preferably, is carried out at ambient temperature. It is an advantage of the invention that the hydrolysis may be performed under relatively mild conditions. A person skilled in the art however would appreciate that the time and temperature may be varied to suit particular reactants and/or to achieve a desired result.

Without wishing to be limited by theory, it is believed that under appropriate hydrolysis conditions the first hydrolysable silane compound is able to rapidly hydrolyse and form silica particles. The silica particles are therefore formed in-situ in the coating composition. The silica particles impart a degree of roughness to the coating that is formed from the coating composition.

Under the same hydrolysis conditions, the second hydrolysable silane compound can participate in hydrolysis reactions to form a hydrolysis product that may be a gel or resin, depending on the silane structure and the solution alkalinity. The hydrolysis product preferably has a low surface free energy.

In one aspect of the invention the second hydrolysable silane compound hydrolyses at a slower rate than that of the first hydrolysable silane compound under the hydrolysis conditions employed. This difference in hydrolysis rates may advantageously assist in the formation of silica particles in situ in the coating composition due to the rapid hydrolysis of the first hydrolysable silane compound compared to that of the second hydrolysable silane compound. The slower rate of hydrolysis of the second hydrolysable silane compound means that this compound generally would not form silica particles but rather, participates in the formation of the hydrolysis product. Accordingly, the hydrolysis product is at least partly derived from the second hydrolysable silane compound.

In one embodiment the hydrolysis product is predominantly obtained from the hydrolysis and condensation of the second hydrolysable silane compound on its own.

In another embodiment, the hydrolysis product is obtained from the hydrolysis and condensation of the second hydrolysable silane compound with at least one other hydrolysable silane compound. In one embodiment, the second hydrolysable silane compound co-hydrolyses and co-condenses with the first hydrolysable silane compound described herein, to form the hydrolysis product. It would be appreciated that not all of the first hydrolysable silane compound may be used to form the silica particles. Accordingly, any quantity of the first hydrolysable silane compound that remains after the silica particles have been formed may be available to react with the second hydrolysable silane compound to provide the hydrolysis product.

In a further embodiment, it is contemplated that one or more further hydrolysable silane compounds may react with the second hydrolysable silane compound in addition to, or instead of, the first hydrolysable silane compound, to form the hydrolysis product. When a further hydrolysable silane compound is used, the further silane compound preferably contains an organofunctional substituent. Such silane compounds may also hydrolyse at a slower rate than the first hydrolysable silane compound under the hydrolysis conditions employed. In one embodiment, the further hydrolysable silane compound includes an organofunctional substituent including a functional group adapted to participate in covalent bonding reactions. In another embodiment, the further hydrolysable silane compound is preferably selected from any one of the trialkoxysilane compounds described above.

A person skilled in the relevant art would understand that the composition of the hydrolysis product may, in part, depend on the nature of the silane compounds employed in the formation of the coating composition and their relative rates of hydrolysis under specified conditions. For example, where the first hydrolysable silane compound is much more reactive than the second hydrolysable silane compound, it is envisaged that the first hydrolysable silane compound would be rapidly hydrolysed to form the silica particles and very little (if any) of the first hydrolysable silane compound would remain available to participate in the reactions forming the hydrolysis product. However, where the first and second hydrolysable silane compounds exhibit a smaller difference in hydrolysis rates or where a large excess of the first hydrolysable silane compound is used, the resulting hydrolysis product may include a mixture of products obtained from the co-hydrolysis and co-condensation of both the first and second hydrolysable silane compounds.

By virtue of the in situ formation of the silica particles and the hydrolysis product, at least a portion of the hydrolysis product is adsorbed onto at least a portion of the surface of the silica particles. Depending on the nature of the hydrolysis product, the hydrolysis product may impart a low surface energy to the silica particles.

The silica particles are capable of taking on a high proportion of the hydrolysis product on their surfaces. In one embodiment, at least a portion of the hydrolysis product coats one or more of the silica particles. Preferably, at least a portion of the hydrolysis product substantially covers the surface of one or more silica particles. Where at least a portion of the hydrolysis product substantially covers the surface of a silica particle, a structure resembling a core-shell particle may be formed. Generally, such core-shell particles have a core including a silica particle and a shell including the hydrolysis product that substantially surrounds the core. As described above, the silica particles can be derived from the first hydrolysable silane compound while the hydrolysis product of the shell region would be at least partly derived from the second hydrolysable silane compound. Thus in accordance with the invention, the core-shell structures may be formed from two or more silane compounds that hydrolyse at different rates under the hydrolysis conditions employed.

It is however envisaged that not all of the hydrolysis product will be adsorbed on to the surface of the silica particles. As such, any portion of the resin which has not adsorbed may function as a binder to immobilize the coated silica particles on a substrate when the coating composition is applied. It is one advantage of the invention that the coating of the silica particles by the hydrolysis product and the formation of core-shell particles not only may reduce the surface free energy of the particles, but may also prevent or reduce agglomeration of the silica particles.

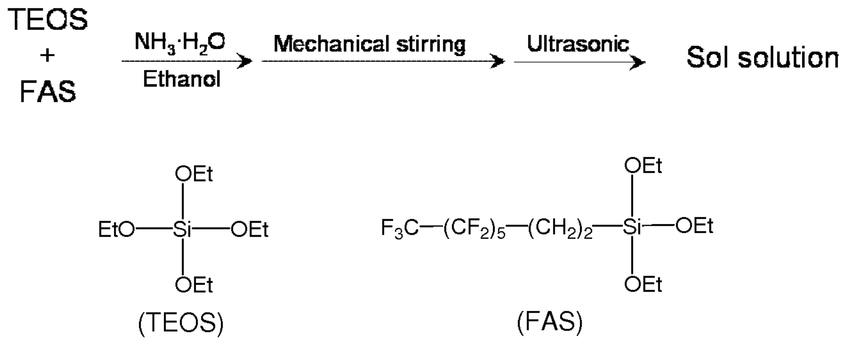
The second hydrolysable silane compound participates in hydrolysis reactions to produce a hydrolysis product (in the third aspect) or a silica resin including a plurality of organofunctional substituents (in the fourth aspect).

In the third aspect of the invention the hydrolysis product may be any product obtained from hydrolysis of the second hydrolysable silane compound, optionally together with at least one other hydrolysable silane compound. In one embodiment, the hydrolysis product is a silica resin or silica sol. Hydrolysis products which are not silica resin may also be formed in addition to, or instead of, the silica resin under the hydrolysis conditions.

Where a silica resin is formed in accordance with the third or fourth aspects of the invention, the silica resin includes a plurality of organofunctional substituents. The formation of the silica resin is typically due to hydrolysis and condensation of at least the second hydrolysable silane compound under the hydrolysis conditions. In this instance, the silica resin contained organofunctional substituents derived from the second hydrolysable silane compound. Examples of suitable organofunctional substituents are described herein.

If desired, the process of the invention may further include the step of sonicating the composition to form a homogeneous mixture. Sonication may be useful if an inhomogeneous mixture is formed after hydrolysis of the silane compounds. An inhomogeneous mixture may be due to aggregation of the silica particles. A milky or cloudy appearance may be indicative of an inhomogeneous mixture. Sonication of the mixture, preferably by ultrasonication, may disrupt these aggregations and allow the silica particles to be more homogeneously dispersed in the coating composition. A clear and transparent appearance for the composition may be indicative of a homogeneous mixture.

In one particularly preferred embodiment, the process of the invention prepares a coating composition by co-hydrolysis of two silane compounds, tetraethyl silicate (TEOS) and tridecafluorooctyl triethoxysilane (FAS), in $NH_3 \cdot H_2O$-ethanol solution. The chemical structures of the silane compounds and the preparation route are shown in **Scheme 1.**



Scheme1: Reaction route of silica sol and chemical structures of TEOS and FAS

Hydrolysis of TEOS only quickly resulted in the formation of silica particles that turned the solution milky. Meanwhile, hydrolysis of FAS on its own resulted in the formation of a thick and clear resin that phase-separated from the reaction solution, indicating a very slow hydrolysis rate. When the two silane compounds were co-hydrolysed in the same $NH_3{\cdot}H_2O$-ethanol solution, the quick hydrolysis of the TEOS resulted in the formation of silica particle cores, while the slowly hydrolysed FAS co-condensed with the TEOS which was not used in the formation of the silica particles to produce a shell layer that covered the surface of the silica particles. The coating composition thus formed is stable and homogeneous and no resin separated from the solution after 12 hours.

It is an advantage of the invention that the process for preparing the coating composition is a one-pot and single step method that generates silica particles and a polymer resin which is preferably a low surface energy resin, in-situ under relatively mild conditions. The in-situ produced coating composition including the particulate silica sol is able to provide a hydrophobic, and preferably superhydrophobic, surface on various substrates. The coating composition may be directly applied to the surface of a substrate to form the hydrophobic coating on the substrate.

The present invention also provides a coating composition prepared by a process as described herein.

Applications

The ability to apply the coating composition of the invention to a variety of substrates and to form a hydrophobic and in particular, a superhydrophobic coating on those substrates enables the invention to be used in a wide range of applications. The coating composition of the invention is particularly useful where characteristics such water, ice or fog repellence and/or resistance of a substrate to fouling or contamination by a substances such as for example, oily substances, is desired to be improved. The coating composition may also form a clear and transparent film on the substrate and as such, would not significantly affect the appearance of the underlying substrate. Also, the coating composition is suitable to form films on many different substrates. It is an advantage of the invention that the hydrophobicity of a treated substrate surface is less dependent on the original characteristics of the underlying substrate.

Thus in accordance with one aspect, the present invention provides a method of improving the water repellence of a substrate including the step of applying a coating composition of the invention to the surface of the substrate.

In another aspect, the present invention provides a method of improving resistance to fouling of a substrate including the step of applying a coating composition of the invention to the surface of the substrate.

The improved properties are provided by applying the coating composition of the invention to the surface of a substrate.

Accordingly in a fifth aspect, the invention provides a method for forming a hydrophobic coating on a substrate including the steps of:

(i) applying to the surface of the substrate a coating composition including:

  (a) a plurality of silica particles, and

(b) a hydrolysis product obtained from the hydrolysis of one or more hydrolysable silane compounds, wherein the at least one of the hydrolysable silane compounds includes at least one organofunctional substituent, and wherein at least a portion of the hydrolysis product covers at least a portion of the surface of the silica particles; and

(ii) drying the coated substrate.

The hydrolysis product may be any hydrolysis product as described herein. Preferably, the hydrolysis product is a silica resin as described herein.

Thus in a sixth aspect, the invention provides a method for forming a hydrophobic coating on a substrate including the steps of:

(i) applying to the surface of the substrate a coating composition including:

(a) a plurality of silica particles, and

(b) a silica resin including a plurality of organofunctional substituents, wherein at least a portion of the silica resin covers at least a portion of the surface of the silica particles; and

(ii) drying the coated substrate.

Typically, one or more silica particles are coated with at least a portion of either the hydrolysis product (in the fifth aspect) or the silica resin (in the sixth aspect). Preferably, at least a portion of either the hydrolysis product (in the fifth aspect) or the silica resin (in the sixth aspect) substantially covers the surface of the silica particles. In one embodiment, the silica particles and either the hydrolysis product (in the fifth aspect) or the silica resin (in the sixth aspect) that covers the particles form core-shell particles having a core including a silica particle and a shell surrounding the core, wherein the shell includes either the hydrolysis product or the silica resin.

The coated substrate may be dried for any length of time and at any suitable temperature. Preferably, the coated substrate is dried at room temperature.

Upon application of the coating composition onto a substrate, the resultant coating may form a nano-structured surface with a low free energy, hence imparting superhydrophobicity to the substrate.

The inventors have found that the hydrophobic coating exhibits good adhesion to the underlying substrate. Without wishing to be limited by theory, it is believed that the sol-gel nature of the coating composition assists to promote adhesion of the coating to the substrate.

In one embodiment, the method may further include the step of (iii) heating the coated substrate for a time sufficient to cure the hydrophobic coating. The curing may result in crosslinking of the hydrolysis product or silica resin in the coating. The coated substrate may be heated at any suitable temperature for any suitable length of time and a person skilled in the art would understand that the temperature and time may be varied to achieve a desired result. Preferably, the coated substrate is heated at a temperature in the range of from about 90 to 130°C. In one preferred embodiment, the coated substrate is heated at 110°C, preferably for about 1 hour.

The substrate may be coated with a single layer of the coating composition or alternatively, with multiple (i.e. two or more) layers of the coating composition. If a multilayer coating is desired, a further quantity of the coating composition may be applied to a coated substrate to form a further coating layer on the substrate. For multiple layers, it is preferred that each layer of the coating composition is allowed to cure and/or dry prior to application of any subsequent layers.

In another embodiment, the hydrolysis product (in the fifth aspect) or silica resin (in the sixth aspect) of the coating composition may include at least one functional group adapted to participate in covalent bonding reactions. Preferably, the hydrolysis product or silica resin includes at least one functional group selected from the group consisting of halo, amino, epoxy, hydroxy, thiol, carboxy and anhydride. More preferably, the hydrolysis product or silica resin includes at least one functional group selected from the group consisting of epoxy, carboxy and anhydride functional groups.

Where the hydrolysis product (in the fifth aspect) or silica resin (in the sixth aspect) includes at least one functional group adapted to participate in covalent bonding reactions, the method may include the step of reacting the functional group of the hydrolysis product or silica resin with an agent under conditions allowing formation of a covalent bond between the agent and the hydrolysis product or silica resin. The covalent reaction results in the grafting of the agent to the hydrolysis product or silica resin of the coating composition. Preferably, the hydrolysis product or the silica resin includes at least one functional group selected from the group consisting of halo, amino, epoxy, hydroxy, thiol, carboxy and anhydride. More preferably, the hydrolysis product or silica resin includes at least one functional group selected from the group consisting of epoxy, carboxy and anhydride functional groups. Such functional groups may covalently react with an agent having complementary functional group such as an amino or hydroxy group. The reaction of the agent with the functional groups of the hydrolysis product or the silica resin may be carried out before application of the coating composition to the surface of a substrate, however it is preferred that the reaction be performed after the coating has been formed on the substrate surface.

In one embodiment, the agent is a hydrophobic agent including an organofunctional substituent capable of imparting hydrophobicity to the coating of the invention. Preferred organofunctional substituents include a moiety selected from the group consisting of C_1 to C_{20} alkyl, C_2 to C_{30} alkenyl, C_3 to C_{10} alkyl epoxy, C_2 to C_{20} aminoalkyl, C_5 to C_{10} aminocycloalkyl, C_5 to C_{10} aryl, C_1 to C_{20} haloalkyl, C_3 to C_{10} cycloalkyl and C_2 to C_{20} cyanoalkyl, more preferably a moiety selected from the group consisting of C_1 to C_{20} alkyl (preferably C_8-C_{20} alkyl), C_3 to C_{10} alkyl epoxy, C_5 to C_{10} aryl and C_1 to C_{20} haloalkyl (preferably C_1 to C_{20} fluoroalkyl), even more preferably a moiety selected from the group consisting of C_8-C_{20} alkyl and C_1 to C_{20} perfluoroalkyl. In one embodiment, the agent is an alkylamine (such as a C_1 to C_{20}

alkylamine, preferably C_8 to C_{20} alkylamine) or a fluoroalkylamine (such as a C_1 to C_{20} perfluoroalkylamine). The reaction of an agent with the functional groups of the hydrolysis product or silica resin may therefore provide a coating including a plurality of organofunctional substituents grafted thereto, wherein the organofunctional substituents are derived from the agent that is covalently bonded to the coating.

In another embodiment, where the hydrolysis product (in the fifth aspect) or silica resin (in the sixth aspect) of the coating composition includes at least one functional group adapted to participate in covalent bonding reactions, the functional groups may participate in covalent crosslinking reactions. Thus, in another embodiment the method of invention may include the step of reacting the functional groups of the hydrolysis product or silica resin under conditions allowing crosslinking of the applied coating composition. For example, if the hydrolysis product includes a mixture of different types of functional groups (e.g. amino and epoxy functional groups) these groups may react together to form a crosslink there between, thereby giving rise to a crosslinked coating. Alternatively, the functional groups of the hydrolysis product or silica resin may react with a crosslinking agent to form a crosslinked coating. The crosslinking reactions may be facilitated by the application of heat, such as during curing of the coating composition. Crosslinked coatings may exhibit greater stability than non-crosslinked coatings.

In a further embodiment, the method of the invention may include the step of reacting the functional groups of the hydrolysis product (in the fifth aspect) or silica resin (in the sixth aspect) of the coating composition with functional groups present on the surface of the substrate under conditions allowing formation of a covalent bond between the applied coating composition and the substrate. The reaction of the respective functional groups may improve the adhesion of the applied coating to the substrate.

In general, conditions for forming covalent bonds between appropriate functional groups can be ascertained by one skilled in the relevant art.

The present invention also provides a coated substrate including a coating composition as described herein.

A nano-structured surface formed by silica particles in combination with a product that has a low surface free energy has been shown in the invention to exhibit at least hydrophobic and typically superhydrophobic properties. The present invention not only allows excellent properties to be imparted to the substrate, the application of the coating composition to a substrate is robust and may be achieved by the use of conventional wet-coating techniques. The present invention therefore provides a one-step method for the hydrophobic treatment of substrates.

EXAMPLES

The present invention is described with reference to the following examples. It is to be understood that the examples are illustrative of and not limiting to the invention described herein.

Materials and measurements

Ethanol, tetraethylorthosilicate (TEOS) and ammonium hydroxide (28% in water) were obtained from Aldrich. Tridecafluorooctyl triethoxysilane (FAS, Dynasylan F 8261), Methyltriethoxysilane (MTES), phenyl triethoxysilane (PTES), Octal triethoxysilane (OTES, Dynasylan octeo), Hexadecyl trimethoxysilan (HETMS, Dynasylan 9116) and 3-Glycidoxypropyltrimethoxysilane (GPTMS) were supplied by Degussa. n-Hexadecylamine was obtained from Aldrich.

The macroscopic images were taken under a scanning electron microscope (SEM, Leo 1530). Transmission electron microscope (TEM, JEM-200 CX JEOL) was used to observe the silica particles. The FTIR (Fourier Transform Infrared) spectra were measured on a FTIR spectrophotometer (Bruker Optics) in ATR mode. The water contact angles were measured using a contact angle meter (KSV CAM200 Instruments Ltd). X-ray photoelectron spectra (XPS) were collected on a VG ESCALAB 220-iXL spectrometer with a monochromated Al K_source (1486.6 eV). Survey spectrum (0–1100 eV) was obtained, followed by high-resolution spectra of the C_{1s}, O_{1s}, F_{1s} and Si_{2p} regions. The sampling area was ca. 3 mm^2. The photoelectron emission angle was 0º with respect to the surface normal. This corresponds to a sampling depth of ca. 10 nm. Spectra were analysed by XPSPEAK41 software.

Example 1

TEOS (5ml) and FAS (FAS/TEOS ratio of 1:10 mol/mol) were dissolved in 25ml ethanol. The solution was mixed with ammonium hydroxide in ethanol solution (6ml 28% $NH_3{\cdot}H_2O$ in 25ml ethanol), and stirred intensively at room temperature for 12hr. The milky mixture was then subjected to 30min ultrasonic treatment (VCX750 Sonics & Materials Inc.), to get a homogeneous suspension, and immediately applied to a substrate. After drying at room temperature, the treated substrate was cured at 110ºC for 1hr. In this study, six different substrates were used, including glass slide, polyester fabric (plain weave, 168g/m^2), wool fabric (plain weave, 196g/m^2), cotton fabric (plain weave, 160g/m^2), electrospun polyacrylonitrile (PAN) nanofibre mat (average fibre diameter 226±21nm, thickness 0.29mm±0.03mm), filter paper (Advantec. Tokyo Roshi Kaisha, Ltd) and silicon wafer (Si-Mat Silicon Materials). The resultant coated substrates were characterised by SEM, FTIR, XPS and contact angle and sliding angle measurements.

The results of water contact angle and sliding angle after application of the fluoro-containing silica sol on to various substrates is shown in Table 1. As seen in Table 1, all the substrates exhibited very high surface contact angle (larger than 170º) and low sliding angle (in the range of 1.7-6.3º) after the coating treatment.

Table 1. Water contact angle data on different substrates*

Substrate	Loading (mg/cm^2)	Contact Angle (degree)		Sliding Angle (degree)
		Before coating	After coating	
Polyester fabric	5.02	117.1	174.2±2.7	2.2±0.1
Cotton fabric	2.62	37.9	173.7±3.2	4.9±0.4
Wool fabric	4.08	108.0	170.2±2.5	5.6±0.4
Nanofibre mat	1.30	132.6	176.9±2.1	1.7±0.1
Filter paper	1.90	0	172.4±2.3	6.3±0.3
Glass slide	0.15	33.5	174.6±1.6	2.3±0.3
Silicon wafer	0.20	63.0	174.2±1.4	2.4±0.2

* FAS/TEOS ratio=1:10 (mol/mol)

The SEM images of coated polyester fibres are shown in Figure 1. Particles with an average particle size around 100 to 300nm were observed to scatter or aggregate in the entire coating area. The contact angle (CA) measurement indicated that the coated surface had a water contact angle and sliding angle of 174±2.7º and 2.2±0.1º, respectively. As depicted in the photographic image in Figure 1, the water formed a nearly spherelike droplet on the treated fabric surface, and such a droplet was able to maintain this shape for a long period of time.

The FTIR spectra of the polyester fabric before and after the coating treatment are shown in Figure 2. After the coating treatment, new peaks occurred at 1087cm^{-1} and 810cm^{-1} corresponding to Si–O–Si asymmetric and symmetric vibration, respectively. The peaks at 1240 and 1190cm^{-1} were characteristic of C-F stretching vibrations.

The chemical composition of the coated surface was also measured by XPS. Figure 3 shows the XPS spectra of the silica coated polyester fabric, corresponding to the C_{1s} and Si_{2p} regions. The binding energies of 294eV, 292eV, 289eV, 285eV are typical of $-CF_3$, $-CF_2$, -CSi and C-H moieties, respectively. The binding energy of Si_{2p} was 104.6eV, suggesting the polyester fabric was covered with the coating.

The XPS measurement also gave information about the atomic fraction of elements on the sample surface. Based on the atomic fraction data, the atomic ratio of element F, C and Si on the coating surface can be calculated, to be $N_F/N_C/N_{Si}$=37.4/26.9/11.7 (molar ratio). This ratio in FAS molecule (excluding three ethoxy groups) can also be calculated, to be 37.4/23.0/2.8 (mol/mol). By comparing the two ratios, it is estimated that about 25% silicon atoms came from FAS, and other 75% from TEOS. Since the FAS/TEOS ratio in the sol preparation was 1/10 (mol/mol), the high FAS moiety on the surface of the silica coating suggested that FAS was mainly concentrated on the silica surface. The high composition of FAS resulted in high concentration of tridecafluorooctyl on the silica surface, rendering the surface with a low free energy.

Images of water droplets on a variety of coated substrates are shown in Figure 4.

A TEM image of the silica particles of the particulate coating is shown in Figure 5. SEM-EDX mapping revealed that the surface elements O, F and Si in addition to bulk carbon, which shows that the silica particles are each coated by a polymer resin containing FAS. The coated silica particles resemble core-shell structures.

Example 2

A range of solutions containing variable ratios of FAS:TEOS ranging from 1:50 to 1:5 (v/v) were prepared in accordance with the procedure of Example 1 and applied to polyester fabric. In addition, either a single coating layer or multiple coating layers were applied to the fabric.

As shown in Figure 6, with the FAS:TEOS ratio changed from 1:50 to 1:5 (v/v), the increase in the FAS proportion led to increased CA value, suggesting that the surface hydrophobicity increases with the increase of FAS proportion in the sol preparation. While it was found that further increasing the FAS/TEOS ratio from 1:5 to 1:3.3 (v/v) reduced the CA value, the coated substrate nevertheless still exhibited hydrophobic properties.

Example 3

TEOS (5ml), tridecafluorooctyl triethoxysilane (1ml) and (3-glycidyloxypropyl) trimethoxysilane (1ml) were dissolved in 25ml ethanol. The solution was mixed with ammonium hydroxide/ethanol solution (6ml 28% $NH_3{\cdot}H_2O$ in 25ml ethanol), and stirred intensively at room temperature for 12hr. The milky mixture solution was then ultrasonicated for 30 min to produce a homogeneous suspension prior to the immediate coating onto substrates. Upon drying at room temperature, the treated substrate was further cured at 110ºC for 1hr. The water contact angle of the coated surface was 172º.

Example 4

TEOS (5ml), and dodecyltriethoxysilane (1ml) were dissolved in 25ml ethanol. The solution was mixed with ammonium hydroxide/ethanol solution (6ml 28% $NH_3{\cdot}H_2O$ in 25ml ethanol), and stirred intensively at room temperature for 12hr. The milky mixture solution was then ultrasonicated for 30 min to produce a homogeneous suspension prior to the immediate coating onto substrates. Upon drying at room temperature, the treated substrate was further cured at 110ºC for 1hr. The water contact angle of the coated surface was 166º.

Example 5

TEOS (5ml), dodecyltriethoxysilane (1ml) and (3-glycidyloxypropyl) trimethoxysilane (1ml) were dissolved in 25ml ethanol. The solution was mixed with ammonium hydroxide/ethanol solution (6ml 28% $NH_3{\cdot}H_2O$ in 25ml ethanol), and stirred intensively at room temperature for 12hr. The milky mixture solution was then ultrasonicated for 30 min to produce a homogeneous suspension prior to the immediate coating onto substrates. Upon drying at room temperature, the treated substrate was further cured at 110ºC for 1hr. The water contact angle of the coated surface was 163º.

Example 6

TEOS (5ml) and phenyl triethoxysilane (1ml) were dissolved in 25ml ethanol. The solution was mixed with ammonium hydroxide in ethanol solution (6ml 28% $NH_3{\cdot}H_2O$ in 25ml ethanol), and stirred intensively at room temperature for 12hr. The mixture was then subjected to 30min ultrasonic treatment to get a homogeneous suspension and immediately applied to a substrate. After drying at room temperature, the treated substrate was cured at 110ºC for 1hr. The surface showed water contact angle of 172.3º (on polyester fabric).

Example 7

TEOS (5ml) and hexadecyl trimethoxysilane (1ml) were dissolved in 25ml ethanol. The solution was mixed with ammonium hydroxide in ethanol solution (6ml 28% $NH_3{\cdot}H_2O$ in 25ml ethanol), and stirred intensively at room temperature for 12hr. The mixture was then subjected to 30min ultrasonic treatment (VCX750 Sonics & Materials Inc.) to get a homogeneous suspension and immediately applied to a substrate. After drying at room temperature, the treated substrate was cured at 110ºC for 1hr. The surface showed water contact angle of 172.5º (on cotton fabric).

Example 8

Compositions containing TEOS (5ml) together with 1ml of tridecafluorooctyl triethoxysilane (FAS), methyltriethoxysilane (MTES), phenyl triethoxysilane (PTES), octal triethoxysilane (OTES) or hexadecyl trimethoxysilane (HETMS) dissolved in 25 ml ethanol were prepared. Each solution was then mixed with ammonium hydroxide/ethanol solution (6ml 28% $NH_3{\cdot}H_2O$ in 25 ml ethanol), and stirred intensively at room temperature for 12 hr. The mixture solutions were then ultrasonicated for 30 min to produce homogeneous suspensions prior to application of the coating compositions onto various substrates.

Polyester fabric (plain weave, 168 g/m^2), wool fabric (plain weave, 196 g/m^2) and cotton fabric (plain weave, 160 g/m^2) were used in this example. The solutions prepared above were padded onto the fabrics and dried at room temperature. Upon drying at room temperature, the treated substrates were further cured at 110ºC for 1hr. The results of contact angle (CA) and sliding angle (SA) measurements are shown in the Table 2 below:

Table 2. Hydrophobicity data of fabric substrates treated by different coating solutions

Coating Composition	Fabric	CA (º)	SA (º)
TEOS/MTES	Cotton	133. 8±3.1	40±0.4
	Wool	141.4±2.9	40±0.6
	Polyester	156.1±2.8	37.0±0.3
TEOS/PTES	Cotton	169.8±3.7	9.4±0.7
	Wool	170.1±3.5	14.9±0.6
	Polyester	172.4±1.5	8.7±0.4
TEOS/OTES	Cotton	163.6±3.1	33.1±0.8
	Wool	166.8±1.9	23.7±0.6
	Polyester	172.0±2.4	9.8±0.5
TEOS/HETMS	Cotton	170.6±2.6	13.3±0.3
	Wool	172.9±3.0	9.6±0.4
	Polyester	173.5±2.5	6.4±0.5
TEOS/FAS	Cotton	173.7±3.2	4.9±0.4
	Wool	170.2±2.5	5.6±0.4
	Polyester	174.2±2.7	2.2±0.1

Each of the coatings formed using FAS, MTES, OTES, PTES and HETMS exhibited a core-shell particulate structure. The silica particles formed using the different systems were also of similar size. Furthermore, the coating showed good coverage of the fabric surface treated by the coating.

In this example, the length of the non-hydrolysable alkyl group was observed to influence the properties of the resulting coating. The alkyl chain length for MTES, OTES and HETMS is 1, 8 and 16 carbons, respectively. It was observed that with the increase in the alkyl chain length, the contact angle value also increased. In addition, comparing the OTES to FAS (in which the six carbons in the alkyl chain was fluorinated), the fluorinated alkyl chain of FAS also led to higher hydrophobicity.

Example 9

Compositions containing TEOS (5ml) and various amounts of GPTMS and the alkyl silanes FAS, OTES or HETMS corresponding to the amounts described in Table 3 were prepared in 25 ml ethanol. The solutions were mixed with ammonium hydroxide/ethanol solution (6ml 28% $NH_3 \cdot H_2O$ in 25 ml ethanol), and stirred intensively at room temperature for 12 hr. The mixture solutions were then ultrasonicated for 30 min to produce homogeneous suspensions prior to application of the compositions onto substrates.

The different coating compositions were then padded onto polyester fabric (plain weave, 168 g/m^2) and dried at room temperature. After drying at room temperature, the treated substrates were further cured at 110ºC for 1hr.

The washing fastness of the coated fabric was then tested by washing the coated fabric with water containing soap (5g/L) and sodium carbonate (2g/L), according Australian Standard 2001.2.25.4-2006. The contact angle of the treated fabric before and after washing was measured. The results are shown in Table 3. The washing fastness can provide an indication of the durability of the coating applied to the fabric.

Table 3. Contact angles of coated polyester fabric before and after washing

GPTMS (ml)	Alkyl Silane (ml)	Water contact angle (º)	
		Before washing	After washing
0.33	FAS (0.66)	159.5±1.5	153.7±2.6
0.20	FAS (0.80)	163.0±2.1	156.0±1.1
0.66	HETMS (0.33)	156.0±2.8	148.1±1.8
0.50	HETMS (0.50)	159.5±1.6	154.6±2.2
0.33	HETMS (0.66)	162.0±1.1	152.4±2.5
0.33	OTES (0.66)	157.8±2.0	145.9±2.7
0.20	OTES (0.80)	162.1±2.2	143.5±3.1

The above result shows that after washing, the coating remains on the fabric and is still able to impart hydrophobic properties to the polyester fabric.

In this example, the use of GPTMS in the coating composition may enable the coating to covalently bond to surface of the underlying fabric substrate and therefore help to improve the durability of the coating.

Example 10 - Multilayer Coating

Polyester (plain weave, 168 g/m^2), wool (plain weave, 196 g/m^2) and cotton (plain weave, 160 g/m^2) fabrics were coated with a composition containing TEOS/GPTMS/FAS (5ml/0.2ml/0.8ml) in accordance with the procedure of Example 9 and the coated fabrics were then further treated by applying a composition containing TEOS (5ml), GPTMS (0.2ml) and FAS (0.8ml) to the coated fabrics to form a second coating layer on the fabric. The washing fastness of the multilayer coating was then tested. The contact angle of the multilayer coating before and after washing was measured and the results are shown in Table 4.

Table 4. Contact angles of fabric with multilayer coating before and after washing

Fabrics	Water contact angle (º)	
	Before washing	After washing
Cotton	160.8±1.5	123.2±1.6
Polyester	163.0±2.1	156.4±1.1
Wool	155.4±2.4	144.1±1.2

Example 11

In this example, TEOS/GPTMS/FAS coated polyester fabrics prepared in accordance with the procedure of Example 9 were dipped into hexadecylamine-ethanol solution (5wt%) then dried at room temperature. After drying, the fabric was cured at 80 ºC for 10min. The hexadecylamine treated fabrics were then rinsed with ethanol and dried at room temperature. The treated polyester fabrics were then tested for washing fastness and contact angle according to the procedure described in Example 9. The results are shown in Table 5.

Table 5. Contact angle of coated polyester fabric treated with hexadecylamine

TEOS (ml)	GPTMS (ml)	FAS (ml)	Water contact angle (º)	
			Before washing	After washing
5	0.33	0.66	170.8±2.4	168.7±1.2
5	0.20	0.80	171.2±7.4	168.3±3.4

This example showed that the hexadecylamine solution was able to react with any epoxy groups derived from GPTMS in the coating to graft hexadecyl groups onto the coating. The hexadecyl groups increased the hydrophobicity of the coated polyester fabrics.

It is understood that various other modifications and/or alterations may be made without departing from the spirit of the present invention as outlined herein.

CLAIMS

1. A coating composition for forming a hydrophobic coating on a substrate, the composition including:

a plurality of silica particles, and

a hydrolysis product obtained from the hydrolysis of one or more hydrolysable silane compounds, wherein the at least one of the hydrolysable silane compounds includes at least one organofunctional substituent,

and wherein at least a portion of the hydrolysis product covers at least a portion of the surface of the silica particles.

2. A coating composition according to claim 1 wherein at least a portion of the hydrolysis product substantially covers the surface of the silica particles.

3. A coating composition according to claim 1 or claim 2 wherein the silica particles and the hydrolysis product covering the surface of the silica particles form core-shell particles, each core-shell particle having a core including a silica particle and a shell including the hydrolysis product substantially surrounding the core.

4. A coating composition according to any one of claims 1 to 3 wherein the hydrolysis product is a silica resin.

5. A coating composition according to any one of claims 1 to 4 wherein each organofunctional substituent includes a moiety independently selected from the group consisting of alkyl, alkenyl, alkynyl, alkyl ethers, alkyl esters, aryl, cycloalkyl, haloalkyl, haloether, cyano, epoxy, amino, aminoalkyl, aminoalkenyl, aminoalkynyl, aminoaryl, aminocycloalkyl and mixtures thereof.

6. A coating composition according to claim 5 wherein each organofunctional substituent includes a moiety independently selected from the group consisting of C_1 to C_{20} alkyl, C_2 to C_{30} alkenyl, C_3 to C_{10} alkyl epoxy, C_2 to C_{20} aminoalkyl,

C_5 to C_{10} aminocycloalkyl, C_5 to C_{10} aryl, C_1 to C_{20} haloalkyl, C_3 to C_{10} cycloalkyl and C_2 to C_{20} cyanoalkyl.

7. A coating composition according to claim 6 wherein each organofunctional substituent includes a moiety independently selected from the group consisting of C_1 to C_{20} alkyl, C_5 to C_{10} aryl, C_3 to C_{10} alkyl epoxy and C_1 to C_{20} haloalkyl.

8. A coating composition according to claim 7 wherein each organofunctional substituent includes a C_8 to C_{20} alkyl moiety or a C_1 to C_{20} perfluoroalkyl moiety.

9. A coating composition according to any one of claims 1 to 8 wherein the hydrolysis product includes at least one functional group adapted to participate in covalent bonding reactions.

10. A coating composition according to claim 9 wherein the functional group is selected from the group consisting of halo, amino, epoxy, hydroxy, thiol, carboxy and anhydride functional groups.

11. A coating composition according to any one of claims 1 to 10 wherein the silica particles have a particle size in the range of from 10 to 900 nm.

12. A coating composition according to any one of claims 1 to 11 wherein the silica particles have a particle size in the range of from 30 to 500 nm.

13. A coating composition according to any one of claims 1 to 12 further including a solvent, wherein the silica particles and the hydrolysis product are dispersed in the solvent.

14. A coating composition according to any one of claims 1 to 13 wherein in use, the composition provides a coating that exhibits a water contact angle of at least about 120 degrees.

15. A coating composition according to any one of claims 1 to 14 wherein in use, the composition provides a coating that exhibits a water contact angle of at least about 150 degrees.

16. A coating composition according to any one of claims 1 to 15 wherein in use, the composition provides a coating that exhibits a water contact angle of at least about 160 degrees.

17. A coating composition according to any one of claims 1 to 16 wherein in use, the composition provides a coating that exhibits a sliding angle of no more than about 35 degrees.

18. A coating composition according to any one of claims 1 to 17 wherein in use, the composition provides a coating that exhibits a sliding angle of no more than about 15 degrees.

19. A process for the preparation of a coating composition for forming a hydrophobic coating on a substrate, the process including the step of mixing a first hydrolysable silane compound with a second hydrolysable silane compound, wherein the second hydrolysable silane compound includes at least one organofunctional substituent, under conditions allowing hydrolysis of the first and second hydrolysable silane compounds to form a coating composition including a plurality of silica particles and a hydrolysis product which is at least partly derived from the second hydrolysable silane compound, wherein at least a portion of the hydrolysis product covers at least a portion of the surface of the silica particles.

20. A process according to claim 19 wherein at least a portion of the hydrolysis product substantially covers the surface of the silica particles.

21. A process according to claim 19 or claim 20 wherein the silica particles and the hydrolysis product covering the surface of the silica particles form core-shell particles, each core-shell particle having a core including a silica

particle and a shell including the hydrolysis product substantially surrounding the core.

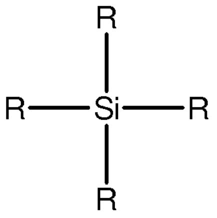
22. A process according to any one of claims 19 to 21 wherein the hydrolysis product is a silica resin.

23. A process according to any one of claims 19 to 22 wherein the hydrolysis is performed in a solution including an alkali and a solvent.

24. A process according to claim 23 wherein the alkali is selected from the group consisting of ammonium hydroxide, amines, imidazole, pyridines and metal hydroxides.

25. A process according to claim 24 wherein the alkali is ammonium hydroxide.

26. A process according to any one of claims 19 to 25 wherein the first hydrolysable silane compound is of general formula (I)

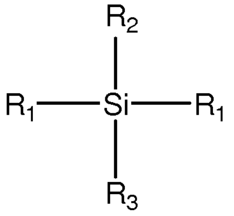


$$R_4Si \quad (I)$$

where

R is a hydrolysable group and at each occurrence is independently selected from the group consisting of alkoxy, alkenyloxy and halo.

27. A process according to any one of claims 19 to 26 wherein the second hydrolysable silane compound is of general formula (II):



(II)

where

R_1 is a hydrolysable group and at each occurrence is independently selected from the group consisting of alkoxy, alkenyloxy and halo,

R_2 is a hydrolysable group selected from the group consisting of alkoxy, alkenyloxy and halo, or

R_2 is a non-hydrolysable organofunctional group including a moiety selected from the group consisting of alkyl, alkenyl, alkynyl, alkylepoxy, alkyl ethers, alkyl esters, aryl, cycloalkyl, haloalkyl, haloether, cyano, epoxy, amino, aminoalkyl, aminoalkenyl, aminoalkynyl, aminoaryl, aminocycloalkyl and mixtures thereof, and

R_3 is a non-hydrolysable organofunctional group including a moiety selected from the group consisting of alkyl, alkenyl, alkynyl, alkylepoxy, alkyl ethers, alkyl esters, aryl, cycloalkyl, haloalkyl, haloether, cyano, epoxy, amino, aminoalkyl, aminoalkenyl, aminoalkynyl, aminoaryl, aminocycloalkyl and mixtures thereof.

28. A process according to claim 27 wherein R_3 includes a moiety independently selected from the group consisting of C_1 to C_{20} alkyl, C_2 to C_{30} alkenyl, C_3 to C_{10} alkyl epoxy, C_2 to C_{20} aminoalkyl, C_5 to C_{10} aminocycloalkyl, C_5 to C_{10} aryl, C_1 to C_{20} haloalkyl, C_3 to C_{10} cycloalkyl and C_2 to C_{20} cyanoalkyl.

29. A coating composition according to claim 28 wherein R_3 includes a moiety independently selected from the group consisting of C_1 to C_{20} alkyl, C_5 to C_{10} aryl, C_3 to C_{10} alkyl epoxy and C_1 to C_{20} haloalkyl.

30. A process according to claim 29 wherein R_3 includes a C_8 to C_{20} alkyl moiety or a C_1 to C_{20} perfluoroalkyl moiety.

31. A process according to any one of claims 26 to 30 wherein R is C_1 to C_4 alkoxy.

32. A process according to any one of claims 27 to 31 wherein R_1 and R_2 are C_1 to C_4 alkoxy.

33. A process according to any one of claims 19 to 32 wherein the ratio of the first hydrolysable silane compound to the second hydrolysable silane compound is the range of from about 200:1 to 1:50 (mol/mol).

34. A process according to any one of claims 19 to 33 further including the step of mixing a further hydrolysable silane compound with the first and second hydrolysable silane compounds.

35. A process according to claim 34 wherein the further hydrolysable silane compound includes an organofunctional substituent having a functional group adapted to participate in covalent bonding reactions.

36. A process according to claim 35 wherein the functional group adapted to participate in covalent bonding reactions is selected from the group consisting of halo, amino, epoxy, hydroxy, thiol, carboxy and anhydride functional groups.

37. A process according to any one of claims 19 to 36 wherein the hydrolysis is performed for about 12 hours at room temperature.

38. A process according to any one of claims 19 to 37 further including the step of sonicating the composition to form a homogeneous mixture.

39. A coating composition prepared by the process of any one of claims 19 to 38.

40. A method for forming a hydrophobic coating on a substrate including the steps of:

(i) applying to the surface of the substrate a coating composition including:

(a) a plurality of silica particles, and

(b) a hydrolysis product obtained from the hydrolysis of one or more hydrolysable silane compounds, wherein the at least one of the hydrolysable silane compounds includes at least one organofunctional substituent, and wherein at least a portion of the hydrolysis product covers at least a portion of the silica particles; and

(ii) drying the coated substrate.

41. A method according to claim 40 wherein at least a portion of the hydrolysis product substantially covers the surface of the silica particles.

42. A method according to claim 40 or claim 41 wherein the silica particles and the hydrolysis product covering the surface of the silica particles form core-shell particles, each core-shell particle having a core including a silica particle and a shell including the hydrolysis product substantially surrounding the core.

43. A method according to any one of claims 40 to 42 wherein the hydrolysis product is a silica resin.

44. A method according to any one of claims 40 to 43 further including the step of heating the coated substrate for a time sufficient to cure the hydrophobic coating.

45. A method according to claim 44 wherein coated substrate is heated at temperature in the range of from about 90 to 130°C.

46. A method according to any one of claims 40 to 45 wherein the hydrolysis product further includes at least one functional group adapted to participate in covalent bonding reactions.

47. A method according to claim 46 wherein the hydrolysis product includes at least one functional group selected from the group consisting of halo, amino, epoxy, hydroxy, thiol, carboxy and anhydride functional groups.

48. A method according to claim 46 or claim 47 further including the step of reacting the functional groups of the hydrolysis product under conditions allowing crosslinking of the applied coating composition.

49. A method according to claim 46 or claim 47 further including the step of reacting the functional groups of the hydrolysis product with functional groups present on the surface of the substrate under conditions allowing formation of a covalent bond between the applied coating composition and the substrate.

50. A method according to claim 46 or claim 47 further including the step of reacting the functional group of the hydrolysis product with an agent under conditions allowing formation of a covalent bond between the agent and the hydrolysis product.

51. A method according to claim 50 wherein the agent includes a moiety selected from the group consisting of C_1 to C_{20} alkyl (preferably C_8 to C_{20} alkyl) and C_1 to C_{20} haloalkyl (preferably C_1 to C_{20} fluoroalkyl).

52. A method according to claim 51 wherein the agent is a C_1 to C_{20} alkylamine or a C_1 to C_{20} fluoroalkylamine (preferably C_1 to C_{20} perfluoroalkylamine).

53. A coated substrate including a coating composition of any one of claims 1 to 18.

54. A method of improving the water repellence of a substrate including the step of applying a coating composition of any one of claims 1 to 18 to the surface of the substrate.

55. A method of improving resistance to fouling of a substrate including the step of applying a coating composition of any one of claims 1 to 18 to the surface of the substrate.

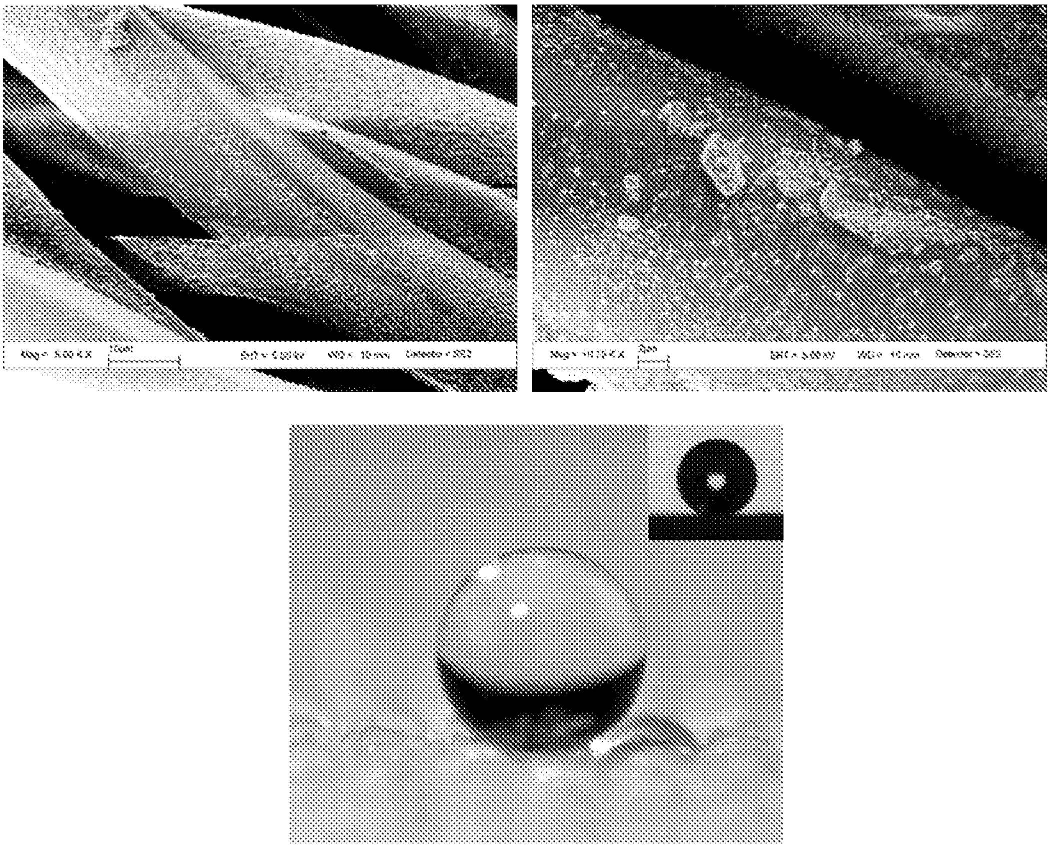


FIGURE 1

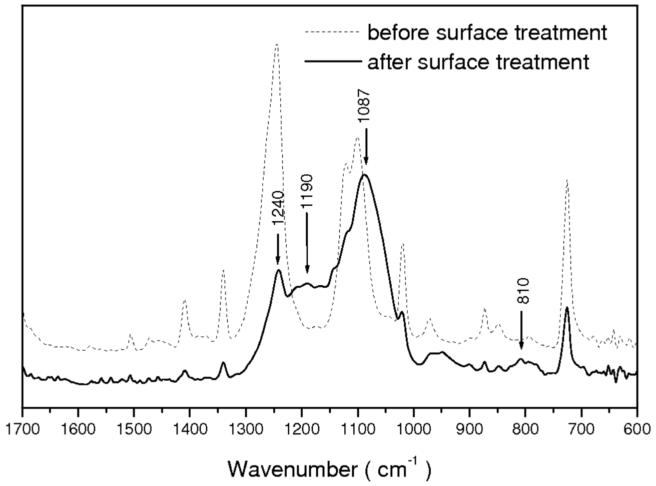

before surface treatment
after surface treatment
1240
1190
1087
810
1700
1600
1500
1400
1300
1200
1100
1000
900
800
700
600
Wavenumber (cm-1)

FIGURE 2

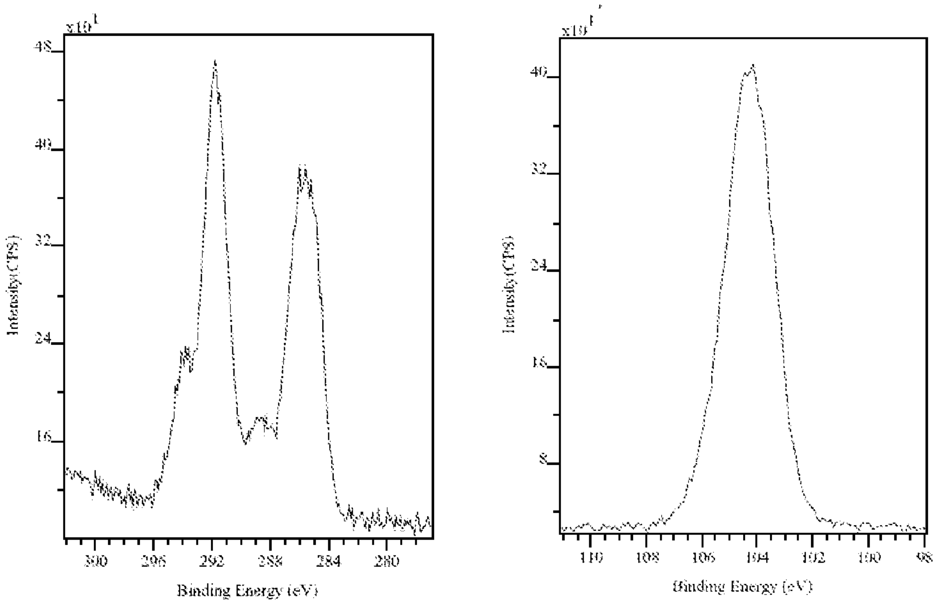


FIGURE 3(a)

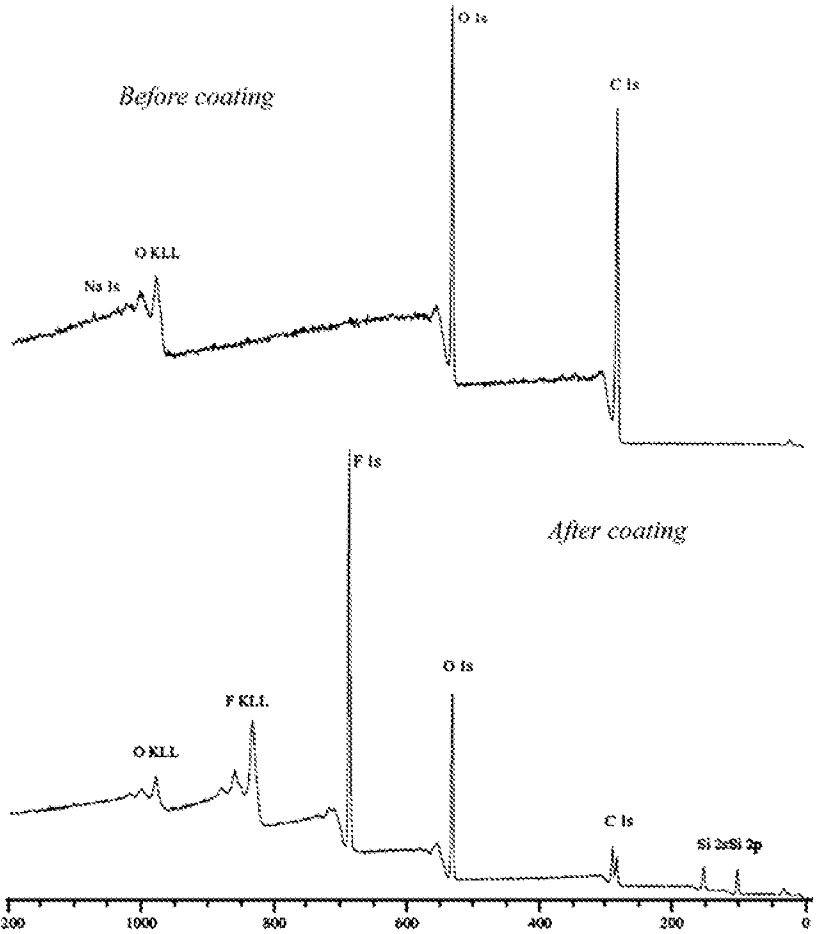
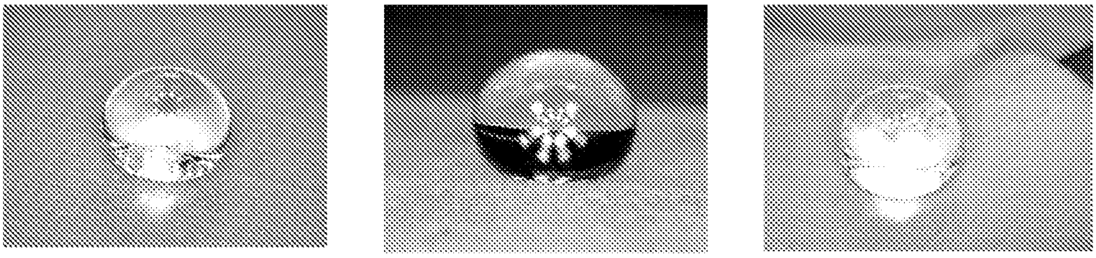
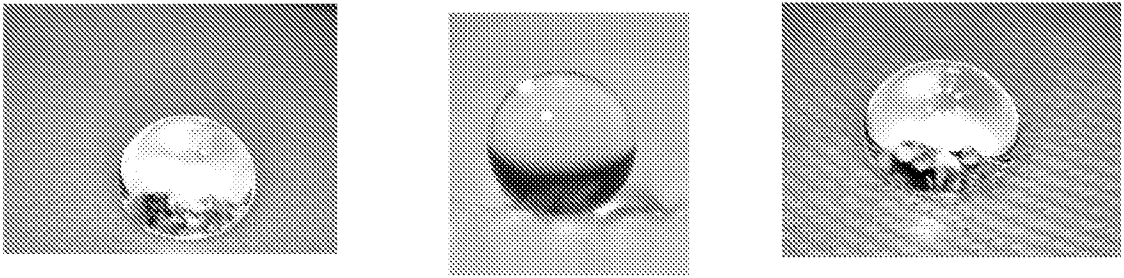


FIGURE 3(b)



cotton glass nanofibre



paper polyester wool

FIGURE 4

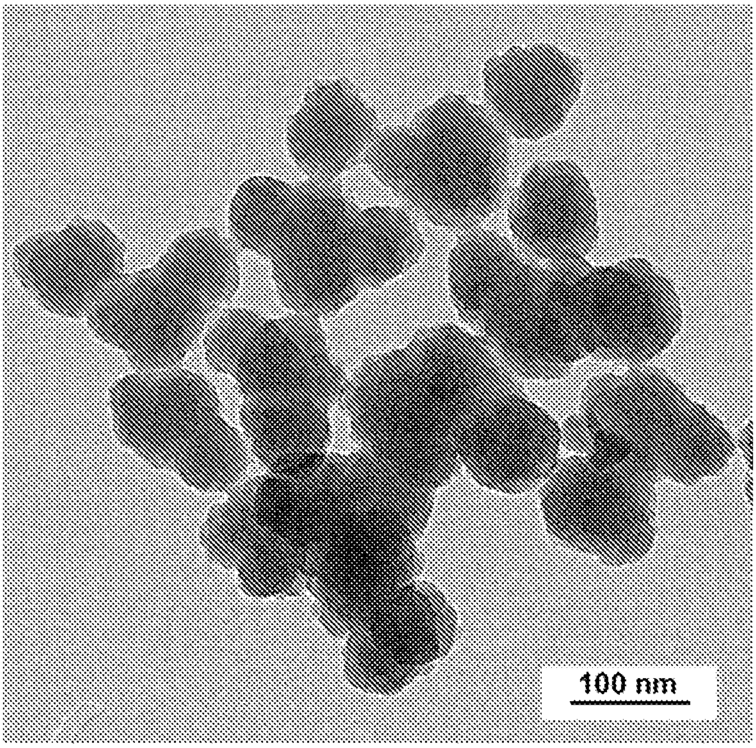


FIGURE 5

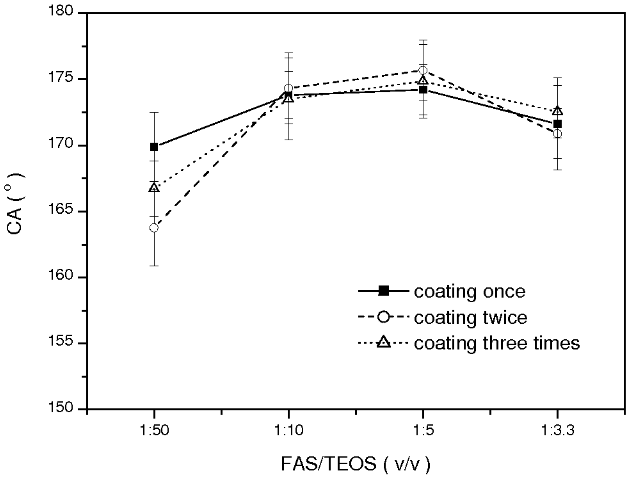

180
175
170
165
160
155
150
CA (°)
1:50
1:10
1:5
1:3.3
FAS/TEOS (v/v)
coating once
coating twice
coating three times

FIGURE 6

INTERNATIONAL SEARCH REPORT

International application No.
PCT/AU2008/001304

A. CLASSIFICATION OF SUBJECT MATTER

Int. Cl.

C09D 1/00 (2006.01) *C08K 3/36* (2006.01) *C09D 183/04* (2006.01)

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)

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)
WPI; EPODOC; CAPLUS: ?hydrophobic?, plurality, coat?, silica or silicon (w) dioxide, ?particulate? or ?particle?, ?silane? or ?siloxane? or ?silicane?, hydrolys? or hydrolyz?, surface? (6a) silica, substrate?, core? or shell?

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 863191 A2 (NIPPON PAINT CO. LTD.) 9 September 1998 (see pg. 8, lines 30-46; pg. 17, lines 23-33; pg. 20, lines 18-34; pg. 23, lines 16-49; Examples, claims)	1-14, 39-51, 53-55
X	US 6506496 B1 (FRUGIER et al.) 14 January 2003 (see Abstract, col. 4, line 38 to col. 7, line 14; Examples, claims)	1-11, 13, 19-22, 26-51, 53-55
X	US 6521290 B1 (KUDO et al.) 18 February 2003 (see Abstract, col. 6, line 64 to col. 7, line 16; Examples, claims)	1-13, 19-43, 46-51, 53-55

☒ 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	"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
"E"	earlier application or patent but published on or after the international filing date	"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
"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)	"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
"O"	document referring to an oral disclosure, use, exhibition or other means	"&"	document member of the same patent family
"P"	document published prior to the international filing date but later than the priority date claimed		

Date of the actual completion of the international search 08 October 2008	Date of mailing of the international search report 20 OCT 2008
Name and mailing address of the ISA/AU AUSTRALIAN PATENT OFFICE PO BOX 200, WODEN ACT 2606, AUSTRALIA E-mail address: pct@ipaustralia.gov.au Facsimile No. +61 2 6283 7999	Authorized officer **SALESH SWAMI** AUSTRALIAN PATENT OFFICE (ISO 9001 Quality Certified Service) Telephone No : +61 2 6283 7939

INTERNATIONAL SEARCH REPORT

International application No.
PCT/AU2008/001304

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 6635735 B1 (ZHANG et al.) 21 October 2003 (see col. 2, line 51 to col. 3, line 6; col. 5, lines 9-37; Examples, claims)	1-13, 19-44, 46-55
X	US 2007/0196656 A1 (ROWELL) 23 August 2007 (see Abstract, para. 0011-0019; 0025-0029; 0045-0060; 0105; 0132; Examples; claims)	1-13, 19-43, 46-54
X	Patent Abstracts of Japan JP 2006-022258 A (MITSUBISHI RAYON CO. LTD.) 26 January 2006 (see Abstract, English machine translation of para. 0008-0036 & Examples retrieved from the JAPIO website).	1-11, 13-18, 39-44, 46-51, 53-55
X	Patent Abstracts of Japan JP 02-003468 A (CATALYSTS & CHEM IND CO. LTD.) 9 January 1990 (see Abstract)	1-13, 19-22, 26-36, 39-43, 46-51, 53-55
X	WO 2001/014497 A1 (UNISEARCH LIMITED) 1 March 2001 (see Abstract, pg. 10, line 30 to pg. 12, line 24; Examples; claims)	1-22, 26-51, 53-55
X	WO 2004/0104116 A1 (DSM IP ASSETS B.V.) 2 December 2004 (see Abstract, pg. 3, line 17 to pg. 4, line 21; pg. 5, line 30 to pg. 7, line 31; pg. 11, lines 15-24; Examples; claims)	1-22, 26-43, 46-55

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.
PCT/AU2008/001304

This Annex lists the known "A" publication level patent family members relating to the patent documents cited in the above-mentioned international search report. The Australian Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent Document Cited in Search Report		Patent Family Member					
EP	0863191	JP	10245504	JP	11124518	JP	11181334
		US	6013724				
US	6506496	EP	0675087	FR	2718143	JP	8053650
US	6521290	EP	0959102	JP	2000044226	JP	2000108507
		JP	2000109529	US	6855759	US	2003134950
US	6635735	EP	1215253	WO	0077105		
US	2007196656	AU	2006277712	AU	2006277713	CA	2617511
		CA	2617513	EP	1919361	EP	1922367
		US	2007187587	WO	2007017700	WO	2007017701
JP	2006022258	NONE					
JP	2003468	NONE					
WO	0114497	AU	65497/00	CA	2383234	CN	1378581
		EP	1210396	HK	1047599	NZ	517308
		US	6743467				
WO	2004104116	EP	1479738	EP	1641889	KR	20060023532
		US	2006286305				

Due to data integration issues this family listing may not include 10 digit Australian applications filed since May 2001.

END OF ANNEX