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- (71) **Applicant:** ROSS TECHNOLOGY CORPORATION
[US/US]; 104 N. Maple Avenue, Leola, Pennsylvania
17540-0646 (US).
- (72) **Inventors:** SIKKA, Vinod, K.; 115 Dansworth Lane, Oak
Ridge, Tennessee 37830 (US). HURLEY, Michael; 1317
Newton Road, Lancaster, Pennsylvania 17603 (US). LEVI,
Zenas W.; 2019 Swarr Run Road, Building L, Lancaster,
Pennsylvania 17601 (US).
- (74) **Agents:** SANDERCOCK, Colin, G. et al; Perkins Coie
LLP, Suite 600, 700 Thirteenth Street, N.W., Washington,
District of Columbia 20005-3960 (US).

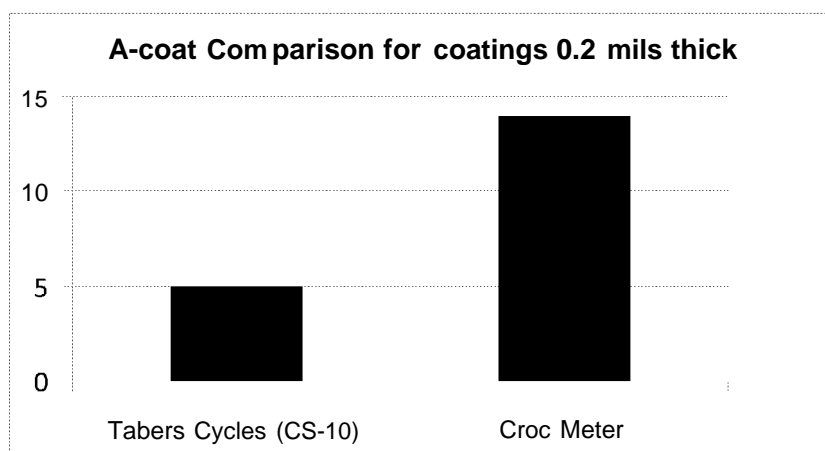
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- (54) **Title:** COMPOSITION AND COATING FOR SUPERHYDROPHOBIC PERFORMANCE



(57) **Abstract:** The present disclosure describes compositions comprising an acrylic polymer binder and nano-particles less than about 100nm that provide a hydrophobic or superhydrophobic coating that may also display oleophobicity. The coating composition may advantageously be prepared using VOC exempt compounds that are compatible with a variety of surface materials including many electronic components. In addition, the coating composition may also be rapidly dried rendering it useful for the rapid preparation of coated objects and surfaces in manufacturing/assembly line environments.



COMPOSITION AND COATING FOR HYDROPHOBIC PERFORMANCE

BACKGROUND AND SUMMARY

This disclosure relates to the preparation of hydrophobic and/or oleophobic coatings that are compatible with various forms of application and the associated packaging including, but not limited to packaging for various forms of spray applications (*e.g.*, standard aerosol spray cans or canisters). Embodiments of coatings described herein provide rapid drying properties. Embodiments of coatings compositions described herein employ volatile organic compounds (VOC) that are exempt under US EPA regulations (VOC-exempt compounds), such as acetone.

The coatings described herein are useful for many applications. As but one example, embodiments of coatings described herein are useful for coating electronic components that are not subject to direct contact and wear, such as circuit boards that can be damaged by liquids, conductive aqueous solutions, and/or high humidity. Embodiments of the coating compositions described herein electronic applications include one or more of compatibility with a variety of electronic components, ease of application using standard spray equipment, rapid drying, and/or a hardness levels that still permit electronic connections to be made using connectors that penetrate the coating to reach contacts.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 shows data from the testing of an embodiment of an acrylic polymer coating described herein.

DETAILED DESCRIPTION

1.0 Definitions

For the purposes of this disclosure a hydrophobic surface is one that results in a water droplet forming a surface contact angle exceeding about 90° and less than 150° at room temperature (about 18° C to about 23 °C). Similarly, for the purposes of this disclosure a superhydrophobic surface is one that results in a water droplet forming a surface contact angle of 150° or greater, but less than the theoretical maximum contact angle of about 180° at room temperature. Some authors further categorize hydrophobic behavior and employ the term "ultrahydrophobic." Since, for the purposes of this disclosure, a superhydrophobic surface has contact angles of 150° to about 180°, superhydrophobic behavior is considered to include ultrahydrophobic behavior. For the purposes of this disclosure, the terms hydrophobicity or hydrophobic (HP) shall include superhydrophobic behavior, unless stated otherwise, and any

and all embodiments, claims, and aspects of this disclosure reciting hydrophobic behavior may be limited to either hydrophobic behavior that is not superhydrophobic (contact angles from 90°-150°) or superhydrophobic behavior (contact angles of 150° or greater).

For the purposes of this disclosure, an oleophobic material or surface is one that results in a droplet of light mineral oil forming a surface contact angle exceeding about 90° and less than 150° at room temperature (about 18 to about 23 °C). Similarly, for the purposes of this disclosure a superoleophobic surface is one that results in a droplet of light mineral oil forming a surface contact angle of 150° or greater, but less than the theoretical maximum contact angle of about 180° at room temperature. For the purposes of this disclosure, the term oleophobicity or oleophobic (OP) shall include superoleophobic behavior, unless stated otherwise, and any and all embodiments, claims, and aspects of this disclosure reciting oleophobic behavior may be limited to either oleophobic behavior that is not superoleophobic (contact angles from 90°-150°) or superoleophobic behavior (contact angles of 150° or greater).

The following procedure can be employed to determine if a coating composition is rapid drying (or rapidly drying) for the purposes of this disclosure. The coating composition is applied at about 2.5 square meters/liter on a substantially planar aluminum test plate that is held substantially constant at a temperature of approximately 23° C. The coating is applied using 5 passes of a substantially equal amount, and each coating becomes dry to the touch (*i.e.*, does not transfer to or stick to a surface brought in contact with the coated area) in less than 60 seconds, provided that solvent in the composition can freely evaporate, but without acceleration of drying by heating or forced air circulation (applying a stream of air).

Embodiments of such coatings generally will have a final thickness of from about 12.7 to about 25.4 microns (*i.e.*, about 0.5 to about 1 mil thickness).

Surfaces coated with rapidly drying compositions typically can be contacted with water about 10 minutes after the application of the last pass without sustaining damage that will affect the coating's hydrophobicity, and are fully useable in less than about one hour at room temperature without accelerating drying by heating or air forced circulation, again provided that solvent can evaporate freely (*e.g.*, the atmosphere is not at or near saturation with solvent so that its evaporation is hindered and the coated surface is maintained at room temperature).

Alkyl as used herein denotes a linear or branched alkyl radical or group. Alkyl groups may be independently selected from *C₁* to *C₂₀* alkyl, *C₂* to *C₂₀* alkyl, *C₄* to *C₂₀* alkyl, *C₆* to *C₁₈* alkyl, *C₆* to *C₁₆* alkyl, or *C₆* to *C₂₀* alkyl. Unless otherwise indicated, alkyl does not include cycloalkyl.

Cycloalkyl as used herein denotes a cyclic alkyl radical or group. Cycloalkyl groups may be independently selected from: C₄ to C₂₀ alkyl comprising one, two, or more C₄ to C₈ cycloalkyl functionalities; C₅ to C₁₈ alkyl comprising one, two, or more C₄ to C₈ cycloalkyl functionalities; C₆ to C₂₀ alkyl comprising one, two, or more C₄ to C₈ cycloalkyl functionalities; C₆ to C₁₈ alkyl comprising one, two, or more C₄ to C₈ cycloalkyl functionalities; or C₆ to C₁₆ alkyl comprising one, two or more C₄ to C₈ cycloalkyl functionalities. Where two or more cycloalkyl groups are present, they may be present as fused rings or in a spiro configuration. One or more hydrogen atoms of the cycloalkyl groups may be replaced by fluorine atoms.

Haloalkyl as used herein denotes an alkyl group in which some or all of the hydrogen atoms present in an alkyl group have been replaced by halogen atoms. Halogen atoms may be limited to chlorine or fluorine atoms in haloalkyl groups.

Fluoroalkyl as used herein denotes an alkyl group in which some or all of the hydrogen atoms present in an alkyl group have been replaced by fluorine atoms.

Perfluoroalkyl as used herein denotes an alkyl group in which fluorine atoms have been substituted for each hydrogen atom present in the alkyl group.

2.0 Description of Embodiments of Coating Components and Properties

It has been found that coating compositions comprising nano-particles treated with agents that provide hydrophobic properties (*e.g.*, silica or fumed silica nano-particles treated with a silanizing agent or siloxane), a rapidly drying polymer binder comprising an acrylic polymer or copolymer, and a volatile organic solvent affords a coating that has dropophobic and/or oleophobic characteristics. Such compositions can be prepared using environmentally acceptable VOC-exempt compounds such as acetone and/or t-butyl acetate (tert butyl acetate). The preparations can be applied by spraying, dipping, or any other suitable method of contacting the composition with a surface. The composition may be used to treat various surfaces including metal, plastic, and fabric.

2.1 Binders

The coating compositions described herein may comprise one or more of a variety of acrylic binders including, but not limited to, polymers or copolymers of methyl methacrylate (MMA), butyl methacrylate (BMA), ethyl methacrylate (EMA) and combinations thereof. In one embodiment, the coating compositions comprise two or more of MMA, BMA, and EMA. In other embodiments, the coating compositions comprise: MMA and BMA (*e.g.*, PARALOID™ B64); MMA and EMA; or BMA and EMA copolymers.

The acrylic binders are typically present from about 0.4% to 10% weight to volume. In some embodiments the acrylic binders are present from about 0.5% to 9%, or about 0.6% to about 8%, or about 0.7% to about 7%, or about 0.8% to about 6%, or about 1% to about 5.5%, or about 2% - about 5% w/v. In other embodiments the binders are present from about 0.2% to about 2%, about 2.1% to about 4.0%, about 4.1% to about 6.0%, about 6.1% to about 8.0%, about 8.1% to about 10%, about 10% to about 12.5%, about 12.5% to about 15%, about 15% to about 17.5%, about 17.5% to about 20%, or above 20% w/v based on the total final volume of the composition. Typically, the acrylic binder will be present in amounts less than 10% w/v or less than 5% w/v.

2.2 Particles

2.2.1 Nano-Particles

Nano-particles treated to be hydrophobic can be employed in the coating composition. Embodiments of such nano-particles include, e.g., silica, alumina and/or TiO_2 . For example, in one embodiment, silica nano-particles suitable for use in the coating composition comprise fumed silica nano-particles (e.g., Nanogel TLD201, CAB-O-SIL® TS-720, or M5 from Cabot Corp., Billerica, MA) that have been reacted with a silanizing agent or treated with a siloxane (e.g. polydimethyl siloxane that may or may not be terminated with a silanol (CAS 63148-62-9 or 70131-67-8)).

In embodiments where a silanizing agent is employed, the silanizing agent may be a compound of the formula (I):



where n is an integer from 1 to 3;

each R is independently selected from

(i) alkyl or cycloalkyl group optionally substituted with one or more fluorine atoms,

(ii) $\text{C}_{1 \text{ to } 20}$ alkyl optionally substituted with one or more substituents independently selected from fluorine atoms and $\text{C}_{6 \text{ to } 14}$ aryl groups, which aryl groups are optionally substituted with one or more independently selected halo, $\text{C}_{1 \text{ to } 10}$ alkyl, $\text{C}_{1 \text{ to } 10}$ haloalkyl, $\text{C}_{1 \text{ to } 10}$ alkoxy, or $\text{C}_{1 \text{ to } 10}$ haloalkoxy substituents,

(iii) $\text{C}_{2 \text{ to } 8}$ or $\text{C}_{6 \text{ to } 20}$ alkyl ether optionally substituted with one or more substituents independently selected from fluorine and $\text{C}_{6 \text{ to } 14}$ aryl groups, which aryl groups are optionally substituted with one or more independently selected halo, $\text{C}_{1 \text{ to } 10}$ alkyl, $\text{C}_{1 \text{ to } 10}$ haloalkyl, $\text{C}_{1 \text{ to } 10}$ alkoxy, or $\text{C}_{1 \text{ to } 10}$ haloalkoxy substituents,

(iv) $C_{6 \text{ to } 14}$ aryl, optionally substituted with one or more substituents independently selected from halo or alkoxy, and haloalkoxy substituents,

(v) $C_{4 \text{ to } 20}$ alkenyl or $C_{4 \text{ to } 20}$ alkynyl, optionally substituted with one or more substituents independently selected from halo, alkoxy, or haloalkoxy, and

5 (vi) $-Z-((CF_2)_q(CF_3))_r$, wherein Z is a $C_{1 \text{ to } 12}$ or a $C_{2 \text{ to } 8}$ divalent alkane radical or a $C_{2 \text{ to } 12}$ divalent alkene or alkyne radical, q is an integer from 1 to 12, and r is an integer from 1 to 4;

each X is an independently selected -H, -Cl, -I, -Br, -OH, $-OR^2$, $-NHR^3$, or $-N(R^3)_2$ group;

10 each R^2 is an independently selected $C_{1 \text{ to } 4}$ alkyl or haloalkyl group; and

each R^3 is an independently selected H, $C_{1 \text{ to } 4}$ alkyl, or haloalkyl group.

In some embodiments, R is an alkyl or fluoroalkyl group having from 6 to 20 carbon atoms.

15 In other embodiments, R is an alkyl or fluoroalkyl group having from 8 to 20 carbon atoms.

In other embodiments, R is an alkyl or fluoroalkyl group having from 10 to 20 carbon atoms.

In other embodiments, R is an alkyl or fluoroalkyl group having from 6 to 20 carbon atoms and n is 3.

20 In other embodiments, R is an alkyl or fluoroalkyl group having from 8 to 20 carbon atoms and n is 3.

In other embodiments, R is an alkyl or fluoroalkyl group having from 10 to 20 carbon atoms and n is 3.

25 In other embodiments, R has the form $-Z-((CF_2)_q(CF_3))_r$, wherein Z is a $C_{1 \text{ to } 12}$ divalent alkane radical or a $C_{2 \text{ to } 12}$ divalent alkene or alkyne radical, q is an integer from 1 to 12, and r is an integer from 1 to 4.

30 In any of the previously mentioned embodiments of compounds of formula (I), the value of n may be varied such that 1, 2 or 3 independently selected terminal functionalities are present. Thus, in some embodiments, n is 3. In other embodiments, n is 2. In still other embodiments, n is 1.

In any of the previously mentioned embodiments of compounds of formula (I), all halogen atoms present in any one or more R groups may be fluorine.

In any of the previously mentioned embodiments of compounds of formula (I), X may be independently selected from H, Cl, $-OR^2$, $-NHR^3$, $-N(R^3)_2$, or combinations thereof. In other

embodiments, X may be selected from Cl , $-\text{OR}^2$, $-\text{NHR}^3$, $-\text{N}(\text{R}^3)_2$, or combinations thereof. In still other embodiments, X may be selected from $-\text{Cl}$, $-\text{NHR}^3$, $-\text{N}(\text{R}^3)_2$ or combinations thereof.

Any coating described herein may be prepared with one, two, three, four or more compounds of formula (I) employed alone or in combination to modify the nano-particles, and/or other components of the coating including filler-particles. The use of silanizing agents of formula (I) to modify nano-particles, or any of the other components of the coatings, will introduce one or more $\text{R}_{3-n}\text{X}_n\text{Si}-$ groups (*e.g.*, $\text{R}_3\text{Si}-$, $\text{R}_2\text{XiSi}-$, or $\text{RX}_2\text{Si}-$ groups) where R and X are as defined for a compound of formula (I). The value of n is 0, 1, or 2, due to the displacement of at least one "X" substituent and formation of at least one bond between a nano-particle and the Si atom (the bond between the nano-particle and the silicon atom is indicated by a dash "-" (*e.g.*, $\text{R}_3\text{Si}-$, $\text{R}^{\wedge}\text{Si}-$, or $\text{RX}_2\text{Si}-$ groups).

In other embodiments, suitable silanizing agents for modifying the nano-particles used in the coating compositions generally comprise those with fluorinated or polyfluorinated alkyl groups (*e.g.*, fluoroalkyl groups) or alkyl groups (hydrocarbon containing groups) including, but not limited to:

tridecafluoro- 1,1,2,2-tetrahydrooctyl)silane (SIT8 173.0);
 (tridecafluoro- 1,1,2,2-tetrahydrooctyl) trichlorosilane (SIT8 174.0);
 (tridecafluoro- 1,1,2,2-tetrahydrooctyl)triethoxysilane (SIT8 175.0);
 (tridecafluoro- 1,1,2,2-tetrahydrooctyl)trimethoxysilane (SIT8 176.0);
 (heptadecafluoro-1,1,2,2-tetrahydrodecyl)dimethyl(dimethylamino)silane (SIH5840.5);
 (heptadecafluoro- 1,1,2,2-tetrahydrodecyl)tris(dimethylamino)silane (SIH5841 .7);
 n-octadecyltrimethoxysilane (SIO6645.0); n-octyltriethoxysilane (SIO6715.0); and
 nonafluorohexyldimethyl(dimethylamino)silane (SIN6597.4);

where the designations given in parentheses are the product numbers from Gelest, Inc., Morrisville, PA.

Nano-particles may be selected to have an average diameter from about 8nm to about 100nm. For example, in embodiments the nano-particles can have an average diameter of about 10 to about 75 nm. In other embodiments the nano-particles may have a size from about 12 to about 60 nm, about 4 to about 50 nm, or about 15 to about 40nm. In other embodiments, the average size of the nano-particles is about 10, about 15, about 20, about 25, about 30 or about 40 nm.

Nano-particles typically may be included in the coating composition in a range of about 0.1% to about 10%, about 0.2% to about 7.5%, about 0.5% to about 6%, about 0.8% to about

5%, or about 1% to about 4% on a weight to volume (w/v) basis. Depending on the particular composition involved, amounts above 10% may also provide acceptable results.

2.2.2 Filler-Particles

Filler-particles, also known as extenders, may optionally be incorporated into the coating compositions to develop surface texture, which increases the durability (abrasion resistance) of the coatings. Filler-particles may be prepared from diverse materials including, but not limited to, particles comprising: wood (*e.g.*, wood dust), glass, metals (*e.g.*, iron, titanium, nickel, zinc, tin), alloys of metals, metal oxides, metalloid oxides (*e.g.*, silica), plastics (*e.g.*, thermoplastics), carbides, nitrides, borides, spinels, diamonds, and fibers (*e.g.*, glass fibers).

Numerous variables may be considered in the selection of filler-particles. These variables include, but are not limited to, the effect the filler-particles have on the resulting coatings, their size, their hardness, their compatibility with the binder, the resistance of the filler-particles to the environment in which the coatings will be employed, and the environment the filler-particles must endure in the coating and/or curing process, including resistance to temperature and solvent conditions.

In embodiments described herein, filler-particles have an average size in a range selected from about 1 micron (μm) to about 300 μm or from about 30 μm to about 225 μm . Within such ranges, embodiments include ranges of filler-particles having an average size of from about 1 μm to about 5 μm , from about 5 μm to about 10 μm , from about 10 μm to about 15 μm , from about 15 μm to about 20 μm , from about 20 μm to about 25 μm , from about 1 μm to about 25 μm , from about 5 μm to about 25 μm , from about 25 μm to about 50 μm , from about 50 μm to about 75 μm , from about 75 μm to about 100 μm , from about 100 μm to about 125 μm , from about 125 μm to about 150 μm , from about 150 μm to about 175 μm , from about 175 μm to about 200 μm , from about 200 μm to about 225 μm , and from about 225 μm to about 250 μm . Also included within the broad range are embodiments employing particles in ranges from about 10 μm to about 100 μm , from about 10 μm to about 200 μm , from about 20 μm to about 200 μm , from about 30 μm to about 50 μm , from about 30 μm to about 100 μm , from about 30 μm to about 200 μm , from about 30 μm to about 225 μm , from about 50 μm to about 100 μm , from about 50 μm to about 200 μm , from about 75 μm to about 150 μm , from about 75 μm to about 200 μm , from about 100 μm to about 225 μm , from about 100 μm to about 250 μm , from about 125 μm to about 225 μm , from about 125 μm to about 250 μm , from about 150 μm to about 200 μm , from about 150 μm to about 250 μm , from about 175 μm to about 250

μη, from about 200 μη to about 250 μη, from about 225 μη to about 275 μη, or from about 250 μη to about 300 μη.

Filler-particles may be incorporated into the coating compositions at various ratios depending on the binder composition and the filler-particle's properties. In some embodiments, the filler-particles may have a content range selected from about 0.01% to about 60% or more by weight. Included within that range are embodiments in which the filler-particles are present, by weight, in ranges from about 0.02% to about 0.2%, from about 0.05% to about 0.5%, from about 0.075% to about 0.75%, from about 0.1% to about 1%, from about 0.5% to about 2.5%, from about 2% to about 5%, from about 5% to about 10%, from about 10% to about 15%, from about 15% to about 20%, from about 20% to about 25%, from about 25% to about 30%, from about 30% to about 35%, from about 35% to about 40%, from about 40% to about 45%, from about 45% to about 50%, from about 50% to about 55%, from about 55% to about 60%, and greater than 60%. Also included within this broad range are embodiments in which the filler-particles are present, by weight, in ranges from about 4% to about 30%, from about 5% to about 25%, from about 5% to about 35%, from about 10% to about 25%, from about 10% to about 30%, from about 10% to about 40%, from about 10% to about 45%, from about 15% to about 25%, from about 15% to about 35%, from about 15% to about 45%, from about 20% to about 30%, from about 20% to about 35%, from about 20% to about 40%, from about 20% to about 45%, from about 20% to about 55%, from about 25% to about 40%, from about 25% to about 45%, from about 25% to about 55%, from about 30% to about 40%, from about 30% to about 45%, from about 30% to about 55%, from about 30% to about 60%, from about 35% to about 45%, from about 35% to about 50%, from about 35% to about 60%, from about 40% to about 60%, from about 0.01% to about 5%, from about 0.03% to about 1%, from about 0.05% to about 0.15%, from about 0.1% to about 2.5%, from about 0.2% to about 5%, from about 0.05% to about 10%, from about 0.1% to about 10%, from about 0.05% to about 15%, or from about 0.05% to about 20%, on a weight basis.

In one embodiment, substantially spherical thermoplastic particles are added to the binder composition to develop surface texture (EXPANCEL[®] microspheres). Such microspheres consist of a polymer shell encapsulating a gas. The average diameter of these hollow spheres typically ranges from 6 to 45 μη and have a density of 1000 to 1300 kg/m³ (8.3—10.8 lbs/US Gallon). Upon heating, the microspheres expand and the volume of the microspheres can increase more than 40 times (with the diameter changing, for example, from 10 to 40 μη), resulting in a density below 30 kg/m³ (0.25 lbs/US Gallon). Typical expansion temperatures range from 80° to 190° C (176°-374° F). When heating the microspheres the

pressure of the gas inside the shell increases and the thermoplastic shell softens, resulting in a dramatic increase of the volume of the microspheres. Cooling the microspheres results in the shell stiffening again and produces lighter (lower density) expanded microspheres.

Filler-particles may be purchased from a variety of suppliers. Some commercially available filler-particles that may be employed in the coatings described herein include those in Table 1 below.

Table 1 Filler-particles

Filler-partich No.	Filler-particle ID	Filler-particle Type	Filler Particle Details	Density (g/cc)	Partick Size Range (μη)	Color	Crush Strength (psi)	Source	Location
1	K1	Glass Bubbles	GPS ^a	0.125	30-120	White	250	3M™	St. Paul, MN
2	K15	Glass Bubbles	GPS ^a	0.15	30-1 15	White	300	3M™	St. Paul, MN
3	S15	Glass Bubbles	GPS ^a	0.15	25-95	White	300	3M™	St. Paul, MN
4	S22	Glass Bubbles	GPS ^a	0.22	20-75	White	400	3M™	St. Paul, MN
5	K20	Glass Bubbles	GPS ^a	0.2	20-125	White	500	3M™	St. Paul, MN
6	K25	Glass Bubbles	GPS ^a	0.25	25-105	White	750	3M™	St. Paul, MN
7	S32	Glass Bubbles	GPS ^a	0.32	20-80	White	2000	3M™	St. Paul, MN
8	S35	Glass Bubbles	GPS ^a	0.35	10-85	White	3000	3M™	St. Paul, MN
9	K37	Glass Bubbles	GPS ^a	0.37	20-85	White	3000	3M™	St. Paul, MN
10	S38	Glass Bubbles	GPS ^a	0.38	15-85	White	4000	3M™	St. Paul, MN
11	S38HS	Glass Bubbles	GPS ^a	0.38	15-85	White	5500	3M™	St. Paul, MN
12	K46	Glass Bubbles	GPS ^a	0.46	15-80	White	6000	3M™	St. Paul, MN
13	S60	Glass Bubbles	GPS ^a	0.6	15-65	White	10000	3M™	St. Paul, MN
14	S60/HS	Glass Bubbles	GPS ^a	0.6	11-60	White	18000	3M™	St. Paul, MN
15	A 16/ 500	Glass Bubbles	Floated Series	0.16	35-135	White	500	3M™	St. Paul, MN
16	A20/ 1000	Glass Bubbles	Floated Series	0.2	30-120	White	1000	3M™	St. Paul, MN
17	H20/ 1000	Glass Bubbles	Floated Series	0.2	25-1 10	White	1000	3M™	St. Paul, MN
18	D32/ 4500	Glass Bubbles	Floated Series	0.32	20-85	White	4500	3M™	St. Paul, MN
19	Expancel 551 DE 40 d42	Plastic Micro-spheres	Dry Expandec	0.042 +0.004	30-50			Akzo Nobel	Dist. by Eka Chem., Inc., Duluth, GA
20	Expancel 551 DE 40 d42+2	Plastic Micro-spheres	Dry Expandec	0.042 +0.002	30-50			Akzo Nobel	Dist. by Eka Chem., Inc., Duluth, GA
21	Expancel 461 DE 20 d70	Plastic Micro-spheres	Dry Expandec	0.07 +0.006	15-25			Akzo Nobel	Dist. by Eka Chem., Inc., Duluth, GA

Filler-particle No.	Filler-particle ID	Filler-particle Type	Filler Particle Details	Density (g/cc)	Partick Size Range (μm)	Color	Crush Strength (psi)	Source	Location
22	Expancel 461 DE 40 d60	Plastic Micro-spheres	Dry Expandec	0.06 +0.005	20-40			Akzo Nobel	Dist. by Eka Chem., Inc., Duluth, GA
23	Expancel 461 DET 4 C d25	Plastic Micro-spheres	Dry Expandec	0.025 +0.003	35-55			Akzo Nobel	Dist. by Eka Chem., Inc., Duluth, GA
24	Expancel 461 DET 8 C d25	Plastic Micro-spheres	Dry Expandec	0.025 +0.003	60-90			Akzo Nobel	Dist. by Eka Chem., Inc., Duluth, GA
25	Expancel 920 DE 40 d30	Plastic Micro-spheres	Dry Expandec	0.030 +0.003	35-55			Akzo Nobel	Dist. by Eka Chem., Inc., Duluth, GA
26	Expancel 920 DET 4 C d25	Plastic Micro-spheres	Dry Expandec	0.025 +0.003	35-55			Akzo Nobel	Dist. by Eka Chem., Inc., Duluth, GA
27	Expancel 920 DE 80 d30	Plastic Micro-spheres	Dry Expandec	0.030 +0.003	55-85			Akzo Nobel	Dist. by Eka Chem., Inc., Duluth, GA
28	H50/ 10000 EPX	Glass Bubbles	Floated Series	0.5	20-60	White	10000	3M™	St. Paul, MN
29	iMK	Glass Bubbles	Floated Series	0.6	8.6-26.6	White	28000	3M™	St. Paul, MN
30	G-3 125	Z-Light Spheres™	CM*	0.7	50-125	Gray	2000	3M™	St. Paul, MN
31	G-3 150	Z-Light Spheres™	CM*	0.7	55-145	Gray	2000	3M™	St. Paul, MN
32	G-3500	Z-Light Spheres™	CM*	0.7	55-220	Gray	2000	3M™	St. Paul, MN
33	G-600	Zeeo-spheres™	CM*	2.3	1-40	Gray	>60000	3M™	St. Paul, MN
34	G-800	Zeeo-spheres™	CM*	2.2	2-200	Gray	>60000	3M™	St. Paul, MN
35	G-850	Zeeo-spheres™	CM*	2.1	12-200	Gray	>60000	3M™	St. Paul, MN
36	W-610	Zeeo-spheres™	CM*	2.4	1-40	White	>60000	3M™	St. Paul, MN
37	SG	Extendo-sphere™	HS ^c	0.72	30-140	Gray	2500	Sphere One	Chattanooga, TN
38	DSG	Extendo-sphere™	HS ^c	0.72	30-140	Gray	2500	Sphere One	Chattanooga, TN
39	SGT	Extendo-sphere™	HS ^c	0.72	30-160	Gray	2500	Sphere One	Chattanooga, TN
40	TG	Extendo-sphere™	HS ^c	0.72	8-75	Gray	2500	Sphere One	Chattanooga, TN
41	SLG	Extendo-sphere™	HS ^c	0.7	10-149	Off White	3000	Sphere One	Chattanooga, TN
42	SLT	Extendo-sphere™	HS ^c	0.4	10-90	Off White	3000	Sphere One	Chattanooga, TN
43	SL-150	Extendo-sphere™	HS ^c	0.62	70	Cream	3000	Sphere One	Chattanooga, TN
44	SLW-150	Extendo-sphere™	HS ^c	0.68	8-80	White	3000	Sphere One	Chattanooga, TN
45	HAT	Extendo-sphere™	HS ^c	0.68	10-165	Gray	2500	Sphere One	Chattanooga, TN
46	HT-150	Extendo-sphere™	HS ^c	0.68	8-85	Gray	3000	Sphere One	Chattanooga, TN

Filler-partich No.	Filler-particle ID	Filler-particle Type	Filler Particle Details	Density (g/cc)	Partick Size Range (μm)	Color	Crush Strength (psi)	Source	Location
47	KLS-90	Extendo-sphere™	HS ^c	0.56	4-05	Light Gray	1200	Sphere One	Chattanooga, TN
48	KLS-125	Extendo-sphere™	HS ^c	0.56	4-55	Light Gray	1200	Sphere One	Chattanooga, TN
49	KLS-150	Extendo-sphere™	HS ^c	0.56	4-55	Light Gray	1200	Sphere One	Chattanooga, TN
50	KLS-300	Extendo-sphere™	HS ^c	0.56	4-55	Light Gray	1200	Sphere One	Chattanooga, TN
51	HA-300	Extendo-sphere™	HS ^c	0.68	10-146	Gray	2500	Sphere One	Chattanooga, TN
52	XIOM 5 12	Thermo-plastic	MPR ^d	0.96	10-100	White	508	XIOM Corp.	West Babylon, NY
53	XIOM 5 12	Thermo-plastic	MPR ^d	0.96	10-100	Black	508	XIOM Corp.	West Babylon, NY
54	CORVEL™ Black 78-7001	Thermo-plastic	Nylon Powder Coating	1.09	44-74	Black		ROHM & HASS	Philadelphia, PA
55	Micro-glass 3082	Fibers	MMEGF	1.05	16X120	White		Fibertec	Bridgewater, MA
56	Micro-glass 9007D	Fibers Silane-Treated	MMEGF	0.53	10X150	White		Fibertec	Bridgewater, MA
57	Tiger Drylac Series 49	Polyester crosslinked with TGIC (triglycidyl isocyanurate"							
58	SoftSand®	Rubber based			90, 180, or 300	Various colors		Soft-Point Indus.	Copley, OH

a -GPS - general purpose series

b - ceramic microspheres

c - hollow spheres

d - modified polyethylene resins

5 *e* - microglass milled E-glass filaments

2.3 Solvents

As mentioned above, the coating compositions comprise a volatile organic solvent.

10 Examples of volatile organic solvents that can be employed for the preparation of the coating systems include, but are not limited to, methanol, ethanol, acetone, methyl ethyl ketone, methyl isobutyl ketone, ethyl acetate, butyl acetate, isobutyl acetate, tertbutyl acetate (t-butyl acetate), toluene, benzene, xylene or combinations thereof. In one embodiment, the coating composition comprises two or more, or three or more, solvents from the group consisting of: acetone, methyl ethyl ketone (MEK), and methyl isobutyl ketone (MIBK). In one embodiment, the coating composition comprises a ketone containing solvent. In other embodiments, the composition comprises acetone, methyl ethyl ketone, methyl isobutyl ketone, butylacetate, tert butyl acetate,

15

a combination of two or more of those solvents, or a combination of three or more of those solvents. In another embodiment, the composition comprises acetone, t-butyl acetate, or a combination of those solvents.

2.3.1 VOC-Exempt Organic Compounds

In one embodiment, the solvent is a VOC-exempt compound, such as acetone. In another embodiment, the solvent comprises aromatic compounds (*e.g.*, one or more, two or more, or all three of toluene, benzene, or xylene).

Volatile organic compounds (VOC) means any compound of carbon, excluding carbon monoxide, carbon dioxide, carbonic acid, metallic carbides or carbonates, and ammonium carbonate, which participates in atmospheric photochemical reactions. This includes any such organic compound other than the following "exempt organic compounds" or "VOC-exempt compounds," which have been determined to have negligible photochemical reactivity:

methane; ethane; methylene chloride (dichloromethane); 1,1,1-trichloroethane (methyl chloroform); 1,1,2-trichloro-1,2,2-trifluoroethane (CFC-113); trichlorofluoromethane (CFC-11); dichlorodifluoromethane (CFC-12); chlorodifluoromethane (HCFC-22); trifluoromethane (HFC-23); 1,2-dichloro 1,1,2,2-tetrafluoroethane (CFC-114); chloropentafluoroethane (CFC-115); 1,1,1-trifluoro 2,2-dichloroethane (HCFC-123); 1,1,1,2-tetrafluoroethane (HFC-134a); 1,1-dichloro 1-fluoroethane (HCFC-141b); 1-chloro 1,1-difluoroethane (HCFC-142b); 2-chloro- 1,1,1,2-tetrafluoroethane (HCFC-124); pentafluoroethane (HFC-125); 1,1,2,2-tetrafluoroethane (HFC-134); 1,1,1-trifluoroethane (HFC-143a); 1,1-difluoroethane (HFC-152a); parachlorobenzotrifluoride (PCBTF); cyclic, branched, or linear completely methylated siloxanes; acetone; perchloroethylene (tetrachloroethylene); 3,3-dichloro- 1,1,1,2,2-pentafluoropropane (HCFC-225ca); 1,3-dichloro-1,1,2,2,3-pentafluoropropane (HCFC-225cb); 1,1,1,2,3,4,4,5,5,5-decafluoropentane (HFC 43-10mee); difluoromethane (HFC-32); ethylfluoride (HFC-161); 1,1,1,3,3,3-hexafluoropropane (HFC-236fa); 1,1,2,2,3-pentafluoropropane (HFC-245ca); 1,1,2,3,3-pentafluoropropane (HFC-245ea); 1,1,1,2,3-pentafluoropropane (HFC-245eb); 1,1,1,3,3-pentafluoropropane (HFC-245fa); 1,1,1,2,3,3-hexafluoropropane (HFC-236ea); 1,1,1,3,3-pentafluorobutane (HFC-365mfc); chlorofluoromethane (HCFC-31); 1-chloro-1-fluoroethane (HCFC-151a); 1,2-dichloro- 1,1,2-trifluoroethane (HCFC-123a); 1,1,1,2,2,3,3,4,4-nonafluoro-4-methoxy-butane ($C_4F_9OCH_3$ or HFE-7100); 2-(difluoromethoxymethyl)- 1,1,1,2,3,3,3-heptafluoropropane ($(CF_3)_2CFCF_2OCH_3$); 1-ethoxy-1, 1,2,2,3,3,4,4,4-nonafluorobutane ($C_4F_9OC_2H_5$ or HFE-7200); 2-(ethoxydifluoromethyl)- 1,1, 1,2,3,3,3-heptafluoropropane ($(CF_3)_2CFCF_2OC_2H_5$); methyl acetate; 1,1,1,2,2,3,3-heptafluoro-3-methoxy-propane ($n-C_3F_7OCH_3$, HFE-7000), 3-

ethoxy- 1,1, 1,2,3,4,4,5,5,6,6,6-dodecafluoro-2- (trifluoromethyl) hexane (HFE-7500),
 1,1,1,2,3,3,3-heptafluoropropane (HFC-227ea), methyl formate (HCOOCH_3); (1)
 1,1,1,2,2,3,4,5,5,5-decafluoro-3-methoxy-4-trifluoromethyl-pentane (HFE-7300); propylene
 carbonate; dimethyl carbonate; t-butyl acetate; and perfluorocarbon compounds which fall into
 5 these classes:

- (i) cyclic, branched, or linear, completely fluorinated alkanes;
- (ii) cyclic, branched, or linear, completely fluorinated ethers with no unsaturations;
- (iii) cyclic, branched, or linear, completely fluorinated tertiary amines with no
 10 unsaturations; and
- (iv) sulfur containing perfluorocarbons with no unsaturations and with sulfur bonds only
 to carbon and fluorine.

2.4 Coating Properties

Embodiments of the coatings disclosed herein, once dried and cured, can have a variety
 of characteristics in addition to displaying hydrophobic and/or oleophobic behavior.

15 The coatings display a defined range of hardness that may be evaluated by any known
 method in the art. In one embodiment, the test employed for hardness is the ASTM D3363 -
 05(2011)e2 Standard Test Method for Film Hardness by Pencil Test. In some embodiments,
 depending on the polymer composition employed and/or any non-acrylic polymers that may be
 combined with the acrylic polymers in the composition, the coatings will display a hardness of
 20 9B or 8B using that hardness scale. In some embodiments, the coatings produced may have a
 hardness of about 7B, 6B or 5B. Accordingly, in some embodiments the coatings produced
 may have a hardness from about 9B to about 8B, 9B to about 7B, 9B to about 6B, 9B to about
 5B, from about 8B to about 7B, from 8B to about 6B, from about 8B to about 5B, from about
 7B to about 6B, 7B to about 5B, or from about 6B to about 5B.

25 The coatings described herein may also have a defined durability in that they can
 withstand some amount of abrasion without a substantial loss of HP/OP properties. The
 durability of the hydrophobicity and/or oleophobicity can range from resistance to moderate
 contact to resistance to abrasion that does not damage the surface by peeling, chipping, or
 marring the binder. Resistance to abrasion may be measured using any method known in the
 30 art including, but not limited to, assessment with a Taber abrasion-testing instrument (*e.g.*, a
 Taber "Abraser") or a Crockmeter.

For the purpose of this application, wherever Taber testing results are recited, the tests
 are conducted on a Taber Model 503 instrument using CS-0 or CS10 wheels with 250 g or
 1,000 g loads as indicated.

Abrasion may also be measured using other instruments such as an AATCC Crockmeter, which may be motorized or operated manually, or by manual semiquantitative "glove rub" testing. For the purpose of this application, wherever testing is conducted using a Crockmeter it is performed using a motorized CM-5 Crockmeter with a 14/20 white rubber septum fitted on the instrument's finger to contact the coating (Ace Glass, Inc., Vineland, NJ, Catalog No. 9096-244). Tests are conducted at about 20° C using a 9 Newton load.

The coating compositions, once dried and cured, have hydrophobic and/or oleophobic properties. In addition, they display chemical resistance to a variety of alcohols and/or hydrocarbons. Embodiments of the dried and cured coatings are may be stable when exposed to compositions with a pH from about 2.0 to about 10.0, about 2.0 to about 6.0, about 5.0 to about 9.0, or about 8.0 to about 10.0.

3.0 Coating Application Method:

The coatings described herein can be applied to surfaces using any means known in the art including, but not limited to, brushing, painting, printing, stamping, rolling, dipping, spin-coating, spraying, or electrostatic spraying.

In one embodiment, the coating compositions described herein are prepackaged in a delivery system/apparatus for spray applications, such as aerosol canisters (*e.g.*, pre-pressurized aerosol cans). In such an embodiment, a propellant may be added to the system/apparatus that serves to drive the components out of their canisters for delivery. Propellants will typically be a gas at 25 °C and 1 atmosphere, but may be in a different phase (liquid) under pressure, such as in a pressurized aerosol delivery system.

In one embodiment, propellants are a gas or combination of gases (*e.g.*, air, nitrogen, carbon dioxide). In another embodiment, propellants are a liquefiable gas having a vapor pressure sufficient to propel and aerosolize the coating composition as it exits the delivery system/apparatus). Some propellants include: liquefied petroleum gases, ethers (*e.g.*, dimethyl ether (DME), diethyl ether and combinations thereof); C₁-C₄ saturated hydrocarbons (*e.g.*, methane, ethane, propane, n-butane, and isobutane); hydrofluorocarbons (HFC) (*e.g.*, 1,1,1,2-tetrafluoroethane (HFC-134a), 1,1,1,2,3,3,3-heptafluoropropane (HFC-227HFC), difluoromethane (HFC-32), 1,1,1-trifluoroethane (HFC-143a), 1,1,2,2-tetrafluoroethane (HFC-134), and 1,1-difluoroethane (HFC-152a)), nitrous oxide, carbon dioxide, and mixtures comprising any two, three or more of the foregoing. In another embodiment, the propellant is a blend of n-butane and propane.

In one embodiment, the propellant is a blend of isobutane, n-butane and propane. In another embodiment, the propellant is nitrous oxide and/or carbon dioxide. In another

embodiment, the propellant comprises hydrofluoroalkanes (HFA) (*e.g.*, HFA-134a (1,1,1,2-tetrafluoroethane) or HFA-227 (1,1,1,2,3,3,3-heptafluoropropane) or combinations of the two). In some embodiments, the propellants may be comprised of greater than 30, 40, 50, 60, 70, 80 or 90 percent of one, two, three, or more VOC-exempt compounds by weight of the propellant.

5 The coatings described herein can be applied to virtually any substrate to provide hydrophobic and/or oleophobic properties. Generally, the surfaces to be coated will be rigid or semi-rigid, but the surfaces can also be flexible, for example in the instance of wires, tapes, rubberized materials, gaskets, and ribbons. The coating compositions may be employed in a variety of applications in which it would be advantageous to provide a rigid, semi-rigid and/or
10 flexible surface with hydrophobic and/or oleophobic properties, for example to coat components used in electronic devices and/or circuitry/circuit boards to render them resistant to water and other aqueous compositions.

 The choice of coatings and coating process that will be used may be affected by the compatibility of the substrate and its surface to the coating process and the components of the
15 coating compositions. Among the considerations are the compatibility of the substrate and its surface with any solvents that may be employed in the application of the coatings and the ability of a desired coating to adhere to the substrate's surface.

 Coatings may take any desired shape or form, limited only by the manner and patterns in which they can be applied. In some embodiments, the coating will completely cover a
20 surface. In other embodiments, the coating will cover only a portion of a surface, such as one or more of a top, side or bottom of an object. In one embodiment, a coating is applied as a line or strip on a substantially flat or planar surface. In such an embodiment, the line or strip may form a spill-resistant border.

 The shape, dimensions and placement of coatings on surfaces can be controlled by a
25 variety of means including the use of masks, which can control not only the portions of a surface that will receive a coating, but also the portions of a surface that may receive prior treatments such as the application of a primer layer or cleaning by abrasion or solvents. For example, where sandblasting or a chemical treatment is used to prepare a portion of a surface for coating, a mask resistant to those treatments would be selected (*e.g.*, a mask such as a rigid
30 or flexible plastic, resin, or rubber/rubberized material). Masking may be attached to the surface through the use of adhesives, which may be applied to the mask agent, the surface, or both.

 In another embodiment, coatings are applied to a ribbon, tape or sheet that may then be applied to a substrate by any suitable means including adhesive applied to the substrate, the

ribbon or tape, or both. Ribbons, tapes and sheets bearing a hydrophobic coating may be employed in a variety of applications, including forming spill-proof barriers on surfaces. Ribbons, tapes, and sheets are generally formed of a substantially flat (planar) flexible material where one side (the top) is made hydrophobic. This includes metal sheets, ribbons, and tapes such as aluminum tape or other tapes (*e.g.*, metal adhesive tape, plastic adhesive tape, paper adhesive tape, fiberglass adhesive tape), wherein one side is coated with the coatings described herein and adhesive is applied to the other side. Once such ribbons, tapes, and sheets are prepared, they can be applied to any type of surface including metal, ceramic, glass, plastic, or wood, for a variety of purposes.

In one embodiment, the coatings are applied to a surface by spraying in a method comprising:

(a) spraying a coating composition on all or part of a surface; and

(b) optionally applying additional layers of the coating composition to all or part of the surface to which one or more previous layers of coating composition were applied. In one embodiment, such spray applications are conducted employing the coating composition packaged in aerosol spray canisters to which a propellant has been added.

4.0 Certain Embodiments

Table 2 and the list of embodiments that follows it provide a series of non-limiting embodiments directed to the coatings and methods described herein. Table 2 lists a series of compositions comprising an acrylic binder, solvent, and nano-particles that are covalently or non-covalently associated with chemical groups that give rise to hydrophobic and/or oleophobic properties (*e.g.*, nano-particles treated with a silanizing agent or nano-particles treated with polydimethylsiloxane). Each potential composition set forth by selecting an acrylic binder, its percentage composition, the type of nano-particle and its percentage composition, and the solvent from the columns in Table 2 is disclosed as if recited separately.

Table 2

Series	Acrylic Binder Comprises	% Binder weight / volume of final composition	Nano-particle	% Nano-particle weight / volume of final composition	Solvent Comprises:
1	MMA Polymer or copolymer; BMA Polymer or copolymer; EMA Polymer or copolymer; MMA/BMA copolymer; MMA/EMA copolymer; or a BMA/EMA copolymer	0.4%-10%, 0.5%-9%, 0.6%-8%, 0.7%-7%, 0.8%-6%, 1%-5.5%, 2%-5%, 2.1%-4.0%, 4.1%-6.0%, or 6.1-8.0%	Fumed silica, TiO ₂ , or Alumina treated with polydimethyl-siloxane or a silanizing agent (<i>e.g.</i> , M5 fumed silica treated with (tridecafluoro- 1,1,2,2-tetrahydrooctyl) trichlorosilane)	0.1% - 10%, 0.2%-7.5%, 0.5%-6%, 0.8%-5%, or 1%-4% w/v	Acetone, Acetone/tertbutyl-acetate Acetone/Ethanol, Acetone/MEK, Acetone/MIKB, Aromatic solvent(s)
2	MMA Polymer or MMA Co-polymer	0.4%- 10% 0.5%-9%, 0.6%-8%, 0.7%-7%, 0.8%-6%, 1%-5.5%, 2%-5%, 2.1%-4.0%, 4.1%-6.0%, or 6.1-8.0%	Fumed silica, TiO ₂ , or Alumina treated with polydimethyl-siloxane or a silanizing agent (<i>e.g.</i> , M5 fumed silica treated with (tridecafluoro- 1,1,2,2-tetrahydrooctyl) trichlorosilane)	0.1% - 10%, 0.2%-7.5%, 0.5%-6%, 0.8%-5%, or 1%-4% w/v	Acetone, Acetone/tertbutyl-acetate Acetone/Ethanol, Acetone/MEK, Acetone/MIKB, Aromatic solvent(s)
3	MMA and BMA copolymer	0.4%- 10%, 0.5%-9%, 0.6%-8%, 0.7%-7%, 0.8%-6%, 1%-5.5%, 2%-5%, 2.1%-4.0%, 4.1%-6.0%, or 6.1-8.0%	Fumed silica, TiO ₂ , or Alumina treated with polydimethyl-siloxane or a silanizing agent (<i>e.g.</i> , M5 fumed silica treated with (tridecafluoro- 1,1,2,2-tetrahydrooctyl) trichlorosilane)	0.1% - 10%, 0.2%-7.5%, 0.5%-6%, 0.8%-5%, or 1%-4% w/v	Acetone, Acetone/tertbutyl-acetate Acetone/Ethanol, Acetone/MEK, Acetone/MIKB, Aromatic solvent(s)
4	EMA copolymer	0.4%- 10% 0.5%-9%, 0.6%-8%, 0.7%-7%, 0.8%-6%, 1%-5.5%, 2%-5%.	Fumed silica, TiO ₂ , or Alumina treated with polydimethyl-siloxane or a silanizing agent (<i>e.g.</i> , M5 fumed silica treated with (tridecafluoro- 1,1,2,2-tetrahydrooctyl)	0.1% - 10%, 0.2%-7.5% , 0.5%-6% 0.8%-5% or 1% - 4% w/v	Acetone, Acetone/tertbutyl-acetate Acetone/Ethanol, Acetone/MEK, Acetone/MIKB, Aromatic solvent(s)

Series	Acrylic Binder Comprises	% Binder weight / volume of final composition	Nano-particle	% Nano-particle weight / volume of final composition	Solvent Comprises:
		2.1%-4.0%, 4.1%-6.0%, or 6.1-8.0%	trichlorosilane)		

4.1 List of Embodiment

1. A composition for coating surfaces and objects giving rise to a hydrophobic coating comprising: an acrylic binder, nano-particles from about 8 nm to about 100 nm associated
5 covalently or non-covalently with a hydrocarbon or fluorohydrocarbon containing group (alkyl or fluoroalkyl group), and a solvent.
2. The composition of embodiment 1, wherein the nano-particles comprise silica, fumed silica, titanium dioxide or alumina.
3. The composition according to embodiments 1 or 2, wherein the solvent comprises a
10 VOC-exempt compound selected from acetone, t-butylacetate and/or combinations thereof.
4. The composition of any of embodiments 1-3, wherein the nano-particles are treated with a polydimethylsiloxane, a silanizing agent, or a combination thereof.
5. The compositions of any of embodiments 1-4, wherein the composition is rapid drying as defined herein. That is, wherein when the composition is applied in an amount of about 2.5
15 square meters/liter on a substantially planar aluminum test plate that is held substantially constant at a temperature of approximately 23° C, such application being divided into a series of five sprays, each such spray comprising about one-fifth of the total composition, the composition produces within sixty seconds following each spray a coating that does not transfer to or stick to a surface brought in contact with the coated area, wherein the drying of the spray
20 is not accelerated by heating or forced air circulation, provided that the solvent in the composition can freely evaporate.
6. The composition of any of embodiments 1-5, wherein the composition dries to a hydrophobic and/or oleophobic coating that resists a loss in hydrophobicity when subject to abrasion greater than 2 cycles using a Taber Abraser equipped with CSIO wheels under a 250 g
25 load and operated at 95 RPM at about 20° C in less than about one hour, 30 minutes, 20 minutes, 10 minutes, or 5 minutes.
7. An apparatus comprising a composition of any of embodiments 1-6.

8. The apparatus of embodiment 7, wherein said apparatus produces an aerosol or spray of said composition for spray application of said coating.
9. The apparatus of embodiment 7 or 8, wherein said apparatus comprises a spray can or a canister containing said composition.
- 5 10. The apparatus of embodiment 8 or embodiment 9 wherein said apparatus further comprises a propellant, which may be contained with the coating composition in the can or canister of embodiment 9.
11. The apparatus of embodiment 10, wherein said propellant is carbon dioxide, pressurized air or nitrogen.
- 10 12. A coating prepared by applying said composition of any of embodiments 1-5.
13. A coating applied by applying said composition with an apparatus of any of embodiments 7-12.
14. A method of coating a surface, or a portion thereof, comprising applying a composition of any of embodiments 1-6.
- 15 15. A method of coating a surface, or a portion thereof, comprising applying an aerosol or spray of said composition using an apparatus according to any of embodiments 7-11.
16. A composition for preparing a hydrophobic and/or oleophobic coating according to any of claims 1-6, comprising an acrylic binder as set forth in Table 2.
17. The composition of embodiment 16, wherein the acrylic binder comprises: a MMA
20 polymer or copolymer; BMA polymer or copolymer; EMA polymer or copolymer; MMA/BMA copolymer; MMA/EMA copolymer; or a BMA/EMA copolymer.
18. The composition of embodiment 16, wherein the acrylic binder comprises a MMA polymer and/or MMA copolymer.
19. The composition of embodiment 16, wherein the acrylic binder comprises a BMA
25 polymer and/or BMA copolymer.
20. The composition of embodiment 16, wherein the acrylic binder comprises an EMA copolymer.
21. A coating prepared by the application of a composition according to any of embodiments 16-20 to a surface.

22. A method of preparing a hydrophobic and/or oleophobic coating or surface comprising applying a composition according to any of embodiments 16-20 to the surface of an object or a part of a surface of an object.

23. A coating according to any of embodiments 12, 13 or 21 having a hardness of at least 9B using the ASTM D3363 - 05(2011) Standard Test Method for Film Hardness by Pencil Test.

24. A coating according to any of embodiments 12, 13 or 21 wherein the coating provides superhydrophobic properties.

25. A coating according to any of embodiments 12, 13 or 21 wherein the coating provides hydrophobic but not superhydrophobic properties.

26. A coating according to any of embodiments 12, 13, 21 or 23-25 that is superhydrophobic and retains its superhydrophobicity for at least 5 cycles (revolutions) of a Taber Abraser using CSIO wheels with a 250g load at 95 rpm at about 20° C and/or 14 strokes on a Crockmeter using a 14/20 white rubber septum fitted on to the Crockmeter to contact the coating (Catalog No. 9096-244, Ace Glass, Inc. , Vineland, NJ) at about 20° C, at a 9 Newton load; loss of superhydrophobic behavior is deemed to be the point at which more than half of the water droplets applied to a substantially planar test surface subject to the action of said CSIO wheels (typically 20 droplets are applied) fails to run (roll) off when the surface is inclined at 5 degrees from horizontal.

27. A composition according to any of embodiments 1-6 or 16-20, wherein said composition further comprises filler-particles.

28. A coating according any of embodiments 12, 13, 21, or 23-26, further comprising filler-particles.

5.0 Examples

Example 1

One example of the coating composition described herein comprises:

- (i) 2% to 4% by weight fumed silica (M5 fumed silica, Cabot Corp.) treated with tridecafluoro-1,1,2,2-tetrahydrooctyl) trichlorosilane;
- (ii) 5% acrylic polymer (*e.g.*, MMA polymer or copolymer, or a MMA/BMA copolymer) w/v based on the total volume of the composition;
- (iii) 91% to 93% acetone or acetone/ethanol as a solvent.

The coating composition can be sprayed via gravity, spray gun, or aerosol spray can. It also can be applied by dipping an object into the mixture. Where it is to be applied by spray can, it is introduced into the can with a compatible propellant.

The sample was tested for wear resistance using three tests.

5 **Example 2**

The formulation of Example 1 is applied via aerosol spray can by:

1. cleaning and drying a target surface to be coated as needed before applying the coating;
2. agitating the composition (*e.g.*, shaking the spray can) for at least 2 minutes, or as needed, before using;
- 10 3. spraying the coating composition on to the surface (*e.g.*, at a distance of approximately 12 inches from target; starting with 3 - 4 light coats. Stop and wait for the coating to dry if the target appears to become "damp"); and
- 15 4. following 3, optionally applying additional amounts of the coating composition on to the surface by spraying 1 - 2 light coat(s) of the composition on the surface every 30 seconds (or more) until a desired thickness is achieved.

Typically steps 3-4 are repeated to apply 5- 6 coats and produce a coating that is effective. The application of 7 - 10 coats will yield a product with higher hydrophobicity and that is more durable. The coating can be applied until desire thickness or "whiteness" from the silica is achieved.

- 20 5. Drying the coating for 0-20 minutes (min.), 0.5-5 min., 5-10 min., 10-15 min., 15-20 min., or 0.5-15 min., before use or handling. The coating is typically dried for 0.5 - 15 minutes before the product is used or handled.

When applied by spray gun, the mixture requires 3 coats applied one after another to yield a surface that has hydrophobic and/or oleophobic characteristics. A dry time of about 15
25 minutes at room temperature without forced air circulation is generally employed prior to handling and wetting even though each application is dry to the touch after as little as 30 seconds to 2 minutes.

When the coating is applied by dipping, the coating composition should have a higher concentration of the treated silica. In dipping, the object is immersed into the mixture and
30 removed to drip dry. Excess coating composition is often removed by shaking. Drying is conducted at room temperature.

Example 3 Coating Tests

Cleaned substantially planar aluminum plates (about 10.2 cm X 10.2 cm squares 1.5 mm thick) are coated with a composition comprising PARALOID™ B-64 as the MMA/BMA copolymer prepared as described in Example 1, with the exception that 0.1% w/v filler is added.

5 The composition is applied by spraying multiple applications of the composition on the surface of the plate to build up having a final thickness of about 12.7 to about 25.4 microns (about 0.5 to about 1 mil thickness). After drying for at least an hour, the aluminum plates are subject to a durability test to determine the point at which the coating loses superhydrophobic behavior by Taber Abraser measurement or by measurement using a Crockmeter.

10 Where loss of superhydrophobic behavior is determined using Taber Abraser testing, the Abraser is equipped with CS-10 (abrasive) wheels with 250 gram load. Tests are conducted at 95 rpm at a speed of 95 rpm. The end of superhydrophobic behavior is judged by the failure of more than half of the water droplets applied to the tested surface (typically 20) to run (roll) off when the surface is inclined at 5 degrees from horizontal.

15 Loss of superhydrophobic behavior can also be determined using an American Association of Textile Chemists and Colorists (AATCC) CM-5 Crockmeter.

Superhydrophobic behavior is judged before and after the surface is subject to the action of a cylindrical 14/20 white rubber septum (Part No. 9096-244, Ace Glass, Inc., Vineland, NJ, having an outside diameter of 13 mm and an inside diameter of 7 mm, contact surface area of
20 94 mm²) fitted on the finger of the Crockmeter. The septum is rubbed across the surface using a motorized CM-5 Crockmeter applying a 9 Newton load. The end of superhydrophobic behavior is judged by the failure of more half of the water droplets applied to the tested surface (typically 20) to run (roll) off when the surface is inclined at 5 degrees from horizontal.

The results of Taber Abraser testing and Crockmeter testing are shown in Figure 1.

25 Coating hardness is determined using ASTM D3363 - 05(2011)e2 Standard Test Method for Film Hardness by Pencil Test. The coating achieves a hardness of 9B or greater.

Claims

1. A composition for coating surfaces and objects giving rise to a hydrophobic coating comprising: an acrylic binder, nano-particles from about 8 nm to about 100 nm associated covalently or non-covalently with alkyl or fluoroalkyl groups, and a solvent, where the solvent
5 comprises a VOC-exempt compound selected from acetone, t-butylacetate and/or combinations thereof.
2. The composition of claim 1, wherein the nano-particles comprise silica, fumed silica, titanium dioxide or alumina.
3. The composition of claim 2, wherein the nano-particles are treated with a
10 polydimethylsiloxane, a silanizing agent, or a combination thereof.
4. The composition of claim 1, wherein when the composition is applied in an amount of about 2.5 square meters/liter on a substantially planar aluminum test plate that is held substantially constant at a temperature of approximately 23 °C, such application being divided into a series of five sprays, each such spray comprising about one-fifth of the total composition,
15 the composition produces within sixty seconds following each spray a coating that does not transfer to or stick to a surface brought in contact with the coated area, wherein the drying of the spray is not accelerated by heating or forced air circulation, provided that the solvent in the composition can freely evaporate.
5. The composition of claim 1, wherein the composition dries to a hydrophobic and/or
20 oleophobic coating that resists a loss in hydrophobicity when subject to abrasion greater than 2 cycles using a Taber Abraser equipped with CSIO wheels under a 250 g load and operated at 95 RPM at about 20° C in less than about one hour.
6. An apparatus comprising a composition of claim 1.
7. The apparatus of claim 6, wherein said apparatus produces an aerosol or spray of said
25 composition for spray application of said coating.
8. The apparatus of claim 7, wherein said apparatus comprises a spray can or a canister containing said composition.
9. The apparatus of claim 8, wherein said can or canister further comprises a propellant.
10. The apparatus of claim 9, wherein said propellant is carbon dioxide, pressurized air, or
30 nitrogen.
11. A coating prepared by applying the composition of claim 1.

12. A method of coating a surface, or a portion thereof, comprising applying a composition of claim 1.

13. A method of coating a surface, or a portion thereof, comprising applying an aerosol or spray of said composition using an apparatus according to claim 7.

5 14. The composition of claim 1, wherein the acrylic binder comprises: a MMA polymer or copolymer; BMA polymer or copolymer; EMA polymer or copolymer; MMA/BMA copolymer; MMA/EMA copolymer; or a BMA/EMA copolymer.

15. The composition of claim 1, wherein the acrylic binder comprises a MMA polymer and/or MMA copolymer.

10 16. The composition of claim 1, wherein the acrylic binder comprises a MMA polymer and/or BMA copolymer.

17. The composition of claim 1, wherein the acrylic binder comprises an EMA copolymer.

18. A hydrophobic and/or oleophobic coating prepared by the application of a composition according to claim 14 to a surface.

15 19. A method of preparing a hydrophobic and/or oleophobic coating or surface, comprising applying a composition according to claim 14 to the surface of an object or a part of the surface of an object.

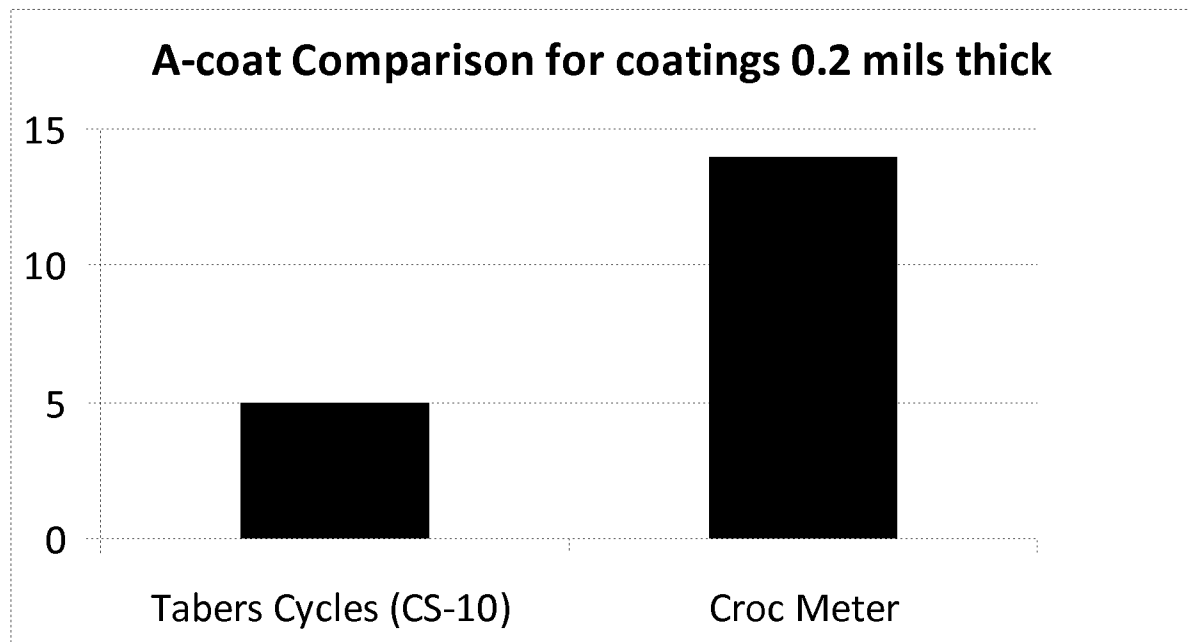
20. A coating according to claim 11 or claim 18, wherein the coating is hydrophobic but not superhydrophobic .

20 21. A coating according to claim 11 or claim 18, wherein the coating is superhydrophobic.

22. A coating according to claim 21 or by applying a composition according to any of claims 14-17 to a surface, wherein said coating has a hardness of at least 9B using the ASTM D3363 - 05(2011)e2 Standard Test Method for Film Hardness by Pencil Test.

25 23. A coating according to claim 22, that retains its superhydrophobicity for at least 2 cycles (revolutions) of a Taber Abraser using CSIO wheels with a 250g load at 95 rpm at about 20° C and/or 14 strokes on a Crockmeter operated with a 9 Newton load at about 20° C, where loss of superhydrophobic behavior is deemed to be the point at which more than half of the water droplets applied to a substantially planar test surface run off when the surface is inclined at 5 degrees from horizontal.

30

Figure 1

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US 12/70200

A. CLASSIFICATION OF SUBJECT MATTER

IPC(8) - C09D 5/00; C09K 3/18 (2013.01)

USPC - 106/2; 106/13

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 - C09D 5/00; C09K 3/18 (2013.01)

USPC - 106/2; 106/13

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
USPC - 442/80; all classes; NPL (Keyword limited, terms below)

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

PatBase, Google Patents, Google Scholar (NPL); Keywords: Acrylic, methacrylate, MMA, BMA, EMA, nanoparticie, coating, silica, spray, aerosol, propellant, polydimethylsiloxane, alkyl fluoroalkyl, acetone, butylacetate, hydrophobic, oleophobic

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 2010/042191 A1 (Bleecher et al.) 15 April 2010 (15.04.2010); page 1, para 3; page 4, para 3; page 5, para 3; page 12, para 5; page 21, para 1-5; page 22, para 3; page 30, para 1; page 47 -page 48; page 40, para 1; page 60, para 2-3; page 61, para 1; page 68, para 1	1-21

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

* Special categories of cited documents:

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

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

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

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

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

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

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

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

"&" document member of the same patent family

Date of the actual completion of the international search

31 January 2013 (31.01.2013)

Date of mailing of the international search report

27 FEB 2013

Name and mailing address of the ISA/US

Mail Stop PCT, Attn: ISA/US, Commissioner for Patents
P.O. Box 1450, Alexandria, Virginia 22313-1450

Facsimile No. 571-273-3201

Authorized officer:

Lee W. Young

PCT Helpdesk: 571-272-4300
PCT OSP: 571-272-7774

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US 12/70200

Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:
2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:
3. ☒ Claims Nos.: 22-23
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying additional fees, this Authority did not invite payment of additional fees.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest



The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.



The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.



No protest accompanied the payment of additional search fees.