Disclosed in certain embodiments are solventless curable coating systems and uses thereof. In one embodiment, an ice-phobic coating formulation includes an elastomer, filler particles, and a cryoprotectant.
FIGURE 2A

1.4 wt% Silane

1.0 wt%

0.03 wt%

0.05 wt% Catalyst

FIGURE 2B

3 wt% Silane

1 wt%

25 wt% Silanol

15 wt%

0.01 wt% Catalyst

0.03 wt%
Mix a siloxane component, a silanol component, and a silane component to form a mixture

Add a catalyst component to the mixture

Heat the mixture immediately after adding the catalyst component to the mixture

End
**Figure 5**

*Viscosity versus Time Profiles*

Graph showing viscosity profiles over time.

**Figure 6**

Chemical structures showing reaction pathways.

*CH$_3$-CH$_2$-H* → *CH$_3$-CH$_2$-CH$_2$*
FIGURE 9

Failure Stress (kPa) vs. Displacement (cm)
FIGURE 10C

Failure Stress (KPa)

Silica microparticles at 13 wt%  Silica nanoparticles at 3 wt%  

FIGURE 10D

Failure Stress (KPa)

Silica at 3 wt%  Graphene at 3 wt%  Polypropylene at 3 wt%
1300
Start

1302
Provide an ice-phobic coating formulation including an elastomer, filler particles, and a cryoprotectant

1304
Apply a primer coating to a surface and allow primer coating to cure

1306
Deposit the ice-phobic coating formulation onto the surface

1308
Allow the ice-phobic coating formulation to cure and form an ice-phobic coating

End

FIGURE 13
SOLVENTLESS CURABLE COATING SYSTEMS AND USES THEREOF

CROSS-REFERENCE TO RELATED APPLICATIONS


TECHNICAL FIELD

[0002] Embodiments of the invention relate generally to coating systems and, more specifically, to solventless curable coating systems and uses thereof.

BACKGROUND

[0003] There is a global trend towards eliminating hydrocarbon solvents in various high volume coating applications of polymeric systems. Alternative systems that are free of volatile organic compounds (VOCs) have utilized, for example, fluorinated solvents, which address some of issues associated with hydrocarbon solvents, such as flammability and volatility. However, fluorinated solvents (e.g., containing fluorinated ethers, fluorinated olefins, etc.) give rise to their own set of concerns, such as ozone depletion potential and high global warming potential (GWP). Moreover, fluorinated solvents tend to be significantly more expensive than hydrocarbon solvents.

[0004] Thus, there exists a need in the art for coating systems that are safer for use, more environmentally-friendly, less expensive, and are capable of meeting end-use performance requirements.

BRIEF DESCRIPTION OF THE DRAWINGS

[0005] The present invention is illustrated by way of example, and not by way of limitation, and will become apparent upon consideration of the following detailed description, taken in conjunction with the accompanying drawings, in which like reference characters refer to like parts throughout, and in which:

[0006] FIG. 1A shows viscosity versus time profiles for a condensation cure system for varying amounts of tin(II) catalyst according to an embodiment of the disclosure;
[0007] FIG. 1B shows viscosity versus time profiles for a condensation cure system illustrating the effects of heating on viscosity behavior over time according to an embodiment of the disclosure;
[0008] FIG. 2A illustrates a two-variable planar representation of formulation parameters according to an embodiment of the disclosure;
[0009] FIG. 2B illustrates a three-variable cubic representation of formulation parameters according to an embodiment of the disclosure;
[0010] FIG. 3A shows a surface plot of viscosity for formulations with silane and catalyst content as variables according to an embodiment of the disclosure;
[0011] FIG. 3B shows a surface plot of viscosity for formulations with catalyst and silanol content as variables according to an embodiment of the disclosure;
[0012] FIG. 3C shows a surface plot of viscosity for formulations with silane and catalyst content as variables according to an embodiment of the disclosure;
[0013] FIG. 3D shows a surface plot of viscosity for formulations with silane and silanol content as variables according to an embodiment of the disclosure;
[0014] FIG. 4 is a block diagram illustrating a method for preparing a solventless curable coating formulating according to an embodiment of the disclosure;
[0015] FIG. 5 shows viscosity versus time profiles for an addition cure system according to an embodiment of the disclosure;
[0016] FIG. 6 is a representation of polymer network formation;
[0017] FIG. 7A is an electron micrograph of a solventless silicone-based coating without filler particles;
[0018] FIG. 7B is an electron micrograph of a solventless silicone-based coating with filler particles;
[0019] FIG. 7C is another electron micrograph of a solventless silicone-based coating with filler particles;
[0020] FIG. 7D is another electron micrograph of a solventless silicone-based coating with filler particles;
[0021] FIG. 8 is a diagram illustrating an ice-pin push out test apparatus;
[0022] FIG. 9 shows ice adhesion load-displacement curves for coatings of different thickness according to embodiments of the present disclosure;
[0023] FIG. 10A shows ice adhesion failure stresses measured for various ice-phobic coatings prepared according to embodiments of the present disclosure;
[0024] FIG. 10B shows ice adhesion failure stresses for ice-phobic coatings utilizing varying amounts of filler particles according to embodiments of the present disclosure;
[0025] FIG. 10C shows ice adhesion failure stresses for ice-phobic coatings utilizing different levels of silica fillers according to embodiments of the present disclosure;
[0026] FIG. 10D shows ice adhesion failure stresses for ice-phobic coatings utilizing different types of filler nanoparticles according to embodiments of the present disclosure;
[0027] FIG. 10E shows ice adhesion failure stresses for ice-phobic coatings utilizing different amounts of glycerol as a cryoprotectant according to embodiments of the present disclosure;
[0028] FIG. 11A is a front view of an erosion test apparatus;
[0029] FIG. 11B is a side view of an erosion test apparatus;
[0030] FIG. 11C is an inside view of an erosion test apparatus;
[0031] FIG. 12A is an optical micrograph of a coating before erosion;
[0032] FIG. 12B is an optical micrograph of a coating with partial erosion;
[0033] FIG. 12C is an optical micrograph of a coating with full erosion; and
[0034] FIG. 13 is a block diagram illustrating a method for preparing an ice-phobic coating in accordance with an embodiment of the disclosure.

DETAILED DESCRIPTION

[0035] Disclosed herein are embodiments of solventless curable coating systems and uses thereof. The embodiments described herein allow for the solventless curable silicone coating system to be prepared over a wide range of coating viscosities. For example, various components of a condensation cure system may be selected to meet a target viscosity, while also maintaining shelf life. Moreover, such systems eliminate the need for any solvents, such as VOC solvents.
Solventless condensation cure systems are advantageous as they enable moisture-based curing at room temperature for thin coating layers. While certain embodiments are described with respect to condensation cure systems, the embodiments are compatible with other systems as well, including addition cure systems and UV cure systems (in which a catalytic curing reaction is activated by UV exposure). Curing may be expedited rapidly for these systems by application of heat.

Certain embodiments are also directed to curable formulations for producing ice-phobic coatings. Ice-phobic coatings play an important role in the aerospace industry. For example, propellers and other components of an aircraft engine utilize coatings based on low surface energy materials to impart hydrophobic properties to the components. Water forms high contact angle droplets on hydrophobic surfaces which can allow a droplet to roll off the surface easily due to the small contact area between the droplet and the surface. However, the dynamics of solid ice formation are more complex than those of water on such surfaces. For example, various factors contribute to the sizes and shapes of ice formations. Moreover, surface roughness of the coating is believed to promote ice adhesion.

The embodiments described herein help to reduce ice adhesion by incorporating low surface energy materials (e.g., hydrophobic elastomers), cryoprotectants, and filler particles into curable coating formulations. Cryoprotectants, such as glycerol, help to reduce ice adhesion failure stress (which relates to an amount of force required to dislodge ice from a surface) compared to coatings without a cryoprotectant. Filler particles improve the durability and erosion resistance of the coatings. In certain embodiments, low loading of filler particles imparts durability while maintaining surface smoothness so as to avoid increasing ice adhesion potential. Embodiments of ice-phobic coating formulations may be based on solventless systems as well as solvent-based systems.

The present invention has been described with reference to specific exemplary embodiments therein. It will, however, be evident that various modifications and changes may be made thereto without departing from the broader scope of the embodiments of the invention as set forth in the appended claims. The specification and drawings are accordingly, to be regarded in an illustrative rather than a restrictive sense.

In the following description, numerous details are set forth. It will be apparent, however, to one skilled in the art, that the present invention may be practiced without these specific details. In some instances, well-known structures and devices are shown in block diagram form, rather than in detail, in order to avoid obscuring the present invention.

As used herein, the term “solventless” refers to a chemical system free of or substantially free of a solvent, such that a total weight percent of solids is at or near 100 wt %.

As used herein, a system that is “substantially free of” a component means that the component, if present in the system, is present below a detectable amount or is present in an amount to having no statistically significant effect on the system (e.g., less than 0.01 ppm).

As used herein, the term “room temperature” or “RT” refers to a temperature ranging from 20°C to about 25°C.

As used herein, when referring to particles, the term “surface area” refers to a maximum molecularly accessible surface area of a material.

The term “particles” when referring materials used as fillers refers to particulate materials ranging in diameter from 1 nm to 1 mm. The morphology of the particles may be crystalline, semi-crystalline, or amorphous, as well as aggregates of smaller particles. Unless stated otherwise, a particle “size” is an average diameter of an ensemble of like particles in which a spherical shape is assumed. In the case of non-spherical particles, such as nanorods or nanotubes, the particle “size” refers to an average value of a largest dimension of like particles. Also, as used herein, the term “nanoparticle” refers to any particle having a maximum dimension less than 1 micrometer (μm), and the term “microparticle” refers to any particle having a minimum dimension greater than or equal to 1 μm.

As used herein, “failure stress” is defined as a maximum or peak value of stress from a load-displacement profile curve. For example, ice adhesion failure stress refers to a maximum stress/load applied to dislodge ice from a surface of a coating.

General embodiments of solventless systems include systems of coatable viscosity may be formulated for each of the three types of systems: condensation systems, addition systems, and ultra-violet (UV) cure systems. Each of these systems can be adapted for meeting end-use requirements (e.g., viscosity, shelf life, etc.) by adjusting various formulation parameters. The embodiments described herein are not limited to coating systems, but can be extended to non-coating applications as well, including, but not limited to, casting, liquid injection molding (LIM), or other molding operations.

Certain embodiments, a condensation cure system includes a siloxane component, a silanol component, a silane component, and a catalyst component.

The siloxane component may include, for example, one or more siloxanes having a wide range of molecular weights and viscosities (e.g., siloxanes available from DOW CORNING, BLUESTAR SILICONES, and GELEST). As an example, a suitable siloxane component may include trimethylsiloxy-terminated polydimethylsiloxane (PDMS) having viscosities ranging from 1 cSt to 20,000,000 cSt. As another example, a suitable low-viscosity PDMS may be DMS-T11 (GELEST) having a viscosity of about 10 cSt. As another example, a suitable low-viscosity PDMS may be DMS-T12 (available from GELEST) having a viscosity of about 20 cSt.

The silanol component may include, for example, one or more silanol-terminated polydimethylsiloxanes having a wide range of molecular weights. As an example, silanols in a viscosity range from 10 cSt to 100,000 cSt (e.g., silanols available from GELEST). As another example, a suitable silanol may be DMS-S31 (available from GELEST) having an average molecular weight of about 26,000 g/mol and a viscosity of about 1,000 cSt. As another example, a suitable silanol may be DMS-32 (GELEST) having an average molecular weight of about 36,000 g/mol and a viscosity of about 2,000 cSt.

The silane component may include, for example, one or more methoxy-, ethoxy-, or acetoxy-silanes (e.g., silanes available from MOMENTIVE and GELEST). As an example, a suitable tri-functional type of silane may be 3-aminopropyltriethoxysilane having a viscosity of about 2
As another example, a suitable tetra-functional type of silane may include tetraethoxysilane (also known as tetraethoxy-orthosilicate). In some embodiments, silane concentrations are typically below 5 wt% (percent weight per total weight).

[0052] The catalyst component may include, for example, tin(II) octoate as a catalyst (e.g., available from SIGMA-ALDRICH). A concentrated solution of catalyst may be prepared in the siloxane component discussed above. In some embodiments, concentrations of the catalyst component may be in a range of 0.01 wt% to 0.1 wt%.

[0053] In certain embodiments, an addition cure system includes a base polymer component, a cross-linking component, and a catalyst component.

[0054] The base polymer component may include, for example, vinyl-siloxane (e.g., vinyl-terminated PDMS) having a viscosity ranging from 1,000 cSt to 60,000 cSt. In one example, a viscosity range of 1 cSt to 100 cSt may be suitable for reactive diluents if no siloxanes are used. As another example, a suitable base polymer component may be DMS-V41 (available from GELEST), which is a vinyl-terminated PDMS having a viscosity of about 10,000 cSt and an average molecular weight of about 62,000 g/mol.

[0055] The cross-linking component may include, for example, methylhydroxiloxane-dimethylsiloxane co-polymer having methylhydroxiloxane content ranging from 15 mol% (percent moles per total moles) to 50 mol%. Molar equivalents of hydrides react with vinyls of vinyl-terminated PDMS to produce a cross-linked network. In one example, a suitable cross-linking component may be HMS-301 (available from GELEST), which is a methylhydroxiloxane-dimethylsiloxane co-polymer having a viscosity about 30 cSt and an average molecular weight of about 2,000 g/mol. In one embodiment, about 3 to 4 parts of cross-linking component for 100 parts of base polymer component is used.

[0056] The catalyst component may include, for example, a platinum complex solution present at a level of 1 ppm to 10 ppm. As an example, the catalyst component may be SPP6830.3 (available from GELEST), which is a platinum-divinyltetramethyl-disiloxane complex in vinyl-terminated PDMS. In one embodiment, 5 ppm to 500 ppm of the platinum complex solution is used.

[0057] In some embodiments, the addition cure system may be formulated as a Part-A and Part-B system, with Part-A corresponding to vinyl-terminated PDMS and a platinum catalyst, and Part-B corresponding to a hydride-functionalized PDMS. As an example, LR 3003-20 (available from WACKER) is an example of a Part-A and Part-B system, which may be used in a liquid injection molding process typical system used in LIM system. Such systems may also be formulated with treated silica.

[0058] In certain embodiments, a UV cure system includes a catalyst component that is activated upon exposure to UV light. UV cure systems are available, for example, from MOVENTIVE, and may be diluted with siloxanes. In some embodiments, a UV system is used for applying a thick coating to a substrate.

[0059] Examples of each system are provided below. Coating formulations for the systems were prepared using various pieces of equipment. A homogenizer (L5M-A High Shear Mixer available from SILVERSON MACHINES, INC.) was used for blending high viscosity silanol or vinyl-siloxane with PDMS to form a uniform solution. Reactive blends were also mixed initially using the homogenizer. An analyzer (Rubber Process Analyzer (RPA) 2000, Serial No. 90 AID 2045, available from ALPHA TECHNOLOGIES, INC.) was used for analyzing rubber cure profiles by obtaining rheological measurements as a function of time and temperature. A viscometer (available from BROOKFIELD ENGINEERING) was used to perform viscosity measurements. It is noted that other equipment may be used to realize the embodiments described herein, as would be appreciated by one of ordinary skill in the art. An optical measuring system (Avant Optical Measuring System, Model 600, OPTICAL GAGING PRODUCTS) was used to measure coating thicknesses before and after erosion tests.

Illustrative Examples of Condensation Cure Systems

[0060] Formulations with four components of siloxane, silanol, silane and catalyst under the condensation cure system were investigated for their viscosity behavior over a time period of hours to days, weeks, and months. FIG. 1A shows viscosity versus time profiles for a condensation cure system formulations each including varying amounts of tin(II) octoate catalyst: 0.030 wt% (plot 102), 0.020 wt% (plot 104), 0.015 wt% (plot 106), 0.010 wt% (plot 108), 0.005 wt% (plot 110), and 0.000 wt% (plot 112). Increased viscosity was observed with increasing amounts of catalyst up to 0.02 wt%, and the viscosity appeared to level off after about 50 hours (about 2 days). The viscosity increased indefinitely until gelting occurred when the catalyst content was at 0.03% or greater.

[0061] FIG. 1B shows viscosity versus time profiles for a condensation cure system illustrating the effects of heating on viscosity behavior over time. Heating the formulations at about 50°C to about 60°C for 1 to 2 hours immediately after addition of the tin (II) octoate catalyst produced more stable viscosity over time (as shown by plots 124 and 126 for lower and higher silane amounts, respectively) as compared to unheated formulations (as shown by plots 120 and 122 for lower and higher silane amounts, respectively). Viscosity measurements were performed at room temperature after cooling each formulation, with the formulations being kept in a closed container. In some instances, skin formations appeared at air interfaces of the formulations due to the presence of moisture, which occurred when formulations remained un-stirred for a significant amount of time.

[0062] Based on the above-described condensation cure formulations with stable viscosity versus time profiles, two- and three-variable design-of-experiment (DOE) systems were developed to allow for tunable viscosity. FIG. 2A illustrates a two-variable planar representation of formulation parameters according to an embodiment of the disclosure. The four corners illustrate bounds of selectable ranges corresponding to silane content (ranging from 1.0 wt% to 1.4 wt%), and catalyst content (ranging from 0.03 wt% to 0.05 wt%), with silanol content being held constant at 23.0 wt% with total weight being adjusted by siloxane. Similarly, FIG. 2B illustrates a three-variable cubic representation of formulation parameters according to an embodiment of the disclosure. The eight corners represent bounds of selectable ranges corresponding to silane content (ranging from 1 wt% to 3 wt%), silanol content (ranging from 15 wt% to 25 wt%), and catalyst content (ranging from 0.01 wt% to 0.03 wt%), with the total weight being adjusted by siloxane.

[0063] Using viscosity data measured for various concentrations of silane and catalyst, statistical fractional factorial fit
analysis was performed for the two-variable DOE using MINITAB statistical software. The fit analysis yielded the following empirical equation:

$$\text{Viscosity} = 330.4 - 41.1\, \text{C}_{\text{Silanol}} + 53.6\, \text{C}_{\text{Silanol}}^2$$

Eq. 1

where \( \text{C}_{\text{Silanol}} \) and \( \text{C}_{\text{Catalyst}} \) correspond to silane and catalyst content, respectively, in units of wt %. Eq. 1 predicts a positive effect of catalyst content on viscosity, a negative effect of silane content on viscosity, and a moderately weak negative effect of the interaction term of silane and catalyst content, with validity expected within the concentration ranges investigated. As an example, it was observed that raising the silane content and lowering the catalyst content will lead towards lower viscosity formulations. This effect is observable in the surface plot shown in FIG. 3A.

[0064] Statistical fractional factorial fit analysis was also performed for the three-variable DOE, which yielded the following empirical equation:

$$\text{Viscosity} = 211.1 - 109.8\, \text{C}_{\text{Silanol}} + 45.5\, \text{C}_{\text{Catalyst}} + 105.3\, \text{C}_{\text{Silanol}}^2$$

Eq. 2

where \( \text{C}_{\text{Silanol}} \), \( \text{C}_{\text{Catalyst}} \), and \( \text{C}_{\text{Silanol}} \) correspond to silane, catalyst, and silanol content, respectively, in units of wt %. Eq. 2 predicts main effects and two-way and three-way interaction effects of the three components. It is predicted that both catalyst and silanol content have a positive effect on viscosity whereas, silane has a negative effect on viscosity.

[0065] FIG. 3A shows a surface plot of viscosity for formulations with silane and catalyst content as variables, silanol content held constant (e.g., at 23 wt %), and total weight adjusted with silanol content, according to an embodiment of the disclosure. FIG. 3A shows a surface plot of viscosity for formulations with catalyst and silanol content as variables, silanol content held constant (e.g., at 1.0 wt %), and total weight adjusted with silanol content, according to an embodiment of the disclosure. FIG. 3A illustrates the positive effect of increasing catalyst and silanol content while holding silanol content constant, as predicted by Eq. 2.

[0066] FIG. 3C shows a surface plot of viscosity for formulations with silane and catalyst content as variables, silanol content held constant (e.g., at 15 wt %), and total weight adjusted with silanol content, according to an embodiment of the disclosure. FIG. 3D shows a surface plot of viscosity for formulations with silane and silanol content as variables, catalyst content held constant (e.g., at 0.01 wt %), and total weight adjusted with silanol content, according to an embodiment of the disclosure. FIGS. 3C and 3D show that viscosity increases by decreasing the silanol content, whereas viscosity increases by increasing either the catalyst or silanol content. Some observed data and predicted values using Eq. 2 are summarized briefly in the Table 1 below.

### Table 1

<table>
<thead>
<tr>
<th>Silanol (wt %) (weight adjusted with 20 cSt siloxane)</th>
<th>Predicted Viscosity (cSt)</th>
<th>Actual Viscosity (cSt) (measured stable viscosity at 5 days)</th>
</tr>
</thead>
<tbody>
<tr>
<td>20%</td>
<td>680</td>
<td>200</td>
</tr>
<tr>
<td>35%</td>
<td>1100</td>
<td>950</td>
</tr>
</tbody>
</table>

[0067] It was observed that the four-component system of siloxane, silanol, silane, and catalyst contains components that can both increase and decrease viscosity with increasing concentration of a given component. This is a rather unexpected behavior observed with silane content in the formulation, and the aforementioned embodiments provide for a convenient design space for a formulator to arrive at a desirable viscosity for a coating composition while maintaining desired end-use performance.

[0068] Without being bound by theory, a possible mechanism for the above behavior may be explained as follows. A condensation cure formulation containing 79 wt % PDMS, 20 wt % silanol of molecular weight 28,000 g/mol, 1 wt % amino-propyl-triethoxysilane of molecular weight 221 g/mol will have an approximate molar composition for a tin(II) catalyzed reaction at RT as: 1 mole silano+4 moles silanol+oligomers of silane-capped-silanol of MW=28,000 g/mol, 56,000 g/mol, etc. A molar ratio of 1 to 6 would translate to 1 to 9 in an equivalents ratio. As the silanol content is decreased in the above system, the ratio of silanol to silane would approach a 1 to 1 ratio in equivalents, which would lead to oligomer formation of an increasingly higher degree of polymerization with silane end-capping. This may explain the behavior of the viscosity as observed above with silane.

[0069] Such a system, upon coating and moisture activated cure, would undergo the following reaction, where alcohol would condense out if an ethoxy-type silane was used: oligomers of silane-capped-silanol + H2O → silanol+silane-capped-silanol = curing-alcohol. It was observed that the initial viscosity for a given formulation at higher levels of catalyst content sometime showed a faster rise in viscosity, which decreased over time to produce a more stable viscosity. This may suggest that a tin(II) catalyzed reaction could have aggregates initially formed, which would subsequently break down resulting in an equilibrium distribution of oligomers.

[0070] Viscosity data for various molecular weights of siloxanes are shown in Table 2 (data from GELESI). Silanols for condensation cure systems and vinyl-terminated silanols for addition cure systems are reported to have molecular weights comparable to siloxanes for the same viscosities. Silanols and vinyl-terminated siloxanes are commercially available in viscosity ranges, respectively, from about 10 cSt to about 100,000 cSt and from about 1 cSt to about 100,000 cSt.

### Table 2

<table>
<thead>
<tr>
<th>Viscosity (cSt)</th>
<th>Avg. Molecular Weight (g/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>237</td>
</tr>
<tr>
<td>10</td>
<td>1,250</td>
</tr>
<tr>
<td>100</td>
<td>5,970</td>
</tr>
<tr>
<td>1000</td>
<td>28,000</td>
</tr>
<tr>
<td>10,000</td>
<td>62,700</td>
</tr>
<tr>
<td>100,000</td>
<td>139,000</td>
</tr>
<tr>
<td>1,000,000</td>
<td>368,000</td>
</tr>
</tbody>
</table>

[0071] While siloxanes are suitable as non-reactive diluents, a blend of low and high molecular weight silanols for condensation cure systems were also prepared. It is believed that the low molecular weight fraction would help control the viscosity during the first stage of the reaction for performing the coating operation. Once coated and subsequently cured, most of this fraction would contribute to network formation.
FIG. 4 is a block diagram illustrating a method for preparing a solventless curable coating formulation according to an embodiment of the disclosure. Although described with respect to components of a condensation cure system, the method may be adapted to other types of systems, including addition and UV cure systems.

At block 402, a siloxane component, a silanol component, and a silane component are mixed together to form a mixture (e.g., using a homogenizer). At block 404, a catalyst component is added to the mixture (e.g., tin(II) octoate), forming a solventless curable coating formulation.

At block 406, the mixture is heated immediately (e.g., within 10 minutes) after adding the catalyst component to the mixture. In one embodiment, concentrations of each of the silanol component, the silane component, and the catalyst component are adjusted based on the siloxane component. In one embodiment, the concentrations are selected to cause the mixture to have a viscosity in a range of 50 cSt to 600 cSt, or any other viscosity described herein with reference to the various embodiments.

Examples of Addition Cure Systems

An exemplary addition cure formulation was prepared using the following components: vinyl-terminated siloxane (DMS-V41) of equivalent weight 31,550 g/mol and viscosity 10,000 cSt as the Part-A component; hydride-siloxane (HMS-301) of equivalent weight 245 g/mol and viscosity 2,000 cSt; platinum catalyst SIP 68303.3; and siloxane of viscosity 100 cSt. Formulations were prepared by placing 100 cSt siloxane in a container, adding vinyl-siloxane to the container, and mixing with a homogenizer. Hydride-siloxane was then added to the mixture, and the mixture was mixed again with the homogenizer. A solution of platinum catalyst was prepared in the siloxane at 1 wt %.

TABLE 3

<table>
<thead>
<tr>
<th>Part-A</th>
<th>Exposure at 60°C for 2</th>
<th>Viscosity at RT over Time (cSt)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Time = 2</td>
<td>Time = 16</td>
</tr>
<tr>
<td>Part-B</td>
<td>Hours (measured at RT)</td>
<td></td>
</tr>
<tr>
<td>10 to 1</td>
<td>None (Control)</td>
<td>330</td>
</tr>
<tr>
<td>10 to 1</td>
<td>Heated at 60°C</td>
<td>Gelled</td>
</tr>
</tbody>
</table>

Viscosity profiles of the same 10 to 1 system were further evaluated using siloxanes of other viscosities as diluents (e.g., 10 cSt and 1000 cSt), demonstrating stable systems consistent with the viscosities of the diluents and their concentrations.

The behavior of viscosity of the addition cure system at RT was similar to that of the condensation cure system, which suggests that an intermediate oligomeric structure is formed with a lower degree of oligomerization of the intermediate. Upon coating and curing, the network structure is formed, as illustrated in FIG. 6. However, the addition cure system was different from the condensation cure system in a significant way in that the former resulted in gelation upon heating, whereas the latter resulted in a more stable system of oligomeric intermediates with improved shelf-life.

While siloxanes are suitable as non-reactive diluents, blends of low and high molecular weight vinyl-capped-siloxanes with hydride-siloxanes were also formulated, as it is believed that the low molecular weight fraction could help control the viscosity during the first stage of the reaction when a coating is to be formed. Once coated and subsequently cured at RT or elevated temperature, most of the low molecular weight fraction is converted into the network formation.

In some embodiments, very thick coating may be made by casting, injection molding, transfer molding, or LIM, and may be produced using the addition cure system. As an example, a Part-A formulation contained vinyl-capped-siloxane polymer, quartz filler, calcium carbonate, and platinum catalyst, which had a viscosity 153,000 cSt. Part-B formulation contained vinyl-capped-siloxane polymer, hydride cross-linker, and blue pigment, which had a viscosity of 6,000 cSt. A mix ratio of Part-A to Part-B was 10 to 1. In a particular application requiring a compliant rubber sheet that would demonstrate release characteristics of ink for printing onto glass and ceramics, the system was diluted using siloxane of 100 cSt at a loading of 20 wt % to 30 wt %. Various other concentrations of diluents were also evaluated. Finally, a formulation was selected that yielded a heat-cured sheet of having a Shore A hardness of 25±5. The sheet demonstrated a specific gravity of 1.16, a tensile strength of 427 psi, and elongation at break of 280%.

To demonstrate mechanical performance and ink-transfer capability, flowable liquid formulations were prepared using PDMS of viscosity 50 cSt or 100 cSt and a two-component platinum cure system. In these formulations, the Part-A component included vinyl-siloxane and platinum catalyst along with an appropriate level of filler, and the Part-B component included vinyl-siloxane and hydride-siloxane cross-linker along with an appropriate level of filler. PDMS was mixed with the Part-A component first as this was the higher viscosity component, followed by adding the
Part-B component to yield a Part-A to Part-B ratio of about 10 to 1. This formulation strategy provided a readily mixable and flowable system, which could be pumped into a flat mold of desired membrane thickness or spin-cast into a sheet of desired thickness. Cured membranes were obtained after heating at 220°F. for 75 minutes.

Table 4 summarizes the parameters and mechanical performance results for three two-component systems (Samples A-C). Results for liquid silicone rubber (LSR) membranes (Samples D-F) are shown for comparative purposes. Samples A-C were each about 55 mil in thickness. Two levels of PDMS oil from about 27% to 39% were evaluated, which provided adequate mechanical performance for ink transfer to a substrate during which the membranes underwent repeated large-scale deformations of about 100% elongation. Mold surface preparation determined the roughness of the surface produced, which was evaluated by atomic force microscopy. A rougher surface resulted in a larger amount of ink pick-up for subsequent transfer to the substrate.

### TABLE 4

<table>
<thead>
<tr>
<th>Composition (wt %)</th>
<th>Sample A</th>
<th>Sample B</th>
<th>Sample C</th>
<th>Sample D</th>
<th>Sample E</th>
<th>Sample F</th>
</tr>
</thead>
<tbody>
<tr>
<td>Part-A</td>
<td>68.5</td>
<td>55.6</td>
<td>68.5</td>
<td>1SR</td>
<td>1SR</td>
<td>LSR</td>
</tr>
<tr>
<td>Part-B</td>
<td>4.1</td>
<td>5.6</td>
<td>4.1</td>
<td>for</td>
<td>for</td>
<td>for</td>
</tr>
<tr>
<td>PDMS(100)</td>
<td>27.4</td>
<td>38.8</td>
<td>27.4</td>
<td>LIM</td>
<td>LIM</td>
<td>LIM</td>
</tr>
<tr>
<td>PDMS(50)</td>
<td></td>
<td></td>
<td></td>
<td>No Oil</td>
<td>No Oil</td>
<td>No Oil</td>
</tr>
<tr>
<td>Sp. Gravity</td>
<td>1.16</td>
<td>1.12</td>
<td>1.17</td>
<td>1.12</td>
<td>1.11</td>
<td>1.09</td>
</tr>
<tr>
<td>Shore A Hardness</td>
<td>25</td>
<td>19</td>
<td>23</td>
<td>22</td>
<td>26</td>
<td>20</td>
</tr>
<tr>
<td>Tensile Strength (psi)</td>
<td>427</td>
<td>313</td>
<td>420</td>
<td>1117</td>
<td>1109</td>
<td>939</td>
</tr>
<tr>
<td>Elongation (%)</td>
<td>280</td>
<td>208</td>
<td>239</td>
<td>893</td>
<td>614</td>
<td>905</td>
</tr>
<tr>
<td>Modulus100 (psi)</td>
<td>188</td>
<td>175</td>
<td>204</td>
<td>70</td>
<td>104</td>
<td>52</td>
</tr>
<tr>
<td>Tear B (lbs/in)</td>
<td>53</td>
<td>39</td>
<td>53</td>
<td>283</td>
<td>100</td>
<td>121</td>
</tr>
<tr>
<td>Thickness (mil)</td>
<td>58 ± 5</td>
<td>55 ± 3</td>
<td>58 ± 5</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ink Transfer</td>
<td>Suitable</td>
<td>Suitable</td>
<td>Suitable</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>AFM Roughness (Ra)</td>
<td>117 ± 41</td>
<td>87 ± 20</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Examples of UV Cure Systems

[0083] An exemplary UV cure system included SILOPREN UV Electro 225-1 Base (viscosity of 70,000 cSt), which is a colorless or translucent system including polyvinyl siloxane, dimethyl-hydrogen-polydimethylsiloxane and silica. The UV cure system further included SILOPREN UV Electro 225-1 Catalyst (viscosity 10,000 cSt), which is a colorless or translucent system including platinum catalyst and polyvinyl siloxane. A UV light source (UV LED SLM™, PHOSEO NE TECHNOLOGY) was used to irradiate the system at a power of 480 W, a peak irradiance of 8 W/cm² at 395 nm and 4 W/cm² at 365 nm.

[0084] This system was similar to the addition cure systems described above, except that the platinum catalyst was generated in response to UV irradiation. Siloxanes can be also be used as diluents, as in condensation or addition cure systems. Material transparency may be adjusted to allow light to pass through for a more effective UV cure.

[0085] The above system of Silopren UV Electro 225-1 at a Base to Catalyst ratio of 98 to 2 was cured readily in a casting mold by exposure to UV light for about 5 minutes to about 10 minutes. A sheet was obtained having a thickness of 2 mm. The cured silicone elastomer sheet showed a Shore A hardness of 23, a tensile strength of 592 psi, and an elongation at break of 674%.

[0086] Other UV cure systems, such as NUVIA-SII, 5031, utilize a single component dual cure silicone, where UV-visible light and moisture curing can be utilized for the same formulation. In such systems, UV curing occurs due to acrylic functionality and moisture curing occurs due to tin(II) catalyzed acetoxy silane.

[0087] In certain embodiments that contained additional filler materials, silica, for example, appeared to have no adverse effect on UV curing, while dark colored filler materials, such as graphite, resulted in skin-curing with limited curing depth through the coating. Indium tin oxide (or tin-doped indium oxide) is one of the most widely used transparent conductive oxides. Embodiments that utilized indium tin oxide allowed for electrical and thermal conductivity and provided optical transparency that facilitated UV curing. Filler materials, such as nanoparticle fillers, are often to impart beneficial properties to the coatings while provide transparency or translucency during curing due to their small sizes. It is noted that condensation and addition cure systems have no associated restrictions regarding transparency or translucency.

Embodiments of Ice-Phobic Coating Formulations

[0088] Certain embodiments of the disclosure relate to ice-phobic coating formulations. Such formulations include low surface energy elastomers including, but not limited to, silicones, fluoro-silicones, and fluoro-elastomers. Embodiments of ice-phobic coating formulations for producing ice-phobic coatings that exhibit advantageous ice adhesion resistance include silicone, nanoparticle fillers, and a cryoprotectant. Moreover, such embodiments may be based on solventless systems or systems utilizing solvents (e.g., non-VOC solvents).

[0089] In certain embodiments, ice-phobic coating formulations include filler particles of various compositions, sizes, and morphologies. Silicone-based formulations that include filler particles at 10 wt % to 30 wt % demonstrated high ice adhesion (quantified as ice adhesion failure stress measured using an “ice-pin test” discussed below), while formulations having less filler particles led to coatings with superior ice-
phobicity (e.g., lower ice adhesion). Filler particles may be included in coating formulations to provide reinforcement and increase erosion resistance of the resulting coating. In some embodiments, nanoparticle fillers, such as surface-treated silica nanoparticles, are effective for these purposes at lower loading amounts.

In some embodiments, the coating formulations include a cryoprotectant, such as glycerol. As an example, a silicone-based formulation containing glycerol at 1 wt % to 3 wt % and silica nanoparticles resulted in low ice adhesion. As another example, a formulation containing glycerol at 1 wt % to 3 wt % and silica nanoparticles at 3 wt % resulted in a coating having the lowest ice adhesion compared to unfilled or silica nanoparticle-filled coatings, and exhibited acceptable erosion resistance. As another example, polytetrafluoroethylene (PTFE) nanoparticles, graphene nanoparticles, and micrometer-scale polypropylene particles at low loading (e.g., about 3 w %) demonstrated low ice adhesion. At high loading (e.g., 33 wt % or greater) of PTFE nanoparticles, the resulting coating demonstrated significantly higher ice adhesion failure stress.

In some embodiments, ice-phobic coating formulations are applied in a liquid state to a solid surface, for example, by spraying or other suitable techniques. In some embodiments, the formulations may be solvent-based or solventless, and the viscosity may be selected to facilitate spraying to achieve a desired coating thickness. For solvent-based formulations, suitable solvents may include VOC solvents and/or non-VOC solvents, which may be used to disperse the formulations. In some embodiments, solventless formulations may be prepared in accordance with any of the condensation, addition, or UV cure systems described herein.

In some embodiments, the elastomer includes one or more of fluoro-elastomer, fluoro rubber of polyethylene type (e.g., having all sub stituents fluor and perfluoralkyl or perfluoroalkoxy groups on the polymer chain), fluoro-silicone (e.g., pre-formulated with silica filler particles), or silicone (polysiloxane). In some embodiments, the elastomer is further formulated with fillers, curatives, and other additives.

In some embodiments, the ice-phobic coating formulation was deposited on a surface treated with a primer, such as a silane-based primer that was moisture cured on the surface. Examples of primers include, but are not limited to, CEMLOK® 680 (available from LORD CORPORATION), SP-270 (available from NUSIL TECHNOLOGY LLC) and PR-1200 (available from DOW CORNING).

In some embodiments, fillers include filler particles, such as silica particles, polypropylene (PP) particles, polytetrafluoroethylene (PTFE) particles, and graphene particles. Silica particles may include silica particles having their surfaces treated with dimethyl-dichlorosilane ("fumed silica"). In some embodiments, the filler particles have an average size ranging from 5 nm to 20 nm (e.g., 17 nm nanoparticles). In some embodiments, filler particles may form aggregates having an average diameter ranging from 100 nm to 300 nm, and greater than 500 nm in some embodiments. Examples of filler particles include micronized polypropylene (MICROPRO 400, MICRO POWDERS, INC.) having an average diameter of about 6 µm, PTFE nanoparticles (nanoFON® 114T, SHAMROCK INDUSTRIES) having an average diameter of about 200 nm and a surface area of 6 to 8 m²/g, and graphene particles (xGnP® C-500, XG SCIENCES, INC.) having an average thickness ranging from 1 nm to 5 nm with an average surface area ranging from 300 m²/g to 750 m²/g. Other types of filler particles include calcium carbonate, titanium dioxide, indium tin oxide, or any other suitable particle for dispersing within a coating formulation.

In some embodiments, a cryoprotectant is included. Cryoprotectants are well recognized for their use in cryopreservation of tissue, cells, and blood-based systems to increase shelf life under freezing conditions. Their mechanism of action includes lowering of ice melting temperature and/or reducing the size of ice crystals. Without cryoprotectants, the formation of large ice crystals can cause damage to cell membranes. Examples of cryoprotectants include, but are not limited to, glycerol, trehalose, dimethylsulfoxide (DMSO), and polyvinyl alcohol (PVA). Any other material capable of reducing melting temperature and/or reducing the size of ice crystals formed may be utilized as a cryoprotectant. Without being bound by theory, it was hypothesized that a compatible cryoprotectant used in an ice-phobic coating formulation could reduce the size of ice crystals formed on the surface of the resulting coating, and thus reduce the overall adhesion of ice to the coating.

Illustrative Examples of Ice-Phobic Coating Formulations

Various sample formulations were investigated for their use in ice-phobic coatings, which are summarized in Table 5. Variations of these samples were also characterized. The samples included various low surface energy polymers, such as fluoro-elastomer, fluoro-silicone, and silicone, had different cure mechanisms, and included varying levels of fillers. Some of the samples were solvated in traditional VOC solvents or a non-VOC solvent, and one sample (Sample 6) was a solventless system. Viscosities of the samples were evaluated at 20 wt % solids with the exception of solventless Sample 6, which was at 100 wt % solids by definition. Viscosities varied depending on the molecular weight of the polymer and filler content in the formulation. The samples were subsequently diluted at varying levels to arrive at a suitable coating viscosity for spraying (e.g., using a pneumatic spray coater), which could vary of a wide range from 100 cSt to 1500 cSt.

**TABLE 5**

<table>
<thead>
<tr>
<th>Sample 1</th>
<th>Sample 2</th>
<th>Sample 3</th>
<th>Sample 4</th>
<th>Sample 5</th>
<th>Sample 6</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chemistry/ Cure Type</td>
<td>silicone/platinum cure</td>
<td>fluoro-elastomer/hexafluorobiphenyl cure</td>
<td>fluoro-silicone/peroxide cure</td>
<td>silicone/platinum cure</td>
<td>silicone/platinum cure</td>
</tr>
<tr>
<td>Silica Filler (wt %)</td>
<td>6</td>
<td>0 (metal oxides at 8)</td>
<td>17</td>
<td>13</td>
<td>0</td>
</tr>
</tbody>
</table>
TABLE 5-continued

<table>
<thead>
<tr>
<th>Sample 1</th>
<th>Sample 2</th>
<th>Sample 3</th>
<th>Sample 4</th>
<th>Sample 5</th>
<th>Sample 6</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solvent Type</td>
<td>VOC</td>
<td>VOC</td>
<td>VOC</td>
<td>non-VOC</td>
<td>non-VOC</td>
</tr>
<tr>
<td>Viscosity (cSt) at 20 wt % Solids Diluted</td>
<td>5,450</td>
<td>105</td>
<td>375</td>
<td>14,750</td>
<td>120</td>
</tr>
<tr>
<td>Solids Content (wt %) for Coating</td>
<td>13.3</td>
<td>20.0</td>
<td>20.0</td>
<td>15.4</td>
<td>20.0</td>
</tr>
<tr>
<td>Coating Viscosity (cSt)</td>
<td>374 ± 8</td>
<td>105</td>
<td>375</td>
<td>1,320</td>
<td>120</td>
</tr>
</tbody>
</table>

Example 1

Water Contact Angle on Coatings

Example 2

Electron Microscopy of Nano-Dispersed Coatings

Example 3

Atomic Force Microscopy of Coatings on Aluminum Surfaces
TABLE 7  
Surface roughness for coatings with different fillers  

<table>
<thead>
<tr>
<th>Coating/Filler Conditions</th>
<th>Measured $R_a$ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample X</td>
<td>2.0</td>
</tr>
<tr>
<td>0 wt % nano-PTFE</td>
<td></td>
</tr>
<tr>
<td>0 wt % silica nanoparticles</td>
<td></td>
</tr>
<tr>
<td>Sample X</td>
<td>2.7</td>
</tr>
<tr>
<td>1 wt % nano-PTFE</td>
<td></td>
</tr>
<tr>
<td>0 wt % silica nanoparticles</td>
<td></td>
</tr>
<tr>
<td>Sample X</td>
<td>3.0</td>
</tr>
<tr>
<td>3 wt % nano-PTFE</td>
<td></td>
</tr>
<tr>
<td>0 wt % silica nanoparticles</td>
<td></td>
</tr>
<tr>
<td>Sample X</td>
<td>6.9</td>
</tr>
<tr>
<td>0 wt % nano-PTFE</td>
<td></td>
</tr>
<tr>
<td>13 wt % silica nanoparticles</td>
<td></td>
</tr>
<tr>
<td>Sample X</td>
<td>7.4</td>
</tr>
<tr>
<td>3 wt % nano-PTFE</td>
<td></td>
</tr>
<tr>
<td>13 wt % silica nanoparticles</td>
<td></td>
</tr>
</tbody>
</table>

Example 4  
Ice-Pin Push Out Test for Evaluating Ice Adhesion Resistance

[0102] The ice-pin push out test (or “ice-pin test”) is a technique developed by the Department of the Army, Engineer Research and Development Center, Cold Regions Research and Engineering Laboratory (CRREL), and is used to quantify ice adhesion to various surfaces. FIG. 8 is a diagram illustrating an ice-pin push out test apparatus 800, which includes a cylindrical pin 802 disposed within an ice mold 808. Disposed on a surface of the pin 802 is a coating formed in accordance with any of the embodiments described herein. The ice mold 808 is supported on a base 806 that provides space for the pin 802 to be displaced through the ice mold 808. To prepare for testing, the ice mold 808 was filled with water with the pin 802 disposed inside and subjected to a temperature of −20°C for at least 24 hours prior to testing to form ice 810. Measurements were then performed by applying a force to a top 805 of a cap 804 using a tensile tester at a deformation rate of 0.051 cm per minute (or 0.02 inches per minute). The lower the resistance force at the ice-pin interface, the more effective the coating was as an ice-phobic coating. Based on the surface area of the pin 802 in contact with ice 810 (defined by the pin 802 size and the ice contact extent 812), the measured failure stress was reported in units of kPa for a given coating thickness. For such measurements, the lowest thickness of coating that was prepared was 25 μm (or 1 mil) and the highest was 250 μm (or 10 mil). A Di-Metric Plus Vision Computer (OGP, INC.) was used for measuring coating thickness, which was suitable for measuring thickness on both flat and cylindrical surfaces in the micrometer range. The results ice adhesion resistance tests for various surface coatings are summarized below.

[0103] FIG. 9 shows ice adhesion load-displacement curves for coatings of different thickness according to embodiments of the present disclosure. Three coatings were prepared at the thicknesses of 25 μm (plot 902), 125 μm (plot 904), and 250 μm (plot 906). It was observed that higher coating thickness resulted in lower failure stress, though the effect was less pronounced at progressively higher thicknesses. In certain embodiments, coatings having thicknesses greater than 100 μm have corresponding ice adhesion failure stresses less than 20 kPa.

[0104] FIG. 10A shows ice adhesion failure stresses measured for various ice-phobic coatings prepared according to embodiments of the present disclosure. Coatings were prepared based on the sample formulations of Table 5, with each coating having a thickness of 25 μm. It was observed that all coatings containing filler particles, which were in the range of about 6 wt % to 30 wt %, showed higher ice adhesion than those containing no filler particles. For example, the coating based on Example 2 (a bisphenol-furyl fluoro-estomer formulation containing about 8 wt % filler) and the coating based on Example 3 (a peroxide-cure fluoro-silicone formulation containing 17 wt % filler) demonstrated high ice adhesion. Other coatings based on filled silicones containing 6 wt % to 30 wt % traditional silica fillers (Sample 4, Sample 7, and Sample 1) also demonstrated comparatively high ice adhesion. The coating formed based on Sample 5 (a filler-free platinum cure system in a non-VOC solvent), the coating based on Sample 6 (a solventless, filler-free platinum cure system), and the coating based on Sample 8 (a condensation cure system with less than 1 wt % titanium dioxide) each demonstrated low ice adhesion (e.g., ice adhesion failure stress less than 20 kPa). While the absence of filler particles resulted in the lowest ice adhesion, it is believed that filler particles help to improve erosion resistance of the coatings. Thus, certain embodiments include filler particles at suitable loading to maximize erosion resistance while minimizing any adverse effect on ice adhesion resistance.

[0105] FIG. 10B shows ice adhesion failure stresses for ice-phobic coatings utilizing varying amounts of filler particles according to embodiments of the present disclosure. The coatings were based on the formulation of Sample 5 including nano-PTFE at different loading amounts (0 wt %, 1 wt %, 3 wt %, and 33 wt %). A thickness of each coating was 25 μm. While low loading levels demonstrated low ice adhesion, higher loading (33 wt %) appeared to have an adverse effect on adhesion resistance.

[0106] FIG. 10C shows ice adhesion failure stresses for ice-phobic coatings utilizing different levels of silica fillers according to embodiments of the present disclosure. A coating based on the formulation of Sample 4 having fused silica at 13 wt % loading was compared against a coating based on the formulation of Sample 5 having silica nanoparticles at 3 wt % loading. While the loading amounts differed, it was expected that 3 wt % loading with silica nanoparticles would yield a comparable set of physical performances otherwise. Lower ice adhesion was observed with the lower loading of silica nanoparticles.

[0107] FIG. 10D shows ice adhesion failure stresses for ice-phobic coatings utilizing different types of filler nanoparticles according to embodiments of the present disclosure. The coatings were prepared based on the formulation of Sample 5 having different filler particles each at a total loading of 3 wt %, with silica nanoparticles (with average sizes ranging from 10 nm to 50 nm), graphene (xGnP® C-500), and polypropylene microparticles (MICROPOR® 400) used as the filler particles. A thickness of each coating was 25 μm. Each coating displayed comparable and relatively low levels of ice adhesion.

[0108] FIG. 10E shows ice adhesion failure stresses for ice-phobic coatings utilizing different amounts of glycerol as a cryoprotectant according to embodiments of the present disclosure. The coatings were prepared based on the formulation of Sample 5 at different loadings of glycerol (0 wt %, 1 wt %, and 3 wt % glycerol) with a constant loading of silica.
nanoparticles (at 3 wt%). A thickness of each coating was 25 µm. It is observed from FIG. 10E that the presence of a relatively small amount of cryoprotectant can significantly reduce ice adhesion failure stress (e.g., by a factor of two to three). It is noted that other cryoprotectants may yield similar results, and thus the embodiments herein are not limited to glycerol.

Example 5

Erosion Resistance of Coatings

Erosion resistance methodologies were adapted from ASTM G76-13, “Standard Test Method for Conducting Erosion Tests by Solid Particle Impingement Using Gas Jets”. An erosion test apparatus included a Problast system (VANIMAN MANUFACTURING CO.) fitted with air flow in-take at a desired pressure at ambient temperature, and a reservoir for holding the grit powder of aluminum oxide of 50 Micron/220 grit. A nozzle diameter was 1.6 mm and a distance of the nozzle from the sample surface (coating on an aluminum coupon) was 10 mm±1 mm at an angle of 90° from the sample surface. Test durations (with grit blasting) were kept at 30, 60, 90, and 120 seconds. The weight loss of the coupons was found to be inconsistent, as the grit material was embedded in the aluminum and the coating upon impact. Therefore erosion was qualitatively measured by taking optical images of the coated surfaces of the coupons at varying times of exposure upon grit blasting. FIGS. 11A-11C show, respectively, front, side, and inside photographs of the erosion test apparatus.

[0110] FIGS. 12A-12C are optical micrographs of varying degrees of erosion of a coating based on Sample 1. A thickness of the coating was 125 µm. FIG. 12A shows the coating with no erosion (prior to grit exposure). FIG. 12B shows the coating with partial erosion, with some aluminum oxide grit particles being embedded in the coating. FIG. 12C shows the coating with full erosion, with the underlying aluminum coupon being visible.

[0111] Table 8 summarizes erosion resistance test results for coatings prepared from a tin-catalyzed silanol-silane system based on a VOC solvent and containing silica nanoparticles (Sample 9). Three different coatings were formed on aluminum coupons and had varying thicknesses. Erosion testing was performed as described above.

<table>
<thead>
<tr>
<th>TABLE 8</th>
<th>Erosion resistance results for Sample 9</th>
</tr>
</thead>
<tbody>
<tr>
<td>Target Thickness of Coating (mil)</td>
<td>1</td>
</tr>
<tr>
<td>Actual Measured Thickness (mil)</td>
<td>1.80 ±0.32</td>
</tr>
<tr>
<td>% Erosion</td>
<td>@ 30 seconds</td>
</tr>
<tr>
<td></td>
<td>@ 60 seconds</td>
</tr>
<tr>
<td></td>
<td>@ 90 seconds</td>
</tr>
</tbody>
</table>

[0112] Table 9 summarizes erosion resistance and ice adhesion failure test results for coatings prepared from a tin-catalyzed silanol-silane system based on a VOC solvent and containing silica nanoparticles (Sample 10). Three different coatings were formed on aluminum coupons and had target thickness of 5 mil (with actual thicknesses of 5.4, 5.9, and 7.6 mil). Erosion testing was performed as described above.

<table>
<thead>
<tr>
<th>TABLE 9</th>
<th>Ice adhesion failure and erosion resistance results for Sample 10</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ice Adhesion Failure Stress @ 1 Mil Thickness (kPa)</td>
<td>Grit Blast Time</td>
</tr>
<tr>
<td>66 ± 15</td>
<td>@ 30 seconds</td>
</tr>
<tr>
<td></td>
<td>@ 60 seconds</td>
</tr>
<tr>
<td></td>
<td>@ 90 seconds</td>
</tr>
</tbody>
</table>

[0113] Table 10 summarizes erosion resistance and ice adhesion failure test results for coatings prepared from a tin-catalyzed silanol-hydride (methyl hydrogen cross-linker with 45% Si—H groups) system based on a VOC solvent and without filler particles (Sample 11). Three different coatings were formed on aluminum coupons and had target thickness of 10 mil (with actual thicknesses of 9.1, 13.3, and 10.3 mil). Erosion testing was performed as described above.

<table>
<thead>
<tr>
<th>TABLE 10</th>
<th>Ice adhesion failure and erosion resistance results for Sample 11</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ice Adhesion Failure Stress @ 1 Mil Thickness (kPa)</td>
<td>Grit Blast Time</td>
</tr>
<tr>
<td>45 ± 6</td>
<td>@ 30 seconds</td>
</tr>
<tr>
<td></td>
<td>@ 60 seconds</td>
</tr>
<tr>
<td></td>
<td>@ 90 seconds</td>
</tr>
</tbody>
</table>

[0114] The results of Table 8 indicate that 1 mil thickness is ineffective against erosion resistance for any exposure time to grit blasting. Table 10 demonstrates erosion resistance results for Sample 11 that are superior to those of Samples 9 and 10, as shown in Tables 8 and 9, respectively. Moreover, Sample 11, which was filler free, also demonstrated superior ice adhesion resistance over sample 10.

[0115] FIG. 13 is a block diagram illustrating a method for preparing an ice-phobic coating in accordance with an embodiment of the disclosure. At block 1302, an ice-phobic coating formulation is provided, the formulation including an elastomer, filler particles, and a cryoprotectant. The components of the formulation may correspond to any of the examples described herein, including combinations and variations thereof.

[0116] At block 1304, a primer coating is applied to a surface and allowed to cure. At block 1306, the ice-phobic coating formulation is deposited onto the surface (e.g., with the primer coating serving as an intermediate layer between the ice-phobic coating formulation and the surface). In some embodiments, the ice-phobic coating formulation is deposited directly onto the surface (e.g., block 1304 is omitted). At block 1308, the ice-phobic coating is allowed to cure and form an ice-phobic coating. In some embodiments, the ice-phobic coating formulation is solventless, and is a condensation cure system, an addition cure system, or a UV cure system. In some embodiments, the ice-phobic coating formulation is solvent-based (e.g., VOC solvent, non-VOC solvent, or combinations thereof).

Further Embodiments

[0117] The following examples pertain to further embodiments. In one aspect of the present disclosure, a solventless curable coating formulation comprises a siloxane component at a first concentration, a silanol component at a second con-
centration, a silane component at a third concentration, and a catalyst component at a fourth concentration, wherein a viscosity of the solventless curable coating formulation ranges from 50 cSt to 1,000 cSt.

[0118] In another aspect of the present disclosure, a solventless curable coating formulation comprises a siloxane component at a first concentration, a vinyl-siloxane component at a second concentration, a hydride-siloxane component at a third concentration, and a catalyst component at a fourth concentration, wherein a viscosity of the solventless curable coating formulation ranges from 50 cSt to 1,000 cSt.

[0119] In yet another aspect of the present disclosure, solventless curable coating formulation comprises a first component at a first concentration, the first component comprising siloxane, a second component at a second concentration, the second component comprising silanol or vinyl-siloxane, a third component at a third concentration, the third component comprising silane or hydride-siloxane, and a fourth component at a fourth concentration, the fourth component comprising a catalyst, wherein a viscosity of the formulation ranges from 50 cSt to 1,000 cSt.

[0120] In one embodiment, the viscosity ranges from 100 cSt to 1,000 cSt, from 50 cSt to 600 cSt, from 250 cSt to 400 cSt, from 100 cSt to 400 cSt, or from 60 cSt to 160 cSt.

[0121] In one embodiment, the siloxane of the first component comprises PDMS.

[0122] In one embodiment, the first concentration of the first component ranges from 84 wt% to 72 wt%, and wherein the siloxane of the first component comprises PDMS.

[0123] In one embodiment, the formulation was heated within a range of 50°C to 60°C for 1 to 2 hours immediately after mixing the second component with the first, second, and third components. In one embodiment, 24 hours after the coating formulation was heated, the viscosity remains stable within 50 cSt.

[0124] In one embodiment, the second concentration of the second component ranges from 15 wt% to 25 wt%, and wherein the silanol of the second component comprises silanol-terminated PDMS.

[0125] In one embodiment, the third concentration of the third component ranges from 1 wt% to 3 wt%. In one embodiment, the third concentration of the third component ranges from 1 wt% to 1.4 wt%. In one embodiment, the silane of the third component comprises one or more of methoxy-silane, ethoxy-silane, and/or acetoxy-silane. In one embodiment, the silane of the third component comprises 3-aminopropyltriethoxysilane. In one embodiment, wherein the silane of the third component comprises tetraethoxysilane.

[0126] In one embodiment, the fourth concentration of the fourth component ranges from 0.001 wt% to 0.1 wt%. In one embodiment, the fourth concentration of the fourth component ranges from 0.01 wt% to 0.05 wt%. In one embodiment, the fourth concentration of the fourth component ranges from 0.01 wt% to 0.05 wt%. In one embodiment, the catalyst of the fourth component comprises tin(II) octate.

[0127] In one embodiment, the second component comprises silanol and the third component comprises hydride-siloxane, and wherein the fourth component comprises a tin catalyst.

[0128] In one embodiment, the formulation further comprises filler particles. In one embodiment, the filler particles comprise one or more of indium tin oxide, silica particles, or graphite.

[0129] In one embodiment, the coating formulation is an ice-phobic coating formulation. In one embodiment, the ice-phobic coating formulation is adapted to form an ice-phobic coating having an ice adhesion failure stress ranging from 1 kPa to 20 kPa.

[0130] In another aspect of the present disclosure, a method comprises spraying the aforementioned solventless curable coating formulation onto a surface.

[0131] In yet another aspect of the present disclosure, a method comprises producing a mold by casting or liquid injection molding the aforementioned solventless curable coating formulation.

[0132] In yet another aspect of the present disclosure, a method comprises mixing a siloxane component, a silanol component, and a silane component to form a mixture, and adding a catalyst component to the mixture. The method further comprises heating the mixture within a range of 50°C to 60°C for 1 to 2 hours immediately after adding the catalyst component to the mixture, wherein an amount of the siloxane component is selected to adjust concentrations of each of the silanol component, the silane component, and the catalyst component, and wherein the concentrations are selected to cause the mixture to have a viscosity in a range of 50 cSt to 600 cSt.

[0133] In yet another aspect of the present disclosure, a method comprises mixing a first volume with a second volume to produce a third volume, wherein the first volume comprises a vinyl-siloxane component, and wherein the second volume comprises a hydride-siloxane component, a siloxane component, and a catalyst component, wherein an amount of the siloxane component is selected to adjust concentrations of each of the vinyl-siloxane component, the hydride-siloxane component, and the catalyst component, and wherein the concentrations are selected to cause the mixture to have a viscosity in a range of 50 cSt to 600 cSt.

[0134] In yet another aspect of the disclosure, an ice-phobic coating formulation comprises an elastomer, filler particles, and a cryoprotectant. In one embodiment, the formulation is a solventless curable coating formulation. In one embodiment, a viscosity of the solventless curable coating formulation ranges from 750 cSt to 1,500 cSt, or from 800 cSt to 1,100 cSt.

[0135] In one embodiment, the elastomer comprises one or more of fluoro- elastomer, fluoro-silicone, or silicone.

[0136] In one embodiment, the filler particles comprise one or more of silica nanoparticles, silica microparticles, polypropylene, polytetrafluoroethylene (PTFE), graphene, calcium carbonate, or titanium dioxide. In one embodiment, the filler particles have an average surface area ranging from 6 m²/g to 8 m²/g.

[0137] In one embodiment, the filler particles comprise fumed silica. In one embodiment, the fumed silica was previously treated with dimethyl-dichlorosilane.

[0138] In one embodiment, the filler particles comprise silica nanoparticles. In one embodiment, the silica nanoparticles have an average size ranging from 10 nm to 50 nm, or from 15 nm to 20 nm. In one embodiment, a weight percent of the silica nanoparticles in the formulation is less than 5 wt%, is less than 4 wt%, ranges from 1 wt% to 5 wt%, or ranges from 2 wt% to 4 wt%. In one embodiment, the silica nano-
particles are present in aggregates having an average size greater than 500 nm, or ranging from 100 nm to 300 nm.

[0139] In one embodiment, the filler particles comprise polypropylene microparticles. In one embodiment, the polypropylene microparticles have an average size ranging from 3 micrometers to 10 micrometers.

[0140] In one embodiment, the filler particles comprise PTFE nanoparticles. In one embodiment, the PTFE nanoparticles have an average size ranging from 100 nm to 300 nm.

[0141] In one embodiment, the filler particles comprise graphene. In one embodiment, the graphene has an average thickness ranging from 1 nm to 5 nm. In one embodiment, the graphene has an average surface area ranging from 300 m²/g to 750 m²/g.

[0142] In one embodiment, the filler particles comprise titanium oxide. In one embodiment, a weight percent of the titanium oxide in the formulation is greater than 0 wt % and less than 1 wt %.

[0143] In one embodiment, the cryoprotectant comprises one or more of glycerol, trehalose, dimethylsulfoxide (DMSO), or polyvinyl alcohol (PVA).

[0144] In one embodiment, the cryoprotectant comprises glycerol at a weight percent in the formulation ranging from 1 wt % to 3 wt %.

[0145] In yet another aspect of the present disclosure, a method for forming an ice-phobic coating comprises providing an ice-phobic coating formulation, the ice-phobic coating formulation comprising an elastomer, filler particles, and a cryoprotectant. The method further comprises depositing the ice-phobic coating formulation onto a surface, wherein the ice-phobic coating formulation forms the ice-phobic coating upon curing.

[0146] In one embodiment, depositing the ice-phobic coating formulation comprises spraying the ice-phobic coating formulation onto the surface.

[0147] In one embodiment, the ice-phobic coating formulation has a viscosity ranging from 750 cSt to 1,500 cSt, or from 800 cSt to 1,100 cSt.

[0148] In one embodiment, the method further comprises applying a primer coating to the surface, wherein the ice-phobic coating formulation is deposited onto the surface after the primer coating is cured. In one embodiment, the primer coating is a silane-based primer coating. In one embodiment, the primer coating is moisture cured.

[0149] In one embodiment, a thickness of the ice-phobic coating is less than 100 micrometers, ranges from 10 micrometers to 40 micrometers, ranges from 115 micrometers to 300 micrometers, or is greater than or equal to 100 micrometers.

[0150] In one embodiment, the ice-phobic coating has an average failure stress ranging from 5 kPa to 20 kPa as measurable using an ice-pin test.

[0151] In yet another aspect of the present disclosure, an ice-phobic coating formulation comprising silicone and glycerol at a weight percent in the formulation ranging from 1 wt % to 3 wt %. In one embodiment, the ice-phobic coating formulation is solventless. In one embodiment, the formulation is substantially free of nanoparticles or microstructures. In one embodiment, the formulation comprises silica nanoparticles at a weight percent in the formulation ranging from 1 wt % to 5 wt %. In one embodiment, the ice-phobic coating formulation is adapted to form an ice-phobic coating having an average ice-adhesion failure stress ranging from 1 kPa to 20 kPa, as measurable using an ice-pin test.

[0152] In the foregoing description, numerous specific details are set forth, such as specific materials, dimensions, processes parameters, etc., to provide a thorough understanding of the present invention. The particular features, structures, materials, or characteristics may be combined in any suitable manner in one or more embodiments. The words “example” or “exemplary” are used herein to mean serving as an example, instance, or illustration. Any aspect or design described herein as “example” or “exemplary” is not necessarily to be construed as preferred or advantageous over other aspects or designs. Rather, use of the words “example” or “exemplary” is intended to present concepts in a concrete fashion. As used in this application, the term “or” is intended to mean an inclusive “or” rather than an exclusive “or”. That is, unless specifically otherwise, or clear from context, “X includes A or B” is intended to mean any of the natural inclusive permutations. That is, if X includes A; X includes B; or X includes both A and B, then “X includes A or B” is satisfied under any of the foregoing instances. In addition, the articles “a” and “an” as used in this application and the appended claims should generally be construed to mean “one or more” unless specified otherwise or clear from context to be directed to a singular form.

[0153] Reference throughout this specification to “an embodiment”, “certain embodiments”, or “one embodiment” means that a particular feature, structure, or characteristic described in connection with the embodiment is included in at least one embodiment. Thus, the appearances of the phrase “an embodiment”, “certain embodiments”, or “one embodiment” in various places throughout this specification are not necessarily all referring to the same embodiment, and such references mean “at least one”.

[0154] Whereas many alterations and modifications of the present invention will no doubt become apparent to a person of ordinary skill in the art after having read the foregoing description, it is to be understood that any particular embodiment described and shown by way of illustration is in no way intended to be considered limiting. Therefore, references to details of various embodiments are not intended to limit the scope of the claims, which in themselves recite those features regarded as the invention.

What is claimed is:

1. A solventless curable coating formulation comprising:
   a first component at a first concentration, the first component comprising siloxane;
   a second component at a second concentration, the second component comprising silanol or vinyl-siloxane;
   a third component at a third concentration, the third component comprising silane or hydride-siloxane; and
   a fourth component at a fourth concentration, the fourth component comprising a catalyst, wherein a viscosity of the formulation ranges from 50 cSt to 1,000 cSt.

2. The formulation of claim 1, wherein the formulation was heated within a range of 50°C to 60°C for 1 to 2 hours immediately after mixing the fourth component with the first, second, and third components, and wherein, 24 hours after the coating formulation was heated, the viscosity remains stable within 50 cSt.

3. The formulation of claim 1, wherein the first concentration of the first component ranges from 84 wt % to 72 wt %, and wherein the siloxane of the first component comprises polydimethylsiloxane (PDMS).

4. The formulation of claim 1, wherein the second concentration of the second component ranges from 15 wt % to 25 wt %.
% wherein the second component comprises silanol and the third component comprises silane, and wherein the silanol of the second component comprises silanol-terminated PDMS.

5. The formulation of claim 1, wherein the third concentration of the third component ranges from 1 wt % to 3 wt %, and wherein the second component comprises silanol and the third component comprises silane, and wherein the silane of the third component comprises one or more of methoxy-silane, ethoxy-silane, acetoxy-silane, 3-aminopropyltriethoxysilane, or tetraethoxysilane.

6. The formulation of claim 1, wherein the fourth concentration of the fourth component ranges from 0.001 wt % to 0.1 wt %, wherein the second component comprises silanol and the third component comprises silane, and wherein the catalyst of the fourth component comprises tin(II) octoate.

7. The formulation of claim 1, wherein the second component comprises silanol and the third component comprises hydride-siloxane, and wherein the fourth component comprises a tin catalyst.

8. The formulation of claim 1, wherein the second component comprises vinyl-siloxane and the third component comprises hydride-siloxane, and wherein the fourth component comprises a platinum catalyst.

9. The formulation of claim 1, wherein the formulation is an ice-phobic coating formulation adapted to form an ice-phobic coating having an ice adhesion failure stress ranging from 1 kPa to 20 kPa.

10. An ice-phobic coating formulation comprising:

- an elastomer;
- filler particles; and
- a cryoprotectant.

11. The formulation of claim 10, wherein the formulation is a solventless curable coating formulation.

12. The formulation of claim 11, wherein a viscosity of the solventless curable coating formulation ranges from 750 cSt to 1,500 cSt.

13. The formulation of claim 10, wherein the elastomer comprises one or more of fluoro-elastomer, fluoro-silicone, or silicone.

14. The formulation of claim 10, wherein the filler particles comprise one or more of silica nanoparticles, silica microparticles, silica nanoparticles, fumed silica, polypropylene, polytetrafluoroethylene (PTFE), graphene, calcium carbonate, or titanium dioxide.

15. The formulation of claim 10, wherein the filler particles comprise silica nanoparticles having an average size ranging from 10 nm to 50 nm, and wherein a weight percent of the silica nanoparticles in the formulation is greater than 0 wt % and less than 5 wt %.

16. The formulation of claim 10, wherein the filler particles comprise polypropylene microparticles, and wherein the polypropylene microparticles have an average size ranging from 3 micrometers to 10 micrometers.

17. The formulation of claim 10, wherein the filler particles comprise PTFE nanoparticles, and wherein the PTFE nanoparticles have an average size ranging from 100 nm to 300 nm.

18. The formulation of claim 10, wherein the filler particles comprise titanium oxide, and wherein a weight percent of the titanium oxide in the formulation is greater than 0 wt % and less than 1 wt %.

19. The formulation of claim 10, wherein the cryoprotectant comprises one or more of glycerol, trehalose, dimethylsulfoxide (DMSO), or polyvinyl alcohol (PVA).

20. The formulation of claim 10, wherein the cryoprotectant comprises glycerol at a weight percent in the formulation ranging from 1 wt % to 3 wt %.

21. The formulation of claim 10, wherein the formulation is adapted to form an ice-phobic coating having an ice adhesion failure stress ranging from 1 kPa to 20 kPa.

22. A ice-phobic coating formulation comprising:

- silicone;
- glycerol at a weight percent in the formulation ranging from 1 wt % to 3 wt %; and
- silica nanoparticles at a weight percent in the formulation ranging from 1 wt % to 5 wt %, wherein the ice-phobic coating formulation is adapted to form an ice-phobic coating having an ice adhesion failure stress ranging from 1 kPa to 20 kPa.

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