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(54) **ELASTOMERIC COATINGS HAVING  
HYDROPHOBIC AND/OR OLEOPHOBIC  
PROPERTIES**

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(57) **ABSTRACT**

This disclosure deals with novel formulations to create highly  
durable hydrophobic, superhydrophobic, oleophobic and/or  
superoleophobic surfaces that can be nearly transparent. The  
formulations of this invention can be applied by dip, spray  
and painting processes.

FIGURE 1

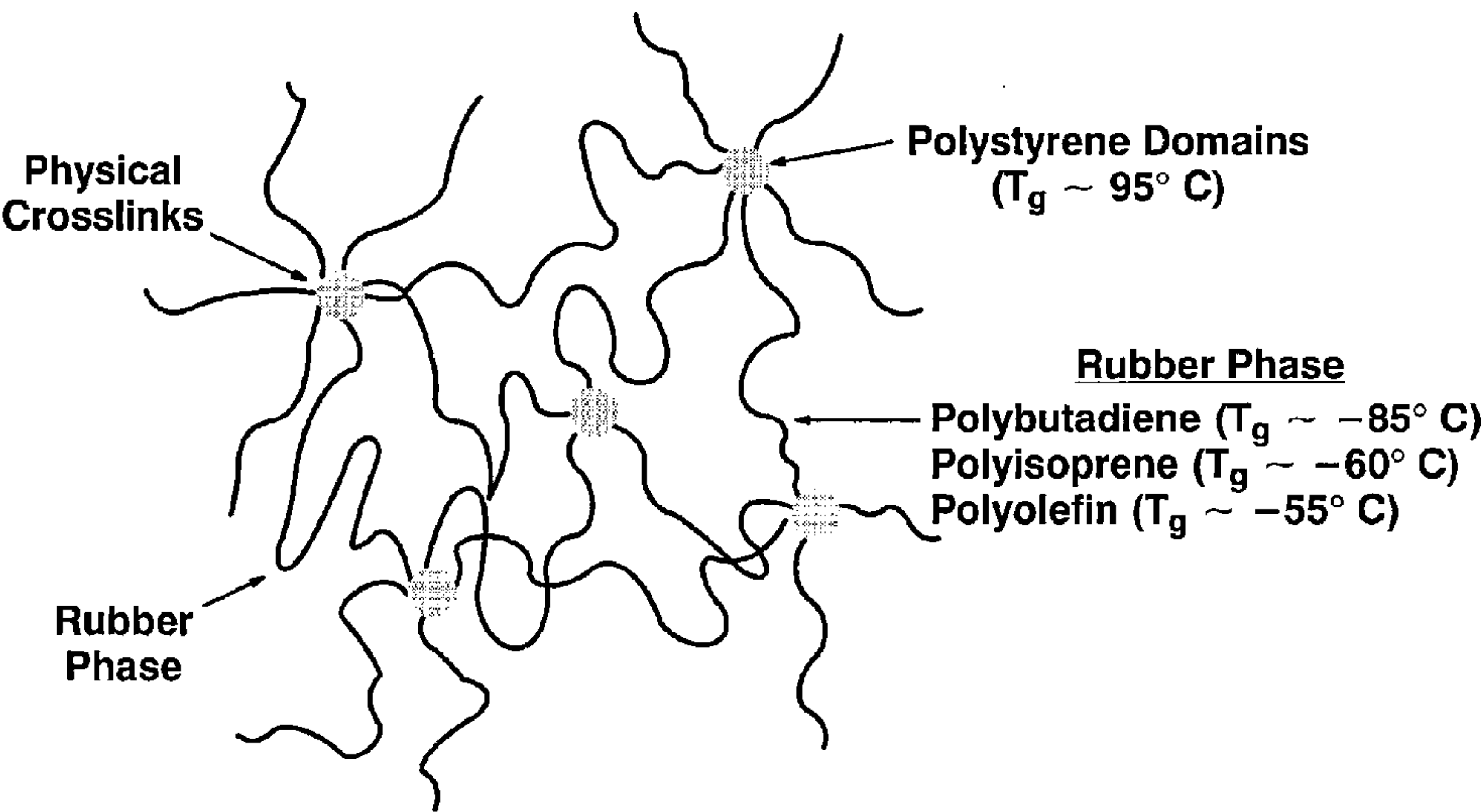


FIGURE 2

Coupled Polymer Structure

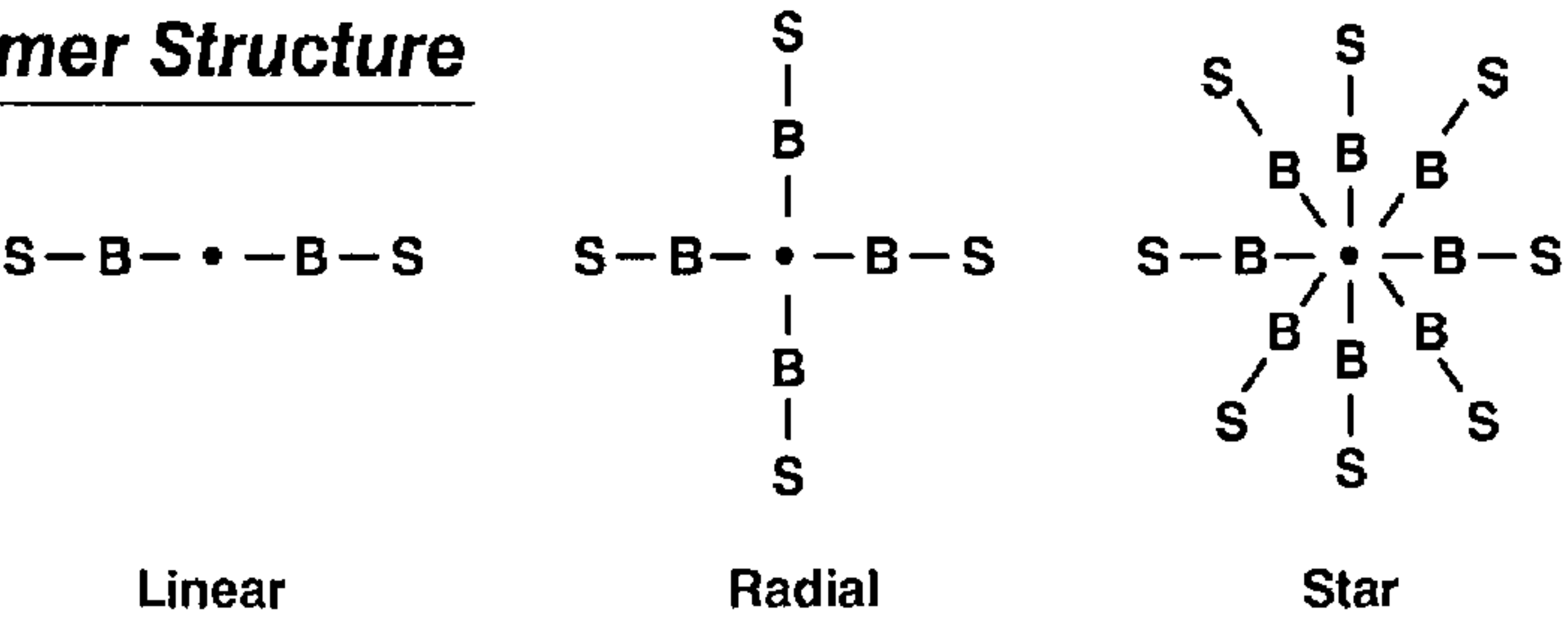
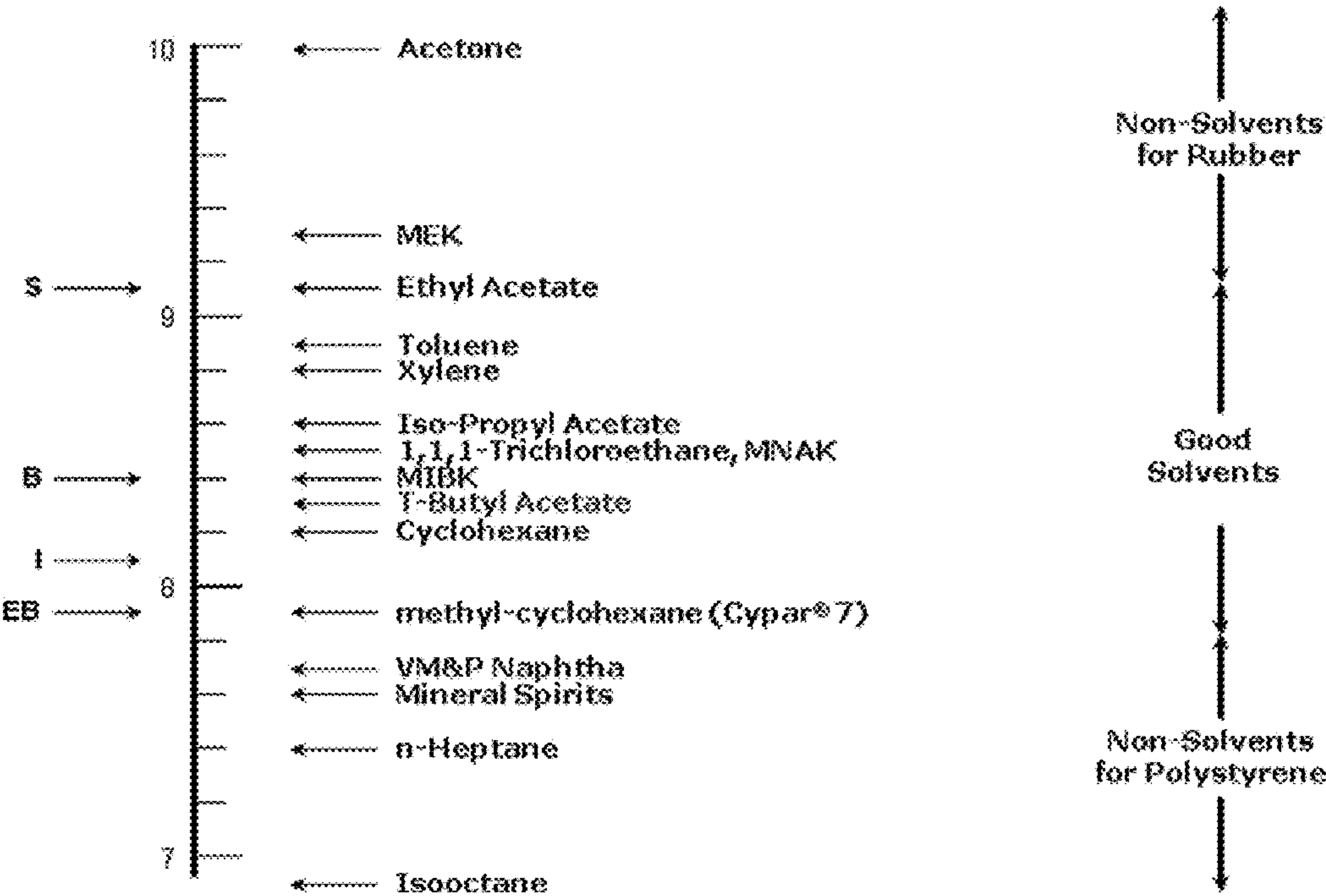
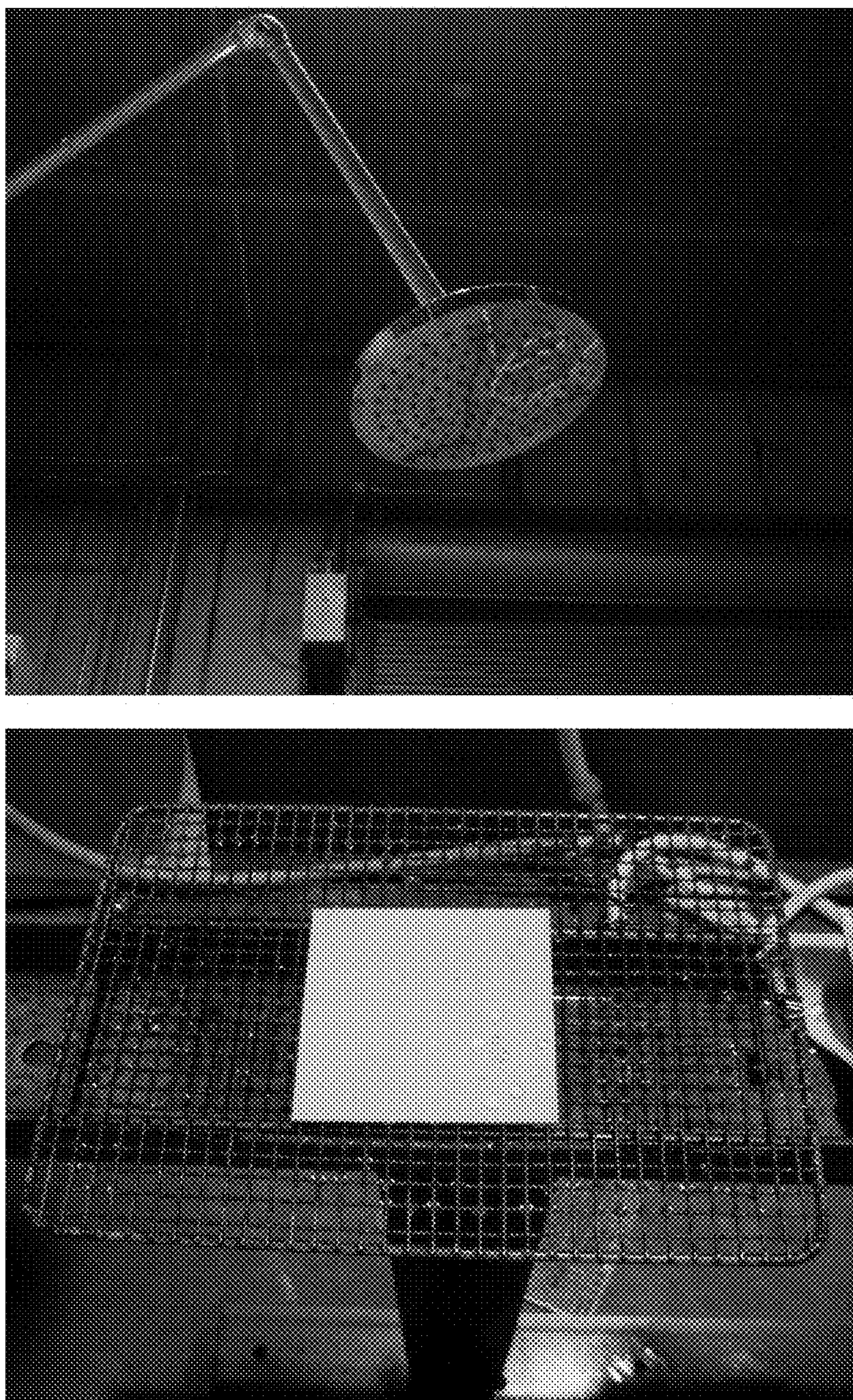


FIGURE 3





**FIGURE 4**





**FIGURE 5**  
**PCoat with Expancel (461 DET d25)**

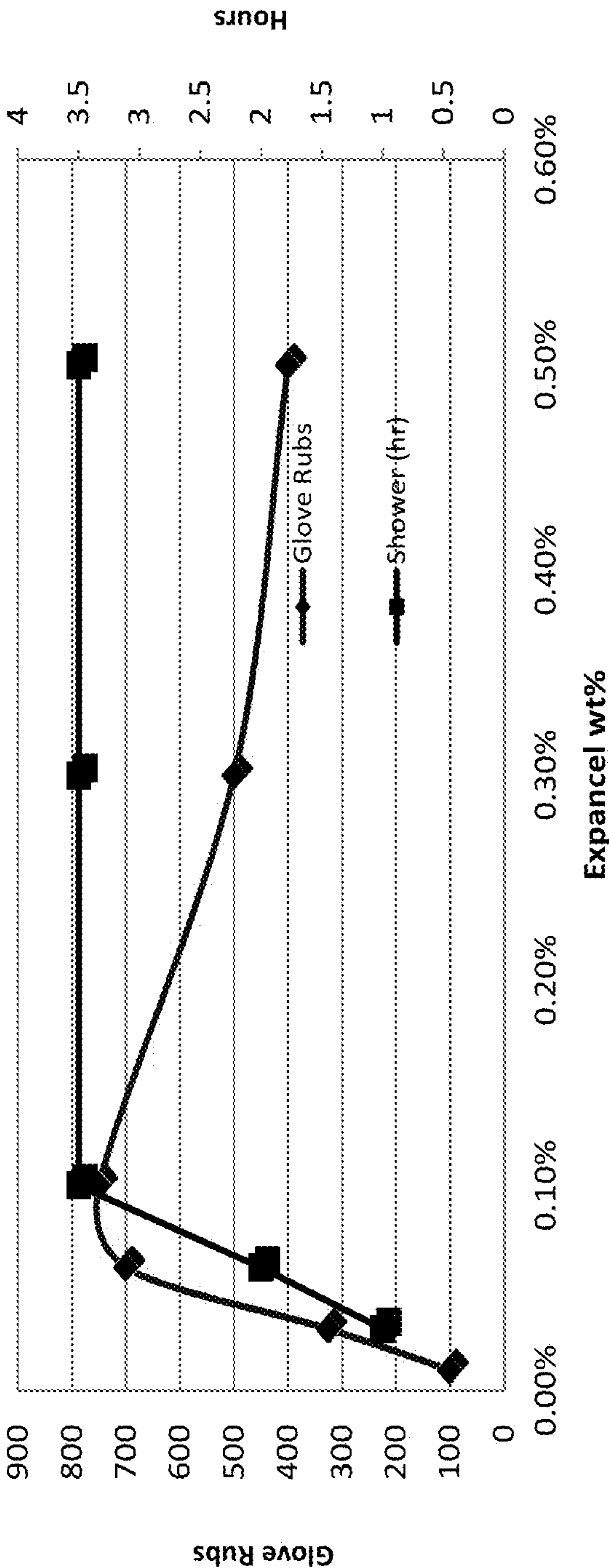


FIGURE 6

Comparison of Expancel® at 1wt% loading

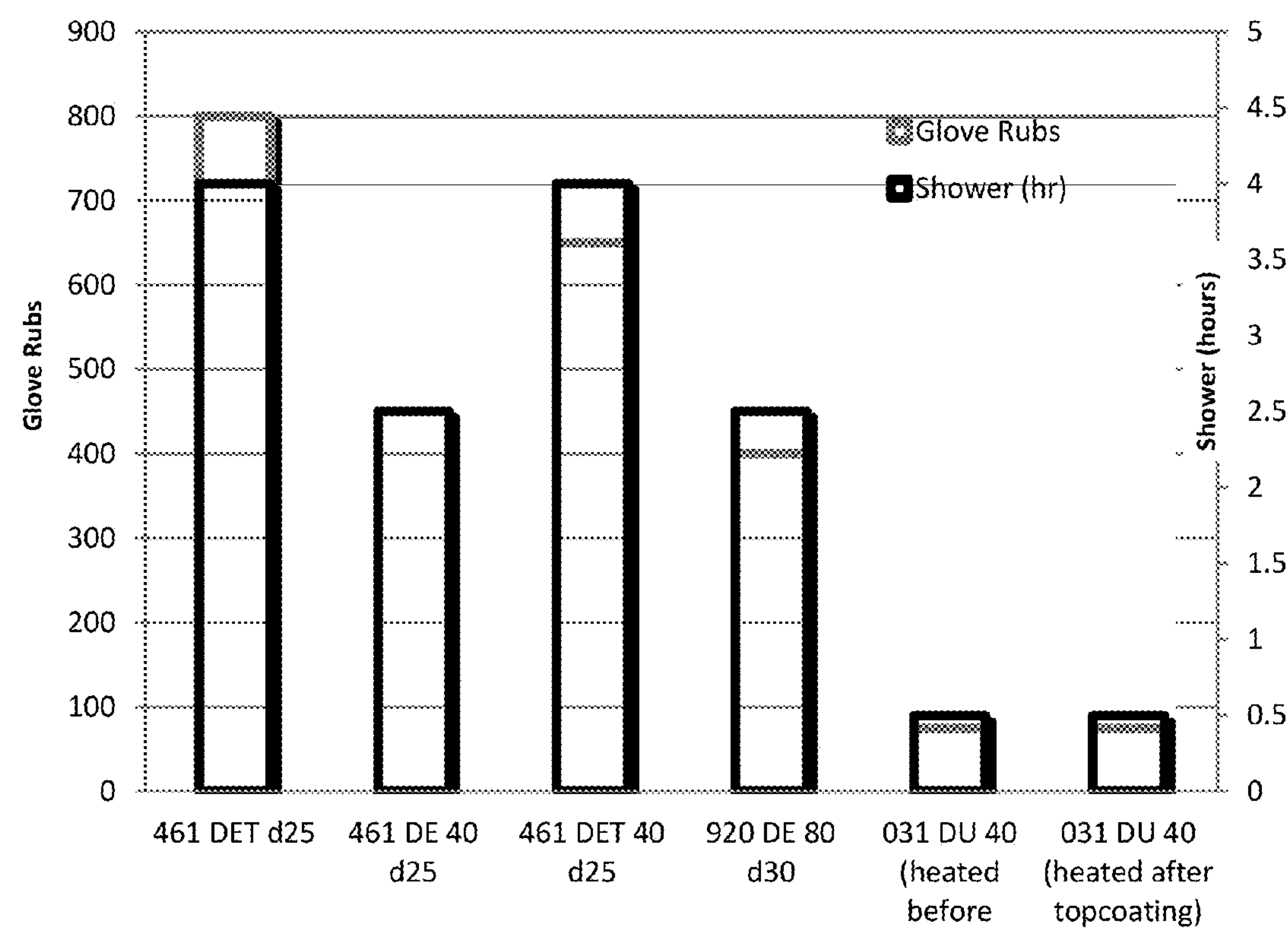
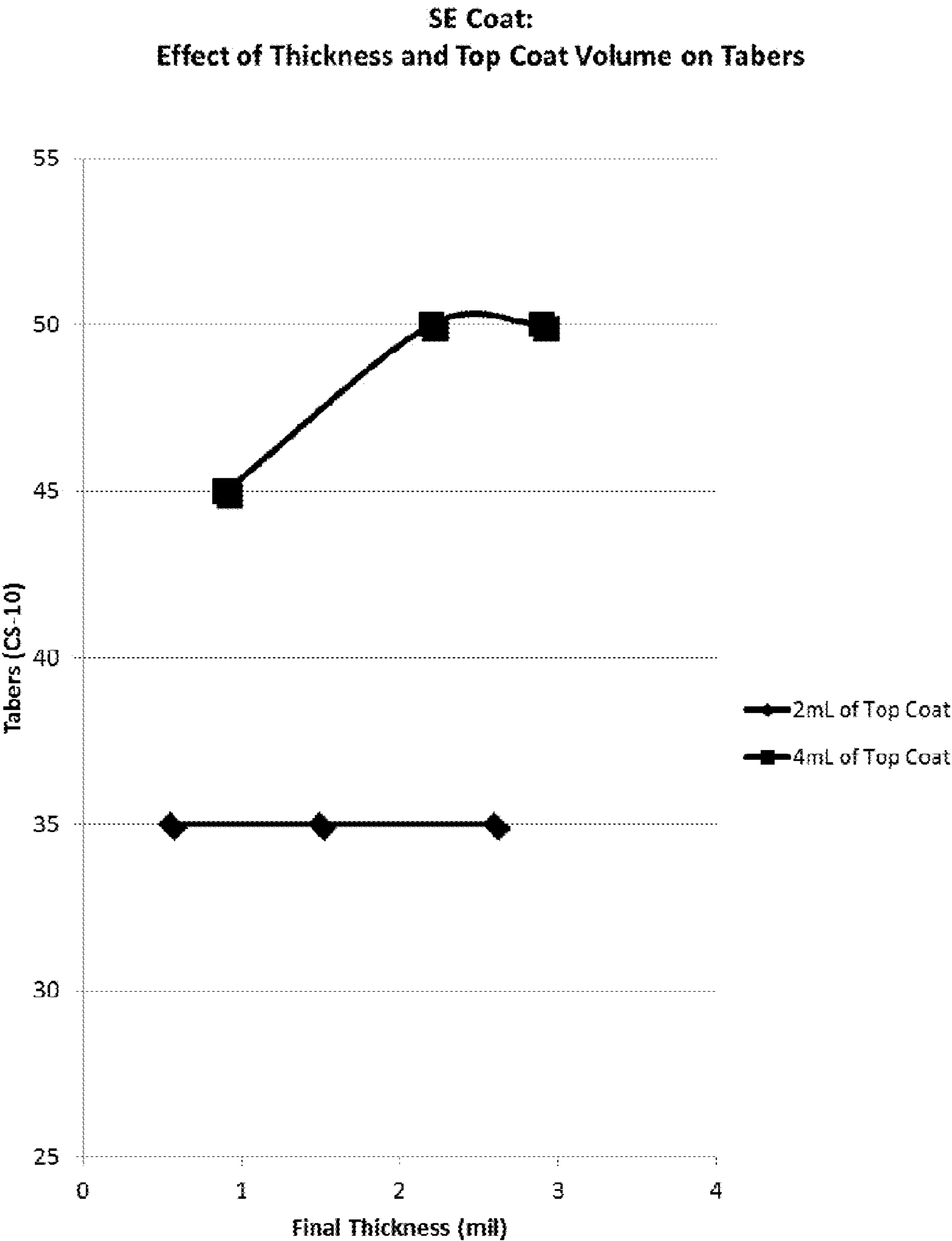
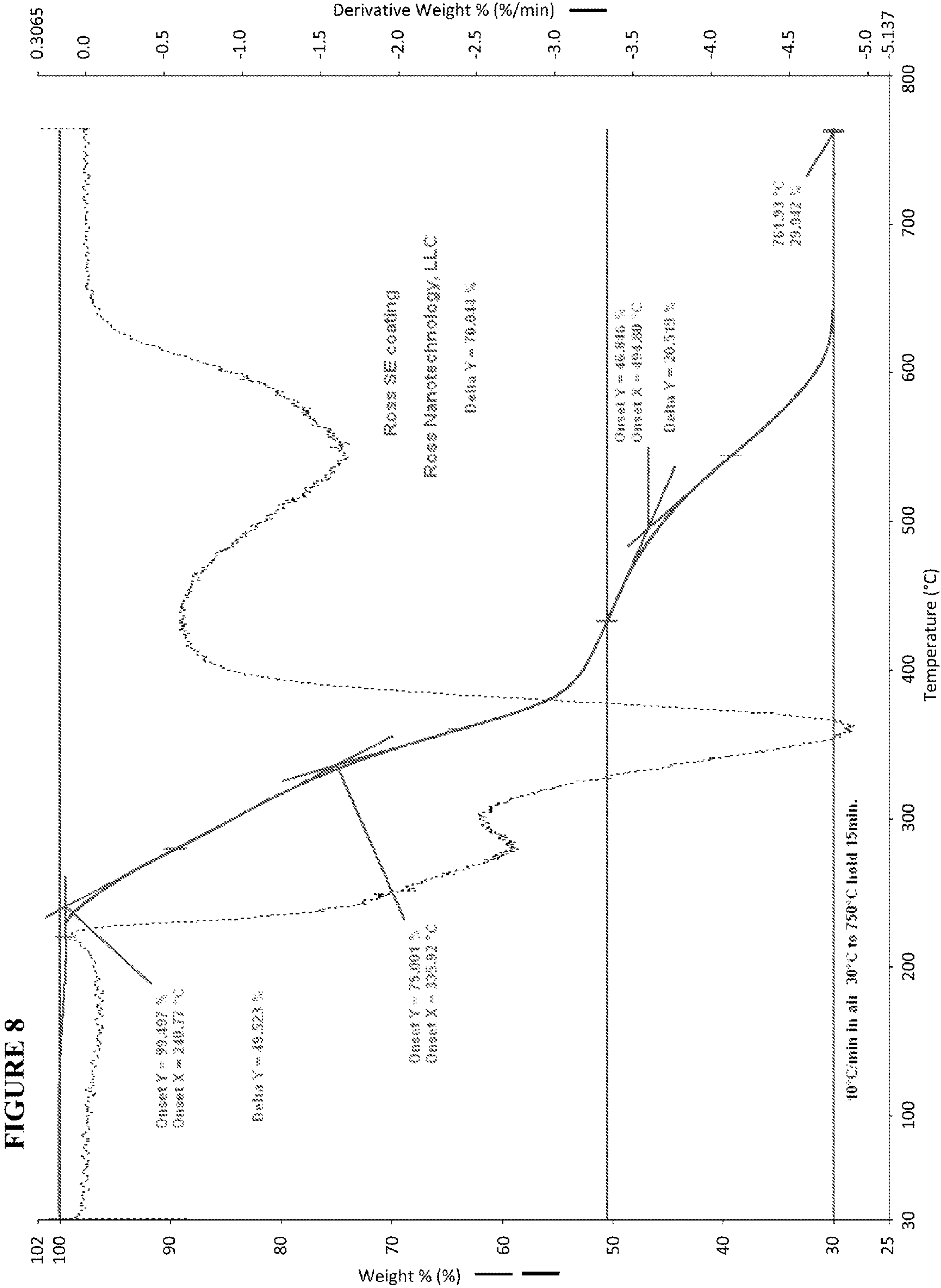
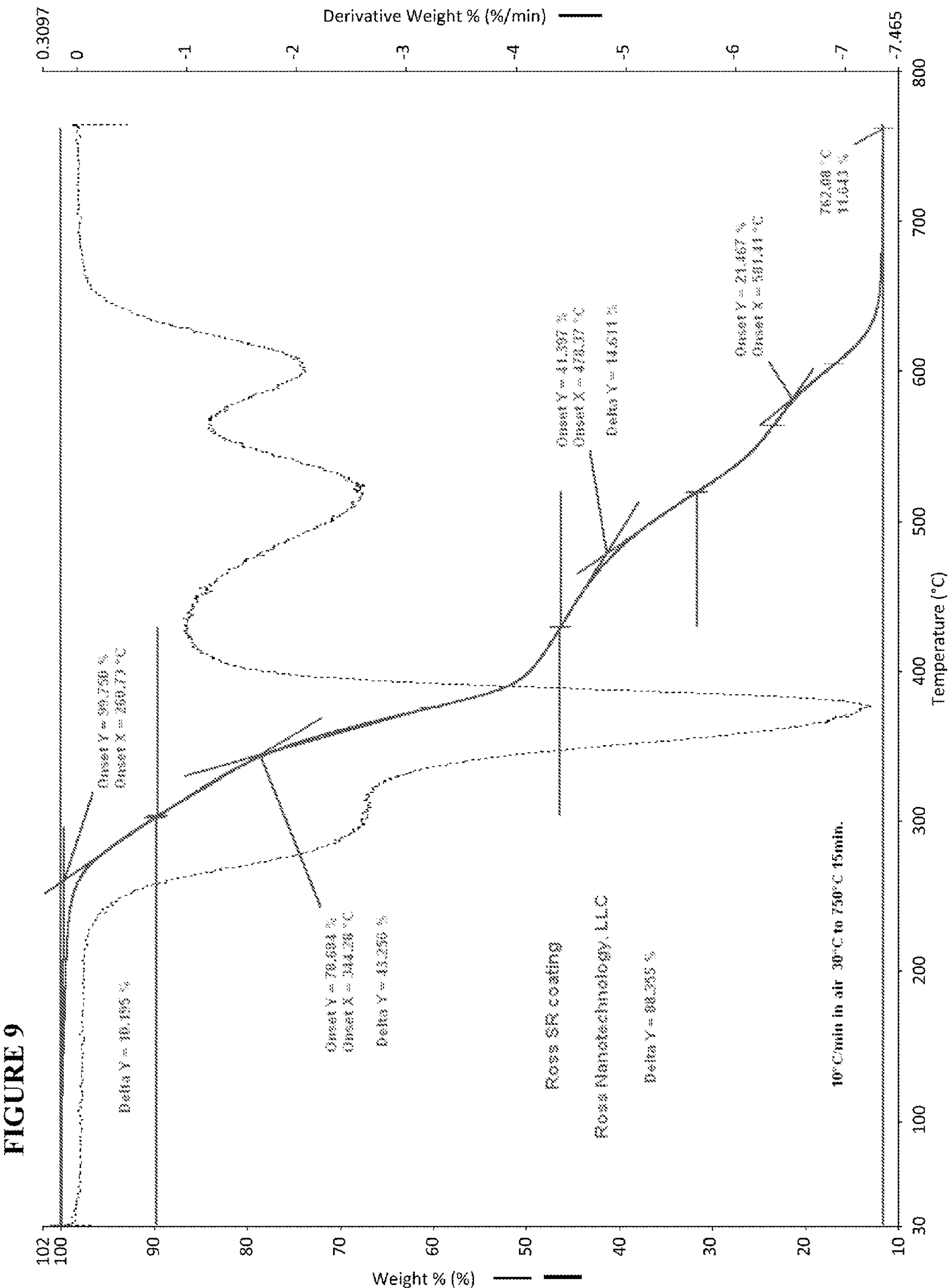


FIGURE 7









## ELASTOMERIC COATINGS HAVING HYDROPHOBIC AND/OR OLEOPHOBIC PROPERTIES

### CROSS REFERENCE TO RELATED APPLICATIONS

**[0001]** This application claims the benefit of U.S. Provisional Application No. 61/663,985, filed Jun. 25, 2012; U.S. Provisional Application No. 61/708,760, filed Oct. 2, 2012; and U.S. Provisional Application No. 61/768,290, filed Feb. 22, 2013, the entirety of each of which application is incorporated herein by reference.

### BACKGROUND

**[0002]** The surfaces of objects that are exposed to the environment come into contact with a variety of agents, including dust, moisture, water, and oils. In industrial applications, surfaces may be exposed to a variety of agents in addition to water, such as aqueous salt solutions, solutions of aqueous acid or base, and chemical components that may be dissolved or suspended in aqueous compositions or other liquids, including those used in manufacturing processes. Not only are the surfaces of objects exposed to a variety of chemical agents, but the temperatures to which the surfaces are exposed can also affect their interaction with those agents and the performance of the coated surfaces of objects. For example, freezing liquids, such as water, can result in frozen deposits tightly attached to the surfaces that prevent access to the surfaces and in some instances prevent proper operation of equipment bound by the frozen liquid. In addition, elevated temperatures can accelerate processes such as corrosion or leaching.

### SUMMARY

**[0003]** Embodiments of coatings and surface treatments are provided herein that can provide advantageous surface properties including, but not limited to, hydrophobicity or superhydrophobicity (collectively HP), oleophobicity or superoleophobicity (collectively OP), and resistance to ice formation, adherence and/or accumulation. Embodiments of the coatings described herein that are HP and OP, and which may also display anti-icing behavior, may be applied to a surface using two or more steps. Embodiments of methods of applying such coatings and surface treatments also are provided, together with embodiments of compositions for applying such coatings and surface treatments, and surfaces and/or objects so treated and coated are provided as well.

### BRIEF DESCRIPTION OF THE DRAWINGS

**[0004]** FIG. 1 is a schematic showing an embodiment of a polystyrene and rubber elastomeric copolymer.

**[0005]** FIG. 2 is a schematic showing various spatial orientations of embodiments of polystyrene and rubber copolymers. S is styrene and B is a rubber phase (i.e. butylene).

**[0006]** FIG. 3 shows some solvents suitable for dissolving styrene (styrenic) block copolymers (SBCs). The scale represents suitable solvents that can be used as SBC copolymers. Letters to the left axis are indicators of: S (styrene), B butylene (polybutadiene), I (polyisoprene), and EB (ethylene/butylene). Those solvents indicated as “Good Solvents” are solvents that tend to dissolve or suspend SBC polymers.

**[0007]** FIG. 4 depicts a shower test apparatus. The upper panel shows the showerhead with 70 nozzles with a 1 mm

diameter orifice arranged in 5 spokes of 5 nozzles and 15 spokes of 3 nozzles about a central point on a circular showerhead. For testing the showerhead delivers approximately 6 liters of potable tap water per minute using about 137900 Pa (Pascals) to 310275 Pa. The lower panel depicts a sample, which is placed about 1.5 meters below the showerhead and subject to the shower.

**[0008]** FIG. 5 shows a plot of “glove rubs,” which are an estimate of the surface resistance to the loss of either or both of HP or OP properties as a function of percentage of EXPANCEL first particles employed in a nearly transparent coating prepared without colorants. The glove rub estimates tend to trend in the same direction as loss of HP or OP properties due to handling, abrasion resistance, and/or the shower time. The weight percent of EXPANCEL particles is given as the percentage of the base coat formulation weight as opposed to a dry weight basis (see Example 1).

**[0009]** FIG. 6 shows the variation in the resistance to the loss of superhydrophobic behavior of an elastomeric binder system due to wear based on “glove rubs” and exposure to a shower of water using five different types of EXPANCEL particles. Duplicate samples containing EXPANCEL 031 DU 400 heated before or after the second component (referred to as “top coat”) comprising hydrophobic fumed silica in acetone is applied. See Example 2 for details.

**[0010]** FIG. 7 shows the effect of coating thickness on coating resistance to the loss of superhydrophobic behavior due to wear based on Taber Abraser testing using a 1,000 g load and CS-10 wheels on 10×10 cm plates treated with 2 or 4 ml of top coat (second component) applied over the base coating. See Example 5 for details.

**[0011]** FIG. 8 shows Thermogravimetric Analysis (TGA) data for a nearly transparent elastomeric coating incorporating EXPANCEL461 EXPANCEL DE 40 D 25 microspheres.

**[0012]** FIG. 9 shows TGA data for an embodiment of a non-transparent HP/OP elastomeric coating incorporating SoftSand™ rubber particles.

### DETAILED DESCRIPTION

**[0013]** Embodiments of elastomeric coating methods, compositions, and treatments are provided that impart a variety of desirable characteristics to objects and their surfaces, including hydrophobicity (including superhydrophobicity), oleophobicity (including superoleophobicity), and/or anti-icing. As used herein, the term “hydrophobicity” and the abbreviation HP includes superhydrophobicity, and the term “oleophobicity” and the abbreviation OP includes superoleophobicity. The abbreviation “HP/OP” is used collectively herein to mean HP and/or OP and may also include anti-icing properties (including ice formation, adherence and/or accumulation). Treating surfaces with coatings having HP/OP characteristics can result in objects and surfaces with a variety of advantageous properties including, but not limited to, resistance to wetting, corrosion, swelling, rotting, cracking or warping, exfoliation, fouling, dust and/or dirt accumulation on surfaces (self cleaning), and resistance to surface ice formation, adherence and/or accumulation. Not only do embodiments of the coating compositions and treatments described herein provide properties including HP/OP, but the coatings also are durable in that they substantially retain those properties despite some amount of mechanical abrasion. In addition to providing durable HP/OP behavior, embodiments of the elastomeric coatings can also remain flexible and provide substantial resistance to cracking, peeling, and delamination



from the coated surface over a wide range of temperatures. Further, embodiments of the coatings can readily be repaired where the surface has been abraded sufficiently to compromise the coating's properties including HP/OP behavior.

**[0014]** Embodiments of the HP/OP elastomeric coatings described herein may be applied in a process comprising two or more steps in which the first component applied comprises an elastomeric binding agent and optionally comprises first particles. Once applied, the coating formed by the first component is termed a "substrate coating," a "base coating," or a "base coat" particularly when dried. Following the application of the elastomer base coat, an amount of second component is applied to the base coat. The second component comprises second particles that are treated to cause the second particles, and the coatings into which they are suitably incorporated, to display advantageous properties including HP/OP and/or anti-icing behavior. The second component may be applied to an elastomeric base coat after the base coat is applied, but before it is dried and/or set. Alternatively, depending on the carrier/solvent used with the second component, the second component may be applied to the elastomer after the base coat is dried and/or set.

**[0015]** The use of second component coating compositions comprising solvents that can be applied to the elastomeric base coat after it has dried and set permits repair of coatings that have been abraded or otherwise damaged to the point where the desired HP/OP properties is/are no longer observed. Provided the base coat is intact, or the base coat has not been damaged to the point that material underlying the base coat is exposed, repair is accomplished by the reapplication of the second component which comprises second particles.

**[0016]** Where the HP/OP elastomeric coatings have been abraded so as to compromise the elastomer binder coating or its properties (e.g., abraded, worn too thin, or damaged to the point where the surface of the coated object or underlying material such as a primer is exposed), the coating may be reapplied to the abraded area (i.e., it may be repaired) by repeating the application of both the first and second components. Suitable repair/preparation of exposed/damaged surfaces and/or underlying primers may be required prior to the reapplication of the elastomeric coating. In contrast, other HP or OP coatings using non-elastomeric binder systems (e.g., polyurethane systems) may not be as readily repaired because the HP/OP behavior of the original coating that remains in place can prevent newly applied coating compositions from binding to the surface.

**[0017]** In one embodiment, a method of applying a HP/OP coating to a substrate comprises the steps of:

**[0018]** a) applying to the substrate a first component comprising: i) an elastomeric binder comprising one or more styrenic block copolymers, and optionally comprising ii) first particles having a size of about 1 micron to about 300 microns (e.g., 10 microns to about 100 microns), to provide a base coating; and

**[0019]** b) applying to the base coating a second component comprising second particles having a size of about 1 nanometer to 25 microns, where the second particles are associated with one or more siloxanes and/or have one or more independently selected alkyl, haloalkyl, or perfluoroalkyl groups covalently bound, either directly or indirectly, to the second particles, and wherein the second component optionally comprises an agent to sus-

pend or assist in suspending the particles (e.g., a solvent such as hexane or tert-butyl acetate).

To assist in the application process, embodiments of the first and second components may include any necessary solvents, liquids or propellants.

**[0020]** In some embodiments of the application method, the base coating is treated with the second component after drying and curing the base coating at room temperature (e.g., about 18 to about 23° C.) or at an elevated temperature (e.g., about 30° to about 100° C., about 30° to about 60° C., about 50° to about 100° C., or about 40° to about 90° C.). In other embodiments, the solvent used to apply the base coat is allowed to evaporate until the coating is no longer liquid and cannot be removed by contact (i.e., dry to the touch); however, the base coating is not fully dried and cured when treated with the second component containing second particles. In still other embodiments, the composition comprising second particles may be applied directly to the base coat before solvents used in the application of the base coating have fully, substantially, or partly evaporated.

**[0021]** Diverse elastomeric binders, first particles, and second particles may be employed in the methods and compositions described herein. In some embodiments, first particles may be filler particles. In some embodiments second particles may be considered nanoparticles. In some embodiments described herein, the coating formed by the application of the first and second components will be nearly transparent to visible light. In other embodiments, the coatings may be colored but nearly transparent to visible light that is not absorbed by the coating components and/or colorants. In still other embodiments, the coatings will have colorants (e.g., insoluble pigments or colored first and/or second particles) that will render them opaque or block the transmission of light. Embodiments of such coating components, materials, and compositions are described more fully below.

**[0022]** A skilled artisan will readily understand that the selection of first particles and second particles needs to include consideration of not only the desired properties of the coating and the ultimate conditions to which the coating will be subject in use, but also the process used to prepare the coating. Where, for example, particles must withstand elevated temperatures or specific solvents in the coating process, they should be selected so as to be suitable for use in the required temperature ranges or in the required solvents. For example, in those embodiments where coatings or the first and/or second particles are intended for use at elevated temperatures (e.g., above room temperature), the particles need to be compatible with the elevated temperatures that the coatings will be subjected to when in use and/or in processes employed to prepare the coatings. Similarly, the particles should be selected to be compatible with solvents used in the application process and with solvents the coatings will become exposed to in use.

**[0023]** In methods described herein, where second particles are applied to a base coat on a substrate, which may be coated with a primer, the methods can produce coatings having (i) a surface in contact with said substrate (or primer) and (ii) an exposed surface that is not in contact with the substrate (or primer) where these surfaces bear different amounts of first particles, second particles, or both first and second particles. In some embodiments the exposed surface can have a greater amount of first and/or second particles on, at, or adjacent to the exposed surface, compared to the amount of first and/or second particles at or adjacent to the surface of the coating



that is in contact with the substrate (or primer). In one embodiment the coatings have a greater amount of second particles on, at, or adjacent to the exposed surface than the surface of the coating that is in contact with the substrate (or primer). In embodiments where a greater amount of first and/or second particles may be present at the exposed surface, the coatings may be considered composite coatings.

**[0024]** The amount of particles in any portion of a coating may be assessed by any means known in the art including, but not limited to, microscopy or electron microscopy. Using those techniques on cross or oblique sections of coatings, the amount (e.g., the number) of particles can be determined. In addition, where it is possible to remove coatings, or where the substrate permits (e.g., it is transparent), the surfaces can be examined directly using microscopy or electron microscopy to determine the amount of particles present at the exposed surface or adjacent to the substrate.

**[0025]** Embodiments of the coatings described herein are durable in that they can withstand some amount of abrasion without a substantial loss of HP/OP properties. To provide an endpoint for the loss of superhydrophobic (SH) behavior as a result of abrasion testing, substantially planar abraded surfaces are tested for their propensity to shed water droplets at an indicated angle of incline (5 degrees unless indicated otherwise). Typically, twenty droplets are placed on the surface to be assessed, which is inclined at the desired angle. The end of SH behavior is indicated when more than half (ten or more drops) stay in place. While such measurements provide a consistent endpoint, a skilled artisan will understand that, even when the endpoint is reached, the abraded surfaces may still be quite hydrophobic, e.g., having water contact angles greater than 130° or 140° in many instances.

**[0026]** Resistance to abrasion may be measured using any method known in the art including, but not limited to, mechanized or manual assessment with a Taber abrasion-testing instrument (e.g., a Taber “Abraser”) or a Crockmeter. Alternatively, a manual measure used to assess the durability of surfaces is a glove rub (GR) test. Each of those tests is described in more detail below.

**[0027]** 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. Unless indicated otherwise, a load of 1,000 g was employed, and tests were conducted at room temperature at a speed of 95 rpm.

**[0028]** Where resistance to the loss of HP is measured with a Crockmeter, a motorized American Association of Textile Chemists and Colorists (AATCC) CM-5 Crockmeter is employed. The finger of the Crockmeter is fitted with a 14/20 white rubber septum having an outside diameter of 13 mm and an inside diameter of 7 mm with a contact surface area of 94 mm<sup>2</sup> (Ace Glass, Inc., Vineland, N.J., Catalog No. 9096-244). The septum is brought into contact with the coating with a force of 9N (Newtons). 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 droplets) to run (roll) off when the surface is inclined at 5 degrees from horizontal. Abrasion resistance may also be measured using a manually operated AATCC Crockmeter.

**[0029]** Although an absolute correlation between Taber Abraser Testing, Crockmeter testing, and glove-rub testing is not provided, the manual glove-rub test is useful as an indication of the durability of the coated surface and its ability to be handled. Coatings applied to primed surfaces incorporat-

ing rigid particles (e.g., EXTENDO SPHERES) typically give a ratio of about 4.5 glove rubs/Taber Abraser cycles (250 g load) with CS-0 wheels and a ratio of about 7.5 glove rubs/Taber cycles with CS-10 wheels. Coatings incorporating flexible first particles (e.g., black rubber particles) typically give a ratio of about 7.6 glove rubs/Taber Abraser cycles (250 g load) with CS-0 wheels and a ratio of about 12.9 with CS-10 wheels. Results are given below for coatings of several thicknesses, where the thickness measurement includes the thickness of the primer layer. The number of strokes observed in Crockmeter testing is generally about one fourth of the number of “glove rubs” observed in the manual glove rub testing. Nearly Transparent Coating with Clear Hollow Rigid Thermoplastic First Particles

Approximate Glove Rubs to loss of SH	CS-0 Wheel			CS-10 Wheel		
	Thickness (mils)	Taber Cycles	Ratio GR/ Taber cycle	Thickness (mils)	Taber Cycles	Ratio GR/ Taber cycle
500	1.1	130	3.8	1	60	8.3
500	2.1	100	5.0	2	70	7.1
500	3.5	110	4.5	3.5	60	8.3
500	4	110	4.5	4.5	80	6.3

Nontransparent Coating with Flexible Black Rubber First Particles

Approximate Glove Rubs to loss of SH	CS-0 Wheel			CS-10 Wheel		
	Thickness (mils)	Taber Cycles	Ratio GR/ Taber cycle	Thickness (mils)	Taber cycles	Ratio GR/ Taber cycle
700	2.7	100	7.0	2.6	60	11.7
700	4.9	90	7.8	4.8	50	14
700	7.5	90	7.8	7.2	50	14
700	9.5	90	7.8	8.5	60	11.7

**[0030]** In addition to resisting the loss of HP/OP properties from abrasion, the compositions provided herein also provide durability in the form of resistance to other conditions. The coatings also resist loss of those properties when subject to:

**[0031]** Submersion in water (the duration a coating resists wetting at different depths in water);

**[0032]** Flowing water (the ability of a coating or surface treatment to resist the impact of flowing water such as a shower of water);

**[0033]** Exposure to liquids other than water (chemical durability and resistance to acids, alkalis, salts, and certain organic solvents such as alcohols);

**[0034]** Ultraviolet (UV) radiation;

**[0035]** Boiling water; and

**[0036]** Salt water, in the form of immersion, spray, or fog.

**[0037]** The elastomer-based coatings described herein have a variety of properties in addition to resisting the loss of HP/OP from abrasion including, but not limited to, resisting ice formation and/or adherence on the coating and flexibility over a wide range of temperatures (e.g., -35° C. to 205° C.).

**[0038]** In one embodiment, the HP/OP elastomeric coatings comprising plastic, glass or rubber first particles (e.g., EXPANCEL spheres or micronized rubber) have a relative



electrical permittivity at 100 MHz from about 0.2 to about 4 at about 22° C. (e.g., a permittivity from about 0.2 to about 1, from about 1 to about 2, from about 2 to about 3, or from about 3 to about 4) as measured by ASTM D150 using a single 0.11 mm thick film, or three layers of 0.11 mm film to achieve a 0.33 mm thickness.

**[0039]** In addition to their other properties, the HP/OP coatings described herein can be described by their characteristic roughness that may be measured by any means known in the art. In some embodiments, the surface roughness is measured using a Mahr Pocket Surf PS1 (Mahr Federal Inc., Providence, R.I.). The roughness of a surface can be expressed using a variety of mathematical expressions including, but not limited to, its Arithmetical Mean Roughness and its Ten-Point Mean Roughness.

**[0040]** The coatings resulting from the application of the compositions provided for herein have in some embodiments a surface with an arithmetical mean roughness in a range selected from: greater than about 3 microns to about 4 microns; from about 4 microns to about 6 microns; from about 4 microns to about 8 microns; from about 4 microns to about 12 microns; from about 4 microns to about 20 microns; from about 5 microns to about 10 microns; from about 5 microns to about 12 microns; from about 5 microns to about 20 microns; from about 6 microns to about 10 microns; or from about 6 microns to about 14 microns.

**[0041]** In other embodiments, the coatings, resulting from the application of the compositions provided for herein, have in some embodiments a surface with a ten point mean roughness selected from: from about 7 microns to about 60 microns; from about 7 microns to about 70 microns; from about 7 microns to about 80 microns; from about 7 microns to about 100 microns; from about 8 microns to about 60 microns; from about 8 microns to about 80 microns; from about 8 microns to about 100 microns; from about 12 microns to about 60 microns; from about 12 microns to about 100 microns; from about 15 microns to about 60 microns; or from about 15 microns to about 100 microns.

**[0042]** A more complete discussion of the coating compositions, their methods of preparation and application, and their properties follows. A skilled artisan will understand that the description and examples set forth herein are provided as guidance, and are not limiting to the scope of the methods and compositions described herein.

## 1.0 DEFINITIONS

**[0043]** For the purposes of this disclosure, a HP material or surface is one that results in a water droplet forming a surface contact angle exceeding about 90° at room temperature (which is about 18° C. to about 23° C. for purposes of this disclosure). Similarly, for the purposes of this disclosure, a SH material or surface is one that results in a water droplet forming a surface contact angle exceeding 150° but less than the theoretical maximum contact angle of 180° at room temperature. As SH surface behavior encompasses water contact angles from about 150° to about 180°, SH behavior is considered to include what is sometimes referred to as “ultrahydrophobic” behavior. For the purpose of this disclosure the term hydrophobic (HP) shall include superhydrophobic (SH) behavior unless stated otherwise, and any and all embodiments, claims, and aspects of this disclosure reciting hydrophobic behavior may be limited to either hydrophobic behav-

ior that is not superhydrophobic (contact angles from 90°-150°) or superhydrophobic behavior (contact angles of 150° or greater).

**[0044]** For the purposes of this disclosure an OP material or surface is one that results in a droplet of light mineral oil forming a surface contact angle exceeding about 90°. Similarly, for the purposes of this disclosure a SOP material or surface is one that results in a droplet of light mineral oil forming a surface contact angle exceeding 150° but less than the theoretical maximum contact angle of 180° at room temperature. For the purpose of this disclosure the term oleophobic (OP) shall include superoleophobic (SOP) 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).

**[0045]** Anti-icing (AI) surfaces are surfaces that are resistant to ice formation and/or accretion in dynamic testing, or that prevent ice that forms from adhering to the surface (i.e., ice that forms can be removed with less force than from untreated metal surfaces).

**[0046]** For the purpose of this disclosure, HP/OP denotes hydrophobic behavior (including superhydrophobic behavior) or properties and/or oleophobic (including superoleophobic behavior) behavior or properties. HP/OP behavior may be understood to include anti-icing properties and any embodiment recited as having HP/OP behavior may be recited as having anti-icing properties, unless stated otherwise in this disclosure.

**[0047]** Durability, unless stated otherwise, refers to the resistance to loss of superhydrophobic or superoleophobic properties due to mechanical abrasion.

**[0048]** Alkyl as used herein denotes a linear or branched alkyl radical or group. Alkyl groups may be independently selected from C<sub>1</sub> to C<sub>20</sub> alkyl, C<sub>2</sub> to C<sub>20</sub> alkyl, C<sub>4</sub> to C<sub>20</sub> alkyl, C<sub>6</sub> to C<sub>18</sub> alkyl, C<sub>6</sub> to C<sub>16</sub> alkyl, or C<sub>6</sub> to C<sub>20</sub> alkyl. Unless otherwise indicated, alkyl does not include cycloalkyl.

**[0049]** Cycloalkyl as used herein denotes a cyclic alkyl radical or group. Cycloalkyl groups may be independently selected from: C<sub>4</sub> to C<sub>20</sub> alkyl comprising one, two, or more C<sub>4</sub> to C<sub>8</sub> cycloalkyl functionalities; C<sub>6</sub> to C<sub>20</sub> alkyl comprising one, two, or more C<sub>4</sub> to C<sub>8</sub> cycloalkyl functionalities; C<sub>6</sub> to C<sub>20</sub> alkyl comprising one, two, or more C<sub>4</sub> to C<sub>8</sub> cycloalkyl functionalities; C<sub>5</sub> to C<sub>18</sub> alkyl comprising one, two, or more C<sub>4</sub> to C<sub>8</sub> cycloalkyl functionalities; C<sub>6</sub> to C<sub>18</sub> alkyl comprising one, two, or more C<sub>4</sub> to C<sub>8</sub> cycloalkyl functionalities; or C<sub>6</sub> to C<sub>16</sub> alkyl comprising one, two or more C<sub>4</sub> to C<sub>8</sub> 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.

**[0050]** 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.

**[0051]** 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.

**[0052]** Perfluoroalkyl as used herein denotes an alkyl group in which fluorine atoms have been substituted for each hydrogen atom present in the alkyl group.



**[0053]** Rubber phase as used herein denotes a portion of styrene block copolymers having synthetic rubber attributes. In SBCs rubber phases are typically flanked or joined by polystyrene units that may function as end blocks. Typical synthetic rubbers include an isoprenoid or a polyolefin such as polybutadiene, polyisoprene, or ethylene/butylene.

**[0054]** For the purpose of this disclosure, unless stated otherwise, when content is indicated as being present on a “weight basis,” the content is measured as the percentage of the weight of the components indicated to the total weight of the composition (including recited/required solvents). Optional solvents are not included in the weight of the composition.

**[0055]** “Colorant” as used herein is a material added to the coating composition to cause a change in color, i.e., become colored. Colorants can be dyes which bind at least a portion of the material to be colored, insoluble pigments that are dispersed in at least a portion of the material to be colored, colored chemicals that are dispersed or dissolved in at least a portion of the material to be colored, or inks, which may be any combination of dyes, pigments and colored chemicals. In some embodiments, first or second particles may comprise colorants or may be prepared from materials that are colored.

## 2.0 ELASTOMERIC BINDERS

**[0056]** Elastomers are polymers that are elastic (i.e., have viscoelasticity), and which generally have a low Young’s modulus and high yield strain compared with other materials. Elastomers may be thermoset materials, which require vulcanization (e.g., covalent crosslinking) during curing, or thermoplastic materials (thermoplastic elastomers), in which the crosslinks are weaker dipole or hydrogen bonds.

**[0057]** Elastomeric binder systems employed to make elastomeric coatings (elastomer based coatings) having HP/OP properties are typically comprised of copolymers of polystyrene and a rubber (a rubber phase) known as Styrenic Block Copolymers (SBCs). SBCs are a class of thermoplastic elastomers consisting of a two-phase structure of hard polystyrene end blocks and soft rubber midblocks. The polystyrene end blocks associate to form domains that lock the molecules into place without vulcanization. Since this is a reversible process, the material can be processed on conventional thermoplastic equipment or dissolved in a suitable solvent for application as a coating. Polystyrene end blocks impart strength and the rubber phase mid-blocks impart elasticity. FIG. 1 shows a schematic of a typical SBC copolymer, where the rubber phase is linked to the polystyrene phase. In SBCs the rubber phase can be a synthetic rubber such as, for example, ethylene/butylene (EB e.g.,  $-\text{[CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}(\text{CH}_2\text{CH}_3)\text{CH}_2\text{]}_n-$ ) ethylene/propylene (EP, e.g.,  $-\text{[CH}_2\text{CH}_2\text{CH}(\text{CH}_3)\text{CH}_2\text{]}_n-$ ), polybutadiene, polyisoprene, or polyolefin (see FIG. 1). FIG. 2 shows that the copolymers can have various spatial orientations such as linear, radial, or star like.

**[0058]** SBC compositions, when used as a base coating, produce highly durable HP/OP coatings as measured by a variety of different methods, including those described herein. Moreover, the coatings are compatible with and adhere tightly to a broad range of materials, permitting a large number and type of objects and substrates to be coated.

**[0059]** SBC elastomers offer a variety of advantages and properties for the preparation of base coats used to prepare HP/OP coatings. As they can be dissolved/suspended in a number of solvents, they may be formulated into composi-

tions that are amenable to application using standard equipment including conventional spray guns and aerosol canisters (e.g., an aerosol spray container comprises a valve assembly, a dip tube, and an actuator). As a base coating composition for use in a multi-step (e.g., two-step, three-step, four-step . . . ) HP/OP coating process, SBC elastomer formulations offer flexibility during application and in the application of the second component of the HP/OP coating process. The elastomeric first component can be applied to form a base coating and the second component, which comprises second particles whose application renders the coating HP/OP, can be applied to the base coating when it is wet, tacky, dry to touch, or even completely dried and cured.

**[0060]** A variety of SBCs may be employed to prepare the HP/OP coatings described herein. In an embodiment the SBC-containing binder compositions comprise a rubber phase comprising ethylene/butylene (EB e.g.,  $-\text{[CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}(\text{CH}_2\text{CH}_3)\text{CH}_2\text{]}_n-$ ). In another embodiment, the SBC-containing binder compositions comprise a rubber phase comprising (poly)butadiene (e.g., styrene-butadiene-styrene (SBS) elastomeric polymers. In other embodiments, the rubber phases of suitable SBC polymer compositions comprise ethylene/propylene (EP e.g.,  $-\text{[CH}_2\text{CH}_2\text{CH}(\text{CH}_3)\text{CH}_2\text{]}_n-$ ), polybutadiene, polyisoprene or polyolefin. In another embodiment, binder compositions used for the preparation of durable HP/OP coatings comprise a mixture of any two, three, or four SBC elastomers having rubber phases comprising: ethylene/butylene butadiene, ethylene/propylene polybutadiene, polyisoprene or polyolefin.

**[0061]** Elastomeric coatings with an elongation at break that is greater than about 500%, 600%, 700%, 750%, or about 800% are generally desirable as binders for preparing the durable HP/OP coatings (e.g., coatings prepared with “Kraton G” elastomers), although elastomeric coating compositions with lower elongation at break values can be employed. The rubber component in the SBC copolymers of such elastomer compositions typically varies from about 69% to about 87%, but the rubber component may be about 65% to about 90%, about 67% to about 75%, about 75% to about 87%, or about 70% to about 80% (based on the weight of the SBC copolymer(s)). Among the commercially available SBC elastomer compositions that can be employed as binders for the HP/OP coating compositions described herein are those developed by KRATON® Polymers U.S. LLC. (Houston, Tex.). Various elastomeric polymers, compositions, and their properties are described, for example, in the KRATON® Polymers’ Fact Sheet K0151 Americas available on the world wide web at: [docs.kraton.com/kraton/attachments/downloads/82021AM.pdf](http://docs.kraton.com/kraton/attachments/downloads/82021AM.pdf).

**[0062]** In one embodiment the elastomers employed as binders may be ethylene butylene (EB) elastomeric polymers which have styrene domains (endblocks) and ethylene/butylene rubber phase midblocks. Such EB elastomers may comprise about 65% to 75% rubber phase midblocks, (e.g., about 65%, about 70% or about 75% rubber phase midblocks) and have an elongation at break of 500 to 800% using ASTM D412 on films cast from toluene solution with the grip separation speed set at 10 inches per minute. Some properties of KRATON® EB elastomers are detailed in Table 1.

**[0063]** In one embodiment the elastomers employed as binders may be styrene-butadiene-styrene (SBS) elastomeric polymers. Such SBS elastomers comprise about 60% to 74% butadiene by weight, and have an elongation at break of from



800 to 900% using ASTM D412 on films cast from toluene solution with the grip separation speed set at 10 inches per minute. Some properties of KRATON® styrene-butadiene-styrene (SBS) elastomeric polymers (KRATON® D SBS) are detailed in Table 2.

TABLE 1

EB Based Polymers*								
Property	G1633 (SEBS) Linear	G1650 (SEBS) Linear	G1651 (SEBS) Linear	G1652 (SEBS) Linear	G1654 (SEBS) Linear	G1657 (SEBS) Linear	G1660 (SEBS) Linear	G1726 (SEBS) Linear
Tensile Strength, MPa <sup>1,2</sup>	—	35	>28	31	>28	23	32	2
300% Modulus MPa <sup>1,2</sup>	—	5.6	—	4.8		2.4	5.5	—
Elongation at Break, % <sup>1,2</sup>	—	500	>800	500	800	750	800	200
Specific Gravity	—	70	70	70	70	47	68	70
Brookfield Viscosity, cps at 25° C.	0.91	0.91	0.91	0.91	0.91	0.89	0.91	0.91
25% w4	—	8,000	>50,000	1,800	>50,000	4,200	8,000	200
10% w4	—	50	1,800	30	410	65	50	10
-Melt Index g/10 min. (5 kg) 200° C.	<1	<1	<1	<1	<1	<8	<1	65
230° C.	<1	<1	<1	5	<1	22	<1	<100
Styrene/Rubber Ratio	30/70 Fluffy	30/70 Powder/	30/70 Powder/	30/70 Powder/	33/67 Powder/	13/87 Dense	31/69 Powder	30/70 Dense
Physical Form	Crumb	Fluffy Crumb	Fluffy Crumb	Fluffy Crumb	Fluffy Crumb	Pellet		Pellet
Diblock, %	—	<1	<1	<1	<1	29	—	70
Comments	FDA	FDA	FDA	FDA	FDA	FDA	FDA	FDA

\*polymers recited in this table supplied by KRATON ®  
<sup>1</sup>ASTM method D412 tensile tester grip separation speed 10 in./min.  
<sup>2</sup>Typical properties determined on film cast from toluene solution.  
<sup>3</sup>Typical values on polymer compression molded at 177° C.  
<sup>4</sup>Neat Polymer concentration in toluene

TABLE 2

SBS Elastomeric Polymers*								
Property	D0243 (SBS) Di-block	D1101 (SBS) Linear	D1102 (SBS) Linear	D1116 (SBS) Radial	D1118 (SBS) Diblock	D1133 (SBS) Linear	D1152 (SBS) Linear	D1153 (SBS) Linear
Tensile Strength, MPa <sup>1,2</sup>	2	32	32	32	2	21	32	28
300% Modulus, MPa <sup>1,2</sup>	1.0	2.8	2.8	2.4	1.2	2.1	2.8	2.9
Elongation at Break, % <sup>1,2</sup>	—	880	880	900	600	800	900	800
Set at Break, % <sup>1,2</sup>	—	10	10	10	40	20	10	—
Hardness, Shore A (10 sec.) <sup>3</sup>	70	69	66	63	64	74	66	70
Specific Gravity	0.94	0.94	0.94	0.94	0.94	0.94	0.94	0.96
Brookfield Viscosity, cps at 25° C. (25% w)	315	4,000	1,100	9,000	630	4,800	1,000	1,650
Brookfield Viscosity, cps at 25° C. (15% w)	—	—	—	2,500	—	420	—	—
Melt Index g/10 min. (200° C./5 kg)	20	<1	14	<1	10	<1	8	3

TABLE 2-continued

SBS Elastomeric Polymers*							
Styrene/Rubber Ratio	33/67	31/69	28/72	23/77	33/67	36/64	29/71
Physical Form	Porous Pellet	Porous Pellet Powder	Porous Pellet	Porous Pellet Powder	Porous Pellet Powder	Porous Pellet	Porous Pellet
Diblock, %	75	16	17	16	78	34	15
							<1
Property	D1155 (SBS) Linear	D1184 (SBS) Radial	D1186 (SBS) Radial	D1189 (SBS) Radial	D1191 (SBS) Radial	D1192 (SBS) Linear	DX405 (SBS) Linear
Tensile Strength, MPa <sup>1,2</sup>	28	28	25	—	—	—	—
300% Modulus, MPa <sup>1,2</sup>	2.9	5.5	3	—	—	—	—
Elongation at Break, % <sup>1,2</sup>	800	820	800	—	—	—	—
Set at Break, % <sup>1,2</sup>	—	10	10	—	—	—	—
Hardness, Shore A (10 sec.) <sup>3</sup>	87	68	74	68	68	66	53
Specific Gravity	0.94	0.94	0.94	0.94	0.94	0.94	0.94
Brookfield Viscosity, cps at 25° C. (25% w)	600	>20,000	—	TBD <sup>5</sup>	>20,000	1,500 v	
Brookfield Viscosity, cps at 25° C. (15% w)	—	1,100	1,200	TBD	1,100	—	2,000
Melt Index g/10 min. (200° C./5 kg)	14	<1	<1	<1	<1	<1	3
Styrene/Rubber Ratio	40/60	31/69	30/70	31/69	33/69	30/70	24/76
Physical Form	Porous Pellet	Porous Pellet Powder	Porous Pellet Powder	Porous Pellet Powder	Porous Pellet Powder	Porous Pellet Powder	Porous Pellet
Diblock, %	<1	16	10	16	18	<1	<1

\*polymers recited in this table supplied by KRATON ®  
<sup>1</sup>ASTM method D412 grip separation speed 10 in./min.  
<sup>2</sup>Typical properties determined on film cast from toluene solution  
<sup>3</sup>Typical values on polymer compression molded at 177° C.  
<sup>4</sup>Neat polymer concentration in toluene  
<sup>5</sup>TBD—To Be Determined

[0064] In another embodiment the elastomers employed as binders may be maleated styrene-ethylene/butylene-styrene (SEBS) elastomeric polymers. Such maleated SEBS elastomers comprise about 65% to about 90% (e.g., about 70% or about 87%) rubber midblocks by weight, and have an elongation at break of 500 to 750% using ASTM D412 on films cast from toluene solution with the grip separation speed set at 10 inches per minute. Maleated SEBS polymers typically have from about 0.8% to about 2.2% (e.g., 0.9% to 2.1% or 1% to 1.7%) of substitution. Some properties of KRATON® styrene-ethylene/butylene-styrene (SEBS) elastomeric polymers (KRATON® FG Polymers) are detailed in Table 3.

TABLE 3

Maleated SEBS Polymers FG Polymer Grades*		
Property	FG1901 (SEBS) Linear	FG1924 (SEBS) Linear
Tensile Strength, MPa <sup>1</sup>	34	23
300% Modulus, MPa <sup>1</sup>	—	—
Elongation at Break, % <sup>1</sup>	500	750
Hardness, Shore A (10 sec) <sup>2</sup>	71	49
Specific Gravity	0.91	0.89



TABLE 3-continued

Maleated SEBS Polymers FG Polymer Grades*		
Property	FG1901 (SEBS) Linear	FG1924 (SEBS) Linear
Brookfield Viscosity, 25% w (toluene solutions) cps at 25° C.	5,000	19,000
10% w	110	270
Melt Index g/10 min (5 kg)		
200° C.	5	11
230° C.	22	40
Styrene/Rubber Ratio	30/70	13/87
Physical Form	Dense Pellet	Dense Pellet
Comments	FDA <sup>3</sup>	1.0% bound
	1.7% bound	functionality
	functionality	

\*polymers recited in this table supplied by KRATON®

<sup>1</sup>ASTM method D412-tensile tester grip separation speed 10 in./min.

<sup>2</sup>Typical values on polymer compression molded at 177° C.

**[0065]** In one embodiment the elastomeric binder comprises triblock copolymers of styrene and ethylene/butylene with a polystyrene content of: about 8% to about 14%, about 12% to about 20%, about 18% to about 28%, about 22% to about 32%, about 26% to about 36%, about 8%, about 9%, about 10%, about 11%, about 12%, about 13%, about 14%, about 16%, about 18%, about 19%, about 20%, about 22%, about 24%, about 26%, about 28%, about 30%, about 32%, about 34%, about 36% or mixtures of any two or more, three or more, or four or more of such triblock copolymers. Any one or more of such triblock copolymers may optionally comprise 1% to 3%, 1.4% to 2.0%, 1% to 1.4%, 1.6% to 3%, or 2% to 3% of bound maleic anhydride (maleated copolymers) and may be linear triblock copolymers. In one such embodiment the binder comprises two different maleated triblock copolymers of styrene and ethylene/butylene with a polystyrene: a first triblock copolymer of styrene and ethylene/butylene with a polystyrene having 0.4% to 1.6% (e.g., 0.5% to 1.5%, 0.6% to 1.4%, or 0.7% to 1.3%) substitution by maleic anhydride by weight of the first triblock copolymer (and optionally less than 0.3% maleic anhydride free); and a second triblock copolymer of styrene and ethylene/butylene with a polystyrene having 1.1% to 2.5% (e.g., 1.3 to 2.3 or 1.4 to 2.4%) substitution by maleic anhydride by weight of the second triblock copolymer. In such an embodiment the first and/or second triblock copolymers may be linear or branched copolymers (e.g., arborols or dendrimers), and the second triblock copolymers may be present in a weight ratio from about 4:1 to about 6.5:1 (e.g., the first copolymer to second copolymer ratio is about 4:1 to about 5.5:1, about 5:1 to about 6:1, or about 5.5:1 to about 6.5:1).

**[0066]** Persons skilled in the art will also recognize other elastomeric binders that may be used in place of or in addition to the elastomeric binders described in this disclosure.

**[0067]** In addition to comprising elastomeric polymers (e.g., SBCs), first particles and solvents, elastomeric binder systems that serve as first components optionally comprise a tackifier. Tackifiers may be present in any suitable amount, including in a range selected from about or from about 0.5% to about 30%; 1% to about 5%, from about 2% to about 8%, from about 3% to about 7%, from about 5% to about 10%, from about 10% to about 15%, from about 15% to about 20%, from about 20% to about 25%, or from about 25% to about 30%. Some suitable tackifiers, including totally synthetic

(e.g., members of the Regalrez® family from Eastman Chemical) or modified resins or rosins are set forth in the section describing primers that follows.

**[0068]** First components, and primers discussed below, may further comprise light stabilizers and UV absorbers (UV stabilizers), fire retardants, and/or antioxidants. For example, Tinuvin® light stabilizing products (e.g., Tinuvin 328 and/or Tinuvin 770DF) produced by BASF®, and/or IRGANOX® antioxidant products (e.g., phenolic or hindered phenolic antioxidants such as IRGANOX® 1520 or IRGANOX® 150L) produced by BASF® may be included in the first component binder composition used to set down the base coat or in a primer. Where light/UV stabilizers, UV absorbers, fire retardants, and/or antioxidants are added to either or both of the first component or the primer, they are generally added in an amount less than 2% by weight (e.g., about 1%, 0.75%, 0.5%, 0.4%, 0.3%, 0.2%, 0.1%, 0.075%, 0.06%, or 0.05%, or in a range selected from about 0.01% to about 2%, from about 0.05% to about 1.0%, or from about 0.75% to about 0.5% by weight), and take the place of a corresponding weight of any solvents that may be present.

**[0069]** In addition to the ease of application, elastomer based coatings that do not contain a colorant or significant amounts of opaque particles are nearly transparent to visible light. Typical light transmission (Total Luminous Transmittance or “TLT”) of an elastomeric binder coating prepared using SBCs having 15 micron thickness is approximately 90% (about 85% to about 92%) with a haze of about 61% (about 55% to about 65%). HP/OP coatings without added colorants that are about 25 microns thick prepared with clear first particles (e.g., EXPANCEL particles or other plastic or glass particles or hollow spheres) and fumed silica second particles treated with a silane (silanizing agent) can be nearly transparent. Such HP/OP coatings typically have a TLT of about 80% (about 75% to about 85%) with a haze of about 90% (about 85% to about 90%) as measure by ASTM D1003-11. For the measurements the instrument was calibrated against air and glass sample blanks and given a TLT of about 90% to about 91% and a haze of about 0.2%. Excluding or removing fine particulate materials such as talc used to increase the properties of commercially available elastomer compositions (e.g., flowability of bulk particulates) may increase TLT and haze values. Such fine particulates used in bulk elastomers may be removed by washing with a suitable solvent or by omitting the material from the elastomer compositions when they are prepared.

**[0070]** A variety of solvents may be employed to dissolve elastomeric binders for the preparation of coating compositions used to prepare the base coat of HP/OP coatings described herein. In some embodiments, the copolymers are dissolved in solvents selected from: methyl ethyl ketone (MEK), ethyl acetate, toluene, 1-chloro-4-(trifluoromethyl)-benzene, xylene or mixed xylenes (including technical grade xylenes), isopropyl acetate, 1,1,1-trichloroethane, methyl isobutyl ketone (MIBK), tertbutyl acetate (t-butyl acetate), cyclohexane, methyl-cyclohexane, or mixtures comprising any two, three, four or more thereof. In one embodiment the solvent(s) are selected from those found in the solubility chart shown in FIG. 3, or mixtures of any two, three, four or more thereof. In another embodiment, the solvent comprises greater than 50%, 60%, 70%, 80%, 90%, 95%, 98% or 99% of a xylene (1,2-xylene, 1,3-xylene, or 1,4-xylene) or a mixture of any two or all three xylenes and optionally ethyl benzene (e.g., a technical grade of xylene comprising 34%-47% 1,3-



xylylene, 9%-21% 1,4-xylylene, 4%-16% 1,2-xylylene, 9%-10% ethylbenzene, 0%-1% toluene, and 0%-1% benzene).

**[0071]** In any of the foregoing embodiments, particularly where coatings are to be nearly transparent, the elastomeric binder components comprise at most insubstantial amounts (e.g., less than about 0.5% by weight of the polymers present in the binder) of colorants or particulates that are insoluble in solvents that dissolve the elastomeric polymers and/or that would block the transmission of visible light. One source of such particulates is materials added for the flowability of bulk polymers in the form of powders, pellets, or flakes (e.g., talc added to bulk SBCs).

### 3.0 PARTICLES EMPLOYED IN HP/OP OLEOPHOBIC COATINGS

#### 3.1 First Particles

**[0072]** Embodiments of the coatings disclosed herein may comprise particles that are added to the binder compositions to improve the mechanical properties of the coating, e.g., the durability of the HP/OP coatings. A wide variety of such particles, which are also known as extenders or fillers, may be added to the binders. Those particles are denoted herein as “first particles” because the coatings described herein may have one or more additional types of particles. Such first particles that can be employed in the HP/OP coatings described herein include, but are 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).

**[0073]** Numerous variables may be considered in the selection of first particles. These variables include, but are not limited to, the effect the first particles have on the resulting coatings, their size, their hardness, their compatibility with the binder, the resistance of the first particles to the environment in which the coatings will be employed, and the environment the first particles must endure in the coating and/or curing process, including resistance to temperature and solvent conditions. In addition, if light is used for curing the coatings or they are intended for extended exposure to sunlight, the particles must be resistant to the required light exposure conditions (e.g., resistant to UV light employed in curing or sunlight).

**[0074]** In embodiments described herein, first particles have an average size in a range selected from about 1 micron ( $\mu\text{m}$ ) to about 300  $\mu\text{m}$  or from about 30  $\mu\text{m}$  to about 225  $\mu\text{m}$ . Within the broader ranges, embodiments include ranges of first particles having an average size of from about 1  $\mu\text{m}$  to about 5  $\mu\text{m}$ , from about 5  $\mu\text{m}$  to about 10  $\mu\text{m}$ , from about 10  $\mu\text{m}$  to about 15  $\mu\text{m}$ , from about 15  $\mu\text{m}$  to about 20  $\mu\text{m}$ , from about 20  $\mu\text{m}$  to about 25  $\mu\text{m}$ , from about 1  $\mu\text{m}$  to about 25  $\mu\text{m}$ , from about 5  $\mu\text{m}$  to about 25  $\mu\text{m}$ , from about 25  $\mu\text{m}$  to about 50  $\mu\text{m}$ , from about 50  $\mu\text{m}$  to about 75  $\mu\text{m}$ , from about 75  $\mu\text{m}$  to about 100  $\mu\text{m}$ , from about 100  $\mu\text{m}$  to about 125  $\mu\text{m}$ , from about 125  $\mu\text{m}$  to about 150  $\mu\text{m}$ , from about 150  $\mu\text{m}$  to about 175  $\mu\text{m}$ , from about 175  $\mu\text{m}$  to about 200  $\mu\text{m}$ , from about 200  $\mu\text{m}$  to about 225  $\mu\text{m}$ , and from about 225  $\mu\text{m}$  to about 250  $\mu\text{m}$ . Also included within this broad range are embodiments employing particles in ranges from about 10  $\mu\text{m}$  to about 100  $\mu\text{m}$ , from about 10  $\mu\text{m}$  to about 200  $\mu\text{m}$ , from about 20  $\mu\text{m}$  to about 200  $\mu\text{m}$ , from about 30  $\mu\text{m}$  to about 50  $\mu\text{m}$ , from about 30  $\mu\text{m}$  to about 100  $\mu\text{m}$ , from about 30  $\mu\text{m}$  to about 200  $\mu\text{m}$ , from about 30  $\mu\text{m}$  to about 225  $\mu\text{m}$ , from about 50  $\mu\text{m}$  to about 100  $\mu\text{m}$ , from about 50  $\mu\text{m}$  to about 200  $\mu\text{m}$ , from about 75  $\mu\text{m}$  to about 150  $\mu\text{m}$ , from about 75  $\mu\text{m}$  to about 200  $\mu\text{m}$ , from about 100  $\mu\text{m}$  to about 225  $\mu\text{m}$ , from about 100  $\mu\text{m}$  to about 250  $\mu\text{m}$ , from about 125  $\mu\text{m}$  to about 225  $\mu\text{m}$ , from about 125

$\mu\text{m}$  to about 250  $\mu\text{m}$ , from about 150  $\mu\text{m}$  to about 200  $\mu\text{m}$ , from about 150  $\mu\text{m}$  to about 250  $\mu\text{m}$ , from about 175  $\mu\text{m}$  to about 250  $\mu\text{m}$ , from about 200  $\mu\text{m}$  to about 250  $\mu\text{m}$ , from about 225  $\mu\text{m}$  to about 275  $\mu\text{m}$ , or from about 250  $\mu\text{m}$  to about 300  $\mu\text{m}$ .

**[0075]** First particles may be incorporated into the elastomer binders at various ratios depending on the binder composition and the first particle's properties. In some embodiments, the first particles may have a content range selected from about 0.01% to about 60% or more by weight. Included within this broad range are embodiments in which the first 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 first 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.

**[0076]** In those embodiments where it is desirable to have coatings that are transparent, substantially transparent, or colored but transparent, it is generally desirable to employ particles that are transparent. In one set of embodiments, plastic (e.g., thermoplastic) microspheres are employed in the binder systems to develop surface texture. In another set of embodiments, glass microspheres are employed in the binder systems to develop surface texture.

**[0077]** In one embodiment, substantially spherical thermoplastic particles are added to the elastomeric binder composition to develop surface texture (e.g., EXPANCEL microspheres or EXPANCEL particles). Such microspheres consist of a polymer shell encapsulating a gas. The average diameter of these hollow spheres typically ranges from 6 to 45  $\mu\text{m}$  and have a density of 1000 to 1300  $\text{kg}/\text{m}^3$  (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  $\mu\text{m}$ ), resulting in a density below 30  $\text{kg}/\text{m}^3$  (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. Some thermoplastic microspheres produced under the EXPANCEL brand (AkzoNobel, distributed by Eka Chemicals, Inc., 2240 Northmont Parkway, Duluth, Ga.



30096, USA) are suitable for use in preparing HP/OP, particularly those that are substantially transparent. See Table 4.

TABLE 4

EXPANCEL particles and properties				
Main types	Varieties	Description	Solid content [%]	Density of EXPANCEL [kg/m <sup>3</sup> ]
Unexpanded microspheres	EXPANCEL WU	Wet. unexpanded micro-spheres	60-80	1000-1300
	EXPANCEL WUF	Wet. unexpanded micro-spheres	60-80	1000-1300
	EXPANCEL DU	Dry, unexpanded micro-spheres	>99	~1000
	EXPANCEL DUT	Dry, treated, unexpanded microspheres	>99	~1000
	EXPANCEL SL	Wet, salted, unexpanded microspheres	40	1200
	EXPANCEL SLU	Wet, unexpanded micro-spheres	44	1200
	EXPANCEL MB	Dry, unexpanded micro-spheres mixed with a matrix, e.g. EVA	65 (EXPANCEL)	1000
Expanded microspheres	EXPANCEL WE	Wet. expanded microspheres	15	~30
	EXPANCEL DE	Dry, expanded microspheres	>99	25-70
	EXPANCEL DET	Dry, treated, expanded micro-spheres	>99	25

[0078] Where HP/OP coatings capable of withstanding higher temperatures are desired, and particularly coatings that are substantially transparent, glass microspheres may be employed in place of thermoplastic microspheres. Such glass microspheres include those produced by 3M™ (St. Paul, Minn.) or Sphere One, Inc. (Chattanooga, Tenn.).

[0079] 3.1.1 Exemplary Sources of First Particles  
[0080] First particles may be prepared from the diverse materials described above. Alternatively, first particles may be purchased from a variety of suppliers. Some commercially available first particles that may be employed in the formation of the HP/OP coatings described herein include those in Table 5.

TABLE 5

First Particles									
First particle No.	First Particle (Filler) ID	First Particle Type	First Particle Details	(g/cc)	Particle Size Range (µm)	Color	Crush Strength (psi)	Source Location	
1	K1	Glass Bubbles	GPS <sup>a</sup>	0.125	30-120	White	250	3M <sup>TMj</sup>	
2	K15	Glass Bubbles	GPS <sup>a</sup>	0.15	30-115	White	300	3M <sup>TMj</sup>	
3	S15	Glass Bubbles	GPS <sup>a</sup>	0.15	25-95	White	300	3M <sup>TMj</sup>	
4	S22	Glass Bubbles	GPS <sup>a</sup>	0.22	20-75	White	400	3M <sup>TMj</sup>	
5	K20	Glass Bubbles	GPS <sup>a</sup>	0.2	20-125	White	500	3M <sup>TMj</sup>	
6	K25	Glass Bubbles	GPS <sup>a</sup>	0.25	25-105	White	750	3M <sup>TMj</sup>	
7	S32	Glass Bubbles	GPS <sup>a</sup>	0.32	20-80	White	2000	3M <sup>TMj</sup>	
8	S35	Glass Bubbles	GPS <sup>a</sup>	0.35	10-85	White	3000	3M <sup>TMj</sup>	
9	K37	Glass Bubbles	GPS <sup>a</sup>	0.37	20-85	White	3000	3M <sup>TMj</sup>	
10	S38	Glass Bubbles	GPS <sup>a</sup>	0.38	15-85	White	4000	3M <sup>TMj</sup>	
11	S38HS	Glass Bubbles	GPS <sup>a</sup>	0.38	15-85	White	5500	3M <sup>TMj</sup>	
12	K46	Glass Bubbles	GPS <sup>a</sup>	0.46	15-80	White	6000	3M <sup>TMj</sup>	
13	S60	Glass Bubbles	GPS <sup>a</sup>	0.6	15-65	White	10000	3M <sup>TMj</sup>	
14	S60/HS	Glass Bubbles	GPS <sup>a</sup>	0.6	11-60	White	18000	3M <sup>TMj</sup>	
15	A16/500	Glass Bubbles	Floated Series	0.16	35-135	White	500	3M <sup>TMj</sup>	
16	A20/1000	Glass Bubbles	Floated Series	0.2	30-120	White	1000	3M <sup>TMj</sup>	
17	H20/1000	Glass Bubbles	Floated Series	0.2	25-110	White	1000	3M <sup>TMj</sup>	
18	D32/4500	Glass Bubbles	Floated Series	0.32	20-85	White	4500	3M <sup>TMj</sup>	
19	Expancel 551 DE 40 d42	Plastic Micro-spheres	Dry Expanded	0.042 ± 0.004	30-50			AkzoNobel <sup>i</sup>	
20	Expancel 551 DE 40 d42 ± 2	Plastic Micro-spheres	Dry Expanded	0.042 ± 0.002	30-50			AkzoNobel <sup>i</sup>	
21	Expancel 461 DE 20 d70	Plastic Micro-spheres	Dry Expanded	0.07 ± 0.006	15-25			AkzoNobel <sup>i</sup>	

TABLE 5-continued

First Particles								
First particle No.	First Particle (Filler) ID	First Particle Type	First Particle Details	(g/cc)	Particle Size Range ( $\mu$ m)	Color	Crush Strength (psi)	Source Location
22	Expancel 461 DE 40 d60	Plastic Micro- spheres	Dry Expanded	$0.06 \pm 0.005$	20-40			AkzoNobel <sup>i</sup>
23	Expancel 461 DET 40 d25	Plastic Micro- spheres	Dry Expanded	$0.025 \pm 0.003$	35-55			AkzoNobel <sup>i</sup>
24	Expancel 461 DET 80 d25	Plastic Micro- spheres	Dry Expanded	$0.025 \pm 0.003$	60-90			AkzoNobel <sup>i</sup>
25	Expancel 920 DE 40 d30	Plastic Micro- spheres	Dry Expanded	$0.030 \pm 0.003$	35-55			AkzoNobel <sup>i</sup>
26	Expancel 920 DET 40 d25	Plastic Micro- spheres	Dry Expanded	$0.025 \pm 0.003$	35-55			AkzoNobel <sup>i</sup>
27	Expancel 920 DE 80 d30	Plastic Micro- spheres	Dry Expanded	$0.030 \pm 0.003$	55-85			AkzoNobel <sup>i</sup>
28	H50/10000 EPX	Glass Bubbles	Floated Series	0.5	20-60	White	10000	3M <sup>TM/j</sup>
29	iMK	Glass Bubbles	Floated Series	0.6	8.6-26.7	White	28000	3M <sup>TM/j</sup>
30	G-3125	Z-Light Spheres <sup>TM</sup>	CM <sup>b</sup>	0.7	50-125	Gray	2000	3M <sup>TM/j</sup>
31	G-3150	Z-Light Spheres <sup>TM</sup>	CM <sup>b</sup>	0.7	55-145	Gray	2000	3M <sup>TM/j</sup>
32	G-3500	Z-Light Spheres <sup>TM</sup>	CM <sup>b</sup>	0.7	55-220	Gray	2000	3M <sup>TM/j</sup>
33	G-600	Zeeo- spheres <sup>TM</sup>	CM <sup>b</sup>	2.3	1-40	Gray	>60000	3M <sup>TM/j</sup>
34	G-800	Zeeo- spheres <sup>TM</sup>	CM <sup>b</sup>	2.2	2-200	Gray	>60000	3M <sup>TM/j</sup>
35	G-850	Zeeo- spheres <sup>TM</sup>	CM <sup>b</sup>	2.1	12-200	Gray	>60000	3M <sup>TM/j</sup>
36	W-610	Zeeo- spheres <sup>TM</sup>	CM <sup>b</sup>	2.4	1-40	White	>60000	3M <sup>TM/j</sup>
37	SG	Extendo- sphere <sup>TM</sup>	HS <sup>c</sup>	0.72	30-140	Gray	2500	Sphere One <sup>f</sup>
38	DSG	Extendo- sphere <sup>TM</sup>	HS <sup>c</sup>	0.72	30-140	Gray	2500	Sphere One <sup>f</sup>
39	SGT	Extendo- sphere <sup>TM</sup>	HS <sup>c</sup>	0.72	30-160	Gray	2500	Sphere One <sup>f</sup>
40	TG	Extendo- sphere <sup>TM</sup>	HS <sup>c</sup>	0.72	8-75	Gray	2500	Sphere One <sup>f</sup>
41	SLG	Extendo- sphere <sup>TM</sup>	HS <sup>c</sup>	0.7	10-149	Off White	3000	Sphere One <sup>f</sup>
42	SLT	Extendo- sphere <sup>TM</sup>	HS <sup>c</sup>	0.4	10-90	Off White	3000	Sphere One <sup>f</sup>
43	SL-150	Extendo- sphere <sup>TM</sup>	HS <sup>c</sup>	0.62	70	Cream	3000	Sphere One <sup>f</sup>
44	SLW-150	Extendo- sphere <sup>TM</sup>	HS <sup>c</sup>	0.68	8-80	White	3000	Sphere One <sup>f</sup>
45	HAT	Extendo- sphere <sup>TM</sup>	HS <sup>c</sup>	0.68	10-165	Gray	2500	Sphere One <sup>f</sup>
46	HT-150	Extendo- sphere <sup>TM</sup>	HS <sup>c</sup>	0.68	8-85	Gray	3000	Sphere One <sup>f</sup>
47	KLS-90	Extendo- sphere <sup>TM</sup>	HS <sup>c</sup>	0.56	4-05	Light Gray	1200	Sphere One <sup>f</sup>
48	KLS-125	Extendo- sphere <sup>TM</sup>	HS <sup>c</sup>	0.56	4-55	Light Gray	1200	Sphere One <sup>f</sup>
49	KLS-150	Extendo- sphere <sup>TM</sup>	HS <sup>c</sup>	0.56	4-55	Light Gray	1200	Sphere One <sup>f</sup>
50	KLS-300	Extendo- sphere <sup>TM</sup>	HS <sup>c</sup>	0.56	4-55	Light Gray	1200	Sphere One <sup>f</sup>
51	HA-300	Extendo- sphere <sup>TM</sup>	HS <sup>c</sup>	0.68	10-146	Gray	2500	Sphere One <sup>f</sup>
52	XIOM 512	Thermo- plastic	MPR <sup>d</sup>	0.96	10-100	White	508	XIOM Corp. <sup>k</sup>
53	XIOM 512	Thermo- plastic	MPR <sup>d</sup>	0.96	10-100	Black	508	XIOM Corp. <sup>k</sup>
54	CORVEL <sup>TM</sup> Black 78-7001	Thermo- plastic	Nylon Powder Coating	1.09	44-74	Black		ROHM & HASS <sup>g</sup>



TABLE 5-continued

First Particles								
First particle No.	First Particle (Filler) ID	First Particle Type	First Particle Details	(g/cc)	Particle Size Range ( $\mu\text{m}$ )	Color	Crush Strength (psi)	Source Location
55	Micro-glass 3082	Fibers	MMEGF <sup>e</sup>	1.05	16 $\times$ 120	White		Fibertec <sup>h</sup>
56	Micro-glass 9007D	Fibers	MMEGF <sup>e</sup>	0.53	10 $\times$ 150	White		Fibertec <sup>h</sup>
57	Tiger Drylac Series 49	Silane- Treated Polyester crosslinked with TGIC (triglycidyl isocyanurate)						Tiger Drylac USA, Inc. <sup>i</sup>
58	Soft- Sand ®	Rubber based			90, 180, or 300	Various colors		SoftPoint Indust. Copley, OH

<sup>a</sup>GPS—general purpose series<sup>b</sup>ceramic microspheres<sup>c</sup>hollow spheres<sup>d</sup>modified polyethylene resins<sup>e</sup>microglass milled E-glass filaments<sup>f</sup>Chattanooga, TN<sup>g</sup>Philadelphia, PA<sup>h</sup>Bridgewater, MA<sup>i</sup>Distributed by Eka Chem., Inc., Duluth, GA<sup>j</sup>St. Paul, MN<sup>k</sup>West Babylon, NY<sup>l</sup>St. Charles, IL

### 3.2 Second Particles

**[0081]** The coatings disclosed herein employ second particles (e.g., nanoparticles), which are particles that bear, or are associated with, hydrophobic and/or oleophobic compounds or moieties (i.e., moieties that are covalently or non-covalently bound). The hydrophobic moieties can be introduced by treating the particles to include moieties such as siloxanes, fluorinated hydrocarbons (e.g., partly or fully fluorinated hydrocarbons) or nonfluorinated hydrocarbons. In an embodiment, second particles suitable for the preparation of elastomer-based HP/OP coatings have a size from about 1 nanometer (nm) to about 25  $\mu\text{m}$  and are capable of binding covalently to one or more chemical moieties (groups or components) that provide the second particles, and the coatings into which they are incorporated, hydrophobicity, and when selected to include fluoroalkyl groups, hydrophobicity and oleophobicity.

**[0082]** In one embodiment the second particles have a surface area over 100, 150, 200, 250, or 300 square meters per gram ( $\text{m}^2/\text{g}$ ) of particulate. In another embodiment, where the particles are fumed silica, the surface area can be about or greater than 150, 175, 200, 225 or 250  $\text{m}^2/\text{g}$ .

**[0083]** Second particles having a wide variety of compositions may be employed in the durable HP/OP coatings described and employed herein. In some embodiments the second particles will be particles comprising metal oxides (e.g., aluminum oxides such as alumina, zinc oxides, nickel oxides, zirconium oxides, iron oxides, or titanium dioxides), or oxides of metalloids (e.g., metalloid oxides such as oxides of B, Si, Sb, Te and Ge) such as glass, silica (e.g., fumed silica), silicates, aluminosilicates, or particles comprising combinations thereof.

**[0084]** In some embodiments, the second particles may have an average size in a range selected from about 1 nm up

to about 25  $\mu\text{m}$  or more. Included within this broad range are embodiments in which the second particles have an average size in a range selected from: about 1 nm to about 10 nm, from about 10 nm to about 25 nm, from about 25 nm to about 50 nm, from about 50 nm to about 100 nm, from about 100 nm to about 250 nm, from about 250 nm to about 500 nm, from about 500 nm to about 750 nm, from about 750 nm to about 1  $\mu\text{m}$ , from about 1  $\mu\text{m}$  to about 5  $\mu\text{m}$ , from about 5  $\mu\text{m}$  to about 10  $\mu\text{m}$ , from about 10  $\mu\text{m}$  to about 15  $\mu\text{m}$ , from about 15  $\mu\text{m}$  to about 20  $\mu\text{m}$ , from about 20  $\mu\text{m}$  to about 25  $\mu\text{m}$ , from about 1 nm to about 100 nm, from about 2 nm to about 200 nm, from about 10 nm to about 200 nm, from about 20 nm to about 400 nm, from about 10 nm to about 500 nm; from about 40 nm to about 800 nm, from about 100 nm to about 1  $\mu\text{m}$ , from about 200 nm to about 1.5  $\mu\text{m}$ , from about 500 nm to about 2  $\mu\text{m}$ , from about 500 nm to about 2.5  $\mu\text{m}$ , from about 1  $\mu\text{m}$  to about 10  $\mu\text{m}$ , from about 2  $\mu\text{m}$  to about 20  $\mu\text{m}$ , from about 2.5  $\mu\text{m}$  to about 25  $\mu\text{m}$ , from about 500 nm to about 25  $\mu\text{m}$ , from about 400 nm to about 20  $\mu\text{m}$ , from about 100 nm to about 15  $\mu\text{m}$ , from about 1 nm to about 50 nm, from about 1 nm to about 400 nm, from about 1 nm to about 500 nm, from about 2 nm to about 120 nm, from about 5 nm to about 100 nm, from about 5 nm to about 200 nm; from about 5 nm to about 400 nm; from about 10 nm to about 300 nm; or from about 20 nm to about 400 nm.

**[0085]** In the above-mentioned embodiments, the lower size of second particles may be limited to particles greater than about 20 nm, about 25 nm, about 30 nm, about 35 nm, about 40 nm, about 45 nm, about 50 nm, or about 60 nm; and the upper size of second particles may be limited to particles less than about 20  $\mu\text{m}$ , about 10  $\mu\text{m}$ , about 5  $\mu\text{m}$ , about 1  $\mu\text{m}$ , about 0.8  $\mu\text{m}$ , about 0.6  $\mu\text{m}$ , about 0.5  $\mu\text{m}$ , about 0.4  $\mu\text{m}$ , about 0.3  $\mu\text{m}$ , about 0.2  $\mu\text{m}$ , or about 100 nm.



**[0086]** Any combination of particle size, particle composition, surface area, and/or percent composition in the coatings recited herein may be employed in preparing elastomer-based HP/OP coatings. Limitations on the upper and lower size of second particles may be used alone or in combination with any of the above-recited size limits on particle composition, surface area, percent composition in the coatings, and the like.

**[0087]** In some embodiments, the coatings may contain first particles in any of the above-mentioned ranges subject to either the proviso that the coatings do not contain only particles (e.g., first or second particles) with a size of 25  $\mu\text{m}$  or less, or the proviso that the coatings do not contain more than an insubstantial amount of second particles with a size of 25  $\mu\text{m}$  or less (recognizing that separation processes for particles greater than 25  $\mu\text{m}$  may ultimately provide an unintended, insubstantial amount of particles that are 25  $\mu\text{m}$  or less). An insubstantial amount of particles is less than 3% by weight or number of those particles, but it can also be less than 0.5%, 1%, or 2% wherever recited.

**[0088]** In other embodiments, second particles have an average size greater than 30  $\mu\text{m}$  and less than 250  $\mu\text{m}$ , and coatings comprising those particles do not contain more than insubstantial amounts of particles (e.g., first and second particles) with a size of 30  $\mu\text{m}$  or less. In yet other embodiments, the coatings do not contain only particles (e.g., first and second particles) with a size of 40  $\mu\text{m}$  or less, or particles with a size of 40  $\mu\text{m}$  or less in substantial amounts. In addition, in still other embodiments, the coatings do not contain only particles (e.g., first and second particles) with a size of 50  $\mu\text{m}$  or less, or particles with a size of 50  $\mu\text{m}$  or less in substantial amounts.

**[0089]** In other embodiments, such as where the second particles are prepared by fuming (e.g., fumed silica or fumed zinc oxide), the second particles may have an average size in a range selected from about 1 nm to about 50 nm, from about 1 nm to about 100 nm, from about 1 nm to about 400 nm, from about 1 nm to about 500 nm, from about 2 nm to about 120 nm, from about 5 nm to about 100 nm, from about 5 nm to about 200 nm, from about 25 nm to about 100 nm, from about 30 nm to about 200 nm, from about 5 nm to about 400 nm, from about 10 nm to about 300 nm, from about 20 nm to about 400 nm, or from about 50 nm to about 400 nm.

**[0090]** As indicated above, second particles are treated to introduce one or more moieties (e.g., groups or components) that impart HP/OP properties to the particles, either prior to incorporation into the compositions that will be used to apply coatings or after incorporation into the coatings. In some embodiments, the second particles are treated with a silanizing agent, a silane, a siloxane or a silazane, to introduce hydrophobic/superhydrophobic and/or oleophobic/superoleophobic properties to the particles (in addition to any such properties already possessed by the particles).

**[0091]** In one embodiment, second particles are silica, silicates, alumina (e.g.,  $\text{Al}_2\text{O}_3$ ), titanium oxide, or zinc oxide that are treated with one or more silanizing agents, e.g., compounds of formula (I) (below). In other embodiments, second particles are comprised of silica, silicates, alumina (e.g.,  $\text{Al}_2\text{O}_3$ ), titanium oxide, or zinc oxide that are treated with a siloxane. In another embodiment, the second particles are silica, silicates, glass, alumina (e.g.,  $\text{Al}_2\text{O}_3$ ), titanium oxide, or zinc oxide, treated with a silanizing agent, a siloxane or a

silazane. In another embodiment, the second particles may be a fumed metal or metalloid (e.g., particles of fumed silica or fumed zinc oxide).

**[0092]** In embodiments where a silanizing agent is employed, the silanizing agent may be a compound of the formula (I):



**[0093]** where n is an integer from 1 to 3;

**[0094]** each R is independently selected from

**[0095]** (i) alkyl or cycloalkyl group optionally substituted with one or more fluorine atoms,

**[0096]** (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,

**[0097]** (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,

**[0098]** (iv)  $\text{C}_{6 \text{ to } 14}$  aryl, optionally substituted with one or more substituents independently selected from halo or alkoxy, and haloalkoxy substituents,

**[0099]** (v)  $\text{C}_{4 \text{ to } 20}$  alkenyl or  $\text{C}_{4 \text{ to } 20}$  alkynyl, optionally substituted with one or more substituents independently selected from halo, alkoxy, or haloalkoxy, and

**[0100]** (vi)  $-\text{Z}-((\text{CF}_2)_q(\text{CF}_3))_r$ , wherein Z is a  $\text{C}_{1 \text{ to } 12}$  or a  $\text{C}_{2 \text{ to } 8}$  divalent alkane radical or a  $\text{C}_{2 \text{ to } 12}$  divalent alkene or alkyne radical, q is an integer from 1 to 12, and r is an integer from 1 to 4;

**[0101]** each X is independently selected from  $-\text{H}$ ,  $-\text{Cl}$ ,  $-\text{I}$ ,  $-\text{Br}$ ,  $-\text{OH}$ ,  $-\text{OR}^2$ ,  $-\text{NHR}^3$ , or  $-\text{N}(\text{R}^3)_2$  group;

**[0102]** each  $\text{R}^2$  is an independently selected  $\text{C}_{1 \text{ to } 4}$  alkyl or haloalkyl group; and

**[0103]** each  $\text{R}^3$  is an independently selected H,  $\text{C}_{1 \text{ to } 4}$  alkyl, or haloalkyl group.

**[0104]** In some embodiments, R is an alkyl or fluoroalkyl group having from 6 to 20 carbon atoms.

**[0105]** In other embodiments, R is an alkyl or fluoroalkyl group having from 8 to 20 carbon atoms.

**[0106]** In other embodiments, R is an alkyl or fluoroalkyl group having from 10 to 20 carbon atoms.

**[0107]** In other embodiments, R is an alkyl or fluoroalkyl group having from 6 to 20 carbon atoms and n is 3.

**[0108]** In other embodiments, R is an alkyl or fluoroalkyl group having from 8 to 20 carbon atoms and n is 3.

**[0109]** In other embodiments, R is an alkyl or fluoroalkyl group having from 10 to 20 carbon atoms and n is 3.

**[0110]** In other embodiments, R has the form  $-\text{Z}-((\text{CF}_2)_q(\text{CF}_3))_r$ , wherein Z is a  $\text{C}_{1 \text{ to } 12}$  divalent alkane radical or a  $\text{C}_{2 \text{ to } 12}$  divalent alkene or alkyne radical, q is an integer from 1 to 12, and r is an integer from 1 to 4.

**[0111]** 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.



[0112] 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.

[0113] In any of the previously mentioned embodiments of compounds of formula (I), X may be independently selected from H, Cl,  $-\text{OR}^2$ ,  $-\text{NHR}^3$ ,  $-\text{N}(\text{R}^3)_2$ , 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.

[0114] 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.,  $\text{R}_3\text{Si}-$ ,  $\text{R}_2\text{X}_1\text{Si}-$ , 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.,  $\text{R}_3\text{Si}-$ ,  $\text{R}_2\text{X}_1\text{Si}-$ , or  $\text{RX}_2\text{Si}-$  groups).

[0115] 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:

[0116] (tridecafluoro-1,1,2,2-tetrahydrooctyl)silane (SIT8173.0);

[0117] (tridecafluoro-1,1,2,2-tetrahydrooctyl)trichlorosilane (SIT8174.0);

[0118] (tridecafluoro-1,1,2,2-tetrahydrooctyl)triethoxysilane (SIT8175.0);

[0119] (tridecafluoro-1,1,2,2-tetrahydrooctyl)trimethoxysilane (SIT8176.0);

[0120] (heptadecafluoro-1,1,2,2-tetrahydrodecyl)dimethyl(dimethylamino)silane (SIH5840.5);

[0121] (heptadecafluoro-1,1,2,2-tetrahydrodecyl)tris(dimethylamino)silane (SIH5841.7);

[0122] n-octadecyltrimethoxysilane (SIO6645.0); n-octyltriethoxysilane (SIO6715.0); and

[0123] 3,3,4,4,5,5,6,6,6-nonafluorohexyldimethyl(dimethylamino)silane (SIN6597.4)

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

[0124] Another group of reagents that can be employed to prepare first or second particles with hydrophobic and/or oleophobic properties include

[0125] (tridecafluoro-1,1,2,2-tetrahydrooctyl)trichlorosilane;

[0126] (tridecafluoro-1,1,2,2-tetrahydrooctyl)triethoxysilane;

[0127] nonafluorohexyldimethylchlorosilane;

[0128] (tridecafluoro-1,1,2,2-tetrahydrooctyl)trimethoxysilane;

[0129] 3,3,4,4,5,5,6,6,6-nonafluorohexyldimethyl(dimethylamino)-silane;

[0130] nonafluorohexylmethyldichlorosilane;

[0131] nonafluorohexyltrichlorosilane;

[0132] nonafluorohexyltriethoxysilane; and

[0133] nonafluorohexyltrimethoxysilane.

[0134] In one embodiment, the coating compositions set forth herein comprise silica second particles treated with nonafluorohexyltrichlorosilane.

[0135] In addition to the silanizing agents recited above, a variety of other silanizing agents can be used to alter the properties of second particles and to provide hydrophobic and/or oleophobic properties. In some embodiments, second particles may be treated with an agent selected from dimethyldichlorosilane, hexamethyldisilazane, octyltrimethoxysilane, or tridecafluoro-1,1,2,2-tetrahydrooctyl trichlorosilane. In such embodiments, the second particles may be silica. Silica second particles treated with such agents may have an average size in a range selected from about 1 nm to about 50 nm, from about 1 nm to about 100 nm, from about 1 nm to about 400 nm, from about 1 nm to about 500 nm, from about 2 nm to about 120 nm, from about 5 nm to about 150 nm, from about 5 nm to about 400 nm, from about 10 nm to about 300 nm, from about 20 nm to about 400 nm, or from about 50 nm to about 250 nm.

[0136] Other agents can be used to modify second particles, including, but not limited to, one or more of: polydimethylsiloxane, gamma-aminopropyltriethoxysilane, Dynasylan® A (tetraethylorthosilicate), hexamethyldisilazane, and Dynasylan® F 8263 (fluoroalkylsilane), any one or more of which may be used alone or in combination with the silanizing agents recited herein.

[0137] Two attributes of silanizing agents that may be considered for the purposes of their reaction with second particles and the introduction of hydrophobic or oleophobic moieties are the leaving group (e.g., X groups of compounds of the formula (I)) and the terminal functionality (e.g., R groups of compounds of the formula (I)). A silanizing agent's leaving group(s) can determine the reactivity of the agent with the first or second particle(s), or other components of the coating, if applied after a coating has been applied. Where the first or second particles are a silicate or silica (e.g., fumed silica) the leaving group can be displaced to form  $\text{Si}-\text{O}-\text{Si}$  bonds. Leaving group effectiveness is ranked in the decreasing order as chloro>methoxy>hydro (H)>ethoxy (measured as trichloro>trimethoxy>trihydro>triethoxy). This ranking of the leaving groups is consistent with their bond dissociation energy. The terminal functionality determines the level of hydrophobicity that results from application of the silane to the surface.

### [0138] 3.2.1 Some Sources of Second Particles

[0139] Second particles such as those comprising fumed silica may be purchased from a variety of suppliers including, but not limited to, Cabot Corp., Billerica, Mass. (e.g., Nanogel TLD201, CAB-O-SIL® TS-720 (silica, pretreated with polydimethylsiloxane), and M5 (untreated silica)) and Evonik Industries, Essen, Germany (e.g., ACEMATT® silica such as untreated HK400, AEROXIDE® silica, AEROXIDE®  $\text{TiO}_2$  titanium dioxide, and AEROXIDE® Alu alumina).

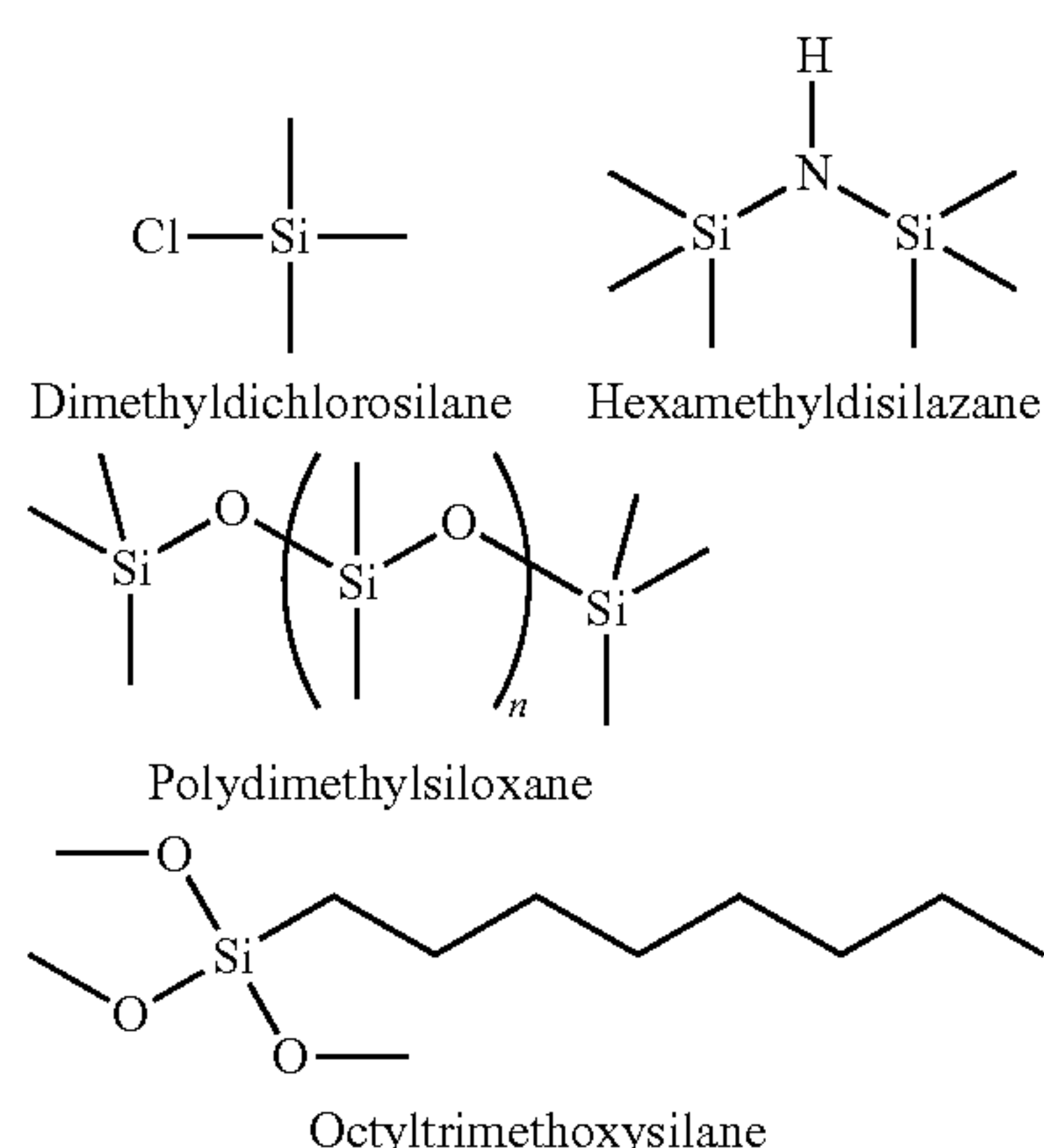
[0140] Some commercially available second particles are set forth in Table 6 along with their surface treatment by a silanizing agent or polydimethyl siloxane.



TABLE 6

Some commercially available second particles					
Product Name	Surface Treatment	Level of Treatment	Nominal BET Surface Area of Base Product (m <sup>2</sup> /g)	Particle Size (nm)	Product Source
M-5	None	None	200	—	Cab-O-Sil
Aerosil ® 200	None	None	200	12	Evonik
Aerosil ® 255	None	None	255	—	Evonik
Aerosil ® 300	None	None	300	7	Evonik
Aerosil ® 380	None	None	380	7	Evonik
HP-60	None	None	200	—	Cab-O-Sil
PTG	None	None	200	—	Cab-O-Sil
H-5	None	None	300	—	Cab-O-Sil
HS-5	None	None	325	—	Cab-O-Sil
EH-5	None	None	385	—	Cab-O-Sil
TS-610	Dimethyldichlorosilane	Intermediate	130	—	Cab-O-Sil
TS-530	Hexamethyldisilazane	High	320	—	Cab-O-Sil
TS-382	Octyltrimethoxysilane	High	200	—	Cab-O-Sil
TS-720	Polydimethylsiloxane	High	200	—	Cab-O-Sil
Aerosil ® R202	Polydimethylsiloxane	—	100	14	Evonik
Aerosil ® R504	Hexamethyldisilazane (HMDS) and aminosilane	—	125-175	—	Evonik
Aerosil ® R812S	HMDS based on Aerosil ® 300	—	220	—	Evonik

BET Surface Area is Brunauer, Emmett and Teller surface area



[0141] As purchased, the particles may be untreated (e.g., M5 silica) and may not possess any HP/OP properties. Such untreated particles can be treated to covalently attach one or more groups or moieties to the particles that give them HP/OP properties, for example, by treatment with the silanizing agents discussed above.

#### [0142] 3.2.2 Dispersants for Second Particles

[0143] Second particles can be applied to a base coating of elastomeric binder after it has been applied to the surface of an object (or a part thereof) in the form of a second component having a composition comprising one or more independently selected second particles as described above (e.g., second particles having a size of about 1 nanometer (nm) to about 25 microns (μm) wherein said particles comprise one or more independently selected alkyl, haloalkyl, or perfluoroalkyl

moieties bound, either directly or indirectly, to said second particles; wherein said second component optionally comprises one or more solvents (liquid dispersants).

[0144] If the elastomeric coating has not dried, or has been subjected to a solvent that dissolves at least the outermost portion of the binder (e.g., renders it sufficiently tacky), second particles may be applied directly to the elastomeric binder by contacting the second particles with the binder. Second particles may be contacted with the surface by any suitable means, including spraying them on the surface using a stream of gas (e.g., air, nitrogen, or an inert gas), exposing the binder coating to particles suspended in a gas, or contacting the base coat of elastomeric binder with a fluidized bed of second particles.

[0145] Second particles can also be applied to a base coating of elastomeric binder in a second coating component that, in addition to the second particles, contains a solvent (dispersant) that dissolves, expands or swells the outermost portion of the binder sufficiently (e.g., renders it tacky) to permit the second particles to become bound in at least the outermost portion of the binder base coat. Where second components of the coating composition comprise a solvent, the second particles are dispersed in the solvent for application. Second particles, and particularly smaller second particles (e.g., 1-50 nm or 1-100 nm), may form aggregates in solvents used as dispersants.

[0146] Suitable solvents include those with a surface energy lower than water including, but not limited to: alcohols, ketones, acetone, methyl ethyl ketone (MEK), ethyl acetate, toluene, xylene, isopropyl acetate, 1,1,1-trichloroethane, methyl isobutyl ketone (MIBK), tertbutyl acetate (t-butyl acetate), cyclohexane, methyl-cyclohexane, or mixtures comprising any two, three, four or more thereof. In an embodiment, the solvents are non-aqueous (e.g., they contain



less than 10%, 5%, 4%, 3%, 2%, 1%, or 0.5% of water by weight or they contain only insubstantial amounts of water). Solvents that are miscible with water are employed in the second coating component in another embodiment. In another embodiment, the solvent comprises a non-aqueous water miscible solvent. In one embodiment, the solvent employed in the second coating component is acetone or is comprised of acetone. In another embodiment the solvent employed in the second coating component is NMP (N-methylpyrrolidone) or is comprised of NMP. In other embodiments, the solvent employed in the second coating composition comprises a mixture of acetone or NMP with water, particularly a minor proportion of water (e.g., less than about 5%, less than about 4%, less than about 2%, less than about 1%, or less than about 0.5% water).

**[0147]** In one embodiment, the second component of the coating composition (i.e., the top coat) comprises:

**[0148]** i) one or more independently selected second particles having a size of about 1 nanometer to about 25 microns, wherein said second particles comprise one or more independently selected alkyl, haloalkyl, or perfluoroalkyl moieties bound, either directly or indirectly, to said second particles; and

**[0149]** ii) optionally, one or more independently selected solvents, wherein when said one or more solvents are present, said second particles may be present in a weight percent range selected from (0.1-1, 1.0-2.0, 0.2-2.0, 0.5-1.5, 0.5-2.0, 0.75-2.5, 1.5-2.0, 1.5-2.5, 2.0-3.0, 2.0-3.5, or 2.5-3.5) based on the weight of the one or more solvents and second particles.

**[0150]** In another embodiment, the second component of the coating composition (i.e., the top coat) comprises:

**[0151]** (i) 0.1 to 3.5 parts by weight (e.g., 0.1-1, 1.0-2.0, 0.2-2.0, 0.5-1.5, 0.5-2.0, 0.75-2.5, 1.5-2.0, 1.5-2.5, 2.0-3.0, 2.0-3.5, or 2.5-3.5) of second particles that comprise one or more independently selected alkyl, haloalkyl, or perfluoroalkyl moieties bound, either directly or indirectly, to said second particles, or one or more siloxanes or silazanes associated with the second particles;

**[0152]** (ii) a fluorinated polyolefin, (e.g., a polymer of tetrafluoroethylene, hexafluoropropylene and vinylidene fluoride, such as Dyneon™ THV); and/or a Fluoroethylene-Alkyl Vinyl Ether (FEVE) copolymer; and

**[0153]** (iii) a solvent for a the remainder of a total of 100 parts by weight.

**[0154]** In another embodiment, the fluorinated polyolefin (e.g., a polymer of tetrafluoroethylene, hexafluoropropylene and vinylidene fluoride, such as Dyneon™ THV), if present, comprises from 0.1 to 1.0 parts by weight (e.g., 0.1-0.5, 0.5-1.0, or 0.3-0.7 parts) of the composition.

**[0155]** In another embodiment, the Fluoroethylene-Alkyl Vinyl Ether (e.g., the constituent polymer found in Lumiflon™), if present, comprises 0.06 to 0.6 parts by weight (e.g., 0.06-0.01, 0.1-0.2, 0.2-0.4, or 0.4-0.6 parts) of the composition. In such an embodiment the FEVE may have an average molecular weight of about 1,000 to 3,000 (e.g., about 1,000-2,000, 2,000-3,000, 1,500-2,500, or about 1,000, about 1,500, about 2,000, about 2,500, or about 3,000 Dalton). Accordingly, one embodiment of the second component comprises per 100 parts by weight:

**[0156]** i) 0.1 to 3.5 parts by weight (e.g., 0.1-1, 1.0-2.0, 0.2-2.0, 0.5-1.5, 0.5-2.0, 0.75-2.5, 1.5-2.0, 1.5-2.5, 2.0-3.0, 2.0-3.5, or 2.5-3.5) of one or more independently selected second particles having a size of about 1 nanometer to about 25 microns, wherein said second particles comprise one or

more independently selected alkyl, haloalkyl, or perfluoroalkyl moieties bound, either directly or indirectly, to said second particles, or one or more siloxanes or silazanes associated with said second particles;

**[0157]** ii) 0.1 to 1.0 parts by weight (e.g., 0.1-0.5, 0.5-1.0, or 0.3-0.7 parts) of a fluorinated polyolefin, (e.g., a polymer of tetrafluoroethylene, hexafluoropropylene and vinylidene fluoride, such as Dyneon™ THV); and/or

**[0158]** 0.06 to 0.6 parts by weight (e.g., 0.06-0.01, 0.1-0.2, 0.2-0.4, or 0.4-0.6 parts) of a Fluoroethylene-Alkyl Vinyl Ether (FEVE) copolymer, having an average molecular weight of about 1,000 to 3,000 (e.g., about 1,000-2,000, 2,000-3,000, 1,500-2,500, or about 1,000, 1,500, 2,000, 2,500, or 3,000 Da);

**[0159]** and

**[0160]** (iii) one or more solvent for a the remainder of a total of 100 parts by weight.

**[0161]** Where the solvent employed in second coating compositions dissolves or renders at least the outermost layer of the elastomeric binder “tacky,” second particles can be introduced into completely dried and cured base coats of elastomeric binder. That permits the repair of worn or abraded coatings that have lost HP/OP behavior over all or part of their surface.

#### 4.0 SURFACE PREPARATION AND PRIMING

**[0162]** To improve the adherence and performance of the coatings described herein the surface to be coated, in whole or in part, should be clean, free of contaminants and capable of supporting the coatings (e.g., not friable).

**[0163]** Performance of the coatings in terms of their durability can be significantly improved by the application of a primer. Any primer compatible with both the surface of the object and the elastomeric coating can be employed.

**[0164]** A variety of primer compositions may be employed. In one embodiment the primers comprise one or more polymers that are elastic (i.e., have viscoelasticity), such as those that comprise the binder used in the first component of the coating compositions described herein (e.g., SBCs). In one embodiment, the primer comprises one or more polymers that are elastic (i.e., have viscoelasticity, e.g., SBCs) and a tackifier. In one embodiment, the primer is a Plasti Dip™ metal primer f938 hp.

**[0165]** In one embodiment, when a tackifier is employed, it may be selected from resins (e.g. rosins and their derivatives; terpenes and modified terpenes; aliphatic, cycloaliphatic and aromatic resins (C5 aliphatic resins, C9 aromatic resins, and C5/C9 aliphatic/aromatic resins); hydrogenated hydrocarbon resins (e.g., Regalrez™ 1094, Eastman Chemical Co., Kingsport Tenn.), and mixtures thereof and/or terpene-phenol resins). In one embodiment the tackifier is an ester of hydrogenated rosin (e.g., FORAL™ 105-E ester of hydrogenated rosin).

**[0166]** In other embodiments the primer is an elastomeric primer comprising triblock copolymers of styrene and ethylene/butylene and an ester of a hydrogenated thermoplastic rosin (e.g., FORAL™ 105-E, Eastman Chemical). The polystyrene content of the triblock copolymers will typically be from about 8% to about 14%, from about 12% to about 20%, from about 18% to about 28%, from about 22% to about 32%, from about 26% to about 36%, about 8%, about 9%, about 10%, about 11%, about 12%, about 13%, about 14%, about 16%, about 18%, about 19%, about 20%, about 22%, about 24%, about 26%, about 28%, about 30%, about 32%, about



34%, or about 36%. Mixtures of any two or more, three or more, or four or more of such triblock copolymers may also be employed in the primer composition, and any one or more of such triblock copolymers may optionally comprise 1% to 3%, 1.4% to 2.0%, 1% to 1.4%, 1.6% to 3%, or 2% to 3% bound maleic anhydride (maleated copolymers). Any of the foregoing triblock copolymers may be linear or branched (e.g., dendrimers or arborols).

**[0167]** In one embodiment wherein the elastomeric primer comprises triblock copolymers of styrene and ethylene/butylene and an ester of a hydrogenated thermoplastic rosin, the primer comprises two different maleated triblock copolymers of styrene and ethylene/butylene with a polystyrene: a first triblock copolymer of styrene and ethylene/butylene with a polystyrene having 0.4% to 1.6% (e.g., 0.5% to 1.5%, 0.6% to 1.4%, or 0.7% to 1.3%) substitution of maleic anhydride by weight of the first triblock copolymer (and optionally less than 0.3% free maleic anhydride); and a second triblock copolymer of styrene and ethylene/butylene with a polystyrene having 1.1% to 2.5% (e.g., 1.3 to 2.3 or 1.4 to 2.4%) substitution of maleic anhydride by weight of the second triblock copolymer. In such an embodiment the first and/or second triblock copolymers may be linear or branched copolymers (e.g., arborols or dendrimers), and the second triblock copolymers may be present in a weight ratio from about 4:1 to about 6.5:1 (e.g., the first copolymer to second copolymer ratio is about 4:1 to about 5.5:1, about 5:1 to about 6:1, or about 5.5:1 to about 6.5:1). The ratio of the total triblock copolymer (first and second) to the ester of a hydrogenated thermoplastic rosin is typically 1:5 to 2.5:5 (triblock copolymers: ester(s) of hydrogenated thermoplastic rosin). Ratios for all three components include 7:1:25, 7.2:1.3:25, 7.6:1.6:25, and 8:1.8:25 (first triblock copolymer: second triblock copolymer: ester of a hydrogenated thermoplastic rosin).

**[0168]** In any of the foregoing embodiments the primers may also comprise insubstantial amounts (e.g., less than about 2% by weight of the polymers present in the binder, such as less than 1.0%, 0.75%, 0.5%, 0.25%, or 0.1%) of colorants or particulates that are insoluble in the solvents that dissolve the elastomeric polymers and/or that would block the transmission of visible light in the dried cured coating (e.g., talc added for the flowability of particles of the polymers as produced).

**[0169]** In any of the foregoing embodiments the primers may also comprise first particles for texture development in the primer and/or the base coat (i.e., a base coat of elastomeric binder with or without first particles).

**[0170]** In another embodiment, when a tackifier is employed it may be a hydrocarbon resin. In one embodiment where hydrocarbon resins are employed, they may be selected from resins such as those prepared from petroleum based feedstocks (e.g., aliphatic (C5), aromatic (C9), DCPD (dicyclopentadiene) resins, or mixtures of these).

**[0171]** Elastomeric primers not only promote bonding to substrate surfaces such as metals, but also provide for improved adhesion to the base coat. In addition, such primers compensate for differences in the coefficient of thermal expansion between the HP/OP coating and the substrate.

**[0172]** In other embodiments, primers comprise polyurethane polymers. Such polyurethane containing primers ("polyurethane primers") demonstrate excellent bonding to many substrates including metallic substrates. When employing a polyurethane primer, it is possible to incorporate first

particles into the primer and/or the base coat (a base coat of elastomeric binder with or without first particles) for texture development. Thus, in addition to promoting adhesion, the primer can also serve to develop texture with increased surface area for improved adhesion of the base coat comprising an elastomeric binder, develop wear resistance, and develop hydrophobicity/oleophobicity. The HP/OP coatings applied over the elastomeric primers or two part polyurethane primers described herein display essentially equal resistance to the loss of hydrophobicity in Taber Abraser wear/abrasion resistance tests (as measured by Taber Abraser cycles) when abrasive (CS-10) and soft (CS-0) wheels are employed.

## 5.0 COATING APPLICATION METHOD

**[0173]** The coatings described herein (including any underlying primer) 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, one or more of a primer, base coat and/or top coat are applied by spraying. In another embodiment, each of a primer (if present), base coat and top coat are applied by spraying.

**[0174]** In one embodiment the first and second coating compositions described herein are separately prepackaged in a delivery system/apparatus for spray applications, such as aerosol canisters (e.g., pre-pressurized aerosol cans). In such an embodiment, the first component and second component can be packaged in separate delivery systems/apparatus. A propellant is 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. The propellant may be a gas (e.g., air or nitrogen) or a liquefiable gas having a vapor pressure sufficient to propel and aerosolize the first and/or second components as they exit their delivery system/apparatus. Some exemplary propellants include: liquefied petroleum gases, ethers (e.g., dimethyl ether (DME) and diethyl ether); C1-C4 saturated hydrocarbons (e.g., methane, ethane, propane, n-butane, and isobutene); 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)), and mixtures comprising any two, three or more of the foregoing. In another embodiment, the propellant is a blend of n-butane and propane.

**[0175]** Generally, the surfaces 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.

**[0176]** The coatings described herein can be applied to virtually any substrate to provide HP/OP properties. The choice of coatings and coating processes that will be used may be affected by the compatibility of the substrate and its surface to the coating process and the component of the 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.

**[0177]** 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 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.

**[0178]** The shape, dimensions and placement of HP/OP coatings on surfaces can be controlled by a 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 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.

**[0179]** In another embodiment HP/OP 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 superhydrophobic 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 or superhydrophobic. 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 an HP/OP coating and adhesive is applied to the other side. Once such HP/OP ribbons, tapes, and sheets are prepared, they can be applied to any type of surface including metal, ceramic, glass, plastic, or wood surfaces, for a variety of purposes.

**[0180]** In one embodiment, HP/OP coatings are applied to the surface of an object by a method comprising:

**[0181]** (a) applying a first component to all or part of the surface of an object; followed by

**[0182]** (b) applying a second component to all or the part of the surface of said object to which said first component was applied.

**[0183]** In another embodiment, HP/OP coatings are applied by a coating method comprising:

**[0184]** (a) applying a first component of a two-component coating composition to all or part of the surface of an object; followed by

**[0185]** (b) applying a second component of the two-component coating composition to all or the part of the surface of said object to which said first component was applied.

**[0186]** In such an embodiment, the first component and second component may be applied using one or more methods selected independently from brushing, painting, printing, stamping, rolling, dipping, spin-coating, or spraying. Such a process is at least a two-step process, but may include additional steps, such as a second application of the second component making it a three or more step process.

**[0187]** In an embodiment, one or both of the first and second components are applied to a surface by spraying in a method comprising:

**[0188]** (a) spraying a first component of a two-component coating composition (e.g., an elastomeric binder and first particles) on all or part of the surface of an object; followed by

**[0189]** (b) spraying a second component of said two-component coating composition (e.g., second particles and optionally a solvent) on all or part of the surface of an object to which said first component was applied. In one embodiment, the spraying may be conducted using first, second, or both components packaged in aerosol spray canisters.

**[0190]** In an embodiment of the above-described coating process, a base coat of elastomeric polymer binder and first particles (e.g., EXPANCEL particles) is applied as the first component. Once the base coat loses sufficient solvent so that it: does not run when a second component is applied; is close to being dry to touch (e.g., is tacky); becomes dry to touch; or is dry, a second coating component (e.g., second particles and an optional dispersant such as acetone) is applied. The solvent in the dispersant helps attach the functional second particles to the binder of the base coat. Other than allowing any solvent used as a dispersant to evaporate no additional curing cycle is needed.

**[0191]** The coating obtained is durable and delivers HP/OP behavior and can be applied to a variety of substrates including metals, ceramics, polymeric and fabrics and in a number of specific applications as set forth below.

## 6.0 APPLICATIONS

**[0192]** The elastomeric coating described herein may be employed in a variety of applications including, but not limited to, coatings for all or part of:

**[0193]** 1) electronic equipment and their electronic components or subassemblies (e.g., circuit boards), including, but not limited to: cell phones, laptop computers, electronic tablets (e.g., iPads), cameras, video games, Global Positioning System (GPS) devices, radios, MP3 and electronic music players, watches, video equipment, security systems, satellite dishes and other portable electronics;

**[0194]** 2) shoes (e.g., athletic shoes, casual shoes, dress shoes) and apparel for medical and recreational use;

**[0195]** 3) toys such as toy vehicles (e.g., trucks, cars), bikes, scooters, playground equipment (e.g., swings, slides, teeter-totters), water toys, and toys for use in bathtubs;

**[0196]** 4) cleaning products—toilet brushes, toilet plungers, mops, dust mops and cloths;

**[0197]** 5) furniture and cooking preparation and serving surfaces including both indoor and outdoor furniture (e.g., lawn/patio furniture and park furniture such as tables, chairs and benches) or employed as spill resistant borders on surfaces that are substantially horizontal.

**[0198]** 6) pet products (e.g., litter boxes, litter scoopers, drinking and food bowls, collars, litter particles, animal beds);

**[0199]** 7) farm tools and home and garden tools including shovels, spades, and rakes;

**[0200]** 8) outdoor and exercise equipment (e.g., skis, snow boards), balls, in-line skates, roller skates);

**[0201]** 9) appliances—portions or entire refrigerator plates (e.g., spill proof borders), freezer liners, parts in washing machines, dishwashers, dehumidifiers, humidifiers, and dryers;

**[0202]** 11) baby/toddler products (e.g., car seats, potty seats, bibs, silverware (made from plastics), cups, plates and diapers (or parts thereof);

**[0203]** 12) food and beverage containers (e.g., bottles and containers for beverages, water, food);



- [0204] 13) sports equipment including balls (e.g., baseballs, tennis balls, footballs, soccer balls), gloves, backpacks, and tents;
- [0205] 14) bedding (sheets, mattresses, pillows, blankets);
- [0206] 15) food processing equipment and kitchen equipment including coatings and/or spill resistant borders for counters, backsplashes, the walls behind counters where food is prepared, and abattoirs (e.g., wall coatings and/or curtains used to section off a slaughter floor);
- [0207] 16) superhydrophobic body spray;
- [0208] 17) automotive parts (e.g., bumpers, internal plastic parts, engine parts, structural parts, fender well (wheel well) liners, and car seats, particularly for convertibles);
- [0209] 18) protective equipment (e.g., helmets, pads, and uniforms);
- [0210] 19) building products (e.g., rain spouts, doors, counters (polymer), flooring, ceilings, screens, and roofing);
- [0211] 20) laboratory equipment (e.g., trays, storage bins, tools, petri dishes, funnels, tubing and animal cages);
- [0212] 21) electrical equipment (e.g., electrical housings, electrical wiring, motors, switches, insulators, and circuit boards);
- [0213] 22) communications equipment (e.g., satellite dishes, antennas, and communications towers);
- [0214] 23) plastic and/or metal tubing and piping (e.g., PVC piping, copper piping, plastic and steel piping);
- [0215] 24) lavatory/bathroom equipment and fixtures (e.g., urinals, toilets, toilet seats, air and/or heat hand drying equipment, potty seat bowls, counters, sinks, and soap dispensers);
- [0216] 25) medical products including: beds and bed parts, bed pans, tubing, tubular products, catheters, stents, surgical tools and operating room equipment (such as robotic surgical tools), operating room equipment (e.g., tables, light fixtures), walls, floors, sinks, imaging equipment/machinery, laboratory testing equipment/machinery, and medical instruments (e.g., medical instruments used in surgical and nonsurgical applications);
- [0217] 26) wound care products, spray-on bandages, regular bandages, and body affecting products (e.g., skin and/or hair spray; and
- [0218] 27) aviation and boating equipment (e.g., airplane fuselage, wings and instrumentation), and boat bottoms, decks, and other places throughout a boat.
- [0219] Use of the coating can be facilitated by providing the first and second components for preparing the coatings described herein in a form that permits facile application. In one embodiment the first and/or second components are pre-packaged in solvent or propellant delivery systems such as aerosol canisters (e.g., aerosol cans).

## 7.0 COATING EVALUATION

- [0220] Coatings prepared using the elastomeric binder first component and second coating composition described herein can be evaluated using one or more criteria including, but not limited to:
- [0221] 1. transparency and appearance, which are evaluated both quantitatively and qualitatively;
- [0222] 2. durability of the SH/OP behavior (wear resistance of the coating) to an applied force using:
  - [0223] 2a. semi-quantitative glove rub test in which the thumb of a latex rubber gloved hand is stroked by hand over the surface of the coating that has been applied to a

substantially planar surface until the coating no longer shows superhydrophobic behavior. This test is a proxy for the ability of the surface to be handled and retain its HP/OP properties. During the test, the area of the surface contacted with the rubber glove is approximately 25 mm×25 mm and the force applied approximately 300 g (or about 0.5 g/square mm). The end of superhydrophobic behavior is judged by the failure of more than half of the water droplets applied (typically 20) to the tested surface to run (roll) off when the surface is inclined at 5 degrees from horizontal. FIG. 4 shows an exemplary testing apparatus used to determine the end of SH/OP,

[0224] 2b. loss of superhydrophobic behavior can also be judged after the surface is subject to the action of a cylindrical rubber finger moved across the surface. The finger is rubbed across the surface using a motorized American Association of Textile Chemists and Colorists (AATCC) CM-5 Crockmeter fitted with a 14/20 white rubber septum (outside diameter of 13 mm and inside diameter of 7 mm with a contact surface area of 94 mm<sup>2</sup>) to contact the coating with a force of 9N (Ace Glass, Inc., Vineland, N.J., Catalog No. 9096-244). 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 droplets) to run (roll) off when the surface is inclined at 5 degrees from horizontal,

[0225] 2c. loss of superhydrophobic behavior when the samples are subject to Taber Abraser testing using CS-10 (abrasive) and/or CS-0 (non-abrasive) wheels at the indicated loads and speeds to determine the point at which the surfaces lose superhydrophobicity. Unless indicated otherwise, a load of 1,000 g is employed. All Taber tests were conducted at a speed of 95 rpm unless stated otherwise. 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,

[0226] 2d. time to the loss of superhydrophobicity under a shower of water. Water is applied from a showerhead placed 152.4 cm (60 inches) above a substantially planar test surface inclined at 5 degrees from the horizontal, the showerhead having 70 nozzles with a 1 mm diameter orifice arranged in 5 spokes of 5 nozzles and 15 spokes of 3 nozzles about a central point on the circular showerhead. The apparatus delivers a shower of 6 liters of water per minute using about 137900 to about 310275 Pa (about 20 to about 45 psi) over an approximately circular area of about 150 cm in diameter at the level of the test surface. The time to loss of superhydrophobic behavior is determined to be the period of time after which water droplets from the shower begin to “stick” to the surface (no longer freely run off the surface) of a sample placed in the shower;

- [0227] 3. coating thickness and/or surface roughness, expressed as the average roughness (Ra) unless stated otherwise. Surface roughness has been found to be an indicator that positively correlates with abrasion resistance (increasing abrasion resistance with increasing roughness);
- [0228] 4. the ability of coated surfaces to resist ice formation in dynamic testing and the adherence of ice to surfaces;
- [0229] 5. electrical properties including resistance and permittivity'



**[0230]** 6. oleophobicity, using either the contact angle of light mineral oil with the coating or by assessing the interaction of droplets of various liquid hydrocarbons having different surface tensions employed in the ATCC 118-1997 Oil Repellancy test with the coating surface. For testing, a coating is applied to a 4×4 inch substantially planar plate. After the plate has dried and cured it is placed on a 5±1 degree slope relative to the horizontal and five droplets of a test hydrocarbon are applied beginning with Kaydol™ (available from CBM Group of N.C. Inc., 1308 N. Ellis Ave., Dunn N.C. 28334). When droplets stick to the coating or wet the coating, the Score (Oil Repellency Grade Number) is assigned. Thus, Kaydol™ droplets rolling off earns a value of 1 or greater, 65:35 Kaydol™: n-hexadecane droplets rolling off earns a value of 2 or greater, and so on. All test are conducted at room temperature.

Score (Oil Repellency Grade Number)	hydrocarbon
0	None (Fails Kaydol™)
1	Kaydol™ (mineral oil)
2	65:35 Kaydol™:n-hexadecane
3	n-hexadecane
4	n-tetradecane
6	n-dodecane
6	n-decane
7	n-octane
8	n-heptane

**[0231]** The oleophobicity of first or second particles (e.g., fumed silica treated with a silane, silazane, silanol, siloxane, fluorinated versions thereof, etc.) can be tested in the same manner. In such tests the first and/or second particles are applied to a clean 4×4 inch aluminum plate by spraying a suspension containing 2% particles 98% acetone by weight to form a coating of particles that cover the aluminum plate. After the plate has dried, the above-listed hydrocarbon liquids are tested on the particle coatings in the same manner as they would be on an elastomeric coating, and the particles scored in the same manner.

## 8.0 CERTAIN EMBODIMENTS

**[0232]** Embodiment 1, has is divided into two sub-embodiments, that are recited below as embodiments 1.1. and 1.2. In embodiment 1.1 the second component comprises second particles and one or more solvents, but does not require a fluoropolymer. In contrast, the second component of sub-embodiment 1.2 requires not only second particles, but also a fluorinated polyolefin and/or a Fluoroethylene-Alkyl Vinyl Ether (FEVE) copolymer, and one or more solvents. In subsequent embodiments, any reference to embodiment 1 refers to either embodiment 1.1 and/or 1.2.

### Embodiment 1.1

**[0233]** A combination of components for forming a coating comprising:

**[0234]** A) a first component which comprises:

**[0235]** i) an elastomeric binder comprising one or more styrenic block copolymers, wherein said elastomeric binder comprises from about 1% to about 30% of said one or more styrenic block copolymers by weight (e.g., about 1% to about 5%, about 5% to about 10%, about

10% to about 15%, about 15% to about 25%, or about 25% to about 30% of said one or more styrenic block copolymers);

**[0236]** ii) optionally, one or more independently selected first particles having a size of about 30 microns to about 225 microns, wherein, when said first particles are present, the first component comprises from about 0.01% to about 5% of said first particles by weight (e.g., about 0.01% to about 5%, about 0.03% to about 1%, about 0.05% to about 0.15%, about 0.1% to about 2.5%, or about 0.2% to about 5% of said first particles by weight); and

**[0237]** iii) one or more independently selected solvents; and

**[0238]** B) a second component which comprises:

**[0239]** i) one or more independently selected second particles having a size of about 1 nanometer to about 25 microns, wherein said second particles comprise one or more independently selected alkyl, haloalkyl, or perfluoroalkyl moieties bound, either directly or indirectly, to said second particles; and

**[0240]** ii) optionally, one or more independently selected solvents, wherein when said one or more solvents are present, said second particles may be present in a weight percent range selected from (0.1-1, 1.0-2.0, 0.2-2.0, 0.5-1.5, 0.5-2.0, 0.75-2.5, 1.5-2.0, 1.5-2.5, 2.0-3.0, 2.0-3.5, or 2.5-3.5) based on the weight of the one or more solvents and second particles.

### Embodiment 1.2

**[0241]** A combination of components for forming a coating comprising:

**[0242]** A) a first component which comprises:

**[0243]** i) an elastomeric binder comprising one or more styrenic block copolymers, wherein said elastomeric binder comprises from about 1% to about 30% of said one or more styrenic block copolymers by weight (e.g., about 1% to about 5%, about 5% to about 10%, about 10% to about 15%, about 15% to about 25%, or about 25% to about 30% of said one or more styrenic block copolymers);

**[0244]** ii) optionally, one or more independently selected first particles having a size of about 30 microns to about 225 microns, wherein, when said first particles are present, the first component comprises from about 0.01% to about 5% of said first particles by weight (e.g., about 0.01% to about 5%, about 0.03% to about 1%, about 0.05% to about 0.15%, about 0.1% to about 2.5%, or about 0.2% to about 5% of said first particles by weight); and

**[0245]** iii) one or more independently selected solvents; and

**[0246]** B) a second component which comprises per 100 parts by weight:

**[0247]** i) 0.1 to 3.5 parts by weight (e.g., 0.1-1, 1.0-2.0, 0.2-2.0, 0.5-1.5, 0.5-2.0, 0.75-2.5, 1.5-2.0, 1.5-2.5, 2.0-3.0, 2.0-3.5, or 2.5-3.5) of one or more independently selected second particles having a size of about 1 nanometer to about 25 microns, wherein said second particles comprise one or more independently selected alkyl, haloalkyl, or perfluoroalkyl moieties bound, either directly or indirectly, to said second particles, or one or more siloxanes or silazanes associated with said second particles;



- [0248] ii) 0.1 to 1.0 parts by weight (e.g., 0.1-0.5, 0.5-1.0, or 0.3-0.7 parts) of a fluorinated polyolefin, (e.g., a polymer of tetrafluoroethylene, hexafluoropropylene and vinylidene fluoride, such as Dyneon™ THV);
- [0249] and/or
- [0250] 0.06 to 0.6 parts by weight (e.g., 0.06-0.01, 0.1-0.2, 0.2-0.4, or 0.4-0.6 parts) of a Fluoroethylene-Alkyl Vinyl Ether (FEVE) copolymer, having an average molecular weight of about 1,000 to 3,000 (e.g., about 1,000-2,000, 2,000-3,000, 1,500-2,500, or about 1,000, 1,500, 2,000, 2,500, or 3,000 Da);
- [0251] and
- [0252] iii) one or more independently selected solvents for a the remainder of a total of 100 parts by weight.
- [0253] 2. The combination of embodiment 1, wherein one or more of the styrenic block copolymers has a rubber phase crosslinked to the polystyrene phase.
- [0254] 3. The combination according to any of embodiments 1 to 2, wherein one or more of the styrenic block copolymers has a rubber phase comprising polybutadiene, polyisoprene, polyolefin or a mixture of any of those rubber phase components (e.g., linear triblock copolymers of styrene and ethylene/butylene with a polystyrene content of about 8% to about 36% by weight (e.g., about 8% to about 12%, about 12% to about 18%, about 18% to about 24%, about 24% to about 30%, about 30% to about 36%, about 10% to about 20%, or about 8%, about 9%, about 10%, about 11%, about 12%, about 13%, about 14%, about 15%, about 17%, about 19%, about 20%, about 22%, about 24%, about 26%, about 28%, about 30%, about 32%, about 34%, about 36%) or mixtures of any two or more, three or more, or four or more of such triblock copolymers, any one or more of which may optionally comprise 1% to 3% or 1.4% to 2.0% maleic anhydride).
- [0255] 4. The combination according to any of embodiments 2 to 3, wherein said rubber component comprises 60%-98%, 60%-70%, 70%-80%, 60%-90%, 80%-90%, 83%-93%, 85%-95%, or 89%-98%, of the elastomer by weight (based on the dry weight of the elastomer present in the first component not including any contribution by the first particles or other materials present in that component).
- [0256] 5. The combination according to any of embodiments 1 to 4, wherein said first component further comprises one or more colorants, UV stabilizers, antioxidants, rheological agents, and/or fillers.
- [0257] 6. The combination according to any of embodiments 1 to 5, wherein said first component further comprises up to 30% by weight of one or more tackifiers (e.g., 1%-5%, 2%-8%, 5%-10%, 10%-15%, 15%-20%, 20%-25%, or 25%-30%).
- [0258] 7. The combination of embodiment 6, wherein said one or more styrenic block copolymers and said one or more tackifiers together comprise up to about 30% by weight of said first component (e.g., up to about 10, 15, 20, 25, or 30%).
- [0259] 8. The combination according to any of embodiments 1 to 7, wherein said elastomeric binder comprises one, two, three, or more triblock copolymers.
- [0260] 9. The combination according to any of embodiments 1 to 8, wherein said elastomeric binder comprises one or more styrenic block copolymers of styrene and ethylene/butylene with a polystyrene content of about 8% to about 36% by weight (e.g., about 8% to about 14%, about 12% to about 20%, about 18% to about 28%, about 22% to about 32%, about 26% to about 36%, about 8%, about 9%, about 10%, about 11%, about 12%, about 13%, about 14%, about 16%, about 18%, about 19%, about 20%, about 22%, about 24%, about 26%, about 28%, about 30%, about 32%, about 34%, about 36%), or mixtures of any two or more, three or more, or four or more of such triblock copolymers.
- [0261] 10. The combination according to any of embodiments 1 to 9, wherein one or more of said styrenic block copolymers present in the elastomeric binder comprise maleic anhydride (e.g., maleated copolymers having 1% to 3%, 1.4% to 2.0%, 1% to 1.4%, 1.6% to 3%, or 2% to 3% maleic anhydride based on the weight of the copolymer).
- [0262] 11. The combination according to any of embodiments 1 to 10, wherein at least one, or at least two, of said one or more styrenic block copolymers is a linear copolymer or a branched copolymer (e.g., a dendrimer or arborol).
- [0263] 12. The combination according to any of embodiments 1 to 11, wherein the elastomeric binder comprises a first and a second maleated triblock copolymer of styrene and ethylene/butylene wherein:
- [0264] said first maleated triblock copolymer of styrene and ethylene/butylene has a polystyrene content from about 8% to about 14%, with 0.4% to 1.6% (e.g., 0.5% to 1.5%, 0.6% to 1.4%, or 0.7% to 1.3%) substitution (content by weight) of maleic anhydride by weight of the first triblock copolymer (and optionally less than 0.3% maleic anhydride free); and
- [0265] said second maleated triblock copolymer of styrene and ethylene/butylene has a polystyrene content of about 22% to about 32%, with 1.1% to 2.5% (e.g., 1.3% to 2.3% or 1.4% to 2.4%) substitution of maleic anhydride by weight of the second triblock copolymer.
- [0266] 13. The combination of embodiment 12, wherein said first and/or second triblock copolymers are independently selected linear or branched (e.g., arborols or dendrimers) copolymers.
- [0267] 14. The combination according to any of embodiments 12 to 13, wherein said first and second triblock copolymers may be present in a weight ratio from about 4:1 to about 6.5:1 (e.g., the first copolymer to second copolymer ratio is: about 4:1 to about 5.5:1; about 5:1 to about 6:1; or about 5.5:1 to about 6.5:1).
- [0268] 15. The combination according to any of embodiments 1-14, wherein said first particles are selected from the group consisting of: glass, ceramic, rubber, plastic, thermoplastic, wood, cellulose, metal oxides, silicon dioxide, silicates, tectosilicates, germanium dioxide, plastic particles, carbide particles, nitride particles, boride particles (e.g., zirconium or titanium boride), spinel particles, diamond particles, fly ash particles, fibers and hollow glass spheres, hollow glass particles or hollow plastic particles (e.g., glass, polymer, plastic or thermoplastic particles, spheres, or microspheres), wherein said first particles optionally comprise a colorant (e.g., colored or pigmented glass particles, plastic particles, rubber particles, hollow glass or hollow plastic particles).
- [0269] 16. The combination according to any of embodiments 1 to 15, wherein said first particles comprise hollow glass or plastic particles (e.g., glass, polymer, plastic or thermoplastic particles or microspheres), and wherein said first particles optionally comprise a colorant.



[0270] 17. The combination according to embodiment 16, wherein said hollow glass or hollow plastic particles have a size (average diameter) in a range selected from the group consisting of 5 to 50 microns, 6 to 45 microns, 5 to 20 microns, 20 to 35 microns, and 35 to 50 microns.

[0271] 18. The combination according to any of embodiments 15 to 17, wherein said hollow plastic particles have a density selected from the group consisting of less than 60 kg/m<sup>3</sup>, less than 50 kg/m<sup>3</sup>, less than 40 kg/m<sup>3</sup>, less than 30 kg/m<sup>3</sup>, or less than 25 kg/m<sup>3</sup>, and wherein said hollow glass particles have a density selected from the group consisting of less than 125 kg/m<sup>3</sup>, less than 150 kg/m<sup>3</sup>, less than 200 kg/m<sup>3</sup>, less than 250 kg/m<sup>3</sup>, less than 300 kg/m<sup>3</sup>, less than 350 kg/m<sup>3</sup>, less than 400 kg/m<sup>3</sup>, less than 450 kg/m<sup>3</sup>, less than 500 kg/m<sup>3</sup>, less than 550 kg/m<sup>3</sup>, less than 600 kg/m<sup>3</sup>, or 600 kg/m<sup>3</sup>.

[0272] 19. The combination according to any of embodiments 1 to 18, wherein the second particles have an average size in a range selected from the group consisting of from: about 1 nm to about 100 nm; about 10 nm to about 200 nm; about 20 nm to about 400 nm; about 10 nm to 500 nm; about 40 nm to about 800 nm; about 100 nm to about 1 micron; about 200 nm to about 1.5 microns; about 500 nm to about 2 microns; about 500 nm to about 2.5 microns; about 1 micron to about 10 microns; about 2 microns to about 20 microns; about 2.5 microns to about 25 microns; about 500 nm to about 25 microns; about 400 nm to about 20 microns; and about 100 nm to about 15 microns.

[0273] 20. The combination according to any of embodiments 1 to 19, wherein said second particles comprise a metal oxide, an oxide of a metalloid (e.g., silica), a silicate, or a glass.

[0274] 21. The combination according to any of embodiments 1 to 20, wherein said second particles are comprised of silica and have an average size in a range selected from: about 1 nm to about 50 nm; about 1 nm to about 100 nm; about 1 nm to about 400 nm; about 1 nm to about 500 nm; about 2 nm to about 120 nm; about 5 nm to about 150 nm; about 5 nm to about 400 nm; about 10 nm to about 300 nm; or about 20 nm to 400 nm.

[0275] 22. The combination according to any of embodiments 1 to 21, wherein said second particles have an average size in the range of from 1 nm to 100 nm or from 2 nm to 200 nm.

[0276] 23. The combination according to any of embodiments 1 to 22, wherein said second particles comprise one or more hydrophobic and/or oleophobic moieties.

[0277] 24. The combination according to any of embodiments 1 to 23, wherein said second particles comprise one or more alkyl, fluoroalkyl, and/or perfluoroalkyl moieties that are covalently bound to the second particles directly, or bound indirectly through one or more atoms bound to the second particles.

[0278] 25. The combination according to any of embodiments 1 to 24, wherein said one or more hydrophobic or oleophobic moieties result from contacting the second particles with one or more silanizing agents of formula (I):



[0279] where n is an integer from 1 to 3;

[0280] each R is independently selected from

[0281] (i) alkyl or cycloalkyl group optionally substituted with one or more fluorine atoms,

[0282] (ii) C<sub>1 to 20</sub> alkyl optionally substituted with one or more substituents independently selected from fluorine atoms and C<sub>6 to 14</sub> aryl groups, which aryl groups are optionally substituted with one or more independently selected halo, C<sub>1 to 10</sub> alkyl, C<sub>1 to 10</sub> haloalkyl, C<sub>1 to 10</sub> alkoxy, or C<sub>1 to 10</sub> haloalkoxy substituents,

[0283] (iii) C<sub>2 to 8</sub> or C<sub>6 to 20</sub> alkyl ether optionally substituted with one or more substituents independently selected from fluorine and C<sub>6 to 14</sub> aryl groups, which aryl groups are optionally substituted with one or more independently selected halo, C<sub>1 to 10</sub> alkyl, C<sub>1 to 10</sub> haloalkyl, C<sub>1 to 10</sub> alkoxy, or C<sub>1 to 10</sub> haloalkoxy substituents,

[0284] (iv) C<sub>6 to 14</sub> aryl, optionally substituted with one or more substituents independently selected from halo or alkoxy, and haloalkoxy substituents,

[0285] (v) C<sub>4 to 20</sub> alkenyl or C<sub>4 to 20</sub> alkynyl, optionally substituted with one or more substituents independently selected from halo, alkoxy, or haloalkoxy, and

[0286] (vi) —Z—((CF<sub>2</sub>)<sub>q</sub>(CF<sub>3</sub>))<sub>r</sub>, wherein Z is a C<sub>1 to 12</sub> or a C<sub>2 to 8</sub> divalent alkane radical or a C<sub>2 to 12</sub> divalent alkene or alkyne radical, q is an integer from 1 to 12, and r is an integer from 1 to 4;

[0287] each X is independently selected from —H, —Cl, —I, —Br, —OH, —OR<sup>2</sup>, —NHR<sup>3</sup>, or —N(R<sup>3</sup>)<sub>2</sub> group;

[0288] each R<sup>2</sup> is an independently selected C<sub>1 to 4</sub> alkyl or haloalkyl group; and

[0289] each R<sup>3</sup> is an independently selected H, C<sub>1 to 4</sub> alkyl, or haloalkyl group.

[0290] 26. The combination according to embodiment 25, wherein each R is selected independently from:

[0291] (a) an alkyl or fluoroalkyl group having from 6 to 20 carbon atoms;

[0292] (b) an alkyl or fluoroalkyl group having from 8 to 20 carbon atoms;

[0293] (c) an alkyl or fluoroalkyl group having from 10 to 20 carbon atoms;

[0294] (d) an alkyl or fluoroalkyl group having from 6 to 20 carbon atoms when n is 2 or 3;

[0295] (e) an alkyl or fluoroalkyl group having from 8 to 20 carbon atoms when n is 2 or 3; and

[0296] (f) an alkyl or fluoroalkyl group having from 10 to 20 carbon atoms when n is 2 or 3.

[0297] 27. The combination according to any of embodiments 25 to 26, wherein R is —Z—((CF<sub>2</sub>)<sub>q</sub>(CF<sub>3</sub>))<sub>r</sub>, wherein Z is a C<sub>1 to 12</sub> divalent alkane radical or a C<sub>2 to 12</sub> divalent alkene or alkyne radical, q is an integer from 1 to 12, and r is an integer from 1 to 4.

[0298] 28. The combination according to any of embodiments 25 to 27, wherein n is 1, 2, or 3.

[0299] 29. The combination according to any of embodiments 25 to 28, wherein all halogen atoms present in any one or more R groups are fluorine atoms.

[0300] 30. The combination according to any of embodiments 25 to 29, wherein each X is independently selected from —H, —Cl, —OR<sub>2</sub>, —NHR<sup>3</sup>, and —N(R<sup>3</sup>)<sub>2</sub>.

[0301] 31. The combination according to any of embodiments 25 to 30, wherein each X is independently selected from —Cl, —OR<sub>2</sub>, —NHR<sup>3</sup>, and —N(R<sup>3</sup>)<sub>2</sub>.

[0302] 32. The combination according to any of embodiments 25 to 31, wherein each X is independently selected from —Cl, —NHR<sup>3</sup>, and —N(R<sup>3</sup>)<sub>2</sub>.



- [0303] 33. The combination according to any of embodiments 1 to 32, wherein two, three, four, or more than four compounds of formula (I) are employed alone or in combination to modify at least one second particle; or wherein said second particles incorporated into said second component have an Oil Repellancy Grade Number greater than or equal to about 1, 2, 3, 4, 5, 6, 7, or 8 when measured as a coating applied to a metal plate in the absence of a binder.
- [0304] 34. The combination according to any of embodiments 1 to 33, wherein said second particles are treated with a silanizing agent selected from the group consisting of: tridecafluoro-1,1,2,2-tetrahydrooctyl)silane; (tridecafluoro-1,1,2,2-tetrahydrooctyl)trichlorosilane; (tridecafluoro-1,1,2,2-tetrahydrooctyl)triethoxysilane; (tridecafluoro-1,1,2,2-tetrahydrooctyl)trimethoxysilane; (heptadecafluoro-1,1,2,2-tetrahydrodecyl)dimethyl(dimethylamino)silane; (heptadecafluoro-1,1,2,2-tetrahydrodecyl)tris(dimethylamino)silane; n-octadecyltrimethoxysilane; n-octyltriethoxysilane; and nonafluorohexyldimethyl(dimethylamino)silane.
- [0305] 35. The combination according to any of embodiments 1 to 34, wherein said second particles are treated with a silanizing agent selected from the group consisting of dimethyldichlorosilane, hexamethyldisilazane, octyltrimethoxysilane, polydimethylsiloxane, and (tridecafluoro-1,1,2,2-tetrahydrooctyl)trichlorosilane.
- [0306] 36. The combination according to any of embodiments 1 to 35, wherein said first component and/or said second component further comprise an independently selected solvent and/or propellant.
- [0307] 37. The combination of embodiment 36, wherein said solvent is an organic solvent or a mixture of two or more organic solvents, and wherein either said organic solvent or said mixture of two or more organic solvents comprises less than 10%, 5%, 2%, or 1% of water by weight.
- [0308] 38. The combination of embodiment 36 or 37, wherein said solvent or propellant comprises greater than 1%, greater than 2%, greater than 5%, up to 10%, up to 20%, or greater than 20% by weight of any one, two, three or more of each of air, nitrogen, an inert gas, an alkane, a ketone, an ether, a halogenated alkane, a halogenated alkene, an aromatic hydrocarbon, an alcohol, methane, ethane, propane, butane, pentane, hexane, heptane, ethylene, propene, acetone, methyl isobutyl ketone (MIBK), methyl ethyl ketone (MEK), dimethylether (DME), diethylether, methyl ethyl ether, methyl tert-butyl ether, chloromethane, dichloromethane, carbontetrachloride, trichlorofluoromethane, dichlorodifluoromethane, methanol, ethanol, propanol, butanol, benzene, toluene, xylene, 1-chloro-4-(trifluoromethyl)-benzene, carbon disulfide, and isomers of any of the foregoing, based upon the total weight of solvent or propellant present in the composition.
- [0309] 39. The combination according to any of embodiments 1 to 38, wherein either the first component and/or second component further comprise a colorant or pigment.
- [0310] 40. The combination according to any of embodiments 1 to 39, wherein said elastomeric binder has an ultimate strength greater than about 20, 21, 22, 23, 24, 26, 28, 30, 32, or 34 Mega Pascals (MPa) (e.g., greater than about 2,500, 2,750, 2,800, 2,900, 3,000, 3,200, 3,500, 3,750, 4,000, 4,250, 4,500, 4,750, or 4,900 psi) according to ASTM D412.
- [0311] 41. A method of forming a hydrophobic coating on a portion of a surface comprising the following steps:
- [0312] (a) applying a first component according to any of embodiments 1 to 40 to at least a portion of the surface, wherein the portion of the surface has optionally been treated with a primer (e.g., an elastomeric primer) on all or part of the surface to which said first component is to be applied; and
- [0313] (b) applying a second component according to any of embodiments 1 (i.e., 1.1 or 1.2) to 40 to all or a portion of the portion coated in step (a),
- [0314] wherein said coating has either hydrophobic or superhydrophobic properties, and optionally is also oleophobic or superoleophobic.
- [0315] 42. The method of embodiment 41, wherein said steps of applying said first component and applying said second component are conducted by methods selected independently from painting, printing, stamping, rolling, dipping, spin-coating, spraying, and electrostatic spraying.
- [0316] 43. A coating prepared by the method according to any of embodiments 41 to 42.
- [0317] 44. The coating of embodiment 43, wherein said coating is superhydrophobic and/or superoleophobic.
- [0318] 45. The coating according to any of embodiments 43 to 44, wherein said coating has an ultimate strength greater than about 20, 21, 22, 23, 24, or 26 mega Pascals (MPa) (e.g., greater than about 2,500, 2,750, 2,800, 2,900, 3,000, 3,200, 3,500, or 3,750 psi) according to ASTM D412.
- [0319] 46. The coating according to any of embodiments 43 to 45, wherein said coating has a modulus at 100% elongation of greater than 10, 11, 12, or 13 mega Pascals (MPa) (e.g., greater than about 1,700, about 1,750, about 1,800, or about 1,850 psi) according to ASTM D412.
- [0320] 47. The coating according to any of embodiments 43 to 46, having an elongation at break of greater than about 100%, 110%, 120%, 140%, 160%, 180%, 200%, 250%, 300%, 350%, 400%, or 420%.
- [0321] 48. The coating according to any of embodiments 43 to 47, having a relative electrical permittivity at 100 MHz from about 0.2 to about 4 at about 22° C. (e.g., a relative electrical permittivity from about 0.2 to about 1, from about 1 to about 2, from about 2 to about 3, or from about 3 to about 4) as measured by ASTM D150 using a 0.11 mm thick film.
- [0322] 49. The coating according to any of embodiments 43 to 48, having a Total Luminous Transmittance of about 75% to about 85% and a haze of about 85% to about 90% as measure by ASTM D1003-11 on a film about 25 microns thick.
- [0323] 50. The coating according to any of embodiments 43-49, wherein said coating is superhydrophobic and retains its superhydrophobicity after being subjected to greater than 20, 25, 30, 40, 50, 60, 70, 80, 90, or 100 cycles on a Taber Abraser using CS-0 or CS-10 wheels and a 250 gram load at 95 rpm at room temperature, wherein the end of superhydrophobicity is determined to be the point when more than half of the water droplets applied to the portion of the surface subject to the action of the wheels do not roll off the surface when the surface is inclined at a 5 degree angle at room temperature.
- [0324] 51. The coating according to embodiment 50, wherein said coating retains its superhydrophobicity after being subjected to greater than 20, 25, 30, 40, 50, 60, 70, 80, 90, or 100 cycles on a Taber Abraser using CS-0 or



CS-10 wheels and a 1,000 gram load at 95 rpm at 20° C.-25° C., wherein the end of superhydrophobicity is determined to be the point when more than half of the water droplets applied to the portion of the surface subject to the action of the wheels do not roll off the surface when the surface is inclined at a 5 degree angle at room temperature.

[0325] 52. The coating according to any of embodiments 43 to 51, wherein said coating is superhydrophobic and when said coating is applied to a planar surface, it continues to display superhydrophobic behavior after being subjected to a continuous shower test of about six liters of water per minute at about 20° C.-25° C. for greater than 0.3, 0.5, 0.6, 1, 2, 3, or 3.5 hours, wherein the duration of superhydrophobic behavior is determined to be the time when more than half of the water droplets applied to a portion of the surface subject to said shower do not roll off the surface when it is inclined at a 5 degree angle at room temperature,

[0326] wherein the shower test is conducted using a showerhead with 70 nozzles with a 1 mm diameter orifice arranged in 5 spokes of 5 nozzles and 15 spokes of 3 nozzles about a central point on a circular showerhead, and wherein the showerhead delivers approximately 6 liters of potable tap water per minute using about 137900 Pa (Pascals) to 310275 Pa (20-45 psi cycle over 5 minutes), and wherein the coating placed about 1.5 meters below the showerhead.

[0327] 53. The coating of embodiment 52, wherein, when said coating is subjected to said continuous shower test for a period of time sufficient to lose superhydrophobic behavior, the coating regains superhydrophobic behavior following drying at 20° C. to 25° C. and one atmosphere of pressure, said shower testing and drying collectively comprising a single test cycle.

[0328] 54. The coating of embodiment 53, wherein said coating regains superhydrophobic behavior following more than 5, 10, 15, 20, 30, 40, 50, 75, 100, 150, or 200 of said test cycles.

[0329] 55. A method according to embodiment 41 or 42, wherein applying according to step (b) is repeated to at least a portion of the coated surface if that portion of the coated surface loses said hydrophobic, superhydrophobic, oleophobic and/or superoleophobic properties, and wherein following the repetition of step (b), the coated portion regains hydrophobic, superhydrophobic, oleophobic and/or superoleophobic properties.

[0330] 56. A method according to embodiment 41 or 42, wherein both steps (a) and (b) are repeated on at least a portion of the coated surface if that portion of the coated surface loses said hydrophobic, superhydrophobic, oleophobic and/or superoleophobic properties, and wherein following the repetition of steps (a) and (b), the coated portion regains hydrophobic, superhydrophobic, oleophobic and/or superoleophobic properties.

[0331] 57. A coated surface, or a portion thereof, resulting from the process of embodiment 55 or 56.

[0332] 58. A product comprising an aerosol spray container (e.g., a metal canister) containing a first component according to any of embodiments 1 to 40 and a propellant.

[0333] 59. The product of embodiment 58, wherein the aerosol spray container comprises a valve assembly, a dip tube, and an actuator.

[0334] 60. A product comprising an aerosol spray container (e.g., a metal canister) containing a second component according to any of embodiments 1 to 40 and a propellant.

[0335] 61. The product of embodiment 60, wherein the aerosol spray container comprises a valve assembly, a dip tube, and an actuator.

[0336] 62. A product comprising an aerosol spray container according to embodiment 58 or 59, and a second aerosol spray container according to embodiment 60 or 61.

## 9.0 EXAMPLES

### Example 1

#### An HP/OP Elastomeric Coating

[0337] One part by weight of elastomeric coating (24% by weight of solids) supplied as clear liquid from PLASTI DIP International, Inc. (Blaine, Minn.) is combined with two parts by weight of xylene and mixed. The mixture of elastomer and xylene is divided into six aliquots and the indicated amounts of EXPANCEL 461 DET d25 (0.01% to 0.5% by weight based on the total weight of the elastomer and xylene mixture) is added to separate aliquots. The aliquots are mixed to form first component compositions. The first component compositions are sprayed onto individual aluminum plates to form a base coat. The base coated aluminum plates are then top coated with a second component consisting of a 2% (w/w) dispersion in acetone of fumed silica particles modified to render them hydrophobic by reacting them with tridecafluoro tetrahydroctyl trichloro silane (fumed silica to silane ratio is 2:1 by weight). Test data for plates is summarized in the table below and the data is plotted in FIG. 5. Coatings formed from PLASTI DIP elastomer have a tensile strength of 3,740 psi (ASTM D-638), salt spray resistance greater than 1,000 hours (ASTM B-117) and elongation at break of 430% (ASTM D-638) without added first or second particles.

Data on HP/OP Elastomeric Coatings from Example 1

EXPANCEL wt %	Glove Rubs	Approximate Taber Abraser Cycles to loss of SH behavior CS-0 wheel CS-10 wheel ( )	Shower (hr)*
0.01%	100	22 (13)	
0.03%	325	72 (43)	1
0.06%	700	156 (93)	2
0.10%	750	167 (100)	3.5
0.30%	500	111 (67)	3.5
0.50%	400	89 (53)	3.5

Taber cycles estimated based upon a value of 4.5 glove rubs per Taber cycle using CS-0 wheels and 7.5 glove rubs per Taber cycle (sample rotation) using CS-10 wheels. The number in parentheses is for the CS-10 data estimate. Taber load was 250 g.

\*Shower test was terminated at 3.5 hours.

[0338] Data in the table above and FIG. 5 show that the abrasion resistance (glove rub performance and estimated Taber cycles) reaches a maximum when about 0.1% of EXPANCEL particles are incorporated into the base coat. Shower time to loss of superhydrophobicity also increases with increasing amounts of EXPANCEL particles incorporated in the base coat. Shower time to loss of superhydrophobic behavior saturates beyond 0.1% addition.

### Example 2

[0339] Six first component mixtures are prepared as in Example 1 using 0.1% of five different types of EXPANCEL particles (duplicate samples containing EXPANCEL 031 DU 400), and the first components are each applied to a different aluminum plate by spraying to form a base coat. The base coating on each plate is then top coated with a second com-



ponent comprising a 2% (w/w) dispersion of fumed silica particles treated with tridecafluoro tetrahydroctyl trichlorosilane suspended in acetone. For samples containing EXPAN-CEL 031 DU 400) the aluminum plates were heated to 80° C. for 2-3 minutes either before or after the application of the second component to expand the EXPAN-CEL particles. Test data for the plates are summarized in the table of performance data, below, and plotted in FIG. 6.

**[0340]** Performance Data by Using 0.1% by Weight of Different EXPAN-CEL Particles in Elastomeric Coating

EXPAN-CEL type	Glove Rubs	Taber Abraser Cycles to loss of SH behavior	Shower (hr)
461 DET d25	800	178 (106)	4
461 DE 40 d25	500	111 (67)	2.5
461 DET 40 d25	650	144 (87)	4
920 DE 80 d30	400	89 (53)	2.5
031 DU 40 (heated before top coating)	75	17 (10)	0.5
031 DU 40 (heated after top coating)	75	17 (10)	0.5

Taber cycles estimated based upon a value of 4.5 glove rubs per Taber cycle using a 250 g load, CS-0 wheels and 7.5 glove rubs per Taber cycle (sample rotation) using CS-10 wheels. The number in parentheses is for the CS-10 data estimate.

**[0341]** Data in the table above and FIG. 6 show that incorporation of EXPAN-CEL 461 DET d25 and EXPAN-CEL 461 DET 40 d25 produces a combination of resistance to the loss of HP/OP when being handled (“handleability” assessed by glove rubs and resistance to Taber abrasion testing), and shower time to loss of superhydrophobicity. Unexpanded EXPAN-CELS 031 DU 40 did not show good performance. The shower times track closely and positively correlate with glove rubs and Taber cycles (higher glove rubs correspond to higher shower time).

### Example 3

#### Scaled Preparation of Fumed Silica Second Particles

**[0342]** A series of aluminum plates primed with PLASTI DIP primer for metals according to the manufacturer’s instructions are base coated as in Example 1, with 0.1% EXPAN-CEL 461 DET d25 particles added to the first component, which is applied by spraying. After the base coat has dried at room temperature, one set of plates is treated with a second component as in Example 1. The second component comprises 20 g of 20-80 nm fumed silica particles having a surface area of about 200 m<sup>2</sup>/g (Evonik Industries, Horsham Pa.), treated in an Osterizer kitchen blender for 10 minutes at room temperature with 10 g of tridecafluoro tetrahydroctyl trichloro silane. A second set of plates is also treated with a second component as in Example 1, using silica from the same supplier prepared in a larger batch using 5,000 g of the silica reacted with tridecafluoro tetrahydroctyl trichloro silane 2,500 g in a 10 kg reactor system at room temperature for 2-3 hours. In this example, after top coats are applied the plates are dried for 15 minutes at 170° F. (77° C.). Two plates treated with fumed silica prepared in the blender and two plates treated with fumed silica prepared in the reactor are subjected to thickness and surface roughness measurements. The point at which the plates lose superhydrophobic behavior is also determined using Taber Abraser equipped with CS-0 wheels at a 1,000 g load and using glove rub testing. Loss of superhydrophobic behavior is deemed to be the point at which

more than half of the water droplets applied to the tested portion of a substantially planar surface inclined at 5 degrees from the horizontal do not roll off the plate.

**[0343]** Data on plates coated with fumed silica particles prepared in the blender is summarized in Table 7, and data on plates treated with fumed silica prepared in the reactor is shown in Table 8.

TABLE 7

Blender Grade NPT 74			
Coating Thickness (mils) Sample #1	Ra Sample #1	Coating Thickness (mils) Sample #2	Ra Sample #2
0.73	2.61	1.1	3.267
0.67	2.66	1.01	3.337
0.49		0.82	
0.76		1.08	
Avg 0.6625	2.635	1.0025	3.302
Glove Rubs 600			
Taber Abraser cycles to loss of SH		50	

TABLE 8

Reactor Grade NPT 74			
Coating Thickness (mils) Sample #1	Ra Sample #1	Coating Thickness (mils) Sample #2	Ra Sample #2
0.92	3.246	1.07	3.027
1.35	3.259	0.94	2.35
0.88		0.86	
1.01		0.88	
Avg 1.04	3.2525	0.9375	2.6885
Glove Rubs 900			
Taber Abraser cycles to loss of SH		30	

The data in Tables 7 and 8 indicate that superhydrophobic coatings prepared with fumed silicas produced in reactors on different scales display similar properties.

### Example 4

#### Transparency and Haze

**[0344]** Glass plates are coated with a near transparent coating based on elastomeric binder systems as in Example 1 with the exception that the plate marked P does not include first particles (EXPAN-CEL particles) in the base coat (first component). The plate marked SE-1 contains 0.1% of EXPAN-CEL particles in the first component. Samples are tested for Haze value and Total Luminous Transmittance (TLT) values using the method described in ASTM D1003. The instrument is calibrated without a sample present using air as a standard. Calibration values are TLT=100 and Haze=0. Clear, clean, uncoated glass plates have average readings of TLT=90.6 and a haze reading of 0.18. Plates lacking first particles (P-coat) have about the same transparency as clear clean glass. The presence of EXPAN-CEL particles in the base coat reduces the transparency by about 10%. The coating haze increases from about 0.18 for glass to about 61% for coatings without first



particles and to about 90% for coatings including EXPAN-CEL particles in the base coating. See Table 9.

TABLE 9

P-Coat Sample (no first particles)	Reading 1	Reading 2	Reading 3	Average Readings
Transmittance	90.50	90.30	90.40	90.4
Haze	60.70	62.40	60.80	61.30
SE-1 Sample (first particles included in the base coat)				
Transmittance	80.00	79.10	80.10	79.73
Haze	88.60	90.80	89.30	89.57

## Example 5

## Effect of Coating Thickness

[0345] Six aluminum plates (10 cm×10 cm) are primed with PLASTI DIP primer for metal (product f938 hp). Pairs of the primed plates are spray coated with first component as in Example 1 (0.1% EXPANCELs) to achieve a base coat thicknesses of about 1, 1.5, or 2.6 ml respectively. One plate at each coating thickness is top coated with 2 ml of the second component as described in Example 1, and the second plate at each coating thickness is top coated with 4 ml of second component. Coating thicknesses, which include the primer thickness, and Taber Abraser data are summarized in Table 10A and data is plotted in FIG. 7.

TABLE 10A

Data summary for plates made with varying coating thicknesses					
Sample	Volume of Topcoat (mL)	Passes of Base Coat	Final Thickness (mil)	Tabers (CS-10) to end of super- hydrophobicity	Notes
1.1	2	1	0.55	35	some tearing
2.1	2	3	1.5	35	no tearing
3.1	2	5	2.6	35	no tearing
1.2	4	1	0.9	45	some tearing
2.2	4	3	2.2	50	no tearing
3.2	4	5	2.9	50	no tearing

[0346] Based on the data above, 2 ml of top coat (0.02 ml/cm<sup>2</sup>) produces no benefits in performance improvement at any thickness. However, when the top coat is increased to 4 ml (0.04 ml/cm<sup>2</sup>), it provides an adequate performance that increases with coating thickness. While not wishing to be bound by any theory, it appears that at the higher application rate the top coat penetrates to some depth into the base coat. When only 2 ml (0.02 ml/cm<sup>2</sup>) is applied the coating may be sufficient to just cover the base coat, but not enough to permit the second particles to penetrate at any significant level that will increase the durability of SH performance. In addition, when the base coat is very thin, tearing becomes the failure mode.

## Example 6

## Effect of Priming with Polyurethane Primer

[0347] Aluminum plates are primed with a two-part polyurethane coating (DESMOPHEN 670BA with DESMODUR N75 BA-XBMS, Bayer Material Science) prepared and applied per manufacturer's instructions. An elastomeric coating as described in Example 1 (0.1% of EXPANCEL 461 DET d25) is employed in the first component. Coated plates are measured for coating thickness (including primer thickness) and their ability to resist the loss of superhydrophobic behavior using a Taber Abraser fitted with CS-10 (abrasive) wheels and CS-0 (soft rubber) wheels at a 1,000 g load is recorded. All end points for loss for superhydrophobic behavior are measured for water droplet roll off with the plates inclined at 5 degrees from the horizontal (5 degree tilt angle). Test data is summarized in Table 10B.

TABLE 10B

Summary of data on Al plates primed with two-part polyurethane as primer			
	Sample		
	1	2	3
	Total Coating and Primer Thickness(mils)	Total Coating and Primer Thickness (mils)	Total Coating and Primer Thickness (mils)
	3.25	3.13	4.7
	3.13	3.06	4.9
	3	3.1	4.16
	3.32	3.45	4.24
	4.15	4.01	4.47
Avg Thickness	3.37	3.35	4.494
	CS-10 Wheel	CS-0 Wheel	Glove Rubs
Tabers CS-10	40		
Tabers CS-0		40	
Glove Rubs			>1000

## Example 7

Nearly Transparent HP/OP Elastomeric Coating with  
Various First Particles

[0348] Elastomeric coatings are prepared on aluminum test plates as described in Example 1, with the exception that the first component contains first particles as indicated in Table 11. The test plates are assessed for loss of superhydrophobic behavior using glove rubs as a rapid test for assessment of handleability and abrasion resistance/durability. Test data for all coated plates are summarized in Table 11.



TABLE 11

Summary of data for non near transparent elastomeric binder system based coatings					
Particle Designation	Particle Type	Particle Size (micron)	Amount weight (%)	Glove Rubs (#s)	Taber Abraser Predicted cycles with CS-0 wheel*
EXPANCEL DET	Thermoplastic Encapsulated with gas	10-40	0.01	100	22
EXPANCEL DET	Thermoplastic Encapsulated with gas	10-40	0.1	750	167
EXPANCEL DET	Thermoplastic Encapsulated with gas	10-40	0.5	400	89
Hollow Glass Spheres K25	Hollow glass spheres	25-90	0.5	800	178
Hollow Glass Spheres K46	Hollow glass spheres	15-70	0.5	>400	>89

\*Projected based on GR/CS-0 = 4.5

[0349] Thermoplastic particles and hollow glass particles yield similar performance in increasing coating durability.

Example 8

Non-Transparent Elastomeric Coatings Prepared with Micronized Rubber First Particles

[0350] PLASTI DIP (24% solids by weight) elastomeric coating (5 parts by weight of the liquid as provided by the supplier) is combined with seven parts by weight of xylene and mixed. To the resulting mixture of elastomer and xylene, micronized rubber particles (Lehigh Technology, Tucker, Ga.) about 4% or about 7.7% by weight are added to separate aliquots (based on the weight of the elastomer and xylene combined). The particles are mixed into each aliquot to form first component compositions. The first component compositions are applied to separate aluminum plates to form base coats, and the base coats are top coated with a second component as described in Example 1.

[0351] Test data showing resistance to the loss of superhydrophobicity based on glove rub testing and Taber testing for the coatings incorporating rubber particles is provided in Table 12. That data shows the incorporation of elastomeric binder used in this example with micronized rubber particles produces highly durable surfaces that show increasing resistance to the loss of hydrophobicity with increasing amounts of rubber first particles incorporated into the binder up to at least 7.69%.

TABLE 12

Summary of data on non near transparent elastomeric binder based coatings					
Particle Designation	Particle Type	Particle Size (μm)	Amount weight (%)	Glove Rubs (#s)	Taber Abraser cycles with CS-0*
Micronized Rubber	Ground Rubber particles	70	4	1450	191

TABLE 12-continued

Summary of data on non near transparent elastomeric binder based coatings					
Particle Designation	Particle Type	Particle Size (μm)	Amount weight (%)	Glove Rubs (#s)	Taber Abraser cycles with CS-0*
Micronized Rubber	Ground Rubber particles	70	7.69	1800	237

\*Projected based on GR/CS-0 wheel ratio of 7.6 for a 250 g load at 95 rpm.

Example 9

Non-Transparent Elastomeric Coating with Micronized Rubber Particles with and without Primer

[0352] Elastomeric coatings are prepared as in Example 8 employing 7.69% of micronized rubber by weight in the first component. The coatings are applied to clean but unprimed aluminum plates or aluminum plates that have been treated with an elastomeric metal primer (PLASTIDIP metal primer) per the manufacturer's instructions. All plates are substantially planar. The top coating step is the same as in Example 8 and Example 1. The coated plates are assessed for resistance to the loss of SH behavior using a Taber Abraser fitted with CS-0 wheels or CS-10 wheels (as indicated) using 1,000 g loads at 95 rpm, resistance to the loss of SH behavior using glove rubs, and coating thickness, which is measured including primer where present. The appearance of coating failures is also recorded for each plate and the data set forth in Table 13.



TABLE 13

Observations from Taber Abraser Testing of Plates With and Without Primer			
		Coating Thickness (mil)	Comments
Coating Without Primer			
without primer			
Taber CS-0	6 cycles	1.5	Rips and Tears
Taber CS-10	10 cycles	1.5	Rips and Tears
Glove Rubs	1200	1.5	No Rips or Tears
With primer			
Coating With Elastomeric Primer			
with elastomeric primer			
Taber CS-0	50 cycles	1.75	No Rips or Tears
Taber CS-10	40 cycles	1.65	No Rips or Tears
Glove Rubs	1600	1.75	No Rips or Tears

**[0353]** The data indicates that samples with and without primer resist the loss of superhydrophobicity with a very large number of glove rubs. Taber Abraser testing results in a loss of that property due to ripping and/or tearing of the coating in the absence of primer. Loss of superhydrophobic behavior is assessed using the above-described droplet run off test with plates inclined at 5 degrees from the horizontal. Priming of the metal surfaces increases the number of Taber cycles the test samples can withstand without losing superhydrophobic

behavior by about 4 to about 8 fold, regardless of whether non-abrasive rubber (CS-0) or abrasive (CS-10) wheels are employed.

#### Example 10

##### Thermal Stability of Elastomeric Coatings

**[0354]** Elastomeric coatings incorporating EXPANCELs as in Example 1, or micronized rubber as in Example 8, are scraped from their plates and used for thermogravimetric analysis (TGA). TGA data for the coatings is plotted in FIGS. 10 and 11, respectively. Details of the test conditions are listed inside each of the graphs. Data from these charts show the following:

**[0355]** 1. The coating containing EXPANCEL is stable up to 241° C. (465° F.)

**[0356]** 2. The coating containing micronized rubber is stable up to 261° C. (502° F.)

Based upon the data presented above the coatings may be used up to temperatures of 200° C. or 400° F.

#### Example 11

##### HP/OP Coatings Employing Varying Proportions of a Styrenic Block Copolymer and Tackifier

**[0357]** Three styrenic block copolymers (SBCs), FG 1901, FG 1924 and RP 6670, each obtained from KRATON®, are dissolved in xylene at 20% by weight. Regalrez™ 1094 tackifier, obtained from Eastman Chemical Company, is dissolved in xylene at 20% by weight. Varying ratios of SBCs and tackifier solutions are mixed and UV stabilizers and antioxidants, 0.1% Irganox® 1520L, 0.056% Tinuvin® 328, and 0.056% Tinuvin® 770DF (% by weight), are added.

**[0358]** Each of the mixtures of SBCs and tackifier formed is used as a first component and HP/OP coatings are prepared as in Example 1, using 0.1% EXPANCEL particles as first particles. The HP/OP coatings were tested for durability using a Taber Abraser equipped with CS-10 wheels and a 1,000 g load. The results are shown in Table 14.

TABLE 14

FG 1901/Regalrez 1094			FG 1924/Regalrez 1094			RP 6670/Regalrez 1094		
Ratio	Glove Rubs	Taber cycles	Ratio	Glove Rubs	Taber cycles	Ratio	Glove Rubs	Taber cycles
43/57	300	35	25/75	300	30	25/75	500	30
50/50	400	40	50/50	750	35	33/66	500	40
57/43	550	45	66/33*	800	20	50/50	750	45
66/33	1000	60				66/33	1500	50
75/25*	350	35				75/25*	1000	50
90/10*	600	25						
100/0*	600	25						

\*Taber testing induced tearing.

#### Example 12

##### HP/OP Coatings Employing Maleated Styrene-Ethylene/Butylene-Styrene (SEBS) Block Copolymers

**[0359]** Coatings were prepared using first components comprising maleated SBCs (e.g., maleated SEBS block copolymers)



TABLE 15

Base Coat Component	Total Component Parts by Weight (Total of 100 parts)	Exemplary Composition Components (By weight where given)
Maleated SBC	7 to 9	One or more maleated Styrene-Ethylene/Butylene-Styrene (SEBS) Block Copolymers (e.g., Kraton FG 1901, FG 1924 and/or RP 6670♦)
Tackifier	3.5 to 7	Nonpolar hydrogenated hydrocarbon resin (e.g., produced by polymerization and hydrogenation of monomeric hydrocarbons) or esterified hydrogenated rosin. e.g., Eastman Regalrez™ 1094 or Foral™ 105E
Antioxidant(s)	0.05 to 0.2	Antioxidant(s) (e.g., phenolic or hindered phenolic antioxidants e.g., Irganox 1520L
First Particles	0.05 to 20	Expancel 461 DET 40 d25 (0.05-0.2%) SoftSand 5-15% Glass bubbles (e.g., K1, S22, or A16/500) 1%-10%
UV stabilizer(s)	0.05 to 0.5	e.g., Tinuvin® 328 and/or 770DF
Solvent	Bring to 100 parts total including all other components	xylene (or mixed xylenes), acetone, n-hexane (or mixed hexanes), 1-chloro-4-(trifluoromethyl)-benzene or mixtures thereof
Top Coat Component	Parts by weight	Source
Reactor Grade NPT 74	0.05 to 6.0 (e.g., 2%)	Ross Technology -- see Example 3
Solvent	Bring to 100 parts by weight total including all other components	xylene (including mixed xylenes or technical grade), acetone, n-hexane (or mixed hexanes), 1-chloro-4-(trifluoromethyl)-benzene or mixtures thereof

♦RP 6670 is a maleated form of KRATON series A polymers, which are hydrogenated block copolymers having styrene copolymerized with ethylene/butylene in the midblock (S-(EB/S)-S). Styrenic block copolymers (SBCs FG 1901, FG 1924 and RP 6670, each obtained from KRATON®), tackifier (Regalrez™ 1094 or FORAL™ 105E obtained from Eastman Chemical Company), UV stabilizers (e.g., Tinuvin® 328 and/or 770DF from BASF), antioxidants (e.g., Irganox® 1520L) and first particles are dissolved/suspended in solvent using solvent to adjust the total components by weight to 100 parts.

**[0360]** The HP/OP coatings were tested for durability using a Taber Abraser equipped with CS-10 wheels and a 1,000 g load. The results are shown in Table 14.

**1. A system for forming a coating comprising:**

**A) a first component which comprises:**

- i) an elastomeric binder comprising one or more styrenic block copolymers, wherein said elastomeric binder comprises from about 10% to about 30% of said one or more styrenic block copolymers by weight;
- ii) optionally, one or more independently selected first particles having a size of about 30 microns to about 225 microns, wherein, when said first particles are present, the first component comprises from about 0.01% to about 5% of said first particles by weight; and
- iii) one or more solvents; and

**B) a second component which either comprises:**

- i) one or more independently selected second particles having a size of about 1 nanometer to about 25 microns, wherein said second particles comprise one or more independently selected alkyl, haloalkyl, or perfluoroalkyl moieties bound, either directly or indirectly, to said second particles, and
- ii) optionally, one or more solvents;

or comprises per 100 parts by weight:

- i) 0.1 to 3.5 parts by weight of one or more independently selected second particles having a size of about 1 nanometer to about 25 microns, wherein said second particles comprise one or more independently selected alkyl, haloalkyl, or perfluoroalkyl moieties bound, either directly or indirectly, to said second

particles, or one or more siloxanes or silazanes associated with said second particles;

- ii) 0.1 to 1.0 parts by weight of a fluorinated polyolefin; and/or

0.06 to 0.6 parts by weight of a Fluoroethylene-Alkyl Vinyl Ether (FEVE) copolymer, having an average molecular weight of about 1,000 to 3,000;

and

- iii) one or more solvent for the remainder of a total of 100 parts by weight; wherein a coating formed by said system has an elongation at break greater than about 200% and an arithmetical mean roughness value from about 3 microns to about 20 microns, or a ten point mean roughness from about 7 microns to about 100 microns.

**2. The system of claim 1, wherein one or more of the styrenic block copolymers has a rubber phase crosslinked to the polystyrene phase.**

**3. The system according to claim 1, wherein one or more of the styrenic block copolymers has a rubber phase comprising polybutadiene, polyisoprene, polyolefin or a mixture of any of those rubber phase components (e.g., linear triblock copolymers of styrene and ethylene/butylene with a polystyrene content of about 8% to about 36% by weight or mixtures of any two or more, three or more, or four or more of such triblock copolymers, any one or more of which may optionally comprise 1% to 3% or 1.4% to 2.0% maleic anhydride).**

**4. The system according to claim 2, wherein said rubber component comprises 60%-80%, of the elastomer by weight, based on the dry weight of the elastomer present in the first**



component not including any contribution by the first particles or other materials present in the first component.

5. The system according to claim 1, wherein said first component further comprises one or more colorants, UV stabilizers, antioxidants, rheological agents, and/or fillers.

6. The system according to claim 1, wherein said first component further comprises up to 30% by weight of one or more tackifiers, wherein said one or more styrenic block copolymers and said one or more tackifiers together comprise up to about 30% by weight of said first component.

7. (canceled)

8. The system according to claim 1, wherein said elastomeric binder comprises one, two, three, or more triblock copolymers.

9. The system according to claim 1, wherein said elastomeric binder comprises one or more styrenic block copolymers of styrene and ethylene/butylene with a polystyrene content of about 8% to about 36% by weight, or mixtures of any two or more, three or more, or four or more of such triblock copolymers.

10. The system according to claim 1, wherein one or more of said styrenic block copolymers present in the elastomeric binder comprise maleic anhydride or a first and a second maleated triblock copolymer of styrene and ethylene/butylene wherein:

said first maleated triblock copolymer of styrene and ethylene/butylene has a polystyrene content from about 8% to about 14%, with 0.4% to 1.6% substitution of maleic anhydride by weight of the first triblock copolymer; and

said second maleated triblock copolymer of styrene and ethylene/butylene has a polystyrene content of about 22% to about 32%, with 1.1% to 2.5% substitution of maleic anhydride by weight of the second triblock copolymer.

11.-14. (canceled)

15. The system according to claim 1, wherein said first particles are selected from the group consisting of: glass, ceramic, rubber, plastic, thermoplastic, wood, cellulose, metal oxides, silicon dioxide, silicates, tectosilicates, germanium dioxide, plastic particles, carbide particles, nitride particles, boride particles (e.g., zirconium or titanium boride), spinel particles, diamond particles, fly ash particles, fibers and hollow glass spheres, hollow glass particles or hollow plastic particles (e.g., glass, polymer, plastic or thermoplastic particles, spheres, or microspheres), wherein said first particles optionally comprise a colorant (e.g., colored or pigmented glass particles, plastic particles, rubber particles, hollow glass or hollow plastic particles).

16.-19. (canceled)

20. The system according to claim 1, wherein said second particles comprise a metal oxide, an oxide of a metalloid, a silicate, or a glass, wherein said second particles have an average size in the range of from 1 nm to 100 nm or from 2 nm to 200 nm.

21.-24. (canceled)

25. The system according to claim 1, wherein said one or more hydrophobic or oleophobic moieties result from contacting the second particles with one or more silanizing agents of 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)  $C_{1 \text{ to } 20}$  alkyl optionally substituted with one or more substituents independently selected from fluorine atoms and  $C_{6 \text{ to } 14}$  aryl groups, which aryl groups are optionally substituted with one or more independently selected halo,  $C_{1 \text{ to } 10}$  alkyl,  $C_{1 \text{ to } 10}$  haloalkyl,  $C_{1 \text{ to } 10}$  alkoxy, or  $C_{1 \text{ to } 10}$  haloalkoxy substituents,
- (iii)  $C_{2 \text{ to } 8}$  or  $C_{6 \text{ to } 20}$  alkyl ether optionally substituted with one or more substituents independently selected from fluorine and  $C_{6 \text{ to } 14}$  aryl groups, which aryl groups are optionally substituted with one or more independently selected halo,  $C_{1 \text{ to } 10}$  alkyl,  $C_{1 \text{ to } 10}$  haloalkyl,  $C_{1 \text{ to } 10}$  alkoxy, or  $C_{1 \text{ to } 10}$  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
- (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 independently selected from  $-H$ ,  $-Cl$ ,  $-I$ ,  $-Br$ ,  $-OH$ ,  $-OR^2$ ,  $-NHR^3$ , or  $-N(R^3)_2$  group;

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.

26. (canceled)

27. The system according to claim 25, wherein R is  $-Z-((CF_2)_q(CF_3))_r$ , 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.

28. The system according to claim 25, wherein n is 1, 2, or 3.

29.-33. (canceled)

34. The system according to claim 1, wherein said second particles are treated with a silanizing agent selected from the group consisting of: (tridecafluoro-1,1,2,2-tetrahydrooctyl) trichlorosilane; (tridecafluoro-1,1,2,2-tetrahydrooctyl)triethoxysilane; (tridecafluoro-1,1,2,2-tetrahydrooctyl)trimethoxysilane; (heptadecafluoro-1,1,2,2-tetrahydrodecyl) dimethyl(dimethylamino)silane; (heptadecafluoro-1,1,2,2-tetrahydrodecyl)tris(dimethylamino)silane; n-octadecyltrimethoxysilane; n-octyltriethoxysilane; nonafluorohexyldimethyl(dimethylamino)silane; dimethyl dichlorosilane; hexamethyldisilazane; octyltrimethoxysilane, and polydimethylsiloxane.

35. (canceled)

36. The system according to claim 1, wherein said first component and/or said second component further comprises an independently selected solvent and/or propellant.

37.-39. (canceled)

40. The system according to claim 1, wherein said elastomeric binder has an ultimate strength greater than about 20 Mega Pascals (MPa) according to ASTM D412.

41-62. (canceled)

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