



(51) International Patent Classification:

**C09D 127/12** (2006.01) **C09D 171/08** (2006.01)  
**C09D 143/04** (2006.01)

(21) International Application Number:

PCT/US2015/038817

(22) International Filing Date:

1 July 2015 (01.07.2015)

(25) Filing Language:

English

(26) Publication Language:

English

(30) Priority Data:

62/020,269 2 July 2014 (02.07.2014) US

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(81) Designated States (unless otherwise indicated, for every

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

(84) Designated States (unless otherwise indicated, for every

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

Published:

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

(54) Title: HYDROPHOBIC COATING COMPOSITION COMPRISING ALKOXY SILANE MONOMER AND FLUORINATED MONOMER IN AN ORGANIC SOLVENT

(57) Abstract: A coating composition is provided that includes the reaction product of a first reactive monomer, a fluorinated second reactive monomer, and optional additional reactive monomers, in an organic solvent. The first reactive monomer can be a monomer of the formula: K - Q - M(R)<sub>x</sub> wherein M is a metallic or metalloid element, each R is a hydrolyzable group independently selected from a halogen, an alkoxy group, or an aryloxy group, x is from 2 to 5, Q is an intermediate group of from zero to 20 carbon atoms, and K is a reactive moiety capable of forming a linear polymer. The fluorinated second reactive monomer can be a reactive moiety capable of reacting with K to form the linear polymer. The amount of the first reactive monomer used to form the reaction product is sufficient to enable the reaction product to form a solution in the organic solvent.



## **HYDROPHOBIC COATING COMPOSITION COMPRISING ALKOXY SILANE MONOMER AND FLUORINATED MONOMER IN AN ORGANIC SOLVENT**

### **CROSS-REFERENCE TO RELATED APPLICATION**

[0001] The present invention claims the benefit of earlier filed U.S. Provisional Application No. 62/020,269, filed on July 2, 2014, which is incorporated herein in its entirety by reference.

### **FIELD OF THE INVENTION**

[0002] The present invention relates to coating compositions, coatings made therefrom, methods of forming coatings on articles, and articles coated with the coatings.

### **BACKGROUND OF THE INVENTION**

[0003] It would be desirable to provide a coating composition that is dissolved in an organic solvent and can be used to form a durable, hydrophobic coating.

### **SUMMARY OF THE INVENTION**

[0004] A coating composition is provided that comprises the reaction product of a first reactive monomer, a fluorinated second reactive monomer, and optional additional reactive monomers, in an organic solvent. The first reactive monomer is a monomer of the formula:  $K - Q - M(R)_x$  wherein M is a metallic or metalloid element, each R is a hydrolyzable group independently selected from a halogen, an alkoxy group, or an aryloxy group, x is from 2 to 5, Q is an intermediate group comprising from zero to 20 carbon atoms, and K is a reactive moiety capable of forming a linear polymer. In some cases, Q has at least one carbon atom. The fluorinated second reactive monomer can comprise a fluorocarbon having one or more carbon atoms, a greater number of fluorine atoms than carbons atoms, and a reactive moiety capable of reacting with K to form the linear polymer. In some cases, the fluorinated second reactive monomer can comprise at least one fluorinated terminal group, for example, at least one trifluoromethyl group. The amount of the first reactive monomer used to form the reaction product, with respect to the amount of the fluorinated second reactive monomer used to form the reaction product, is sufficient to enable the reaction product to form a solution in the organic solvent. The present invention also provides a coating comprising a condensed product of the reaction product.

[0005] The present invention also provides a coating composition as described herein, that further comprises micro-scale particles, nano-scale particles, or a combination thereof. The

micro-scale particles can be substantially in the range of from about 100 nanometers in diameter to about 500 microns in diameter. The nano-scale particles can be substantially in the range of from about one nanometer in diameter to about 1 micron in diameter. The nano-scale particles can be hydrophobic, and the nano-scale particles, if present, can be present in an amount sufficient to form a surface comprising a condensed product of the reaction product and exhibiting a contact angle to water of 140° or more at 20°C.

[0006] The present invention also provides a layer or surface having elevated, recessed, or elevated and recessed, features that can have at least one height or depth dimension that is greater than about half of at least one width dimension. For example, the feature can comprise hills, each rising 50 microns from a base surface, wherein the crests of the hills are separated from one another by no more than 100 microns. The layer or surface can be coated with a coating comprising a condensed product of the reaction product of the coating composition described herein. The coating can have a thickness that is less than about half of the width dimension.

#### **DETAILED DESCRIPTION OF THE INVENTION**

[0007] In accordance with one or more embodiments of the present invention, herein, the term “(meth)acrylate” refers to derivatives of acrylic acid that may or may not be derivatives of methacrylic acid, whereas the term methacrylate refers to derivatives specifically of methacrylic acid. In other words, the parenthetical component “(meth)” in the term “(meth)acrylate” means that the acrylate can optionally, but does not have to, contain a methyl moiety. Exemplary derivatives encompassed by the term “(meth)acrylate” include acrylates such as  $\text{CH}_2\text{CHCO}_2\text{H}$  and  $\text{CH}_2\text{C}(\text{CH}_3)\text{CO}_2\text{H}$ , salts such as  $\text{CH}_2\text{CHCO}_2\text{-Na}^+$  and  $\text{CH}_2\text{C}(\text{CH}_3)\text{CO}_2\text{-Na}^+$ , esters such as  $\text{CH}_2\text{CHCO}_2\text{CH}_3$  and  $\text{CH}_2\text{C}(\text{CH}_3)\text{CO}_2\text{CH}_3$ , and polymers of these species.

[0008] Herein the term “perfluorohexyl(ethyl) (meth)acrylate” is used to designate a perfluoroalkyl acrylate that can be perfluorohexyl acrylate, perfluorohexylethyl acrylate, perfluorohexyl methacrylate, or perfluorohexylethyl methacrylate. Likewise, the term “perfluorohexyl(methyl) (meth)acrylate” is used to designate a perfluoroalkyl acrylate that can be perfluorohexyl acrylate, perfluorohexylmethyl acrylate, perfluorohexyl methacrylate, or perfluorohexylmethyl methacrylate.

[0009] The term “condensed,” as used herein, can mean cross-linked, inter-reacted, gelled, networked, 3-dimensionally networked, and the like.

[0010] Unless otherwise defined, the phrase “reactive monomers” refers collectively to the first reactive monomer and the fluorinated second reactive monomer.

[0011] The coating composition provided comprises the reaction product of a first reactive monomer, a fluorinated second reactive monomer, and optional additional reactive monomers, in an organic solvent. The first reactive monomer can be a monomer of the formula:  $K - Q - M(R)_x$  wherein M is a metallic or metalloid element, each R is a hydrolyzable group independently selected from a halogen, an alkoxy group, or an aryloxy group, x is from 2 to 5, Q is an intermediate group comprising from zero to 20 carbon atoms, and K is a reactive moiety capable of forming a linear polymer. The fluorinated second reactive monomer can comprise a fluorocarbon having one or more carbon atoms, for example, 3 to 20 carbon atoms, a greater number of fluorine atoms than carbons atoms, at least one fluorinated terminal group, for example, a trifluoromethyl group, and a reactive moiety capable of reacting with K to form a linear polymer. The relative amount of the first reactive monomer used to form the reaction product, with respect to the amount of the fluorinated second reactive monomer used to form the reaction product, is sufficient to enable the reaction product of the first reactive monomer, the fluorinated second reactive monomer, and the optional additional reactive monomers, to form a solution in the organic solvent.

[0012] The first reactive monomer can be present in an amount of from about 20% by weight to about 60% by weight based on the total combined weights of the first reactive monomer and the fluorinated second reactive monomer. In one or more embodiments, the first reactive monomer can be present in an amount of from about 20% by weight to about 45% by weight, from about 25% by weight to about 40% by weight, or from about 25% by weight to about 30% by weight, based on the total combined weight of the first reactive monomer and the fluorinated second reactive monomer. In one or more embodiments, the fluorinated second reactive monomer can be present in an amount of from about 40% by weight to about 80% by weight based on the total combined weight of the first reactive monomer and the fluorinated second reactive monomer, for example, at from about 55% by weight to about 80% by weight, at from about 60% by weight to about 75% by weight, or at from about 70% by weight to about 75% by weight.

[0013] The reaction product of the coating composition can be formulated to be condensible to form a coating surface having a surface area populated with 20% by area, 30% by area, 40% by area, or 50% by area, or more, fluorinated terminal groups and exhibiting a surface energy of about 22 dynes/cm or lower. The reaction product of the coating composition can be formulated to be condensible to form a coating surface having an outermost surface area populated with 50% by area or more trifluoromethyl groups and exhibiting a surface energy of about 17 dynes/cm or lower.

[0014] In one or more embodiments, K can be ethylenically unsaturated, a (meth)acrylate, or an epoxide. In one or more embodiments, K can comprise a diol or a diisocyanate. Q can comprise a methyl moiety, an ethyl moiety, a propyl moiety, a butyl moiety, a cycloalkyl moiety, an aryl moiety, a divalent moiety, a trivalent moiety, or a combination thereof. Each R can independently be a halogen, a methoxy group, an ethoxy group, a propoxy group, another alkoxy group, or an aryloxy group. The first reactive monomer can be a trimethoxysilyl propyl methacrylate. The coating composition can further comprise at least one fluorescent or optically identifiable component.

[0015] The coating composition can further comprise a tetraalkoxysilane, a fluoroalkylsilane, a poly(perfluoroether)silane, a poly(perfluoroether)disilane, a poly(perfluoroether)tetrasilane, an organometallic compound, an organometalloid compound, a dipodal silane compound, a silicate, a titanate, an aluminate, a phosphate, or a combination thereof. The fluorinated second reactive monomer can be perfluorohexyl(ethyl) (meth)acrylate, perfluorohexyl(methyl) (meth)acrylate, perfluorohexyl(alkyl) (meth)acrylate, or a combination thereof. The fluorinated second reactive monomer can comprise a perfluoropolyether(alkyl) (meth)acrylate.

[0016] One or more optional additional reactive monomers can be present in the coating composition, and each of the one or more optional additional reactive monomers present can independently comprise a poly(perfluoropolyether) (meth)acrylate, a perfluorooctyl (meth)acrylate, a perfluorohexyl (meth)acrylate, an isobornyl (meth)acrylate, an allyl (meth)acrylate, a phenoxyethyl (meth)acrylate, a cyclohexyl (meth)acrylate, an isodecyl (meth)acrylate, an ethylhexyl (meth)acrylate, an alkyl (meth)acrylate, or an isooctyl (meth)acrylate. The organic solvent can be selected from water, acetone, methanol, ethanol, isopropanol, methyl isobutyl ketone, tetrahydrofuran, ethoxyethylether, methoxyethylacetate, methoxyethanol, ethyl acetate, acetic acid, butyl acetate, methyl ethyl ketone, triethyl phosphate, dichloromethane, acetonitrile, dimethylformamide, dimethyl sulfoxide, hexamethylphosphoric triamide, and combinations thereof.

[0017] The organic solvent can be an aprotic solvent, a protic solvent, or a combination thereof. The organic solvent can be substantially free of hydroxyl containing compounds. The organic solvent can comprise two or more solvents that synergistically enhance solubility and stability of the reaction product. The organic solvent can comprise acetone or ethyl acetate. The reaction product of the first reactive monomer and the fluorinated second reactive monomer, and the organic solvent, can comprise from about 50% by weight to about 100% by weight of the total weight of the coating composition, for example, from about 70% by weight to about 100% by weight, from about 90% by weight to about 100% by weight, or

from about 95% by weight to about 100% by weight. The coating composition can consist of or consist essentially of the reaction product and the organic solvent. The coating composition can consist of or consist essentially of the reaction product of the first reactive monomer and the fluorinated second reactive monomer, in the organic solvent. If a coating composition as described herein is combined with one or more other components that alone causes the resulting composition to not form a solution in the organic solvent, then the resulting composition would not consist essentially of the first reactive monomer and the fluorinated second reactive monomer in the organic solvent.

[0018] In one or more embodiments of the present invention, the organic solvent can be present in an amount of from about 0% by weight to about 99% by weight, from about 20% by weight to about 80% by weight, from about 50% by weight to about 95% by weight, or from about 90% by weight to about 99% by weight, based on the total combined weight of the first reactive monomer, the fluorinated second reactive monomer, and the organic solvent.

[0019] A coating, layer, film, or article are also provided and can comprise a condensed product of the reaction product of any of the coating compositions described herein.

[0020] A method is provided that comprises: applying the coating composition to a surface; removing the organic solvent; and hydrolyzing and condensing the reaction product on the surface. The surface can be a surface of a membrane, a porous material, a non-porous material, a cellular telephone, a cellular telephone component, an electronics appliance, a household appliance, an electronics component, an electronic circuit, an integrated circuit, a fluidic device, an electrowetting device, an air filter, a gas vent, a speaker opening, or a device or apparatus that would become inoperable if directly in contact with a liquid. The surface can be the surface of a laboratory vessel, a radar dish, a radome, a windshield, a rainshield, a vehicular surface, an architectural surface, outdoor furniture, a household good, an article of clothing or footwear, a kitchen article, a kitchen surface, a bath article, a bathroom surface, an antenna, a microwave antenna, a dish, a reflector, a sign, a visual signaling device, a scanner window, a lens, a liquid crystal display, a video display, a touch screen, or a combination thereof. The surface can be a surface of a laboratory vessel, and the laboratory vessel can be selected from the group consisting of pipette tips, microcentrifuge tubes, vials, syringes, microtiter plates, microscope slides, microscope slide assemblies, sample chambers for analytical devices, and tubing. The method can further comprise heating the coating composition, after it is applied to the surface, to accelerate condensation of the reaction product. The heating can be carried out at 30°C or higher, 40°C or higher, 50°C or higher, from about 40°C to about 50°C, or at 100°C or higher. The hydrolyzing and condensing can be carried out in an atmosphere having a relative humidity of 40% or higher,

and optionally comprising an acid vapor or an alkaline vapor, to accelerate condensation of the reaction product. In some embodiments, the atmosphere can have a relative humidity of 30% or higher, 35% or higher, 40% or higher, 45% or higher, or 50% or higher. In some embodiments, the coating composition can form covalent bonds to the surface of an article being coated.

[0021] The coating composition can further comprise micro-scale particles, nano-scale particles, or a combination thereof, wherein the micro-scale particles are substantially in the range of from about 100 nanometers in diameter to about 500 microns in diameter, the nano-scale particles are substantially in the range of from about one nanometer in diameter to about 1 micron in diameter. The nano-scale particles can be hydrophobic. The nano-scale particles, if present, can be present in an amount sufficient to form a surface comprising a condensed product of the reaction product and exhibiting a contact angle to water of 140° or more at 20°C. At least 90% by weight of the micro-scale particles can be within the target size range, for example, at least 95% by weight. At least 90% by weight of the nano-scale particles can be within the target size range, for example, at least 95% by weight. The micro-scale particles can be substantially in the range of from about 30 microns to about 1 micron in diameter, and the nano-scale particles can substantially be in the range of from about 300 nanometers to about 10 nanometers in diameter.

[0022] Both the micro-scale particles and the nano-scale particles can be present in the composition, and if so, the average diameter of the micro-scale particles can be about 10 to about 1,000 times larger than the average diameter of the nano-scale particles, for example, from 10 to 10,000 times larger than the average diameter of the nano-scale particles, from 10 to 100,000 times larger than the average diameter of the nano-scale particles, or from 10 to 500,000 times larger than the average diameter of the nano-scale particles. The micro-scale particles can be hydrophobic. The micro-scale particles can be substantially covered with nano-scale particles, and the nano-scale particles can be hydrophobic, extremely hydrophobic, or oleophobic. At least one of said micro-scale particles or nano-scale particles can comprise fluorine in a form independently selected from branched perfluoroalkyl groups, un-branched perfluoroalkyl groups, and poly(perfluoropolyether) groups. The nano-scale particles can be present and hydrophobic, and can be present in such an amount that a surface comprising the condensed product of the reaction product exhibits a contact angle to water of 160° or more at 20°C.

[0023] According to one or more embodiments of the present invention, by saying that the micro-scale particles are substantially in the range of from about 100 nanometers in diameters to about 500 microns in diameters, what is meant is that, of the total weight of micro-scale

particles, at least 80% by weight of the micro-scale particles have a diameter that falls within the diameter size range of from about 100 nanometers to about 500 microns, for example, at least 90% by weight of the micro-scale particles have diameters that fall within the range. Accordingly, even if some of the micro-scale particles have diameters that fall outside of this range, only a small portion of the micro-scale particles would fall outside the size range, for example, 20% by weight or less or 10% by weight or less, based on the total weight of the micro-scale particles.

[0024] Herein, by saying the nano-scale particles are substantially in the range of from about 1 nanometer in diameter to about 1 micron in diameter, what is meant is that, of the total weight of the nano-scale particles, at least 80% by weight of the nano-scale particles are nano-scale particles having a diameter within the size range of from about 1 nanometer to about 1 micron, for example, at least 90% by weight based on the total weight of nano-scale particles.

[0025] The micro-scale particles and the nano-scale particles can be of the same or different materials. In some embodiments, at least 95% by weight of the total weight of the micro-scale particles are of a diameter that is larger than the diameter size range of the nano-scale particles, at least 95% by weight of the nano-scale particles, based on the total weight of the nano-scale particles, are of a diameter that is smaller than the diameter size range of the micro-scale particles. In one or more embodiments of the present invention, there is no overlap between the size range of substantially all of the micro-scale particles and the size range of substantially all of the nano-scale particles.

[0026] Suitable micro-scale particle and nano-scale particle materials that can be used, with and without hydrophobic, extremely hydrophobic, or superhydrophobic coatings or surface properties, can comprise various materials, shapes, and forms. Materials including glass, metals, metalloids, minerals, ceramics, calcinated materials, plastics, polyolefins, pigments, Teflon® powders, siliconized glass, fluorosiliconized inorganic pigments, and micronized cellulose can be used. According to embodiments of the invention, a composite, superhydrophobic surface is formed by adding micro-scale and/or nano-scale particles to a coating composition as described herein, and then subsequently coating and condensing the coating composition on a surface of an article. Micro-scale and nano-scale particles exhibiting narrow or wide particle size distributions can also be used.

[0027] Inert powders and particles can be used for the micro-scale particles and/or nano-scale particles, for example, for applications where the resultant coating is exposed to liquids that are other than aqueous in nature. One particle type that can be used is a silanized glass particulate material having a 0.3 micron average particle size diameter, available as



TULLANOX HM 250 or TULLANOX HM 250D, from Tulco, Inc., of Ayer, Massachusetts. Other micropowders that can be used are TEFLON® MP 1200 and MP 1600, available from DuPont Polymer Products Department, Wilmington, Delaware, and have average particle diameters of about 4 µm and 200 nm, respectively. Other suitable nano-scale powders and particles that can be used include AEROSIL R208 and 200 particles, having an average particle size of 20 nanometers, available from Evonic, of Parsippany, New Jersey.

[0028] Microfibers and nanofibers are another class of surface roughening agents and can be used in the coating compositions of the present invention. Inert, hydrophobic, extremely hydrophobic, or superhydrophobic microfibers and nanofibers are useful according to some embodiments of the invention, for example, in some embodiments requiring mechanical strength. An exemplary microfiber that can be used is a cellulose microfiber having an average diameter of about 4 microns and an average length of about 40 microns, for example, TECHNOCEL® 40 available from CFF GmbH & Co. KG of Gehren, Germany. Microfibers of longer lengths are also useful. Other fibers, such as nanotubes, as well as carbon, ceramic, metal, metalloid and glass microfibers and nanofibers are also useful.

[0029] A coating, film, or layer comprising a condensed product of the reaction product of the coating composition is also provided. The condensed product can have an exposed surface. Micro-scale and/or nano-scale particles can be present in the coating, and the micro-scale and/or nano-scale particles can be present in such an amount that at least some of the micro-scale and/or nano-scale particles are substantially exposed at the exposed surface. A top coating can be provided on top of the exposed surface, and the top coating can comprise nano-scale particles that are substantially in the range of from about 1 nanometer in diameter to about 1 micron in diameter. The nano-scale particles of the top coating can be hydrophobic or later rendered hydrophobic, oleophobic, or both. The top coating can comprise an exposed top coating surface and the exposed top coating surface can exhibit a contact angle to water of 140° or more at 20°C. The micro-scale particles and the nano-scale particles can independently be selected from the group consisting of an oxide, a salt, a mineral, a calcinated material, a metal, a metalloid, a rare-earth element, a ferromagnetic element or compound, silicon, carbon, an organosilicon, an organometallic, an organometalloid, a glass, a ceramic, a mineral, a plastic, a polymer, a cellulosic, a protein, a mineralized micro-organism, a seed, a pollen, an organism, a crystal, and a combination thereof. The micro-scale particles and the nano-scale particles can independently comprise particles having a physical form of a special shape. The shape can be selected from the group consisting of a sphere, a hollow body, an ovoid, a rod, a tube, a loop, a platelet, a fiber, a crystal, a porous body, a self-assembled body, a seed, a pollen, a life form, a particle covered body, a fractal body, an

irregular body, an amorphous body, a molecular cage, a dendrimer, and combinations thereof. Micro-scale and nano-scale particles of the present invention can be aligned or oriented advantageously by electrostatic, magnetic, and other means.

[0030] A layer or surface is also provided that has elevated, recessed, or elevated and recessed micro features and/or nano features, and the features can have at least one height or depth dimension that is greater than about half of at least one width dimension. The layer or surface can be coated with a coating comprising a condensed product of the reaction product of the coating composition of the present invention, and the coating can have a thickness that is less than about half of said at least one width dimension. The coating can have a thickness substantially less than half of said at least one width dimension. The coating can have an exposed surface that exhibits a contact angle to water of 140° or more at 20°C. The exposed surface of the coating can exhibit a contact angle to water of 160° or more at 20°C. The composition can further comprise a substantially non-volatile, hydrophobic liquid that is a liquid at, at least one temperature in the range of from about -30°C to about 30°C. The liquid can be either substantially inert or selectively reactive.

[0031] An article coated on at least a portion of a surface thereof with a condensed product of the reaction product of the coating composition of the present invention, is also provided. The article can comprise a porous or non-porous material, a fibrous material, a membrane, a fabric, a woven or non-woven material, a sintered material, or the like. The portion of the surface can exhibit resistance to penetration by decane, as determined by the AATCC Oil Repellency Drop Test, Test Method 118. The portion of the surface can exhibit resistance to penetration by octane, as determined by the AATCC Oil Repellency Drop Test, Test Method 118.

[0032] Particular articles that can be coated according to the present invention include those having an operational surface comprising plastic, sintered material, woven or non-woven material, textured material, semiconductor, glass, ceramic, or metal, or a primed or pre-coated surface. The invention can also be used on operational surfaces which are porous, smooth, rough, pitted, foamed, grooved, cross-hatched, striated, patterned, embossed, particle-covered, abraded, etched, machined, lithographed, printed, sintered, woven, textured, molded, having patterned physical features, or any combination thereof.

[0033] According to embodiments of the present invention, methods are provided for forming extremely hydrophobic and oleophobic coatings on articles such as cell phones, computers, circuit boards, integrated circuits, touch screens, and other devices that would otherwise be rendered inoperable if contacted by a liquid. Articles to be coated according to a process of the present invention can contain or consist of natural materials, wood, stone,

plastic, metal, metalloid, ceramic, or glass. Herein, the term "hydrophobic" refers to a surface exhibiting an average surface energy of about 35 dynes/cm or less, "extremely hydrophobic" refers to a surface exhibiting an average surface energy of about 25 dynes/cm or less, and "oleophobic" refers to a surface exhibiting an average surface energy of about 20 dynes/cm or less.

**[0034]** In addition to the materials mentioned above, examples of other suitable materials that can be coated with the compositions and reaction products of the present invention include polyolefins, polyamides, polyesters, silicones, polyurethanes, epoxies, acrylics, polyacrylates, polyesters, polysulfones, polymethacrylates, polycarbonate, PEEK, polyimide, polystyrene, and fluoropolymers such as PTFE TEFLON®, FEP TEFLON®, TEFZEL®, poly(vinylidene fluoride), PVDF, and perfluoroalkoxy resins. TEFLON® and TEFZEL® products are available from E.I du Pont de Nemours and Company of Wilmington, Delaware. Glass products including silica glass can also be coated. One exemplary glass product is PYREX® (available from Corning Glass, Corning, New York). Ceramic or oxide surfaces can be coated according to embodiments of the invention. Cellulosic products such as paper and reinforced paper containers can be coated to form coated articles according to the invention. Metal and metalloid surfaces can be coated according to the invention, as can surfaces of glass, silicon, silicon compounds or ceramics that have or have not been primed with silane-containing materials or other adhesion promoting materials. Primed metal, primed glass, primed ceramic, and primed oxide surfaces can be coated according to embodiments of the invention. Article surfaces that have been pre-coated with epoxies, silicones, urethanes, acrylics, or other materials can also be coated according to embodiments of the invention.

**[0035]** Articles can also be coated with two different coating compositions according to embodiments of the present invention. According to some embodiments of the present invention, an article is coated with a first composition and then with a second, different, composition. At least one of the coatings, for example, the first coating, can comprise micro-scale particles. At least one of the coatings, for example, the second coating or a top coating, can comprise nano-scale particles.

**[0036]** In some embodiments of the present invention, microscopic fibers such as cellulose or glass microfibers can be used with or in place of micro-scale particles to provide surface roughness and high contact angles to water, for example, of about 120° or greater or of about 150° or greater, at 20°C. Cellulose and/or glass microfibers can be used which have average diameters of from about one to about 500 microns and lengths of from about 20 to about 500 microns or more. The microfibers can be admixed to increase the mechanical strength of the coating.

[0037] According to embodiments of the invention, microscopically rough hydrophobic surfaces having a high repellency to water can be produced by employing foaming and/or pore-forming agents in the compositions and processes of the invention. Foaming and pore-forming agents that can be used include spirocarbonates, diazo compounds, compressed gases, dissolved gases, volatile liquids, and combinations thereof. The agents can be activated by heat, light, or vacuum during the drying, curing, and/or hardening of the coating composition. Pores of the present invention can be substantially filled with hydrophobic or extremely hydrophobic liquids.

[0038] A coating can be provided by adhering a surface roughening agent, for example, a micropowder or nanopowder, to the surface of an un-condensed product of the reaction product of the coating composition of the present invention. A coating can be formed wherein the surface roughening agent is adhered to a hydrophobic surface. The adherence of the surface roughening agent to the surface can be due to one or more mechanisms including, but not limited to, sintering the agent onto the surface, curing a component of the surface and/or a component of the agent, melting the surface and/or the agent, a combination thereof, or the like. The surface roughening agent, for example, a micropowder or nanopowder, can be dusted onto the surface, carried by a solvent, applied in a fluidized bed, or electrostatically sprayed. In some embodiments, the micro-sized or nano-sized particles may be applied to a surface in either single or multiple layers.

[0039] The coating compositions of the present invention can be diluted with an appropriate solvent or medium to obtain a coating solids content, or a non-volatile components content, of from about 0.01% by weight to about 80% by weight, from about 0.05% by weight to about 50%-by weight, from about 0.1% by weight to about 30% by weight, from about 0.5% by weight to about 20% by weight, from about 1.0% by weight to about 10% by weight, or from about 0.1% by weight to about 2% by weight, based on the total weight of the coating composition, depending upon the application technique and desired coating properties.

[0040] According to some embodiments of the invention, branched fluoroalkyl monomers containing terminal fluorinated groups or trifluoromethyl groups can be used as reactive monomers or polymerized product in the coating solutions according to some embodiments of the present invention. An example of a suitable branched monomer for such purposes is a perfluorinated iso-octyl monomer having two terminal trifluoromethyl groups.

[0041] Additives can be incorporated into or polymerized with the reaction product, the coating compositions, and/or the reactive monomers to provide coatings, according to the present invention, that have improved toughness, chemical resistance, hardness, softness, processability, elasticity, adhesion, color, texture, thickness, and/or UV-resistance. Additives

of hydrophobic can be used. Chemically resistant additives can be used. Additives including non-trifluoromethyl-containing reactants and/or monomers can be added in amounts ranging from 1% by weight to about 95% by weight and are described in more detail below.

[0042] The compositions of the present invention are useful for any article that is intended or unintended, for example, by accident, to be exposed to the elements or sources of liquid, that is, intended or unintended to be exposed to the environment, to precipitation, to emersion in fresh water, sea water, or other fluids, including damaging gases, exposed to daily UV radiation, or to freezing or elevated temperatures, or for any article that is generally or otherwise unprotected or unsheltered. The compositions of the present invention provide surfaces that can be weatherable, rust resistant, corrosion resistant, able to maintain the appearance of a surface, able to withstand contact with precipitation without degradation, chemically resistant, and mechanically resilient. Compositions can also be provided, according to various embodiments, that can comprise or be combined with other fluorinated and non-fluorinated polymers, monomers, oligomers, reactants, solids, liquids, non-volatile liquids, or the like, to extend or improve the range of surface, thermal, electrical, magnetic, electromagnetic, mechanical, chemical, or optical properties.

[0043] The coating compositions of the present invention, can further comprise, or in some cases the fluorinated second reactive monomer can be one or more of: a copolymer of at least one fluorine-containing monomer; a perfluoropolymer; tetrafluoroethylene; perfluoro-2,2-dimethyl-1,3-dioxole (PDD); fluoroethylene-propylene; a polymer containing difluoromethylene; a functionalized fluoropolymer; the polymerization product of a branched trifluoromethyl-containing monomer; or combinations thereof.

[0044] According to some embodiments of the present invention, the coating composition can include an aromatic or aliphatic polyurethane. According to some embodiments of the present invention, the coating can comprise the polymerization product of an isocyanate-containing monomer. Optionally, the coating can further comprise a cellulosic; a polyester; the polymerization product of an unsaturated monomer; a condensation polymer; a silicone polymer; an epoxy; or combinations thereof.

[0045] The present invention also provides a coated surface for formed articles having a rough surface or articles having a rough surface which rough surface is formed of the composition. The coating or composition comprises at least one fluorinated component including a fluorinated monomer or a polymerization product thereof. The fluorinated monomer can have from about 3 to about 40 fluorine atoms and at least one trifluoromethyl group. The formed rough surface has features smaller than about 500 microns in at least one dimension. The coated or formed outermost surface provides a surface area that is atomically

30% to 75% by area or more fluorine, difluoro methane, or trifluoromethane and a surface energy of about 22 dynes/cm or lower. The formed rough surface can comprise a pattern of features.

[0046] Adhesion promoting monomers can be added to the coating formulations of the invention. If used, adhesion promoting monomers can be added in amounts of from about 1% by weight to about 40% by weight, or from about 5% by weight to about 20% by weight, based on the weight of the reaction product making up the coating composition. Adhesion promoting monomers which can be used include alkoxy terminated monomers and methacrylate esters and acrylate esters listed as adhesion promoting monomers on page 16 of the 1994 Sartomer Product Catalog.

[0047] The methods of the present invention can comprise diluting the coating composition prior to applying the composition to a surface of an article. The coating composition can be diluted to between about 0.01% by weight and 20% by weight reaction product or coating composition, or from about 0.1% by weight to about 2% by weight reaction product or coating composition.

[0048] An exemplary method for applying a coating composition of the present invention comprises dip-coating an article into a coating composition solution or suspension. Other coating methods can also be used, including spray coating, tumbling in solution, brush coating, padding, spraying, fogging, transferring, painting, printing, stenciling, screen printing, pad printing, ink jet printing, and doctoring. For articles having interior walls defining a reservoir portion, the area of the article around and defining an opening to the reservoir can also be coated. For simultaneously coating a large number of small articles, each having a reservoir portion, a tumbling method of coating can be used. Ultrasonic energy may be used to facilitate coating. Articles may be placed in at least a partial vacuum to cause filling of cavities and filling of volumes between small features.

[0049] Dip coating can be used according to one or more embodiments of the present invention, to apply the coating composition. After coating an article with the coating composition, the coating can be allowed to dry and solvent can be allowed to dry or driven off. After forming a first coating according to the present invention, the methods of the invention can also comprise applying at least one other coating composition.

[0050] In yet another embodiment of the present invention, it has been discovered that certain composite, superhydrophobic coatings can be rendered substantially more durable and resistant to water film formation and loss of performance due to ultraviolet light degradation and mechanical abrasion, by including in the composite coating a hydrophobic liquid that is mobile, even as a component of a coated composition. The mobile component can remain

mobile throughout the period of intended use of the coating. Herein, the term “mobile” refers to a component of a coating composition or coated composition that can migrate or move through or on the condensed composition to become present at a surface of a coating made from the composition or to repair mechanical damage to the condensed composition. The hydrophobic mobile component can be a substantially or fully non-volatile fluorinated compound, for example, a non-volatile fluorinated oil. The mobile component can be a non-volatile fluorinated liquid that remains liquid at, at least one temperature within the range of from about -30°C to about 30°C. The coating compositions of the present invention can contain the hydrophobic mobile liquid, in an amount sufficient to improve the hydrophobicity and/or the lifespan of the hydrophobic nature of the coating. The mobile liquid can be present in the coating composition in an amount of from about 0.001% by weight to about 20% by weight based on the total weight of non-volatile components in the coating composition, for example, in an amount of from about 0.1% by weight to about 10% by weight, or from about 1% by weight to about 5% by weight.

[0051] According to one or more embodiments of the present invention, the melting point of the hydrophobic mobile compound can be below about 30°C, and the compound can be liquid at below about 20°C. The hydrophobic mobile compound can be substantially non-volatile, for example, at room temperature, or at 100°C.

[0052] According to various embodiments of the present invention, a kit is provided that can include, separately, or in any combination, the various components of the coating composition. Instructions for use can be provided in the kit. According to various embodiments, a method of coating a surface using the kit is provided. The method can involve combining some or all of the components of the kit to form a coating composition and then coating a surface with the coating composition. Alternatively, the method can involve pre-coating a surface to be coated with one or more of the above described kit components, and subsequently coating the pre-coated surface with one or more of the remaining components. The method can include hardening or curing one or more components or component mixtures with heat, moisture, or UV radiation, or by drying the one or more components or component mixtures before, or after, coating the one or more components or component mixtures onto a surface.

[0053] The present invention includes the following aspects/embodiments/features in any order and/or in any combination:

1. A coating composition comprising the reaction product of a first reactive monomer, a fluorinated second reactive monomer, and optional additional reactive monomers, in an organic solvent,

the first reactive monomer being a monomer of the formula:  $K - Q - M(R)_x$  wherein M is a metallic or metalloid element, each R is a hydrolyzable group independently selected from a halogen, an alkoxy group, or an aryloxy group, x is from 2 to 5, Q is an intermediate group comprising from zero to 20 carbon atoms, and K is a reactive moiety capable of forming a linear polymer,

the fluorinated second reactive monomer comprises a fluorocarbon having one or more carbon atoms, a greater number of fluorine atoms than carbons atoms, and a reactive moiety capable of reacting with K to form said linear polymer, and

the amount of the first reactive monomer used to form the reaction product, relative to the amount of the fluorinated second reactive monomer used to form the reaction product, is sufficient to enable the reaction product of the first reactive monomer, the fluorinated second reactive monomer, and the optional additional reactive monomers, to form a solution in the organic solvent.

2. The coating composition of any preceding or following aspect/embodiment/feature, wherein the first reactive monomer is present in an amount of from about 20% by weight to about 60% by weight based on the total combined weight of the first reactive monomer and the fluorinated second reactive monomer.

3. The coating composition of any preceding or following aspect/embodiment/feature, wherein the fluorinated second reactive monomer comprises a trifluoromethyl group and the reaction product is formulated to be condensible to form a coating surface having a surface area populated with 30% by area or more trifluoromethyl groups and exhibiting a surface energy of about 22 dynes/cm or lower.

4. The coating composition of any preceding or following aspect/embodiment/feature, wherein the fluorinated second reactive monomer comprises a trifluoromethyl group and the reaction product is formulated to be condensible to form a coating surface having a surface area populated with 50% by area or more trifluoromethyl groups and exhibiting a surface energy of about 17 dynes/cm or lower.

5. The coating composition of any preceding or following aspect/embodiment/feature, wherein K is ethylenically unsaturated, a (meth)acrylate, or an epoxide.

6. The coating composition of any preceding or following aspect/embodiment/feature, wherein K comprises a diol or a diisocyanate.

7. The coating composition of any preceding or following aspect/embodiment/feature, wherein Q comprises a methyl moiety, an ethyl moiety, a propyl moiety, a butyl moiety, a cycloalkyl moiety, an aryl moiety, a divalent moiety, a trivalent moiety, or a combination thereof.



8. The coating composition of any preceding or following aspect/embodiment/feature, wherein each R, is independently selected from a halogen, a methoxy group, an ethoxy group, a propoxy group, another alkoxy group, or an aryloxy group.

9. The coating composition of any preceding or following aspect/embodiment/feature, wherein the first reactive monomer is a trimethoxysilyl propyl methacrylate.

10. The coating composition of any preceding or following aspect/embodiment/feature, further comprising at least one fluorescent or optically identifiable component.

11. The coating composition of any preceding or following aspect/embodiment/feature, further comprising a tetraalkoxysilane, a fluoroalkylsilane, a poly(perfluoroether)silane, an organometallic compound, an organometalloid compound, a dipodal silane compound, a silicate, a titanate, an aluminate, a phosphate, or a combination thereof.

12. The coating composition of any preceding or following aspect/embodiment/feature, wherein the fluorinated second reactive monomer is perfluorohexyl(ethyl) (meth)acrylate, perfluorohexyl(methyl) (meth)acrylate, or a combination thereof.

13. The coating composition of any preceding or following aspect/embodiment/feature, wherein the fluorinated second reactive monomer comprises a perfluoropolyether (meth)acrylate.

14. The coating composition of any preceding or following aspect/embodiment/feature, wherein one or more of said optional additional reactive monomers is present in the coating composition, and each of said one or more optional additional reactive monomers present independently comprises poly(perfluoropolyether) (meth)acrylate, a perfluorohexyl (meth)acrylate, an isobornyl (meth)acrylate, an allyl (meth)acrylate, a phenoxyethyl (meth)acrylate, a cyclohexyl (meth)acrylate, an isodecyl (meth)acrylate, an ethylhexyl (meth)acrylate, or an isooctyl (meth)acrylate.

15. The coating composition of any preceding or following aspect/embodiment/feature, wherein the organic solvent is selected from acetone, ethanol, isopropanol, methyl isobutyl ketone, tetrahydrofuran, ethoxyethylether, methoxyethylacetate, methoxyethanol, ethyl acetate, butyl acetate, methyl ethyl ketone, triethyl phosphate, and combinations thereof.

16. The coating composition of any preceding or following aspect/embodiment/feature, wherein the organic solvent is an aprotic solvent, a protic solvent, or a combination thereof.

17. The coating composition of any preceding or following aspect/embodiment/feature, wherein the organic solvent is substantially free of hydroxyl containing compounds.

18. The coating composition of any preceding or following aspect/embodiment/feature, wherein the organic solvent comprises two or more solvents that synergistically enhance solubility and stability of the reaction product.

19. The coating composition of any preceding or following aspect/embodiment/feature, wherein the organic solvent comprises acetone or ethyl acetate.

20. The coating composition of any preceding or following aspect/embodiment/feature, wherein the reaction product of the first reactive monomer and the fluorinated second reactive monomer, and the organic solvent, comprise from about 95% by weight to about 100% by weight based on the total weight of the coating composition.

21. A coating comprising a condensed product of the reaction product of the coating composition of aspect/embodiment/feature 1, 28, 38, 39, or 41, shown herein.

22. A method comprising:

applying the coating composition of any of aspect/embodiment/feature 1, 28, 38, 39, or 41, to a surface;

removing the organic solvent; and

hydrolyzing and condensing the reaction product on the surface.

23. The method according to any preceding or following method, wherein the surface is a surface of a membrane, a porous material, a non-porous material, a cellular telephone component, an electronics appliance component, an electronics component, an air filter, a gas vent, a speaker opening, a microphone opening, a headphone jack, a computer interface port, or a component, device, or apparatus that would become inoperable if directly in contact with a liquid.

24. The method according to any preceding or following method, wherein the surface is the surface of a laboratory vessel, a radar dish, a radome, a windshield, a rainshield, a vehicular surface, an architectural surface, outdoor furniture, a household good, an article of clothing or footwear, a kitchen article, a kitchen surface, a bath article, a bathroom surface, an antenna, a microwave antenna, a dish, a reflector, a sign, a visual signaling device, a scanner window, a lens, a liquid crystal display, a video display, a touch screen, or a combination thereof.

25. The method according to any preceding or following method, wherein the surface is a surface of a laboratory vessel, and the laboratory vessel is a member selected from the group consisting of pipette tips, microcentrifuge tubes, vials, syringes, microtiter plates, microscope slides, microscope slide assemblies, sample chambers for analytical devices, and tubing.

26. The method according to any preceding or following method, further comprising heating the coating composition, after the applying to the surface, at a temperature of 50°C or higher, to accelerate condensation of the reaction product.

27. The method according to any preceding or following method, wherein the hydrolyzing and condensing is carried out in an atmosphere having a relative humidity of 40% or higher, and optionally comprising an acid vapor or an alkaline vapor, to accelerate condensation of the reaction product.

28. The coating composition of any preceding or following aspect/embodiment/feature, further comprising micro-scale particles, nano-scale particles, or a combination thereof, wherein the micro-scale particles are substantially in the range of from about 100 nanometers in diameter to about 500 microns in diameter, the nano-scale particles are substantially in the range of from about one nanometer in diameter to about 10 microns in diameter, the nano-scale particles are hydrophobic, and the nano-scale particles, if present, are present in an amount sufficient to form a surface comprising a condensed product of the reaction product and exhibiting a contact angle to water of 140° or more at 20°C.

29. The coating composition of any preceding or following aspect/embodiment/feature, wherein the micro-scale particles are substantially in the range of from about 30 microns to about 1 micron in diameter, and the nano-scale particles are substantially in the range of from about 300 nanometers to about 10 nanometers in diameter.

30. The coating composition of any preceding or following aspect/embodiment/feature, wherein both the micro-scale particles and the nano-scale particles are present, the average diameter of the micro-scale particles is about 10 to about 1000 times larger than the average diameter of the nano-scale particles, and the micro-scale particles are hydrophobic.

31. The coating composition of any preceding or following aspect/embodiment/feature, wherein at least one of said micro-scale particles or nano-scale particles comprise fluorine in a form independently selected from branched perfluoroalkyl groups, un-branched perfluoroalkyl groups, and poly(perfluoropolyether) groups.

32. The coating composition of any preceding or following aspect/embodiment/feature, wherein the nano-scale particles are present, are hydrophobic, and are present in such an amount that a surface comprising the condensed reaction product exhibits a contact angle to water of 160° or more at 20°C.

33. A coating comprising a condensed product of the reaction product of the coating composition of any of the preceding or following aspects/embodiments/features.

34. A coating comprising a condensed product of the reaction product of the coating composition of any of the preceding or following aspects/embodiments/features, wherein the

condensed product has an exposed surface, the micro-scale particles are present, and the micro-scale particles are present in such an amount that at least some of the micro-scale particles are exposed at the exposed surface.

35. The coating of any preceding or following aspect/embodiment/feature, further comprising a top coating on top of the exposed surface, wherein the top coating comprises nano-scale particles that are from about 1 nanometer in diameter to about 10 microns in diameter, the nano-scale particles are hydrophobic, the top coating comprises an exposed top coating surface, and the exposed top coating surface exhibits a contact angle to water of 140° or more at 20°C.

36. The coating composition of any preceding or following aspect/embodiment/feature, wherein the micro-scale particles and the nano-scale particles are independently selected from the group consisting of an oxide, a salt, a calcinated material, a metal, a rare-earth element, silicon, carbon, an organosilicon, an organometallic, an organometalloid, a glass, a ceramic, a mineral, a metal, a plastic, a polymer, a cellulosic, a protein, a mineralized micro-organism, a seed, a pollen, an organism, a crystal, and a combination thereof.

37. The coating composition of any preceding or following aspect/embodiment/feature, wherein the micro-scale particles and the nano-scale particles are independently particles having a physical form in a shape selected from the group consisting of a sphere, a hollow body, an ovoid, a rod, a tube, a loop, a platelet, a fiber, a crystal, a porous body, a self-assembled body, a seed, a pollen, a life form, a particle covered body, a fractal body, an irregular body, an amorphous body, a molecular cage, a dendrimer, and a combination thereof.

38. A layer or surface having elevated, recessed, or elevated and recessed features having at least one height or depth dimension that is greater than about half of at least one width dimension, said layer or surface coated with a coating comprising a condensed product of the reaction product of the coating composition of any preceding or following aspect/embodiment/feature, the coating having a thickness that is less than about half of said at least one width dimension.

39. A layer or surface having elevated, recessed, or elevated and recessed features having at least one height or depth dimension that is greater than about half of at least one width dimension, said layer or surface coated with a coating comprising a condensed product of the reaction product of the coating composition of any preceding or following aspect/embodiment/feature, the coating having a thickness that is substantially less than said at least one width dimension, and wherein the coating has an exposed surface that exhibits a contact angle to water of 140° or more at 20°C.

40. A composition of any preceding or following aspect/embodiment/feature, wherein the exposed surface of the coating exhibits a contact angle to water of 160° or more at 20°C.

41. A layer or surface having elevated, recessed, or elevated and recessed features having at least one height or depth dimension that is greater than about half of at least one width dimension, said layer or surface coated with a coating comprising a condensed product of the reaction product of the coating composition of any preceding or following aspect/embodiment/feature, the coating having a thickness that is substantially less than said at least one width dimension, wherein the coating has an exposed surface that exhibits a contact angle to water of 140° or more at 20°C.

42. The composition of any preceding or following aspect/embodiment/feature, wherein said exposed surface of said coating exhibits a contact angle to water of 160° or more at 20°C.

43. The composition of any one of aspects/embodiments/features 1, 28, 38, 39, or 41, further comprising a substantially non-volatile, hydrophobic liquid that is a liquid at, at least one temperature in the range of from about -30°C to about 30°C.

44. The composition of any preceding or following aspect/embodiment/feature, wherein the liquid is either substantially inert or selectively reactive.

45. An article coated on at least a portion of a surface thereof with a condensed product of the reaction product of the coating composition of any one of aspects/embodiments/features 1, 28, 38, 39, or 41.

46. An article coated on at least a portion of a surface thereof with a condensed product of the reaction product of the coating composition of any one of aspects/embodiments/features 1, 28, 38, 39, or 41, wherein the article comprises a porous material, a membrane, a fabric, a woven material, or a sintered material, and the portion of the surface exhibits resistance to penetration by decane, as determined by the AATCC Oil Repellency Drop Test, Test Method 118.

47. An article coated on at least a portion of a surface thereof with a condensed product of the reaction product of the coating composition of any of aspects/embodiments/features 1, 28, 38, 39, or 41, wherein the article comprises a porous material, a membrane, a fabric, a woven material, or a sintered material, and the portion of the surface exhibits resistance to penetration by octane, as determined by the AATCC Oil Repellency Drop Test, Test Method 118.

[0054] The entire contents of all references cited in this disclosure are incorporated herein in their entireties, by reference. Further, when an amount, concentration, or other value or parameter is given as either a range, preferred range, or a list of upper preferable values and

lower preferable values, this is to be understood as specifically disclosing all ranges formed from any pair of any upper range limit or preferred value and any lower range limit or preferred value, regardless of whether ranges are separately disclosed. Where a range of numerical values is recited herein, unless otherwise stated, the range is intended to include the endpoints thereof, and all integers and fractions within the range. It is not intended that the scope of the invention be limited to the specific values recited when defining a range.

[0055] Other embodiments of the present invention will be apparent to those skilled in the art from consideration of the present specification and practice of the present invention disclosed herein. It is intended that the present specification and examples be considered as exemplary only with a true scope and spirit of the invention being indicated by the following claims and equivalents thereof.

**WHAT IS CLAIMED IS:**

1. A coating composition comprising the reaction product of a first reactive monomer, a fluorinated second reactive monomer, and optional additional reactive monomers, in an organic solvent,

the first reactive monomer being a monomer of the formula:  $K - Q - M(R)_x$  wherein M is a metallic or metalloid element, each R is a hydrolyzable group independently selected from a halogen, an alkoxy group, or an aryloxy group, x is from 2 to 5, Q is an intermediate group comprising from zero to 20 carbon atoms, and K is a reactive moiety capable of forming a linear polymer,

the fluorinated second reactive monomer comprises a fluorocarbon having two or more carbon atoms, a greater number of fluorine atoms than carbons atoms, and a reactive moiety capable of reacting with K to form the linear polymer, and

the amount of the first reactive monomer used to form the reaction product, relative to the amount of the fluorinated second reactive monomer used to form the reaction product, is sufficient to enable the reaction product of the first reactive monomer, the fluorinated second reactive monomer, and the optional additional reactive monomers, to form a solution in the organic solvent.

2. The coating composition of claim 1, wherein the first reactive monomer is present in an amount of from about 20% by weight to about 60% by weight based on the total combined weight of the first reactive monomer and the fluorinated second reactive monomer.

3. The coating composition of claim 1, wherein K is ethylenically unsaturated, a (meth)acrylate, or an epoxide.

4. The coating composition of claim 1, wherein Q comprises a methyl moiety, an ethyl moiety, a propyl moiety, a butyl moiety, a cycloalkyl moiety, an aryl moiety, a divalent moiety, a trivalent moiety, or a combination thereof.

5. The coating composition of claim 1, wherein each R is independently selected from a halogen, a methoxy group, an ethoxy group, a propoxy group, an alkoxy group, or an aryloxy group.

6. The coating composition of claim 1, wherein the first reactive monomer is a trimethoxysilyl propyl methacrylate.

7. The coating composition of claim 1, further comprising at least one fluorescent or optically identifiable component.
8. The coating composition of claim 1, further comprising a tetraalkoxysilane, a fluoroalkylsilane, a poly(perfluoroether)silane, an organometallic compound, an organometalloid compound, a dipodal silane compound, a silicate, a titanate, an aluminate, a phosphate, or a combination thereof.
9. The coating composition of claim 1, wherein the fluorinated second reactive monomer is perfluorohexyl(ethyl) (meth)acrylate, perfluorohexyl(methyl) (meth)acrylate, or a combination thereof.
10. The coating composition of claim 1, wherein the fluorinated second reactive monomer comprises a perfluoropolyether (meth)acrylate.
11. The coating composition of claim 1, wherein the organic solvent is an aprotic solvent, a protic solvent, or a combination thereof.
12. The coating composition of claim 1, wherein the organic solvent comprises two or more solvents that synergistically enhance solubility and stability of the reaction product.
13. The coating composition of claim 1, wherein the reaction product of the first reactive monomer and the fluorinated second reactive monomer, and the organic solvent, comprise from about 95% by weight to about 100% by weight based on the total weight of the coating composition.
14. A coating comprising a condensed product of the reaction product of the coating composition of claim 1.
15. A method comprising:
  - applying the coating composition of claim 1 to a surface;
  - removing the organic solvent; and
  - hydrolyzing and condensing the reaction product on the surface.



16. The method of claim 15, wherein the surface is a surface of a membrane, a porous material, a non-porous material, a cellular telephone component, an electronics appliance component, an electronics component, an air filter, a gas vent, or a component, device, or apparatus that would become inoperable if directly in contact with a liquid.

17. The method of claim 15, further comprising heating the coating composition, after the applying to the surface, at a temperature of 50°C or higher, to accelerate condensation of the reaction product.

18. The method of claim 15, wherein the hydrolyzing and condensing is carried out in an atmosphere having a relative humidity of 40% or higher, and the atmosphere optionally comprises an acid vapor or an alkaline vapor to accelerate condensation of the reaction product.

19. An article coated on at least a portion of a surface thereof with a condensed product of the reaction product of the coating composition of claim 1.

20. An article coated on at least a portion of a surface thereof with a condensed product of the reaction product of the coating composition of claim 1, wherein the article comprises a porous material, a membrane, a fabric, a woven material, or a sintered material, and the portion of the surface exhibits resistance to penetration by decane, as determined by the AATCC Oil Repellency Drop Test, Test Method 118.

## INTERNATIONAL SEARCH REPORT

International application No.

PCT/US15/38817

## A. CLASSIFICATION OF SUBJECT MATTER

IPC(8) - C09D 127/12, 143/04, 171/08 (2015.01)

CPC - C09D 127/12, 143/04, 171/08

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)

IPC(8): C09D 127/12, 143/04, 171/08, 201/10; C08L 27/12, 43/04, 71/08, 101/10 (2015.01)

CPC: C09D 127/12, 143/04, 171/08, 201/10; C08L 27/12, 43/04, 71/08, 101/10

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)

PatSeer (US, EP, WO, JP, DE, GB, CN, FR, KR, ES, AU, IN, CA, INPADOC Data); ProQuest; IP.com; Google/Google Scholar; EBSCO; coating, polymerize, react, hydrolyze, condense, monomer, metal, metalloid, silicon, silyl, silane, siloxane, fluorinated, fluorine, perfluoro, solvent, alkoxide, acrylate, methacrylate, ethylenically unsaturated, trimethoxysilyl propyl methacrylate, polyether, decane, AATCC

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 7,288,282 B2 (GRAHAM, WF et al.) 30 October 2007; column 2, lines 52-57; column 5, lines 37-52; column 7, lines 24-32; column 11, lines 53-56; column 12, lines 50-61; column 13, lines 14-20, 33-67; column 14, lines 1-22; column 18, lines 64-67; claims 1-3, 8, 11	1-6, 8-9, 11, 13-14, 19
Y		7, 10, 12, 15-18, 20
Y	US 2008/0262154 A1 (BEHRENS, SH et al.) 23 October 2008; abstract; paragraph [0093]	7
Y	US 6,204,350 B1 (LIU, JJ et al.) 20 March 2001; abstract; column 4, lines 13-18; column 10, lines 31-41; column 14, lines 57-61; column 22, lines 5-12; column 26, lines 19-22; column 31, lines 47-54; claims 48-49	10, 15-18
Y	US 6,649,272 B2 (MOORE, GGI et al.) 18 November 2003; abstract; column 2, lines 35-48; column 11, lines 33-47	12
Y	US 8,216,321 B2 (DERUELLE, M et al.) 10 July 2012; abstract; column 16, lines 56-62	20
A	US 5,623,037 A (SIMEONE, G et al.) 22 April 1997; entire document	1-20
A	US 7,579,056 B2 (BROWN, JF) 25 August 2009; entire document	1-20

☐ Further documents are listed in the continuation of Box C.☐ See patent family annex.

\* Special categories of cited documents:

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

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

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

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

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

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

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

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

"&amp;" document member of the same patent family

Date of the actual completion of the international search

02 September 2015 (02.09.2015)

Date of mailing of the international search report

06 OCT 2015

Name and mailing address of the ISA/

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