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Figure 1

Un-coated fabric

Dip coating

Coated fabric

(57) Abstract: The present invention generally relates to liquid repellent article. In particular, the invention relates to a liquid repellent article comprising a micro-rough substrate and a substantially particle-free, nano-rough low surface energy coating on the substrate. The invention also relates to a process for preparing the liquid repellent article.



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LIQUID REPELLENT ARTICLE AND PROCESS FOR THE PREPARATION OF THE ARTICLE

TECHNICAL FIELD

[0001] The present invention generally relates to a liquid repellent article. In particular, the invention relates to a liquid repellent article comprising a micro-rough substrate and a substantially particle-free, nano-rough low surface energy coating on the substrate. The invention also relates to a process for preparing the liquid repellent article. The invention is particularly directed to liquid repellent textile articles, such as clothing, that comprise a substantially particle-free, nano-rough low surface energy coating, and to a process for the preparation of such textile articles.

BACKGROUND

[0002] Liquid repellent coatings have the potential to impart self-cleaning and contamination-resistant surface properties to a range of materials. For example, fabrics imbued with liquid repellency are particularly useful for the development of protective clothing, which offers the wearer protection against toxic, flammable or corrosive liquids. However, despite progress made in developing liquid repellent articles and coatings, challenges still remain that hinder their effective, widespread use in practice.

[0003] Clothing and other textile articles having liquid repellent properties can be obtained by applying a liquid repellent coating, such as an amphiphobic or superamphiphobic coating, on to a fabric substrate. Amphiphobic and superamphiphobic coatings have both hydrophobic and oleophobic properties, with the ability to repel both water and oil. Amphiphobic coatings typically exhibit a contact angle of greater than 90 degrees to water and oil, while superamphiphobic coatings generally exhibit a contact angle of greater than 150 degrees to water and oil.

[0004] Amphiphobic or superamphiphobic properties may be conferred to a material by forming a surface having a rough topography and low surface free energy on the material. To form these surfaces, one approach involves the preparation of a coating composition containing a low surface energy binder and either micro- or nanoparticles

dispersed in the binder, which may be applied to the material as a coating treatment. The microparticles and nanoparticles employed in prior art coatings are typically either added to the coating or are formed *in situ*.

[0005] However, the use microparticles and nanoparticles to provide rough surfaces in liquid repellent coatings can be of concern for textile articles as the particles may affect the handling, wear and comfort of the textiles. There may also be potential health and safety issues surrounding the presence of microparticles and nanoparticles in the coatings.

[0006] Another problem faced by liquid repellent surfaces is that they can have poor repellency to low surface tension liquids, particularly those with a surface tension of less than 35 mN/m. Since low surface tension liquids are widely used in daily life and industry, the inability to repel these liquids has been an issue that restricts the wide use of many liquid repellent textiles.

[0007] A further important challenge for liquid repellent textiles is coating durability. For instance, many coatings on fabrics have low durability and can only withstand limited washing and abrasion before its ability to effectively repel liquids is compromised.

[0008] It would be desirable to provide a liquid repellent article and a process for preparing a liquid repellent article that addresses or ameliorates one or more problems of the prior art.

[0009] The discussion of documents, acts, materials, devices, articles and the like is included in this specification solely for the purpose of providing a context for the present invention. It is not suggested or represented that any or all of these matters formed part of the prior art base or were common general knowledge in the field relevant to the present invention as it existed before the priority date of each claim of this application.

[0010] Where the terms "comprise", "comprises", "comprised" or "comprising" are used in this specification (including the claims) they are to be interpreted as specifying the presence of the stated features, integers, steps or components, but not precluding

the presence of one or more other features, integers, steps or components, or group thereof.

SUMMARY OF THE INVENTION

[0011] The present invention relates generally to a liquid repellent article and to a process for the preparation of a liquid repellent article. The liquid repellent article is capable of repelling both water and oil. In particular, the present invention provides an amphiphobic article, preferably a superamphiphobic article.

[0012] In one aspect the present invention provides a liquid repellent article comprising a substrate having a micro-rough surface and a substantially particle-free coating on the micro-rough surface of the substrate, wherein the coating comprises at least one low surface energy polymer and at least one coupling agent and has a nano-rough topography, and wherein the article is capable of repelling both water and oil.

[0013] The substrate employed in the liquid repellent article of the invention has a micro-rough surface. In some embodiments, the substrate having a micro-rough surface may be selected from the group consisting of porous substrates, fibrous substrates (e.g. wovens, non-wovens, knitted, braided), fibres, yarns, porous films and foams. In a particular set of embodiments, the substrate may be selected from the group consisting of a mesh, paper and fabric substrate.

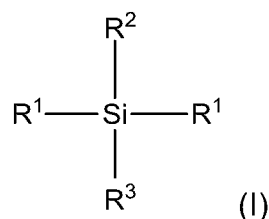
[0014] The liquid repellent article of the present invention also comprises a substantially particle-free low surface energy coating on the micro-rough surface of the substrate. The low surface energy coating has a nano-rough topography. In one set of embodiments the substantially particle-free coating has a RMS roughness of between 10 to 200 nm.

[0015] The low surface energy coating employed in the liquid repellent article is substantially free of particles such as microparticles and nanoparticles. In one set of embodiments the coating comprises less than 0.5% (w/v) particles.

[0016] In accordance with embodiments of the invention, the substantially particle-free coating present in the liquid repellent article comprises at least one coupling agent. In one set of embodiments, the substantially particle-free coating comprises a silane

coupling agent. Exemplary silane coupling agents may comprise at least one hydrolysable group and at least one non-hydrolysable group. The non-hydrolysable group may comprise a moiety selected from the group consisting of hydrocarbyl and halocarbyl moieties. Preferably the non-hydrolysable group imparts low surface energy properties to the coupling agent.

[0017] In some embodiments, the silane coupling agent is of formula (I):



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 group comprising a moiety selected from the group consisting of alkyl, alkenyl, alkynyl, alkylepoxy, alkyl ethers, alkyl esters, aryl, cycloalkyl, fluoroalkyl, fluoroether, fluoroester, fluoroaryl, and polyhedral oligomeric silsequioxane; and

R^3 is a non-hydrolysable group comprising a moiety selected from the group consisting of alkyl, alkenyl, alkynyl, alkylepoxy, alkyl ethers, alkyl esters, aryl, cycloalkyl, fluoroalkyl, fluoroether, fluoroester, fluoroaryl, and polyhedral oligomeric silsequioxane.

[0018] In one set of embodiments, the substantially particle-free coating comprises an amount of coupling agent in a range of from about 0.5 to 10% (v/v), preferably from about 1 to 5% (v/v).

[0019] In accordance with embodiments of the invention, the substantially particle-free coating present in the liquid repellent article also comprises at least one low surface

energy polymer. In one set of embodiments, the coating comprises a polymer having a surface free energy of no more than about 50 mN/m at 20°C.

[0020] In some embodiments, the substantially particle-free coating comprises a low surface polymer selected from the group consisting of polyolefins, fluoropolymers, perfluoropolymers, vinyl polymers, polysiloxanes, polyesters, polyurethanes, polycarbonates, copolymers thereof, and mixtures thereof. In exemplary embodiments, the low surface energy polymer may be selected from the group consisting of polyethylene, polyisobutylene, polystyrene, poly(α -methyl styrene), polyvinylchloride, poly(vinylidene fluoride), poly(vinylidene fluoride-co-hexafluoropropene), poly(vinyl acetate), polytrifluoroethylene, polytetrafluoroethylene, poly(chlorotrifluoroethylene), poly(ethyl acrylate), poly(ethyl methacrylate), poly(butyl methacrylate), poly(iso-butyl methacrylate), poly(hexyl methacrylate), poly(tetramethylene oxide), polydimethylsiloxane, polycarbonates, polyesters, polyurethanes, fluorinated olefin-based polymers, fluoroacrylates, fluorosilicone acrylates, fluorourethanes, and mixtures thereof.

[0021] The substantially particle-free coating may comprise a suitable amount of low surface energy polymer and the quantity may depend on the desired thickness and/or coverage of coating on the underlying substrate. In one set of embodiments, the coating comprises an amount of low surface energy polymer in a range selected from the group consisting of from about 0.2 to 10% (w/v), from about 0.5 to 5% (w/v), and from about 1 to 3% (w/v).

[0022] In another aspect, the present invention provides a process for the preparation of a liquid repellent article comprising the steps of:

applying a substantially particle-free coating composition comprising a low surface energy polymer, coupling agent, and a volatile carrier to a micro-rough surface of a substrate; and

evaporating the volatile carrier from the coating composition applied on the substrate to thereby form a substantially particle-free coating on the substrate,

wherein the coating comprises the low surface energy polymer and coupling agent and has a nano-rough topography, and

wherein the article is capable of repelling both water and oil.

[0023] The process of the present invention provides an effective and facile method for forming a liquid repellent article that is capable of repelling a range of different liquids and most particularly is capable of repelling water and oil. The process of the invention advantageously avoids the need to employ particles such as nanoparticles and microparticles in the manufacture of the liquid repellent article.

[0024] The process of the invention employs a substantially particle-free coating composition comprising a low surface energy polymer, a coupling agent, and a volatile carrier. The coating composition may comprise at least one low surface energy polymer and at least one coupling agent selected from any one of those described herein. The low surface energy polymer and coupling agent are typically dissolved in the volatile carrier.

[0025] In one set of embodiments, it is preferred that the coating composition be a homogeneous liquid comprising the polymer, coupling agent and volatile carrier in a single phase.

[0026] In one set of embodiments, the volatile carrier comprises at least one volatile solvent. Volatile solvents useful in the process of the invention may have a vapour pressure of at least 10 kPa at 20°C. It is preferred that the volatile carrier be capable of rapidly evaporating under ambient conditions. In some embodiments, the volatile carrier may comprise at least one volatile solvent selected from the group consisting of alcohols (preferably C1-C4 alcohols), glycols, ethers, esters, ketones, amides, and halohydrocarbon solvents. Exemplary volatile solvents may be selected from the group consisting of trichloroethane, trichloroethylene, methylene chloride, chloroform, carbon tetrachloride, tetrachlorethylene, methanol, ethanol, propanol, butanol, ethylene glycol, diethyl ether, ethyl acetate, acetone, N, N-dimethylformamide, and tetrahydrofuran.

[0027] In one set of embodiments, the volatile carrier comprises an aqueous mixture of the volatile solvent. The ratio of water, when used, to volatile solvent will depend on the nature of the volatile solvent and other components of the composition as well as the drying conditions to be used. In one set of embodiments, the volume ratio of

water:volatile solvent is no more than 1:1 such as no more than 1:2, no more than 1:4 or no more than 1:8.

[0028] The coating composition may comprise a suitable amount of low surface energy polymer and coupling agent and the quantity may depend on factors such as the solubility of the polymer and coupling agent in the volatile carrier, as well as the desired thickness and/or coverage of resulting coating.

[0029] In embodiments of the process, the coating composition may comprise an amount of coupling agent in a range of from about 0.5 to 10% (w/v), preferably from about 1 to 5% (w/v).

[0030] In embodiments of the process, the coating composition may comprise an amount of low surface energy polymer in a range selected from the group consisting of from about 0.2 to 10% (w/v), from about 0.5 to 5% (w/v), and from about 1 to 3% (w/v).

[0031] In accordance with the process of the invention, the coating composition is applied to a substrate having a micro-rough substrate. Exemplary substrates having micro-rough surfaces may be selected from any one of those described herein. In one set of embodiments, the substrate may be selected from the group consisting of porous substrates, fibrous substrates (e.g. wovens, non-wovens, knitted, braided), fibres, yarns, films and foams. In a particular set of embodiments, the substrate may be selected from the group consisting of a mesh, paper and fabric substrate.

[0032] Any suitable technique may be used to apply the coating composition, including dipping, spraying, brushing, padding, roll coating, curtain coating, or any combination of such techniques.

[0033] Following application of the coating composition, the volatile carrier is evaporated from the applied composition. Evaporation results in the removal of a substantial proportion of the volatile carrier and in the formation of a coating comprising the low surface energy polymer and coupling agent on the micro-rough substrate surface.

[0034] It can be desirable for volatile solvent present in the carrier to undergo rapid evaporation. In some embodiments, rapid evaporation means that a substantial

proportion (such as least 50%, at least 60%, at least 70%, at least 80% or at least 90%) of the volatile solvent is removed from the coating composition applied to the substrate in a time period of less than 10 minutes, preferably less than 8 minutes, more preferably less than 5 minutes. However, a person skilled in the art would understand that the time period for solvent evaporation can vary, as it might depend on variables such as the thickness and surface area of the applied coating, as well as the environmental conditions under which the volatile carrier is removed.

[0035] The evaporation of the volatile carrier may occur under a range of conditions, including under ambient conditions or at elevated temperature. In one set of embodiments, evaporation of the volatile carrier from the coated substrate occurs at an elevated temperature, preferably at a temperature in the range of from about 60 to 140°C.

[0036] The evaporation of the volatile carrier may also be facilitated by the use of a flow of air, which may be directed across the coating composition applied to the substrate. In some embodiments, the evaporation of the volatile carrier occurs in the presence of a flow of air. In one set of embodiments, a flow of air is used in conjunction with an elevated temperature to facilitate rapid evaporation of the volatile carrier.

[0037] In one set of embodiments the process of the invention may further comprise the step of curing the substantially particle-free coating formed on the substrate. The curing step is preferably carried out at elevated temperature. In some embodiments, the curing step is carried out at a temperature in a range of from about 50 to 160°C. The curing step may facilitate covalent reactions of the coupling agent, either with itself or other components of the coating composition, or with the substrate, to crosslink the coupling agent or to help bond the coating to the substrate.

[0038] Following evaporation of the volatile carrier and optionally, the curing step, a substantially particle-free low surface energy coating is formed on the substrate. The coating comprises the low surface energy polymer and coupling agent. The coating formed by the process of the invention also comprises a nano-rough topography. The nanostructure of the coating is such that the surface of the coating is nano rough. The nano-rough topography is achieved without the need to incorporate particles

such as microparticles or nanoparticles in the coating, or the need to disperse particles in between the coating and the underlying substrate. As a result, the liquid repellent article of the present invention may be substantially particle-free.

[0039] The substantially particle-free nano-rough coating covers the micro-rough surface of the substrate and operates in conjunction with the substrate to impart liquid repellent properties to the resulting article. In particular, the liquid repellent properties are such that the article is capable of repelling both water and oil. Other liquids or solvents, in particular, low surface tension liquids, may also be repelled by the articles of the present invention.

[0040] The present invention also provides a liquid repellent article prepared by the process of any one of the embodiments described herein.

[0041] An article that is liquid repellent generally means that the article provides a high liquid contact angle for a liquid that is in contact with the article. In some embodiments the liquid repellent article of one or more aspects of the invention may provide a liquid contact angle of at least about 90 degrees, at least about 120 degrees, or at least about 150 degrees.

[0042] In one set of embodiments, a liquid repellent article of one or more aspects of the invention is amphiphobic and capable of repelling both water and oil. Typically, this means that the article provides a liquid contact angle of at least about 90 degrees, at least about 120 degrees, or at least about 150 degrees, for each of water and oil in contact with the coating. High contact angles are generally indicative of a liquid repellent surface. In some embodiments, the liquid repellent article may be superamphiphobic.

[0043] The liquid repellent article of one or more aspects of the invention possesses a number of advantageous properties, such as being capable of self-cleaning as well as being durable and resistant to damage by abrasion, chemicals, high temperature treatment and repeated washing. The liquid repellent article of embodiments of the invention may furthermore retain an acceptable aesthetic appearance and be air permeable.

[0044] In one set of embodiments a liquid repellent article of one or more embodiments of the invention is capable of withstanding at least 100 washing cycles, when tested according to AATCC Test Method 61-2006.

[0045] In one set of embodiments a liquid repellent article of one or more embodiments of the invention is capable of withstanding 10,000 cycles of abrasion, when tested according to ASTM D4966-98.

[0046] In one set of embodiments, the coating present in the liquid repellent article is capable of self-healing after damage, thus imparting self-healing properties to the article. In some embodiments, the self-healing property is repeatable.

[0047] In some embodiments, the liquid repellent article is a textile article comprising a fabric substrate and a substantially particle-free low surface energy coating as described herein on a surface of the fabric substrate. The low surface energy coating has a nano-rough topography. The present invention therefore is particularly useful in the preparation of textile articles that are highly repellent to liquids, and may be used to resist damage and soils, such as protective clothing.

BRIEF DESCRIPTION OF THE DRAWINGS

[0048] Embodiments of the invention will herein be illustrated by way of example only with reference to the accompanying drawings in which:

[0049] Figure 1 is a schematic illustrating a process for the preparation of a liquid repellent article in accordance with an embodiment of the invention;

[0050] Figure 2 is a schematic illustrating the formation of a liquid repellent textile article in which a fabric substrate is coated with a composition comprising a silane coupling agent and a low surface energy polymer in accordance with an embodiment of the invention;

[0051] Figure 3 shows an image of droplets of ethanol, water, olive oil and hexadecane on a liquid repellent article of an embodiment of the invention and an image of a comparative uncoated substrate that is not liquid repellent;

[0052] Figure 4 is a graph illustrating the change in contact angle (CA) over time for droplets of ethanol, water, olive oil and hexadecane on a liquid repellent article of an embodiment of the invention;

[0053] Figure 5 is a graph illustrating the dependency of contact angle (CA) and sliding angle (SA) with liquid surface tension for a liquid repellent article of an embodiment of the invention;

[0054] Figure 6 is an image showing that a liquid repellent article of an embodiment of the invention maintains liquid repellent properties after immersion in 40% KOH and 40% H₂SO₄ for 12 hours;

[0055] Figure 7 is a graph illustrating a change in contact angle for various liquids in contact with liquid repellent articles of embodiments of the invention comprising varying ratios of coupling agent and polymer in the coating.

DETAILED DESCRIPTION

[0056] The present invention provides a liquid repellent article that is capable of repelling both water and oil. Advantageously, the liquid repellent article of the invention does not require the presence of particles, such as microparticles and nanoparticles, in order to achieve rough surface topographies which are conventionally required to impart liquid repellency.

[0057] In one aspect the present invention provides a liquid repellent article comprising a substrate having a micro-rough surface and a substantially particle-free low surface energy coating on the micro-rough surface of the substrate, wherein the coating has a nano-rough topography, and wherein the article is capable of repelling both water and oil.

[0058] Preferably, the low surface energy coating comprises at least one low surface energy polymer and at least one coupling agent.

[0059] Thus in accordance with one aspect, the present invention provides a liquid repellent article comprising a substrate having a micro-rough surface and a substantially particle-free coating on the micro-rough surface of the substrate, wherein the coating comprises at least one low surface energy polymer and at least one

coupling agent and has a nano-rough topography, and wherein the article is capable of repelling both water and oil.

[0060] The liquid repellent article of the invention has both hydrophobic and oleophobic properties. The liquid repellent article can therefore be regarded as an amphiphobic article and in some embodiments, is a superamphiphobic article.

[0061] The liquid repellent article of the present invention comprises a substrate having a micro-rough surface. A substrate having a micro-rough surface generally has non-planar topography that may arise as a result of the morphology or surface features of the substrate. Generally, the substrate comprises microscale roughness with uneven surface features evident on a micrometre scale.

[0062] In one set of embodiments, a substrate with a "micro-rough" surface may have a surface comprising profile peaks having a height in a range from 0.1 μm to 50 μm and a distance between the profile peaks in a range from 1 μm to 50 μm . In some embodiments, a micro-rough surface of a substrate may comprise profile peaks having a height and distance in a range of 5 μm to 30 μm .

[0063] In some embodiments, a substrate having a micro-rough surface may be selected from the group consisting of porous substrates, woven substrates, non-woven substrates, braided substrates, fibres, yarns, films (including thin films) and foams. The substrate may further be a flexible substrate.

[0064] In one set of embodiments, the substrate is a porous substrate. Porous substrates comprise at least one opening, and may comprise a plurality of openings, in the substrate. Such substrates are generally air permeable. Porous substrates that may be used can be in any form, including in the form of sheets, webs, foams and films. Examples of porous substrates include woven and non-woven fabrics and textiles, foam sheets and woven and non-woven papers. In some embodiments, the substrate may be a thin porous substrate having a thickness selected from the group consisting of less than about 10 mm, less than about 5 mm or less than about 1 mm.

[0065] In one set of embodiments, the substrate may be a textile substrate. Examples of textile substrates include woven, non-woven, knitted or braided fabrics, fibres, filaments, yarns, etc.

[0066] In one set of embodiments, the substrate may be a fabric substrate. A skilled person would understand that fabric substrates have a micro-rough surface. The fabric substrate may be woven, non-woven, braided or knitted substrate, and may be formed from synthetic or natural fibres, either alone or blended in any combination thereof. In some embodiments, the fabric substrate may comprise a fibre selected from the group consisting of cotton, cellulose, wool, cashmere, angora, silk, and combinations thereof. In exemplary embodiments, the fabric substrate comprises cotton, wool or silk. Fabric substrates may also be considered porous substrates due to their air permeability.

[0067] The liquid repellent article of the invention also comprises a substantially particle-free coating. As used herein, a reference to a composition or coating being “substantially particle-free” generally means that the composition or coating contains (on a w/v basis) less than 5%, less than 2%, less than 1%, or less than 0.5% particles. Most preferably, the coating contains no particles.

[0068] The term “particle” as used herein is generally a reference to microparticles and nanoparticles. Such particles have been used in liquid repellent coatings, such as hydrophobic or amphiphobic coatings described in the prior art and desirably, are not employed in the liquid repellent article of the present invention, nor are they employed in processes or coatings used to form the liquid repellent article of the invention. Microparticles that are excluded from the present invention described herein generally have at least one particle dimension in the micrometre (μm) range, while nanoparticles that are excluded from the present invention generally have at least one particle dimension in the nanometre scale. In general, it is desirable that nanoparticles having a particle dimension of 5 nm or greater be excluded or substantially excluded from liquid repellent articles, coatings and coating compositions as described herein.

[0069] Percentages referred to herein are generally percentages by volume (e.g. %w/v) unless otherwise specified.

[0070] In embodiments of the invention described herein, the substantially particle-free coating of the liquid repellent article comprises a low surface energy polymer and a coupling agent.

[0071] A variety of low surface energy polymers may be used in the coating. The low surface energy polymer may be selected from any polymer that is able to effectively reduce the surface energy of a substrate to which the coating has been applied. Low surface energy polymers are available commercially and may also be synthesised from appropriate monomers using various polymerisation techniques. In some embodiments it may be desirable for the low surface energy polymers employed in the coating be non-crosslinked.

[0072] In one set of embodiments, the coating comprises at least one low surface energy polymer having a surface free energy selected from the group consisting of no more than about 50 mN/m, no more than about 40 mN/m, and no more than about 35 mN/m at 20°C.

[0073] The substantially particle-free coating may comprise a single type of low surface energy polymer, or it may comprise a mixture of two or more different types of such polymers.

[0074] When the coating comprises a plurality of low surface energy polymers (i.e. two or more polymers) it is desirable that each polymer has a surface free energy of no more than about 50 mN/m, no more than about 40 mN/m, and no more than about 35 mN/m, at 20°C. It is further desirable that the polymers be compatible with one another and miscible with the other components of the coating so as to form of a single phase. In some embodiments it is desirable that the components of the low surface energy coating do not phase separate.

[0075] In one set of embodiments, the coating may comprise at least one polymer selected from the group consisting of polyolefins, halogenated polymers (such as fluoropolymers and perfluoropolymers), vinyl polymers, polysiloxanes, polyesters, polyurethanes, polycarbonates, copolymers thereof, and mixtures thereof. In some embodiments, polyolefins, fluoropolymers and perfluoropolymers may be preferred.

[0076] In a particular set of embodiments, the coating may comprise a polymer selected from the group consisting of polyethylene (including low density polyethylene and copolymers of polyethylene and polycyclic olefin), polyisobutylene, cyclic olefin copolymers such as ethylene-norbornene copolymer, polystyrene, poly(α -methyl styrene), polyvinylchloride, poly(vinylidene fluoride), poly(vinylidene fluoride-co-

hexafluoropropene), poly(vinyl chloride), poly(vinyl acetate), polytrifluoroethylene, poly(chlorotrifluoroethylene), poly(methyl acrylate), poly(ethyl acrylate), poly(methyl methacrylate), poly(ethyl methacrylate), poly(butyl methacrylate), poly(iso-butyl methacrylate), poly(hexyl methacrylate), poly(tetramethylene oxide), polydimethylsiloxane, polyetheretherketone (PEEK), polycarbonates, polyesters, polyurethanes, fluorinated olefin-based polymers, fluoroacrylates, fluorosilicone acrylates, fluorourethanes, and mixtures thereof.

[0077] The surface free energies of some exemplary polymers that may be present in the coating are shown in Table 1.

Table 1

Polymer	Surface free energy at 20 °C (mN/m)
Linear polyethylene	35.7
Branched polyethylene	35.3
Polyisobutylene	33.6
Polystyrene	40.7
Poly- <i>a</i> -methyl styrene	39.0
Polyvinyl fluoride	36.7
Polyvinylidene fluoride	30.3
poly(vinylidene fluoride-co-hexafluoropropylene)	19.2
Polytrifluoroethylene	23.9
Polyvinylchloride	41.5
Polychlorotrifluoroethylene	30.9
Polyvinylacetate	36.5

Polymer	Surface free energy at 20 °C (mN/m)
Polymethylacrylate	41.0
Polyethylacrylate	37.0
Polymethylmethacrylate	41.1
Polyethylmethacrylate	35.9
Polybutylmethacrylate	31.2
Polyisobutylmethacrylate	30.9
Poly(t-butylmethacrylate)	30.4
Polyhexylmethacrylate	30.0
Polytetramethylene oxide	31.9
Polydimethylsiloxane	19.8
Polycarbonate	34.2
Cyclic Olefin Copolymer (COC)	30.1
Polyetheretherketone	42.1
Low density Polyethylene	31.5

[0078] In one set of embodiments, the coating may comprise at least one polymer selected from the group consisting of low density polyethylene, poly(vinylidene fluoride), poly(vinylidene fluoride-co-hexafluoropropene), poly(vinyl chloride), poly(vinyl acetate), polytrifluoroethylene, polytrifluoroethylene, polyvinyl fluoride, poly(chlorotrifluoroethylene), cyclic olefin copolymer, polydimethylsiloxane and mixtures thereof.

[0079] The substantially particle-free coating may comprise a suitable amount of low surface energy polymer. In one set of embodiments, the coating comprises an amount of low surface energy polymer selected from the group consisting of from about 0.2 to 10% (wt/v), from about 0.5 to 5% (wt/v), and from about 1 to 3% (wt/v).

[0080] The coating employed in the liquid repellent article of the invention also comprises a coupling agent. The coupling agent is preferably a low surface energy coupling agent. Low surface energy coupling agents may comprise at least one moiety that imparts low surface energy properties. Thus the coating may possess enhanced low surface energy properties due to the presence of the coupling agent. Enhancements in low surface energy properties may be provided by the coupling agent and low surface energy polymer operating in combination or synergistically in the coating.

[0081] In one set of embodiments, the coupling agents useful for the present invention may comprise at least one low surface energy moiety selected from the group consisting of hydrocarbyl and halocarbyl moieties. Specific examples of low surface energy moieties include alkyl, aryl, haloalkyl (preferably fluoroalkyl or perfluoroalkyl) and haloaryl (preferably fluoroaryl) moieties.

[0082] In addition to imparting low surface energy properties, the coupling agent may assist to enhance adhesion or bonding of the coating with the underlying substrate.

[0083] The selection of coupling agent may be dependent on the type of low energy polymer employed in the coating and the nature of the substrate of the liquid repellent article. A single type of coupling agent may be employed, or a combination of two or more different types of coupling agent.

[0084] In one set of embodiments, the coupling agent is a silane coupling agent. Silane coupling agents are compounds comprising a silane head group and functional groups that are capable of bonding with different materials. Bonding interactions between the silane coupling agent and different materials may occur through hydroxyl groups present in the coupling agent.

[0085] As used herein with reference to a coupling agent, the term “silane head group” refers to a moiety comprising a silicone (Si) atom and a hydrolysable group covalently bonded to the Si atom.

[0086] In one form, it is desirable that silane coupling agents employed in the coating comprise at least one low surface energy group, and may comprise a plurality (such as two or three) low surface energy groups. In such silane coupling agents, the silane head can bond with polar groups present on a substrate surface, while the low surface energy group has strong affinity with the low surface energy polymer. In this way, the coupling agent may act as a binder between the substrate and polymer in the coating to promote adhesion between the materials.

[0087] In some embodiments, exemplary silane coupling agents may comprise a hydrolysable group and at least one non-hydrolysable group. Preferably the non-hydrolysable group imparts low surface energy properties to the coupling agent. In such embodiments, the non-hydrolysable group may be considered to be a low surface energy group. In some embodiments, the non-hydrolysable group may be selected from the group consisting of hydrocarbyl and halocarbyl groups.

[0088] In one set of embodiments the silane coupling agent may comprise a non-hydrolysable group comprising a moiety selected from the group consisting of alkyl, aryl, haloalkyl (preferably fluoroalkyl or perfluoroalkyl) and haloaryl (preferably fluoroaryl). In some embodiments, exemplary alkyl and haloalkyl may comprise at least 4 carbon atoms while exemplary aryl and haloaryl may comprise at least 6 carbon ring atoms.

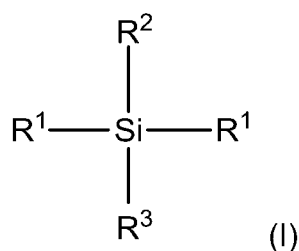
[0089] In one set of embodiments, the silane coupling agent may comprise at least one non-hydrolysable group comprising a moiety selected from the group consisting of C₁ to C₂₀ alkyl, C₂ to C₃₀ alkenyl, C₃ to C₁₀ alkyl epoxy, C₅ to C₂₀ aryl, C₁ to C₂₀ haloalkyl, C₃ to C₂₀ cycloalkyl and C₂ to C₂₀ cyanoalkyl. More preferably, the non-hydrolysable group comprises a moiety selected from the group consisting of C₁ to C₂₀ alkyl, C₅ to C₁₀ aryl and C₁ to C₂₀ haloalkyl (such as C₁ to C₂₀ perfluoroalkyl moiety).

[0090] In one set of embodiments, the silane coupling agent may comprise a non-hydrolysable group comprising a long chain alkyl moiety. Long chain alkyl may

comprise at least 4 carbon atoms and may be C₈-C₂₀ alkyl. Long chain alkyl may help to provide a coating having greater liquid repellency than coatings formed with silane compounds having shorter alkyl substituents. Some examples of long chain alkyl are octyl and hexadecyl.

[0091] In another set of embodiments, the silane coupling agent may comprise a non-hydrolysable group comprising a haloalkyl moiety. In one form, the haloalkyl may be fluoroalkyl or perfluoroalkyl. In one embodiment, the non-hydrolysable group comprises a C₁ to C₂₀ perfluoroalkyl moiety. An exemplary perfluoroalkyl moiety is - (CH₂)₂-(CF₂)₅-CF₃. 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.

[0092] In some embodiments, silane coupling agents employed in the process and coating of the invention have a structure of formula (I):



where

R¹ is a hydrolysable group and at each occurrence is independently selected from the group consisting of alkoxy, alkenyloxy and halo;

R² is a hydrolysable group selected from the group consisting of alkoxy, alkenyloxy and halo; or

R² is a non-hydrolysable group comprising a moiety selected from the group consisting of alkyl, alkenyl, alkynyl, alkylepoxy, alkyl ethers, alkyl esters, aryl, cycloalkyl, fluoroalkyl, fluoroether, fluoroester, and polyhedral oligomeric silsequioxane; and

R³ is a non-hydrolysable group comprising a moiety selected from the group consisting of alkyl, alkenyl, alkynyl, alkylepoxy, alkyl ethers, alkyl esters, aryl, cycloalkyl, cyanoalkyl, fluoroalkyl, fluoroether, fluoroester, and polyhedral oligomeric silsequioxane.

[0093] In some embodiments of formula (I), R³ comprises a moiety selected from the group consisting of C₁ to C₂₀ alkyl, C₂ to C₃₀ alkenyl, C₅ to C₁₀ aryl, C₁ to C₂₀ haloalkyl, C₃ to C₁₀ cycloalkyl and C₂ to C₂₀ cyanoalkyl.

[0094] In some embodiments of formula (I), R³ comprises a moiety selected from the group consisting of C₁ to C₂₀ alkyl, C₅ to C₁₀ aryl, and C₁ to C₂₀ haloalkyl.

[0095] A person skilled in the relevant art would understand that the hydrolysable group of the coupling agent may be reactive under hydrolysis conditions and under such conditions, may form covalent bonds with appropriate functional groups present on other molecules or compounds. When a silane coupling agent undergoes hydrolysis and forms a covalent bond with another molecule, a hydrolysate of the coupling agent is produced.

[0096] In one set of embodiments, the coating of the liquid repellent article may comprise a hydrolysate of at least one silane coupling agent. The silane coupling agent may be selected from any one of those described herein.

[0097] In comparison to the hydrolysable group, the non-hydrolysable group is not reactive under hydrolysis conditions. The non-hydrolysable group can generally impart low surface energy properties to the coupling agent.

[0098] In some embodiments of formula (I), R³ comprises a moiety selected from the group consisting of C₈ to C₂₀ alkyl, and C₁ to C₂₀ perfluoroalkyl.

[0099] In one embodiment the silane coupling agent may be a trialkoxysilane. Trialkoxysilanes include three hydrolysable groups and one non-hydrolysable group. The non-hydrolysable group preferably comprises a moiety as described herein. Examples of suitable trialkoxysilanes that may be used in accordance with the invention are as follows:

Alkyl

[0100] 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, Octyl triethoxysilane.

Alkenyl

[0101] Trimethoxy(vinyl)silane, Trimethoxy(7-octen-1 -yl)silane, Amyltriethoxysilane, 3-(Trimethoxysilyl)propyl methacrylate, Allyltriethoxysilane, 3- (Trimethoxysilyl)propyl acrylate.

Cycloalkyl

[0102] Cyclopentyltriethoxysilane, (Triethoxysilyl)cyclohexane, [2-(Cyclohexenyl)ethyl]triethoxysilane.

Halo

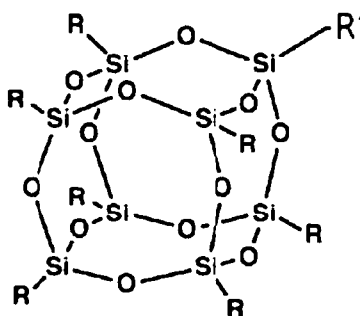
[0103] (4-Chlorophenyl)triethoxysilane, (3-Chloropropyl)tris(trimethylsiloxy)silane, (3-Bromopropyl)trimethoxysilane, (3-Chloropropyl)trimethoxysilane, (3-Chloropropyl)triethoxysilane, (Pentafluorophenyl)triethoxysilane, Triethoxy(4-(trifluoromethyl)phenyl)silane, 1 H, λ /-/,2/-/,2/-/-Perfluorooctyltriethoxysilane, Trimethoxy(3,3,3-trifluoropropyl)silane, Tridecafluorooctyl triethoxysilane, Tridecafluorooctyl triethoxysilane.

Aryl

[0104] Triethoxyphenylsilane, Triethoxy-p-tolylsilane, Triethoxy(4-methoxyphenyl)silane, Trimethoxy(2-phenylethyl)silane , Triethoxy(1 -phenylethenyl)silane.

[0105] One or more of the above trialkyoxysilanes may be used in the coating composition and coating as described herein.

[0106] In some embodiments, silane coupling agents employed in the coating of the liquid repellent article of the invention may be selected from polyhedral oligomeric silsequioxane agents having a structure of formula (II):

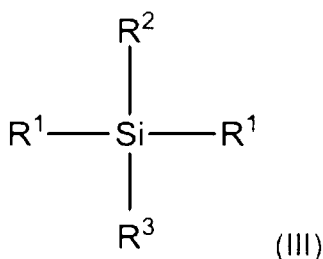


(II)

where

R is a non-hydrolysable group comprising a moiety selected from the group consisting of alkyl, alkenyl, alkynyl, alkylepoxy, alkyl ethers, alkyl esters, aryl, cycloalkyl, haloalkyl, haloether, haloester, polyhedral oligomeric silsequioxane, and fluorinated derivatives thereof; and

R' is of formula (III):



(III)

wherein in formula (III):

at least one of R² and R³ is covalently bonded to formula (II), through a -C-Si-bond;

R^2 and R^3 when not bonded to formula (II) represents a hydrolysable group comprising a moiety selected from the group consisting of alkoxy, alkenyloxy and halo; and

R^1 is a hydrolysable group and at each occurrence is independently selected from the group consisting of alkoxy, alkenyloxy and halo.

[0107] Some specific examples of a silane coupling agent of formula (II) include 1H,1H,2H,2H-heptadecafluorodecyl polyhedral oligomeric polysilsequioxane (heptadecafluorodecyl POSS) and iso-butyl polyhedral oligomeric polysilsequioxane (iso-butyl POSS).

[0108] A skilled person would understand that silane coupling agents of formula (II) belong to the class of polyhedral oligomeric silsequioxane coupling agents. Such coupling agents are generally regarded as large molecular entities. While they might be considered to be particulate in nature, the molecular size of these compounds is generally less than 2 nm, and thus they are not considered to be nanoparticles and are not excluded from coatings and coating compositions of embodiments of the invention described herein.

[0109] In one set of embodiments, the coating of the liquid repellent article may comprise at least one silane coupling agent of formula (I) and (II), and mixtures thereof.

[0110] In some embodiments, the silane coupling agent may comprise one or more functional moieties that confer additional functionality or properties to the coating. Examples of functional moieties include chromophores, luminescents, UV absorbing agents, antimicrobial agents, and antistatic agents. When present, the functional moiety may be included as a moiety within a non-hydrolysable group of the coupling agent. Such functionalised silane coupling agents have been described in the prior art such as Lin *et al*, *Fibers Polym.* 2008, 9(5):521-6; Zareba-Grodz *et al*, *Journal of Luminescence*, 2006, 119–120(0):148-52; Mohorčič *et al*, *J Mater Sci: Mater Med.* 2010, 21(10):2775-82; and Jafari *et al*, *J Coat Technol Res.* 2014, 11(4):587-93, the disclosures of which are incorporated herein by reference.

[0111] In one set of embodiments, the coupling agent may be a fluorinated hydrocarbyl silane. Generally, fluorinated hydrocarbyl silanes comprise silicon atoms bonded to four chemical groups. One or more of these groups contains fluorinated alkyl or aryl moieties that are not hydrolysable, and the remaining group(s) attached to the silicon atoms are typically alkoxy (i.e. hydrocarbon attached to oxygen), or halide (e.g. chlorine) group(s).

[0112] As used herein, the terms "alkyl", "alkenyl and alkynyl" refers to both linear (straight chain) and branched hydrocarbon structures.

[0113] In exemplary embodiments, the coupling agent may be a fluorinated silane coupling agent selected from the group consisting of 1H, 1H, 2H, 2H-perfluorodecyltriethoxysilane $(\text{CF}_3(\text{CF}_2)_7(\text{CH}_2)_2\text{Si}(\text{OCH}_2\text{CH}_3)_3)$, 3,3,3-trifluoropropyltrimethoxysilane $(\text{CF}_3(\text{CH}_2)_2\text{Si}(\text{OCH}_3)_3)$, tridecafluoro-1,1,2,2-tetrahydrooctyl-1-triethoxysilane $(\text{CF}_3(\text{CF}_2)_5(\text{CH}_2)_2\text{Si}(\text{OCH}_2\text{CH}_3)_3)$, $\text{CF}_3(\text{CH}_2)_2\text{SiCl}_3$, $\text{CF}_3(\text{CF}_2)_5(\text{CH}_2)_2\text{SiCl}_3$, $\text{CF}_3(\text{CF}_2)_7(\text{CH}_2)_2\text{Si}(\text{OCH}_3)_3$, $\text{CF}_3(\text{CF}_2)_5(\text{CH}_2)_2\text{Si}(\text{OCH}_3)_3$, $\text{CF}_3(\text{CF}_2)_7(\text{CH}_2)_2\text{SiCl}_3$, $\text{CF}_3(\text{CF}_2)_7(\text{CH}_2)_2\text{SiCH}_3\text{Cl}_2$, $\text{CF}_3(\text{CF}_2)_7(\text{CH}_2)_2\text{SiCH}_3(\text{OCH}_3)_2$, and mixtures thereof.

[0114] The coupling agent may be present in the coating of the liquid repellent article in a suitable amount. In one set of embodiments, the coating comprises an amount of coupling agent in a range of from about 0.5 to 10% (w/v), or from about 1 to 5% (w/v).

[0115] In one set of embodiments, the liquid repellent article comprises a substantially particle-free coating comprising at least one low surface energy polymer selected from the group consisting of low density polyethylene, poly(vinylidene fluoride), poly(vinylidene fluoride-co-hexafluoropropene), polytrifluoroethylene, polyvinyl fluoride, cyclic olefin copolymer, polydimethylsiloxane and poly(chlorotrifluoroethylene); and a coupling agent selected from the group consisting of fluorinated hydrocarbyl silane coupling agents and polyhedral oligomeric silsesquioxane coupling agents.

[0116] The substantially particle-free coating of the liquid repellent article also has a nano-rough topography. In one set of embodiments, the substantially particle-free coating has an average root mean square (RMS) roughness of at least 10 nm, at least 12 nm, or at least 15 nm. In some embodiments, the coating has a RMS

roughness of between 10 to 200 nm, preferably between 15 to 100 nm. Topography and roughness of the coating may be characterised using conventional techniques, such as atomic force microscopy (AFM).

[0117] In some embodiments, the coating of the liquid repellent article may comprise optional additives, which may be used to confer additional properties to the coating and/or article or enable the aesthetic appearance (e.g. colour) of the coating and/or article to be modified. Examples of optional additives may include but are not limited to antistatic agents, ultraviolet (UV) absorbers, stabilisers, antioxidants, lubricants, pigments or other opacifiers, dyes, plasticisers, suspending agents, anti-fouling agents, insect repellents, and the like.

[0118] In one form of the invention the liquid repellent article comprises a fabric substrate and a substantially particle-free coating on the fabric substrate, wherein the coating comprises a low surface energy polymer and a coupling agent and has a nano-rough topography, and wherein the article is capable of repelling both water and oil. Liquid repellent articles comprising a fabric substrate may be textile articles, such as clothing.

[0119] It has been found that the substantially particle-free nano-rough coating is optically transparent, such that the aesthetic appearance of the underlying substrate is not substantially modified. This property may be advantageous when the coating is used in liquid repellent textile articles where it might be desired to preserve the appearance of the underlying fabric substrate. However, where desired, the appearance of the coating may be modified through the inclusion of appropriate optional additives. For example, pigments or dyes may be incorporated in the coating to modify its colour.

[0120] When used with porous substrates, it has also been found that the substantially particle-free nano-rough coating does not modify the porosity of the underlying substrate or its permeability to air. For example, fabric substrates may be considered to be “breathable” due to the permeability of the fabric web to air and moisture. It has been found that the coating does not interfere with the breathability of the fabric and in some instances, may enhance breathability. Therefore, liquid repellent textile articles of the present invention may possess acceptable or

favourable breathability. When the liquid repellent textile article is an article of clothing, breathability may aid a wearer's comfort.

[0121] The present invention also provides a process for the preparation of a liquid repellent article. The process of the invention allows the article to be prepared in a simple and convenient manner, without the need to employ particles, such as microparticles and nanoparticles, to produce the rough topography that is normally required to impart liquid repellency.

[0122] In accordance with one aspect there is provided a process for the preparation of a liquid repellent article comprising the steps of:

applying a substantially particle-free coating composition comprising a low surface energy polymer, coupling agent, and a volatile carrier to a micro-rough surface of a substrate; and

evaporating the volatile carrier from the coating composition applied on the substrate to thereby form a substantially particle-free coating on the substrate;

wherein the coating comprises the low surface energy polymer and coupling agent and has a nano-rough topography, and

wherein the article is capable of repelling both water and oil.

[0123] The process of the invention employs a substantially particle-free coating composition. It is an important feature of the invention that the coating composition be "substantially particle-free". As described herein, this generally means that the composition contains (on a w/v basis) less than 5%, less than 2%, less than 1%, or less than 0.5% particles. Most preferably, the composition contains no particles.

[0124] The coating composition comprises a low surface energy polymer and a coupling agent. The coating composition comprises at least one low surface energy polymer and at least one coupling agent and may, in some embodiments, comprise a plurality of low surface energy polymers and/or coupling agents. Suitable low surface energy polymers and coupling agents may be selected from any one of the low surface energy polymers and coupling agents described herein.

[0125] In one set of embodiments, the coating composition comprises at least one low surface energy polymer having a surface free energy selected from the group consisting of no more than about 50 mN/m, no more than about 40 mN/m, and no more than about 35 mN/m at 20°C.

[0126] In some embodiments, the polymer may be selected from the group consisting of polyolefins, halogenated polymers (such as fluoropolymers and perfluoropolymers), vinyl polymers, polysiloxanes, polyesters, polyurethanes, polycarbonates, copolymers thereof, and mixtures thereof. In some embodiments, polyolefins, fluoropolymers and perfluoropolymers may be preferred.

[0127] In a particular set of embodiments, the coating composition may comprise a polymer selected from the group consisting of polyethylene (including low density polyethylene), polyisobutylene, cyclic olefin copolymers such as ethylene-norbornene copolymer, polystyrene, poly(α -methyl styrene), polyvinylchloride, poly(vinylidene fluoride), poly(vinylidene fluoride-co-hexafluoropropene), poly(vinyl chloride), poly(vinyl acetate), polytrifluoroethylene, poly(chlorotrifluoroethylene), poly(methyl acrylate), poly(ethyl acrylate), poly(methyl methacrylate), poly(ethyl methacrylate), poly(butyl methacrylate), poly(iso-butyl methacrylate), poly(hexyl methacrylate), poly(tetramethylene oxide), polydimethylsiloxane, polyetheretherketone (PEEK), polycarbonates, polyesters, polyurethanes, fluorinated olefin-based polymers, fluoroacrylates, fluorosilicone acrylates, fluorourethanes, and mixtures thereof.

[0128] In one set of embodiments, the coating composition comprises an amount of low surface energy polymer in a range of from about 0.2 to 10% (w/v), preferably from about 0.5 to 5% (w/v), more preferably about 1 to 3% (w/v).

[0129] In one set of embodiments, the coating composition comprises at least one silane coupling agent. Examples of suitable silane coupling agents are described herein. Exemplary silane coupling agents comprise at least one non-hydrolysable group. Non-hydrolysable groups present in the silane coupling agent may be low surface energy groups.

[0130] In one set of embodiments, the silane coupling agent may comprise at least one non-hydrolysable group comprising a moiety selected from the group consisting of C₁ to C₂₀ alkyl, C₂ to C₃₀ alkenyl, C₃ to C₁₀ alkyl epoxy, C₅ to C₂₀ aryl, C₁ to C₂₀

haloalkyl, C₃ to C₂₀ cycloalkyl and C₂ to C₂₀ cyanoalkyl. More preferably, the non-hydrolysable group comprises a moiety selected from the group consisting of C₁ to C₂₀ alkyl, C₅ to C₁₀ aryl and C₁ to C₂₀ haloalkyl (such as C₁ to C₂₀ perfluoroalkyl moiety).

[0131] In one form of the process, the coating composition comprises at least one silane coupling agent selected from the group consisting of silane coupling agents of formula (I) or (II) as described herein, and mixtures thereof.

[0132] In embodiments of the process, the coating composition may comprise an amount of coupling agent in a range of from about 0.5 to 10% (w/v), preferably from about 1 to 5% (w/v).

[0133] In one set of embodiments, the coating composition comprises at least one low surface energy polymer selected from the group consisting of low density polyethylene, poly(vinylidene fluoride), poly(vinylidene fluoride-co-hexafluoropropene), polytrifluoroethylene, polyvinyl fluoride, cyclic olefin copolymer, polydimethylsiloxane and poly(chlorotrifluoroethylene); and a coupling agent selected from the group consisting of fluorinated hydrocarbyl silane coupling agents and polyhedral oligomeric silsesquioxane coupling agents.

[0134] In one set of embodiments, the coating composition may comprise a functionalised silane coupling agent as described herein. Functionalised silane coupling agents may comprise one or more functional moieties selected from the group consisting of chromophores, luminescents, UV absorbing agents, antimicrobial agents, and antistatic agents.

[0135] The coating composition employed in the process of the invention also comprises a volatile carrier. The volatile carrier is selected to be miscible with, and capable of dissolving the low surface energy polymer and coupling agent so that a homogenous coating composition is formed with little or no phase separation evident. In one form, the coating composition is a liquid composition having a single phase. It is desirable that the volatile carrier be capable of evaporation under selected conditions once the coating composition has been applied to the surface of a substrate.

[0136] In one set of embodiments, the volatile carrier comprises at least one volatile solvent. The solvent is desirably one that is capable of dissolving the low surface energy polymer and coupling agent so as to provide a homogeneous solution.

[0137] In some embodiments the volatile carrier may comprise a mixture of two or more volatile solvents. In such embodiments it is preferred that the volatile solvents be compatible and miscible with one another.

[0138] A variety of volatile solvents may be employed in volatile carrier of the coating composition. Preferred volatile solvents are capable of vaporising under ambient conditions. Exemplary volatile solvents may have a saturated vapour pressure of at least 10 kPa at 20°C.

[0139] In some embodiments, the volatile solvent may be selected from esters such as methyl acetate, ethyl acetate and butyl acetate; alcohols such as methanol, ethanol, propanol and butanol; glycols such as ethylene glycol; amides such as dimethylacetamide and N, N-dimethylformamide; dimethylsulfoxide; ketones such as acetone, methyl ethyl ketone, methyl isobutyl ketone, methyl amyl ketone, cyclohexanone and N-methylpyrrolidinone; sulfolane; ethers such as diethyl ether, tetrahydrofuran, 2-methyl tetrahydrofuran and methyl tetrahydrofurfuryl ether; cyclic esters such as delta-valerolactone and gamma-valerolactone; fluorinated solvents such as perfluoro-2-butyltetrahydrofuran; hydrofluoroethers, and halohydrocarbons such as trichloroethane, trichloroethylene, methylene chloride, chloroform, carbon tetrachloride and tetrachlorethylene. The volatile solvents may be used alone or in admixture.

[0140] Preferred volatile solvents may be selected from the group consisting of trichloroethane, trichloroethylene, methylene chloride, chloroform, carbon tetrachloride, tetrachlorethylene, methanol, ethanol, propanol, butanol, ethylene glycol, diethyl ether, ethyl acetate, acetone, N, N-dimethylformamide, and tetrahydrofuran, most preferably acetone.

[0141] The coating composition preferably comprises volatile carrier in an amount of from 75 to 99% (wt/v) of the total composition, preferably in an amount of from 80 to 98% (wt/v) of the total composition. In some embodiments of the invention it is

desirable that a substantial proportion of the coating composition be volatile carrier. In one preference, the volatile carrier consists essentially of volatile solvent.

[0142] In some embodiments, the volatile carrier may further comprise a propellant. The term "propellant" is used herein to refer to materials that are aerosol spray propellants and generally have a boiling point lower than room temperature. Propellants may be used to provide for aerosol delivery of the coating composition. When present in the coating composition, the propellant is generally used in admixture with the volatile solvent and together with the solvent, forms the volatile carrier. Propellants are not considered as part of the volatile solvent in compositions of the invention and amounts based on the weight of the composition do not include propellants or materials having a boiling point below 25°C.

[0143] In some instances propellants such as hydrofluorocarbons, hydrocarbons, hydrochlorofluorocarbons, compressed gases, and their mixtures may be used in aerosol or spray application of the coating composition. Examples of suitable propellants include ethane, propane, isobutene, dimethyl ether, HFO-1234ze, HFC-134a, HFC-152a, and mixtures thereof. The selection of propellant would be dependent on the solubility and miscibility of the propellant with the volatile solvent, polymer and coupling agent contained in the coating composition.

[0144] The coating composition may comprise optional additives. The optional additives may include but are not limited to, antistatic agents, ultraviolet (UV) absorbers, stabilisers, antioxidants, lubricants, pigments or other opacifiers, dyes, plasticisers, anti-fouling agents, insect repellents, and the like. It is preferred that any optional additives also be soluble in the coating composition such that a homogeneous composition is maintained.

[0145] To form the coating composition, the low surface energy polymer and coupling agent are typically mixed with and dissolved in the volatile carrier. Any optional additives may also be dissolved in the volatile carrier. In one set of embodiments, it is preferred that the coating composition be a homogeneous liquid comprising the polymer, coupling agent and volatile carrier in a single phase.

[0146] In one set of embodiments, the coating composition employed in the process of the invention consists of a low surface energy polymer, a coupling agent and a

volatile carrier. In one preference, the coating composition consists of 0.5 to 10% (w/v) low surface energy polymer and 1 to 5% (w/v) coupling agent, with the balance of the composition being a volatile carrier comprising at least one volatile solvent. In one preference, the volatile carrier consists of volatile solvent.

[0147] In one form the process of the invention, the process may also comprise a step of providing a substantially particle-free coating composition comprising a low surface energy polymer, coupling agent, and a volatile carrier.

[0148] Thus in some embodiments, a process for the preparation of a liquid repellent article comprises the steps of:

providing a substantially particle-free coating composition comprising a low surface energy polymer, coupling agent, and a volatile carrier;

applying the coating composition to a micro-rough surface of a substrate; and

evaporating the volatile carrier from the coating composition applied on the substrate to thereby form a substantially particle-free coating on the substrate;

wherein the coating comprises the low surface energy polymer and coupling agent and has a nano-rough topography; and

wherein the article is capable of repelling both water and oil.

[0149] In accordance with embodiments of the process of the invention, the coating composition is applied to a substrate having a micro-rough surface. The coating composition is applied to at least one surface of the substrate, but may be applied to a plurality of surfaces. It is requirement that the surface to which the coating composition is applied be a micro-rough surface.

[0150] The coating composition may be applied to the micro-rough surface of a substrate using conventional techniques, such as by dipping, spraying, brushing, padding, roll coating, curtain coating, or any combination of such techniques. The desired method of application may depend on the type of substrate being coated. The coating composition may be applied in a continuous manner, e.g. by coating a moving web or other substrate, to provide a roll or length of coated article.

[0151] The coating composition may be applied to a range of different substrates having a micro-rough surface.

[0152] In one set of embodiments, a substrate having a micro-rough surface may be selected from the group consisting of non-porous substrates, porous substrates, woven substrates, non-woven substrates, braided substrates, fibres, yarns, films (including thin films) and foams. The substrate may further be a flexible substrate.

[0153] In one set of embodiments, the coating composition is applied to a surface of a porous substrate. Porous substrates may be in the form of sheets, webs, foams and films. Examples of porous substrates include woven and non-woven fabrics and textiles, foam sheets and woven and non-woven papers.

[0154] In one set of embodiments, the coating composition is applied to a surface of a textile substrate. Examples of textile substrates include woven, non-woven, knitted or braided fabrics, fibres, filaments, yarns, etc. A skilled person would understand that textile substrates would possess a surface having microscale profile features.

[0155] In one form, the substrate is a fabric substrate and the coating composition is applied to one or more surfaces of the fabric. The fabric substrate may be a woven, non-woven, braided or knitted substrate and may be formed from synthetic or natural fibres, either alone or blended in any combination thereof. In some embodiments, the fabric substrate may comprise a fibre selected from the group consisting of cotton, cellulose, wool, cashmere, angora, silk, and combinations thereof. In one preference, the fabric substrate comprises cotton, wool or silk.

[0156] After the coating composition is applied to a micro-rough surface of a substrate, a coated substrate may be formed. The volatile carrier is then removed from the applied coating composition by evaporation. The volatile nature of the carrier (including solvents and other volatile compounds contained in the carrier) promotes its rapid evaporation.

[0157] In some embodiments, evaporation of the volatile carrier may proceed under passive conditions at ambient temperature. In some embodiments, evaporation of the volatile carrier may be facilitated by exposing the coated substrate to elevated temperatures and/or by flowing air over the coated substrate.

[0158] In one set of embodiments, the volatile carrier comprises or consists of at least one volatile solvent and the process of the invention comprises the step of evaporating the volatile solvent from the coating composition applied on the micro-rough surface of the substrate.

[0159] It can be desirable for the volatile solvent to undergo rapid evaporation. In some embodiments, rapid evaporation means that a substantial proportion (such as at least 50%, at least 60%, at least 70%, at least 80% or at least 90%) of the volatile solvent is removed from the coating composition applied on the substrate in a time period of less than 10 minutes, preferably less than 8 minutes, more preferably less than 5 minutes. However, a person skilled in the art would understand that the time period for solvent evaporation can vary, as it might depend on variables such as the thickness and surface area of the applied composition.

[0160] In one set of embodiments, the coated substrate may be heated at an elevated temperature in a range of from about 40 to 200°C, preferably from about 60 to 140°C to facilitate evaporation of the volatile carrier. The temperature may be selected based on the boiling point of the volatile solvent and/or the glass transition temperature (T_g) of the low surface energy polymer. Heat may be applied by a range of devices, including convection or forced-air ovens, infrared heaters, or other sources of thermal energy.

[0161] Heating of the coated substrate may occur for a time period sufficient to result in evaporation of a desired quantity of volatile carrier and a skilled person would understand that the time period may depend on the selected temperature, the nature of the volatile carrier and the desired processing time.

[0162] In some embodiments, heating of the coated substrate may occur for a time period selected from the group consisting of at least 5 minutes, at least 10 minutes, at least 15 minutes, at least 20 minutes and at least 30 minutes. A skilled person would appreciate that higher temperatures will generally require shorter time periods.

[0163] In one form of the process of the invention, a combination of airflow and elevated temperature may be used to evaporate the volatile carrier. The combination of airflow and elevated temperature may be employed concurrently or sequentially. For example, the coated substrate may be initially dried at room temperature in the

presence of a flow of air to remove at least some of the volatile carrier and form a partially dried coated substrate. The flow of air may be provided by a fan or similar device. The partially dried coated substrate may then be heated at an elevated temperature to evaporate and remove the remaining quantity of volatile carrier. Alternatively, the volatile carrier may be removed from the coated substrate at an elevated temperature in the presence of a flow of air, which may be provided by a fan-assisted oven or similar apparatus.

[0164] Upon evaporation of the volatile carrier, a dried and substantially particle-free coating is then formed on the substrate.

[0165] In one set of embodiments the process of the invention may further comprise the step of curing the substantially particle-free coating formed on the substrate. The curing step is preferably carried out at elevated temperature. In some embodiments, the curing step is carried out at a temperature in a range of from about 40 to 200°C or in a range from about 60 to 160°C. The curing step may facilitate covalent reactions of the coupling agent, either with itself or other components of the coating composition, or with the substrate, to crosslink the coupling agent or help with bonding of the coating to the substrate.

[0166] In some embodiments, evaporation of the volatile carrier and curing of the coating may occur within a single vessel. For example, the coated substrate may be conveyed to an oven and heated in the oven at elevated temperature. The elevated temperature enables the volatile solvent to be removed by evaporation and also facilitates curing of the coupling agent.

[0167] The coating formed by the process of the invention is a low surface energy coating and comprises the low surface energy polymer and the coupling agent. The coating formed by the process of the invention also has a nano-rough topography.

[0168] In one set of embodiments, the nano-rough coating produced by the process of the invention has an average root mean square (RMS) roughness of at least 10 nm, at least 12 nm, or at least 15 nm. In some embodiments, the coating has a RMS roughness of between 10 to 200 nm, preferably between 15 to 100 nm. A skilled person would be able to ascertain roughness and surface topography using conventional techniques such as atomic force microscopy (AFM).

[0169] Without wishing to be limited by theory, it is believed that the coating produced in the process of the invention has a nanostructured topography and forms a nanoscale rough surface on top of or over the micro-rough surface of the underlying substrate. It is believed that the nano-rough topography of the coating is produced through rapid evaporation of the volatile carrier from the coating applied to the substrate. The rapid evaporation of the volatile carrier is believed to result in fast solidification of the coating. This rapid solidification locks the morphology of the polymer and coupling agent contained in the coating as a very limited time is available for the components of the coating to flatten and smooth out along the substrate surface. As a result, the coating acquires a nano-rough topography or nano-rough surface.

[0170] It is further believed that the liquid repellent properties of the article of the invention arise due to the combination of effects provided by the low surface energy nano-rough coating and the micro-rough substrate. It is believed that the nano-rough coating and the micro-rough substrate can operate in combination or synergistically to provide the advantages of the liquid repellent article that are observed. It is therefore an important feature of the invention that the liquid repellent article comprises a micro-rough substrate and a nano-rough low surface energy coating, where the coating is moreover substantially free of particles.

[0171] In some embodiments, the substantially particle-free coating formed on the substrate has a surface free energy of no more than about 40 mN/m, no more than about 38 mN/m, no more than about 35 mN/m, or no more than about 30 mN/m, at 20°C.

[0172] In one preference, the substantially particle-free coating comprises at least one low surface energy polymer and at least coupling agent. In some embodiments the coupling agent is desirably a low surface energy coupling agent.

[0173] The low surface energy coupling agent may be silane coupling agent comprising a low surface energy group as described herein. A low surface coupling agent may advantageously enable higher surface energy polymers to be used, provided that the combination of coupling agent and polymer together produce a coating having a low surface energy (e.g. a surface energy of no more than about 40

mN/m, no more than about 38 mN/m, no more than about 35 mN/m, or no more than about 30 mN/m, at 20°C).

[0174] When silane coupling agents are used, it is believed that molecules of silane coupling agent can aggregate in the coating composition to form micelle-like structures so that the molecules can remain stable within the low surface energy polymer matrix. If the coupling agent comprises a hydrolysable group, condensation reactions between the hydrolysed molecules of silane agent may take place, which can stabilise the micellar structures because of the stronger interactions between silane molecules within the micelle. Because of their small size, the micellar aggregates may have some mobility within the polymer matrix, especially when the coating is at a temperature that is above the glass transition temperature (T_g) of the polymer. The micelles may stably orientate at the air-solid interface of the polymer coating. When orientated at the air-solid interface, the micelles may contribute to the nano-rough topography of the coating. When the surface energy of the micelle is lower than that of the polymer, the micelle at the air-solid interface of the coating can contribute to lower the overall surface free energy of the coating and hence enhance liquid repellency.

[0175] It is an advantage of the invention that a liquid repellent article is able to be produced in a simple method, with no additional pre- or post-treatment required to control roughness and/or surface chemical composition. Advantageously, the process of the invention enables amphiphobic articles and superamphiphobic articles to be prepared in a facile manner.

[0176] It should be appreciated that the described process is scalable between a laboratory set up and industrial set up and may be carried out in batch-wise or for continuous manner.

[0177] In another aspect, the present invention provides a liquid repellent article prepared by a process of any one of the embodiments described herein.

[0178] The liquid repellent article of one or more aspects of the invention is capable of repelling both water and oil. Liquid repellent articles of the present invention are hydrophobic and provide a contact angle of at least about 90 degrees, at least 120 degrees, or at least 150 degrees, for water. Liquid repellent articles of the present

invention are also oleophobic and provide a contact angle of at least about 90 degrees, at least 120 degrees, or at least 150 degrees, for oil.

[0179] The liquid repellent article may provide approximately the same liquid contact angle or different liquid contact angles for water and oil. As an example, the liquid repellent article may provide a contact angle of at least 150 degrees for water and a contact angle of at least 120 degrees for oil. Thus while the observed liquid contact angles for water and oil may differ, the article remains hydrophobic and oleophobic and able to repel both water and oil.

[0180] An oil may be a hydrocarbon compound or lipid substance that is liquid at room temperature. Generally, oils have a low surface tension, such as for example, a surface tension of 35 mN/m or less at 20°C.

[0181] In some embodiments, the liquid repellent article is capable of repelling other solvents and liquids in addition to water and oil.

[0182] In one form, liquid repellent articles of one or more embodiments of the invention provide a liquid contact angle of at least about 90 degrees, at least 120 degrees, or at least 150 degrees, for a liquid in contact with the article.

[0183] A liquid repellent article of one or more aspects of the invention advantageously exhibits combined hydrophobic and oleophobic properties and may in some embodiments exhibit superhydrophobic and superoleophobic properties where water and oil display contact angles (CAs) at least 120 degrees or at least 150 degrees when in contact with the article. In such embodiments the articles in accordance with the invention may therefore be regarded as superamphiphobic. A liquid contact angle above 150 degrees allows liquids to form nearly spherical shapes on coated substrate surfaces. Such contact angles can be maintained for a long period of time on the coated surfaces.

[0184] The liquid contact angle is often determined by measuring the liquid-solid angle of a liquid drop of given volume with a horizontally laid surface. A skilled person would appreciate that high liquid contact angles (i.e. 90 degrees or higher) are indicative of highly effective liquid repellent surfaces. The desired liquid contact angle

is preferably exhibited by both water and oil when in contact with a liquid repellent article of embodiments described herein.

[0185] In one set of embodiments, liquid repellent articles of one or more aspects of the present invention are capable of repelling low surface tension liquids. Low surface tension liquids may have a surface tension of 35 mN/m or less at 20°C. In such embodiments, the liquid having a surface of 35 mN/m or less exhibits a liquid contact angle of at least 90 degrees, at least 120 degrees or at least 150 degrees, when in contact with a liquid repellent article of the present invention. Low surface tension liquids may include organic solvent liquids such as hydrocarbons including ethanol and hexadecane and halohydrocarbons such as chloroform.

[0186] A liquid repellent article of one or more aspects of the invention also exhibits a low sliding angle (SA). A skilled person would understand that the sliding angle is a measure of the critical angle at which a droplet of liquid (such as water or oil) will slide down an inclined plane. The sliding angle may be indicative of the relative liquid repellency of the article. In one embodiment, the liquid repellent article may exhibit a liquid sliding angle selected from the group consisting of no more than about 35 degrees, no more than about 20 degrees, no more than about 15 degrees, and no more than about 10 degrees.

[0187] In a further aspect, the present invention provides a liquid repellent textile article comprising a fabric substrate and a substantially particle-free low surface energy nano-rough coating on a surface of the fabric substrate.

[0188] In a further aspect, the present invention provides a liquid repellent textile article comprising a fabric substrate and a substantially particle-free coating on a surface of the fabric substrate, wherein the coating comprises a low surface energy polymer and a coupling agent and has a nano-rough topography.

[0189] A skilled person would understand that the fabric substrate employed in the liquid repellent textile article would comprise a micro-rough surface.

[0190] In one set of embodiments of a liquid repellent textile article as described herein, the low surface energy polymer may be at least one selected from those described herein.

[0191] In one set of embodiments of a liquid repellent textile article as described herein, the coupling agent may be a silane coupling agent. Suitable silane coupling agents may be selected from any one of those described herein.

[0192] In embodiments of a liquid repellent textile article as described herein, the fabric substrate of the textile article may be a woven, non-woven, braided or knitted fabric formed from synthetic or natural fibres, either alone or blended in any combination thereof. In some embodiments, the fabric substrate may comprise a fibre selected from the group consisting of cotton, cellulose, wool, cashmere, angora, silk, and combinations thereof. In one preference, the fabric substrate comprises cotton, wool or silk.

[0193] In another aspect, the present invention also provides a method of preparing a liquid repellent textile article comprising the steps of:

applying a substantially particle-free coating composition comprising a low surface energy polymer, coupling agent, and a volatile carrier to a surface of a fabric substrate; and

evaporating the volatile carrier from the applied coating composition to thereby form a substantially particle-free coating on the fabric substrate;

wherein the coating comprises the low surface energy polymer and coupling agent and has a nano-rough topography, and

wherein the textile article is capable of repelling both water and oil.

[0194] The coating composition may be applied to the fabric substrate by means of spray, brush, roll coating, curtain coating, or any combination of these application techniques.

[0195] In some embodiments, the liquid repellent textile article provides a contact angle selected from the group consisting of at least about 90 degrees, at least about 120 degrees, or at least 150 degrees, for water and oil in contact with the article.

[0196] In certain embodiments, the liquid repellent textile article is hydrophobic and provides a contact angle selected from the group consisting of at least about 90

degrees, at least about 120 degrees, or at least 150 degrees, for water in contact with the article.

[0197] In certain embodiments, the liquid repellent textile article is oleophobic and provides a contact angle selected from the group consisting of at least about 90 degrees, at least about 120 degrees, or at least 150 degrees, for oil in contact with the article.

[0198] The liquid repellent article produced of one or more aspects of the present invention possesses a number of advantageous properties as discussed below.

[0199] The liquid repellent article of the invention is durable. The article is able to resist physical and chemical damage without loss of its liquid repellent properties. For instance, the liquid repellent article is able to repel corrosive chemicals such as strong acids and strong alkali, which enables the article to resist chemical damage. The article is also capable of withstanding repeated physical abrasion, rubbing or mechanical stress.

[0200] In one set of embodiments, a liquid repellent article of one or more aspects of the invention is capable of withstanding 10,000 cycles of abrasion, when tested according to ASTM D4966-98. This test indicates that the article is able to maintain the ability to repel water and oil after 10,000 cycles of abrasion.

[0201] When damaged, the liquid repellent article of the invention is capable of undergoing self-healing to repair the damage. In some embodiments, repeated self-healing is possible. Self-healing may be possible as the coating on the article may be capable of repairing itself after damage. Damage may occur by chemical means (e.g. by radiation or oxidation induced damage) or by physical means (e.g. by abrasion, cutting or short time burning). Such damage may introduce high surface energy groups in the coating and article, which can lead to a loss of liquid repellency.

[0202] Without wishing to be limited by theory, it is believed that the ability of the liquid repellent article to self-heal and regain liquid repellency may be due to the ability of the components in the coating of the article to reorientate in the coating to cover any high surface energy groups that may be introduced as a result of damage. For instance, it is believed that the low surface energy polymer may be capable of rotating

in the coating in order to cover and conceal high surface energy groups. Alternatively, or in addition, micellar structures comprising low surface energy coupling agent may migrate to the air-solid interface of the coating to conceal high surface energy groups.

[0203] The liquid repellent article is also able to withstand repeated washing. This property is advantageous for textile articles which are generally washed repeatedly in order to remove stains and soils.

[0204] In one set of embodiments, a liquid repellent article of one or more aspects of the invention is capable of withstanding at least 100 washing cycles, when tested according to AATCC Test Method 61-2006. In some embodiments, the repellent article is capable of withstanding at least 200, at least 400, or at least 600 washing cycles, when tested according to AATCC Test Method 61-2006. This test indicates that articles of the invention, such as liquid repellent textile articles, are able to maintain their ability to repel water and oil despite repeated washing cycles.

[0205] The liquid repellent article is also resistant to high temperature treatment and may be exposed to high temperature, such as immersion in boiling water, without suffering from a significant loss of liquid repellency.

[0206] The invention will now be described with reference to the following examples. It is to be understood that the examples are provided by way of illustration of the invention and that they are in no way limiting to the scope of the invention.

EXAMPLES

Coating Evaluation

Chemical Resistance

[0207] Chemical resistance of a coated fabric was tested by reference to a standard method for evaluation of protective clothing (*Protection against liquid chemicals - Test method for resistance of materials to penetration by liquids, ISO6530:2006*). Before testing, coated fabric samples were placed in a conditioned room (temperature 20 ± 2 °C, humidity $65 \pm 5\%$) for 24 hours. A coated fabric sample (size, 10 cm × 10 cm) was placed on a 30° tilted plate then acid (40% H₂SO₄) or alkali (40% KOH) was poured on

the sample surface continuously for 10 seconds. The test was performed at 20 ± 2 °C. A stronger acid (98% H_2SO_4) was also used to test the chemical stability. Briefly, 1 mL 98% H_2SO_4 was dropped continuously on an inclined fabric sample, followed by leaving the fabric at room temperature for 40 seconds.

Washing Durability

[0208] Washing durability of a coated fabric was examined by reference to a standard method for testing washing fastness of fabrics (*AATCC Test Method 61-2006 test No 2A*). The test was performed using a standard laundering machine (Fong, Fong's National Engineering CO.LTD, Hong Kong, China) equipped with 500 mL (75 mm × 75 mm) stainless-steel lever-lock canisters. The coated fabric sample (size, 50 mm × 150 mm) was laundered in a 150 mL aqueous solution containing 0.15% (w/w) AATCC standard reference detergent WOB. During laundering, the temperature was controlled at 49 °C, and the stirring speed was 40 ± 2 rpm. After 45 minutes of laundering, the laundered sample was rinsed with tap water, and then dried at room temperature without spinning. Contact angle and sliding angle were then measured. This standard washing procedure is equivalent to five cycles of home machine launderings. For convenience, we used equivalent number of home laundering in this work.

Abrasion Resistance

[0209] Abrasion resistance of a coated fabric was tested using the Martindale method according to ASTM D4966. The test was performed under a commercial Martindale abrasion tester (I.D.M Instrument Design & Maintenance). In our experiment, the untreated wool fabric was used as abradant, 12 kPa of pressure was employed, which is often used to evaluate the coated fabrics for heavy duty upholstery usages.

Blade Scratching Test

[0210] An evaluation of the resistance of a coated fabric to blade scratching was performed with a sharp blade. The coated fabric sample was placed on a flat plate. A flat blade was mounted vertically on a frame with the blade edge in close contact to the top surface of the fabric sample. 0.8 kg weight was loaded on the blade, which did

not cut the fabric. The blade was then dragged in a direction perpendicular to the length of the blade.

Abrasion Resistance:

[0211] The ability of a coated fabric to resist abrasion was tested using a fine sandpaper (1200 grit 9 " × 11 ").

Bending Modulus

[0212] The bending modulus of coated fabrics was measured by the cantilever method using a M003B Shirley stiffness tester (BS 3356, BS 9703 part 7 and ASTM D1388). Bending modulus (Q , g/cm²) was calculated according to the equations:

$$Q = \frac{12G \times 10^{-6}}{g^3} \quad (1)$$

$$G = 0.10MC^3 \quad (2)$$

where G (mg·cm) is the flexural rigidity of the fabric sample, and M (mg·cm⁻²) is the areal density of the fabric. C (cm) and g (cm) are bending length and fabric thickness, respectively. The fabric thickness was measured using a thickness tester (MESDAN micrometer). The measurements were carried out in both warp and weft directions.

Surface Energy Measurements

[0213] Surface energy was measured based on contact angle using the Wu's method (Journal of Polymer Science Part C: Polymer Symposia, 1971, **34**(1): p 19-30). Tetraethylene glycol and deionized water were used as probe solvents. Dispersion and polar components were calculated based on the average contact angle from five measurements.

Other Characterizations

[0214] Scanning electron microscope (SEM, Supra 55VP) and transmission electron microscope (TEM, JEM-200 CX JEOL) were used to observe the coating morphology. Surface roughness of the coatings was measured using atomic force microscope (AFM, Asylum Research). Contact angles were measured by a contact angle

goniometer (KSV CAM 101) using liquid droplets of 5 μL in volume. Sliding angles were measured using a purpose-made device consisting of a sample holder and a digital angle meter. Air permeability was tested by FX 3300 Air permeability Tester according to the Standard (SIST EN ISO 9237-1999). The test pressure of 125 kPa was used for all the samples. All the CA and air permeability values were the mean of 5 measurements.

Example 1

[0215] 1H,1H,2H,2H-perfluorodecyltriethoxysilane ($\text{C}_{16}\text{H}_{19}\text{F}_{17}\text{O}_3\text{Si}$) (FAS coupling agent), poly(vinylidene fluoride-co-hexafluoropropylene) (PVDF-HFP) and acetone were obtained from Aldrich and used as received. The coating composition was prepared by mixing PVDF-HFP (1.0 g) and FAS (0.75 mL) in acetone (50 mL) and stirring with a magnetic stirring bar for 30 minutes at 50 $^{\circ}\text{C}$ to get a homogenous solution.

[0216] A fabric substrate (plain weave polyester, 168 g/m^2 , thickness = 520 μm) was washed in a water containing a detergent. After cleaning, the fabric was rinsed with water and then dried prior to use. The fabric substrate was immersed in the above coating composition for 1 minute using a dip coating method. After squeezing the extra liquid from the fabric using two rubber rollers, the coated fabric was dried directly at 130 $^{\circ}\text{C}$ for 10 minutes with a fan at 60 km/h.

[0217] Figure 2 shows the chemical structure of the materials employed in the coating composition and the procedure to prepare the coating on the fabric substrate. Acetone is a high volatile solvent, and under a high temperature with high speed fan, it evaporated rapidly, thus, a nano-rough -structure of PVDF-HFP polymer layer was formed. Surface roughness measured by AFM imaging indicated that the root mean square (RMS) roughness of the fabric changed from 9.82 nm to 15.1 nm after coating treatment, confirming that a rough coating layer can be formed after the rapid evaporation of the solvent.

[0218] As seen in Figure 3, the coated fabric is able to repel a range of liquids, as it was observed that water, olive oil, hexadecane and ethanol formed spherical droplets when in contact with the coated fabric. In comparison, these liquids spread out when in contact with a comparative uncoated fabric due to wetting effects.

[0219] As shown in Figure 4, the coated fabric provided liquid contact angles (CA) of 162°, 156°, 154° and 146°, and sliding angles (SA) of 4°, 15°, 22° and 35°, to water, olive oil, hexadecane and ethanol, respectively. All CAs had little change with time. For ethanol, the droplet evaporated off in 10 minutes, while water drop evaporated completely in 40 minutes.

[0220] Figure 5 shows the dependency of CA and SA on the surface tension of liquids. It is clearly indicated that the coated fabric is capable of repelling liquids with a surface tension greater than 22.3 mN/m.

[0221] The protective ability of the coated fabric against liquid chemicals was tested by reference of a standard test method (Protective clothing - Protection against liquid chemicals for resistance of materials to penetration by liquids, ISO 6530: 2005). 40% H₂SO₄ and 40% KOH aqueous solutions were poured onto the coated fabric samples. Both acid and base liquids rolled off completely from the coated fabric surface. After 10 seconds of pouring, the fabric was still dry and maintained its original superamphiphobicity. Moreover, the coating can withstand hot acid and alkaline, pouring 90°C 40% H₂SO₄ and 40% KOH onto the fabric for 10 seconds, the fabric was still kept dry and super-liquid repellent property, indicating the excellent chemical stability. In contrast, when the liquids were poured on to uncoated fabric, both acid and base liquids spread into the fabrics immediately.

[0222] The chemical stability was further evaluated by immersing the coated fabric in 40% H₂SO₄ or 40% KOH for 12 hours, rinsing the fabric with water, and then measuring the CA and SA after drying the fabric at room temperature. Over 12 hours, the fabrics showed almost no change in the CA, while the SA had a slight increase. As seen in Figure 6, the coated fabrics after acid/base immersion were able to maintain their liquid repellent properties. In comparison, corroded areas were observed on an uncoated fabric after 12 hours immersing in 40% KOH or 40% H₂SO₄ under SEM.

[0223] To further probe the protective ability against strong acid, a coated and uncoated fabric was immersed in 98% H₂SO₄. 98% H₂SO₄ is known to have strong oxidation and corrosion, and it can damage almost all materials. The coated fabric, after immersion in 98% H₂SO₄ for 40 seconds, did not appear to suffer from any

observable damage or degradation. Furthermore, such a treatment did not appear to affect the coated fabric's liquid repellency. However, when an uncoated fabric is immersed in 98% H_2SO_4 under the same condition, immediate degradation took place in the contact zone. In addition, on the coated polyester fabric, 98% H_2SO_4 drops formed a sphere-like bead which can stay on the fabric for at least 1 hour. After cleaning off the acid, the fabric was still superamphiphobic.

[0224] Apart from chemical damages, physical damages such as abrasion with a fabric, rubbing with a rough material, and scratching with a sharp blade are also important causes to the degradation of liquid repellency. During daily use, fabrics are more likely damaged by gentle abrasion, such as wearing and rubbing with other fabrics. The abrasion durability of the coated fabric was tested using the Martindale method, a standard method to test the abrasion resistance of fabrics. After 10,000 abrasion cycles, the coated fabric appeared to showed an improvement in liquid repellency (increased CA), which can be explained as the increased surface roughness due to abrasion.

[0225] Resistance to abrasion (sandpaper rubbing) and blade scratching was also tested. The results show the CA and SA changes with sandpaper (1200 grit 9" × 11") rubbing cycles. Similar to the Martindale abrasion, sandpaper rubbing also led to a slight increase in CA but a decrease in SA. After 500 cycles of rubbing, the CA increased to 171°, 160°, 152° and 146° for water, olive oil, hexadecane and ethanol, while SA reduced to 2.5°, 14°, 18° and 33°, respectively. SEM imaging indicated that some coating materials was scraped from fiber surface, which increased surface roughness (RMS is 144 nm after rubbing). Although rubbing also broke and removed some fibers from the fabric, the newly-exposed fibers were still coated with PVDF-HFP/FAS. The increased surface roughness on the entire fabric and the single fibers enhanced the liquid repellent property. Blade scratching was observed to have a similar effect on CA and SA.

[0226] Washing is an essential treatment for the practical uses of fabrics. During washing, the fabric undergoes mechanical stresses in addition to chemical agents. The synergistic effect of chemical and physical actions accelerates the detachment of coating layer on fiber substrate. The washing durability of the coated fabric was evaluated by reference of a standard machine laundry process. The coated fabric can

withstand at least 600 cycles of machine wash without losing its liquid repellency. After 600 washing cycles, the SA of the coated fabric just had a slight increase, while the CA maintained unchanged.

[0227] Also, the treated fabric can withstand boiling treatment in water. One hour of boiling in water did not affect the liquid repellency of the coated fabric and the CA for all the liquids studied had no change. However, the boiling treatment led to a slight increase in SA. After 1 hour of boiling in water, the SA increased to 6°, 21°, 27° and 43° for water, olive oil, hexadecane and ethanol, respectively.

[0228] Furthermore, the PVDF-HFP/FAS coating has a self-healing property to recover its liquid repellent properties after chemical damage. To demonstrate this, the coated fabric was deliberately treated with a vacuum plasma using air as gas source. The plasma treatment introduces polar functional groups such as oxygen, hydroxyl and carboxylic acid groups to the coating surface. Such a plasma treatment made the coating surface both hydrophilic and oleophilic with a CA of 0°. When the plasma treated fabric was heated at 130° for 5 minutes, the liquid repellency was restored. The treated fabric was able to be repeatedly damaged and repaired and retained its liquid repellent properties even after 60 cycles of plasma and self-healing.

[0229] Table 1 shows the effect of the coating treatment on fabric properties. The coating had almost no influence on the air permeability, but slightly affected the fabric rigidity and the permeability to moisture. For colored fabrics, it was hard to distinguish the color change after coating treatment. The color difference data (ΔE) was less than 1 (Table 1). The ΔE value of 1 is the smallest color difference that human eye can distinguish, and any materials of ΔE less than 1.0 is indistinguishable. To evaluate the coating transparency, a dense PVDF-HFP/FAS film was prepared on a glass slide. The coated glass slide looked transparent. The transmission spectrum also confirmed that the PVDF-HFP/FAS layer was highly transparent, hence did not influence the fabric original color.

Table 1 Effect of coating treatment on fabric properties

Property	Uncoated	PVDF-HFP/FAS coated
Air permeability ($\text{cm}^3 \cdot \text{cm}^{-2} \cdot \text{s}^{-1}$)	21 ± 2	22 ± 3
Moisture permeability ($\text{g} \cdot \text{m}^{-2} \cdot \text{day}^{-1}$)	7580	7180
Bending modulus (g/cm^2)	11.5 (warp)/11.9 (weft)	15.2 (warp)/15.5 (weft)
Color change (ΔE value)	-	0.8~1.0

Example 2

[0230] Polystyrene (PS) solution was prepared by dissolving PS (2.5 g) in chloroform (100 ml). After 30 minutes of magnetic stirring, a homogeneous solution was formed. Tridecafluorooctyl triethoxysilane was then added into the polymer solution with magnetic stirring for 30 minutes. Fabric substrates were immersed into the coating solution for 1 minute. After squeezing to remove excess solution, the coated fabrics were dried at 110 °C for 30 minutes. In this study, 4 different fabrics were used, including polyester fabric (plain weave, 168g/m²), cotton fabric (plain weave, 146g/m²), wool fabric (plain weave, 196 g/m²), and electrospun polyacrylonitrile (PAN) nanofibres mat (average fibre diameter 370 ± 22 nm, thickness 0.35 ± 0.01 mm). The resultant coated substrates were characterised contact angle and sliding angle measurements. The results are shown in Table 2.

Table 2

Fabrics	Testing liquids	Contact angle	Sliding angle
Polyester	Water	$168^\circ \pm 3^\circ$	$3^\circ \pm 1^\circ$
	Cooking oil	$155^\circ \pm 3.5^\circ$	$9^\circ \pm 2.5^\circ$
	Hexadecane	$151^\circ \pm 2.5^\circ$	$15^\circ \pm 1.5^\circ$
Cotton	Water	$166^\circ \pm 3.2^\circ$	$4^\circ \pm 1.5^\circ$
	Cooking oil	$153^\circ \pm 3.6^\circ$	$10^\circ \pm 2^\circ$
	Hexadecane	$150^\circ \pm 2.5^\circ$	$17^\circ \pm 2.5^\circ$

Fabrics	Testing liquids	Contact angle	Sliding angle
Wool	Water	$170^{\circ} \pm 2^{\circ}$	$2^{\circ} \pm 0.8^{\circ}$
	Cooking oil	$157^{\circ} \pm 3.5^{\circ}$	$8^{\circ} \pm 2.5^{\circ}$
	Hexadecane	$153^{\circ} \pm 2.5^{\circ}$	$12^{\circ} \pm 2.5^{\circ}$
PAN nanofibres mat	Water	$165^{\circ} \pm 2.5^{\circ}$	$3^{\circ} \pm 1^{\circ}$
	Cooking oil	$156^{\circ} \pm 3.5^{\circ}$	$10^{\circ} \pm 2.2^{\circ}$
	Hexadecane	$152^{\circ} \pm 2.5^{\circ}$	$16^{\circ} \pm 1.8^{\circ}$

Example 3

[0231] Hexadecyltrimethoxysilane ranging from 0.5 g to 5 g was added into the as-prepared 3% (wt/v) polyetheretherketone (PEEK)-THF solution. The solution was stirred for 1 hour to get a homogeneous solution was formed, which can be directly sprayed onto the substrates. As shown in Figure 7, with the FDTs:PEEK ratio changing from 1:6 to 1:1.5 (wt/wt), CA value increases for both water and oil fluids.

Example 4

[0232] Polycarbonate (PC) 5g was dissolved in 100 ml methylene chloride. 2 ml phenyl triethoxysilane silane was then added in the as-prepared PC solution under magnetic stirring to get a homogeneous coating solution. The solution can be applied onto the substrates directly by different coating techniques, such as spraying, padding and dip-coating. The coated fabric substrates were further dried at 130 °C for 10 minutes. All the coated substrates showed superamphiphobic surface. For example, the CAs of the coated wool fabric are 166° to water, 158° to cooking oil and 150° to hexadecane, respectively.

Example 5

[0233] 3.5 g PVDF was dissolved in 100 ml acetone. After 1 hour stirring, 1 g (isobutyl)₇Si₈O₁₂ (POSS) heptyl silane was added and the solution was stirred for another 30 minutes to form a stable coating solution. The solution was added to a sealed container and blended with a propellant, such as isobutene. The mixture was then sprayed onto fabric substrate. After drying at 140 °C for 10 minutes, the coated fabric exhibited superamphiphobic surface, with CAs are 167°, 158° and 155° to water, cooking oil and hexadecane, respectively.

Example 6

[0234] Polyisobutylene (PIB) 2.5 g was dissolved in 100 ml dichloromethane under stirring for 2 hours to get a homogeneous polymer solution. To further reduce the surface free energy, octyl triethoxysilane was then added in the coating solution with continuous stirring for 30 minutes to form a superamphiphobic coating solution. Dip-coating the fabric substrates in the solution and the coated substrates were finally heated at 130 °C for 1 hour. After coating, the fabric showed high liquid repellency to both water and oil liquid.

Example 7

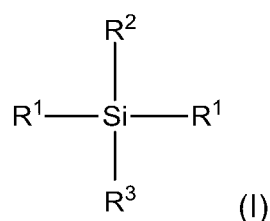
[0235] Low density polyethylene (LDPE) 2 g was dissolved in 100 ml xylene, the solution was mixed with (iso-butyl)-POSS heptyl silane, and stirred intensively at room temperature for 3 hours to produce homogeneous coating solution. Brush painting was used to apply the coating solution onto the substrates. The coated substrates were then dried at 130 °C for 20 minutes. After coating, the porous film turned superamphiphobic, with CAs of 155° and 150° to water and soybean oil.

Example 8

[0236] Poly(styrene-butadiene-styrene) (SBS) 4 g was dissolved in 100 ml tetrahydrofuran (THF)/water solution (THF/water = 9/1, v/v). 2 ml fluorinated alkyl silane was then added in the as-prepared SBS solution under magnetic stirring to get a homogeneous coating solution. The solution can be applied onto the substrates directly by different coating techniques, such as spraying, padding and dip-coating. The coated fabric substrates were further dried at 120 °C for 30 minutes. The coated substrates showed super-repellent to water and oils. The CAs of the coated polyester fabric are 166° to water and 152° to cooking oil.

CLAIMS

1. A liquid repellent article comprising a substrate having a micro-rough surface and a substantially particle-free coating on the micro-rough surface of the substrate, wherein the coating comprises at least one low surface energy polymer and at least one coupling agent and has a nano-rough topography, and wherein the article is capable of repelling both water and oil.
2. An article according to claim 1, wherein the substrate is a porous substrate.
3. An article according to claim 1 or claim 2, wherein the substrate is selected from the group consisting of a mesh, paper and fabric substrate.
4. An article according to any one of claims 1 to 3, wherein the substantially particle-free coating has a RMS roughness of between 10 to 200 nm.
5. An article according to any one of claims 1 to 4, wherein the coating comprises a silane coupling agent.
6. An article according to claim 5, wherein the silane coupling agent is of formula (I):



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 group comprising a moiety selected from the group consisting of alkyl, alkenyl, alkynyl, alkylepoxy, alkyl ethers, alkyl esters, aryl,

cycloalkyl, fluoroalkyl, fluoroether, fluoroester, fluoroaryl, and polyhedral oligomeric silsequioxane; and

R^3 is a non-hydrolysable group comprising a moiety selected from the group consisting of alkyl, alkenyl, alkynyl, alkylepoxy, alkyl ethers, alkyl esters, aryl, cycloalkyl, fluoroalkyl, fluoroether, fluoroester, fluoroaryl, and polyhedral oligomeric silsequioxane.

7. An article according to any one of claims 1 to 6, wherein the coating comprises an amount of coupling agent in a range of from about 0.5 to 10% (v/v), preferably from about 1 to 5% (v/v).

8. An article according to any one of claims 1 to 7, wherein the coating comprises a polymer having a surface free energy of no more than about 50 mN/m at 20°C.

9. An article according to any one of claims 1 to 8, wherein the coating comprises a polymer selected from the group consisting of polyolefins, fluoropolymers, perfluoropolymers, vinyl polymers, polysiloxanes, polyesters, polyurethanes, polycarbonates, copolymers thereof, and mixtures thereof.

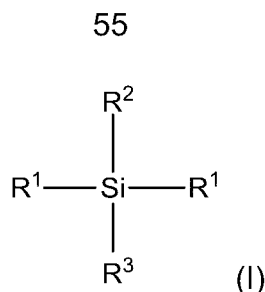
10. An article according to any one of claims 1 to 9, wherein the coating comprises a polymer selected from the group consisting of polyethylene, polyisobutylene, polystyrene, poly(α -methyl styrene), polyvinylchloride, poly(vinylidene fluoride), poly(vinylidene fluoride-co-hexafluoropropene), poly(vinyl acetate), polytrifluoroethylene, , poly(chlorotrifluoroethylene), poly(ethyl acrylate), poly(ethyl methacrylate), poly(butyl methacrylate), poly(iso-butyl methacrylate), poly(hexyl methacrylate), poly(tetramethylene oxide), polydimethylsiloxane, polycarbonates, polyesters, polyurethanes, fluorinated olefin-based polymers, fluoroacrylates, fluorosilicone acrylates, fluorourethanes, cyclic olefin copolymer, and mixtures thereof.

11. An article according to any one of claims 1 to 10, wherein the coating comprises an amount of low surface energy polymer in a range of from about 0.2 to 10% (w/v), preferably from about 0.5 to 5% (w/v), more preferably about 1-3% (w/v).

12. An article according to any one of claims 1 to 11, wherein the coating comprises less than 0.5% (w/v) of particles.

13. An article according to any one of claims 1 to 12, wherein the article provides a liquid contact angle of at least 90 degrees for both water and oil.
14. An article according to any one of claims 1 to 13, wherein the article provides a liquid contact angle of at least 120 degrees for both water and oil.
15. An article according to any one of claims 1 to 14, wherein the article provides a liquid contact angle of at least 150 degrees for both water and oil.
16. An article according to any one of claims 1 to 15, which is capable of withstanding at least 100 washing cycles, when tested according to AATCC Test Method 61-2006.
17. An article according to any one of claims 1 to 16, which is capable of withstanding 10,000 cycles of abrasion, when tested according to ASTM D4966-98.
18. An article according to any one of claims 1 to 17, wherein the coating is capable of self-healing after damage.
19. A process for the preparation of a liquid repellent article comprising the steps of:
 - applying a substantially particle-free coating composition comprising a low surface energy polymer, coupling agent, and a volatile carrier to a micro-rough surface of a substrate; and
 - evaporating the volatile carrier from the coating composition applied on the substrate to thereby form a substantially particle-free coating on the substrate,
 - wherein the coating comprises the low surface energy polymer and coupling agent and has a nano-rough topography, and
 - wherein the article is capable of repelling both water and oil.
20. A process according to claim 19, wherein the substrate is a porous substrate.
21. A process according to claim 19 or claim 20, wherein the substrate is selected from the group consisting of a mesh, paper and fabric substrate.

22. A process according to any one of claims 19 to 21, wherein the substantially particle-free coating has a RMS roughness of between 10 to 200 nm.
23. A process according to any one of claims 19 to 22, wherein the volatile carrier comprises at least one volatile solvent.
24. A process according to claim 23, wherein the volatile solvent has a vapour pressure of at least 10 kPa at 20°C.
25. A process according to any one of claims 19 to 24, wherein the volatile carrier comprises at least one volatile solvent selected from the group consisting of alcohols (preferably C1-C4 alcohols), glycols, ethers, esters, ketones, amides, and halohydrocarbon solvents.
26. A process according to any one of claims 19 to 25, wherein the volatile carrier comprises at least one volatile solvent selected from the group consisting of trichloroethane, trichloroethylene, methylene chloride, chloroform, carbon tetrachloride, tetrachlorethylene, methanol, ethanol, propanol, butanol, ethylene glycol, diethyl ether, ethylacetate, acetone, N,N-dimethylformamide, and tetrahydrofuran.
27. A process according to any one of claims 19 to 26, wherein the evaporation of the volatile carrier occurs at an elevated temperature, preferably at a temperature in the range of from about 60 to 140°C.
28. A process according to any one of claims 19 to 27, wherein the evaporation of the volatile carrier occurs in the presence of a flow of air.
29. A process according to any one of claims 19 to 28, wherein the coupling agent is a silane coupling agent.
30. A process according to claim 29, wherein the silane coupling agent is of formula (I):



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 group comprising a moiety selected from the group consisting of alkyl, alkenyl, alkynyl, alkylepoxy, alkyl ethers, alkyl esters, aryl, cycloalkyl, fluoroalkyl, fluoroether, fluoroester, fluoroaryl, and polyhedral oligomeric silsequioxane; and

R^3 is a non-hydrolysable group comprising a moiety selected from the group consisting of alkyl, alkenyl, alkynyl, alkylepoxy, alkyl ethers, alkyl esters, aryl, cycloalkyl, fluoroalkyl, fluoroether, fluoroester, fluoroaryl, and polyhedral oligomeric silsequioxane.

31. A process according to any one of claims 19 to 30, wherein the coating composition comprises an amount of coupling agent in a range of from about 0.5 to 10% (v/v), preferably from about 1 to 5% (v/v).

32. A process according to any one of claims 19 to 31, wherein the low surface energy polymer has a surface free energy of no more than about 50 mN/m at 20°C.

33. A process according to any one of claims 19 to 32, wherein the low surface energy polymer is selected from the group consisting of polyolefins, fluoropolymers, perfluoropolymers, vinyl polymers, polysiloxanes, polyesters, polyurethanes, polycarbonates, copolymers thereof, and mixtures thereof.

34. A process according to any one of claims 19 to 33, wherein the low surface energy polymer is selected from the group consisting of polyethylene,

polyisobutylene, polystyrene, poly(α -methyl styrene), polyvinylchloride, poly(vinylidene fluoride), poly(vinylidene fluoride-co-hexafluoropropene), poly(vinyl acetate), polytrifluoroethylene, , poly(chlorotrifluoroethylene), poly(ethyl acrylate), poly(ethyl methacrylate), poly(butyl methacrylate), poly(iso-butyl methacrylate), poly(hexyl methacrylate), poly(tetramethylene oxide), polydimethylsiloxane, polycarbonates, polyesters, polyurethanes, fluorinated olefin-based polymers, fluoroacrylates, fluorosilicone acrylates, fluorourethanes, cyclic olefin copolymer, and mixtures thereof.

35. A process according to any one of claims 19 to 34, wherein the coating composition comprises an amount of low surface energy polymer in a range of from about 0.2 to 10% (w/v), preferably from about 0.5 to 5% (w/v), more preferably about 1-3% (w/v).

36. A process according to any one of claims 19 to 35, wherein the coating composition is applied by means of dipping, spraying, padding, brushing, roll coating, or any combination thereof.

37. A process according to any one of claims 19 to 36, wherein the coating composition comprises less than 0.5% (w/v) of particles.

38. A process according to any one of claims 19 to 37, wherein the article provides a liquid contact angle of at least 90 degrees for both water and oil.

39. A process according to any one of claims 19 to 38, wherein the article provides a liquid contact angle of at least 120 degrees for both water and oil.

40. A process according to any one of claims 19 to 39, wherein the article provides a liquid contact angle of at least 150 degrees for both water and oil.

41. A liquid repellent article prepared by the process of any one of claims 19 to 40.

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Figure 1



Figure 2

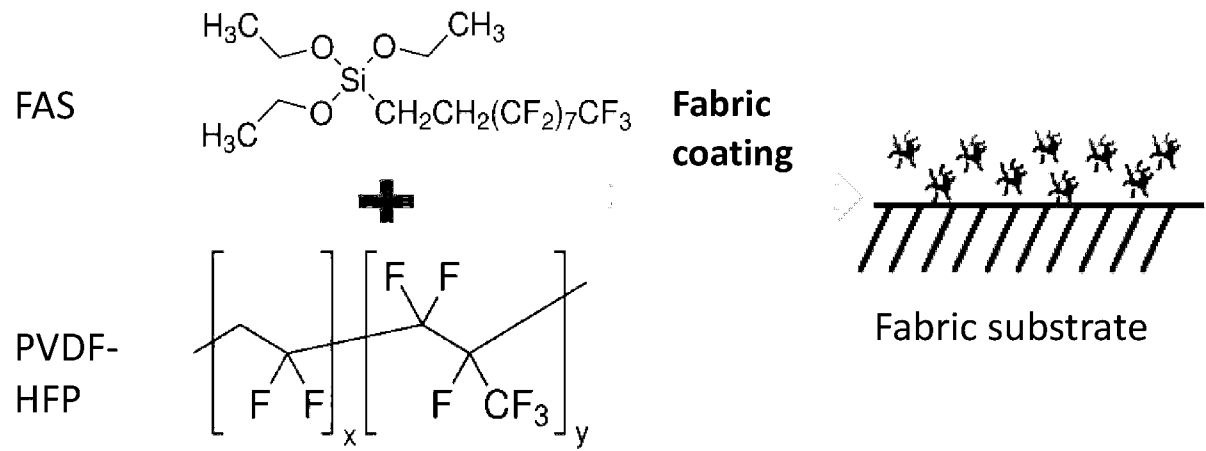
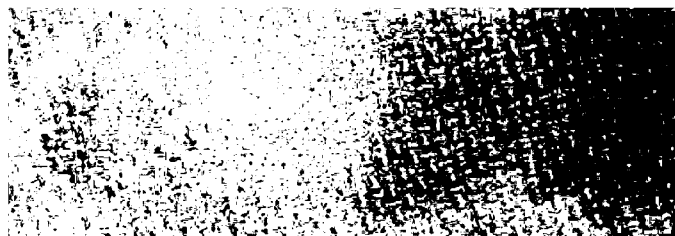
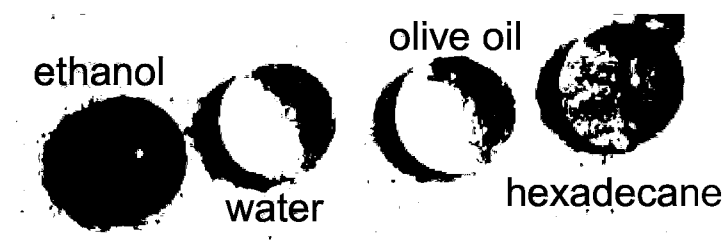


Figure 3

Un-coated fabric



Coated fabric



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Figure 4

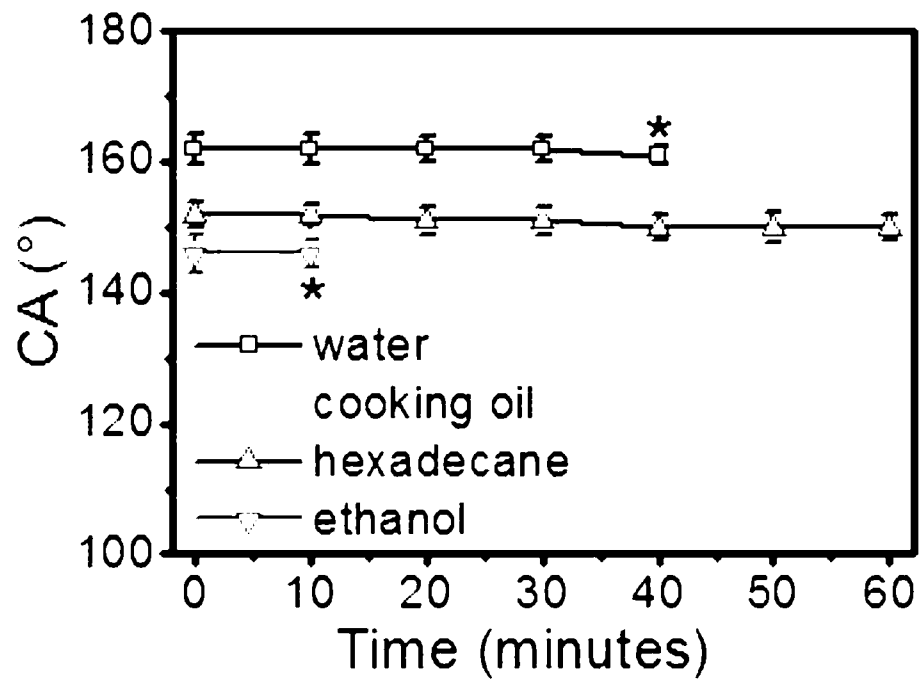
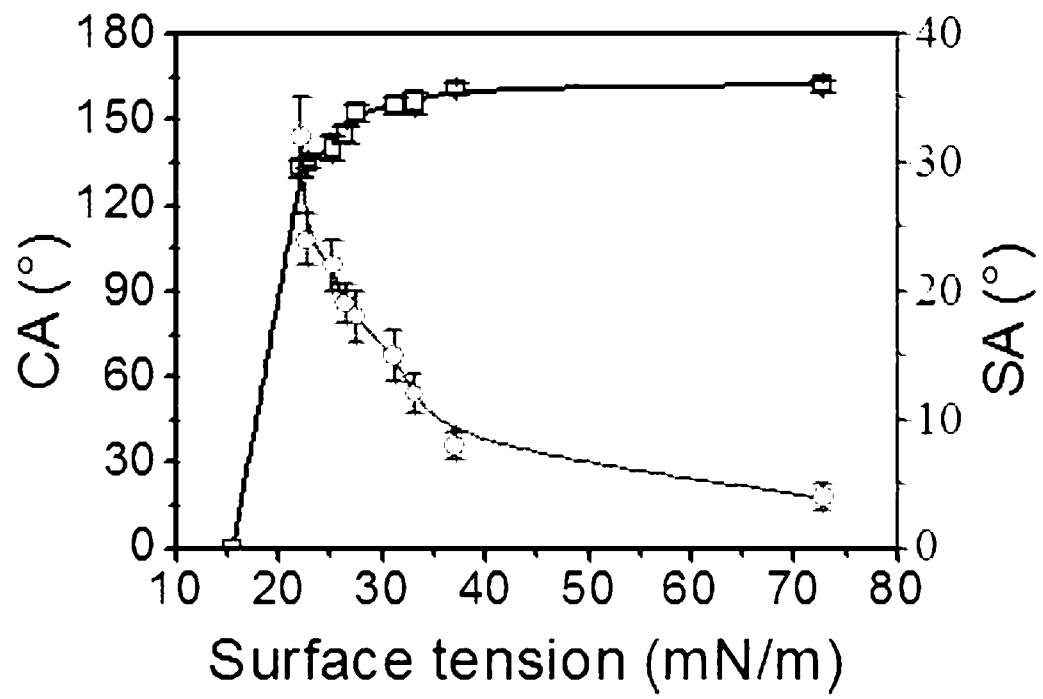


Figure 5



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Figure 6

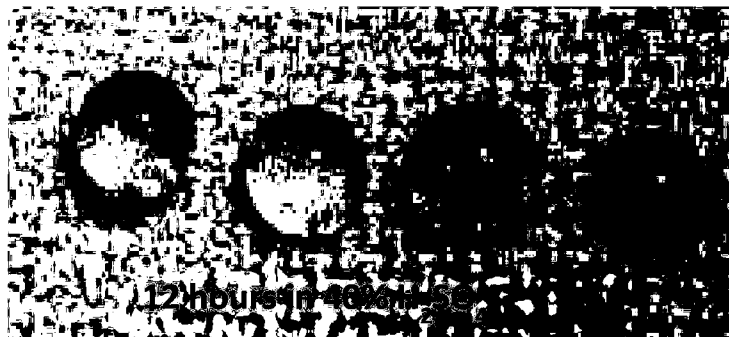
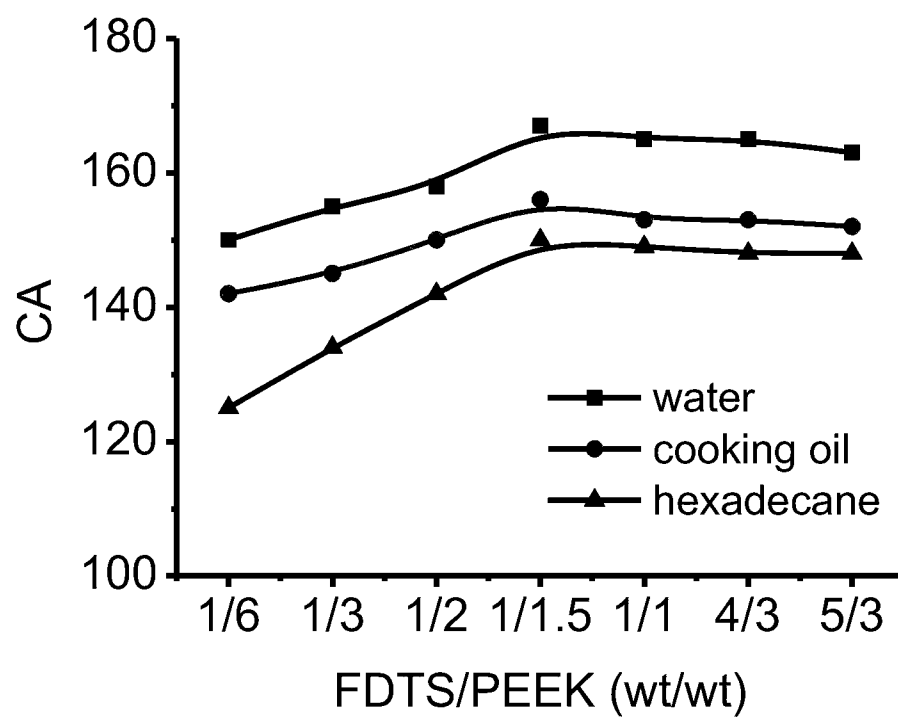


Figure 7



INTERNATIONAL SEARCH REPORT

International application No.
PCT/AU2015/000585

A. CLASSIFICATION OF SUBJECT MATTER

C08L 83/00 (2006.01) C09D 183/00 (2006.01) C08L 27/00 (2006.01) C09D 127/00 (2006.01) C08L 69/00 (2006.01)
C09D 169/00 (2006.01) A61D 13/00 (2006.01) C07F 7/02 (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)

WPIAP, EPODOC, GOOGLE SCHOLAR, ESPACENET (Superamphiphobic, Hydrophobic, Oleophobic, Coupling agent, Silane, Silsesquioxane, POSS, Silicone, Siloxane, Fluoropolymer, poly(vinylidene fluoride-co-hexafluoropropylene), Polystyrene, Polyetheretherketone, Polycarbonate, PVDF, Polyisobutylene, Polyethylene, Water, Oil, Liquid, Repellent, Mesh, Paper, Fabrics, Fibre, Textile, Substrate, Surface, Coat, Impregnate and associated terms)

ESPACENET : Applicant / Inventors Name Search

PAMS (NOSE), AUSPAT, INTESS: Applicant /Inventors name searched in internal databases provided by IP Australia

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
	Documents are listed in the continuation of Box C	



Further documents are listed in the continuation of Box C



See patent family annex

* "A"	Special categories of cited documents: 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
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"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 16 December 2015		Date of mailing of the international search report 16 December 2015	
Name and mailing address of the ISA/AU AUSTRALIAN PATENT OFFICE PO BOX 200, WODEN ACT 2606, AUSTRALIA Email address: pct@ipaustalia.gov.au		Authorised officer Balaji Rengarajan AUSTRALIAN PATENT OFFICE (ISO 9001 Quality Certified Service) Telephone No. +61 3 99359648	

INTERNATIONAL SEARCH REPORT		International application No.
C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		PCT/AU2015/000585
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	ZHOU, H. et al., "Robust, Self-Healing Superamphiphobic Fabrics Prepared by Two-Step Coating of Fluoro-Containing Polymer, Fluoroalkyl Silane, and Modified Silica Nanoparticles", Advanced Functional Materials, 2013, Vol. 23, pages 1664–1670. (See abstract; page 1664, column 2, last para-1668, column 2, para 5; page 1669, column 1, para 2-column 2, first para; Figures 1-4; Supporting Information)	1-41
X	ZHOU, H. et al., "Fluoroalkyl Silane Modified Silicone Rubber/Nanoparticle Composite: A Super Durable, Robust Superhydrophobic Fabric Coating", Advanced Materials, 2012, Vol. 24, pages 2409–2412. (See page 2409, column 2, para 2-page 2411, column 2, para 4; page 2411, column 2, last para-page 2412, column 1, first para; Figures 1-3; Supporting information)	1-41
X	WANG, H. et al., "One-step Vapour-Phase Formation of Patternable, Electrically Conductive, Superamphiphobic Coatings on Fibrous Materials", Soft Matter, 2011, Vol. 7, pages 8158-8161. (See abstract; page 8158, column 2, last para-page 8161, column 1, para 3; Figures 1-4; Electronic Supplementary Information)	1-41
X	Robust, Electro-Conductive, Self-Healing Superamphiphobic Fabric Prepared by One-Step Vapour-Phase Polymerisation of Poly(3,4-ethylenedioxythiophene) in the Presence of Fluorinated Decyl Polyhedral Oligomeric Silsesquioxane and Fluorinated Alkyl Silane", Soft Matter, 2013, Vol. 9, pages 277–282. (See abstract; page 278, column 1, para 4-page 281, column 2, para 5; Figures 1-3; Electronic Supplementary Information)	1-41
X	CN 102977292 A (CAS GUANGZHOU CHEMISTRY CO LTD) 20 March 2013, English Translation retrieved from Google Patents database (See paras 0085-0112; Examples 4-5; claims)	1-41
X	WO 2012/115986 A1 (ROSS TECHNOLOGY CORPORATION) 30 August 2012 (See pages 56-62, Examples 9-12; claims)	1-41
X A	WANG, H. et al., "Durable, Self-Healing Superhydrophobic and Superoleophobic Surfaces from Fluorinated-Decyl Polyhedral Oligomeric Silsesquioxane and Hydrolyzed Fluorinated Alkyl Silane", Angewandte Chemie International Edition, 2011, Vol. 50, pages 11433–11436. (See the whole document) (As above)	41 1-40
X A	WO 2009/029979 A1 (DEAKIN UNIVERSITY) 12 March 2009 (See the whole document) (As above)	41 1-40
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