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(54) Titre : POLYMERES REDUISANT L'ADHERENCE DE LA GLACE  
(54) Title: ICE ADHESION REDUCING POLYMERS

(57) Abrégé/Abstract:

The present disclosure relates to polymers which are cross-linked reaction products of a reactive siloxane and/or a polyisocyanate and/or a polyol, a polyamine and/or reactive coating capable of reducing the ability of ice to adhere to the surface of an object, in particular aircraft or other vehicles, methods of producing the polymers and their use in coating surfaces.



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(54) Title: ICE ADHESION REDUCING POLYMERS

(57) Abstract: The present disclosure relates to polymers which are cross-linked reaction products of a reactive siloxane and/or a polyisocyanate and/or a polyol, a polyamine and/or reactive coating capable of reducing the ability of ice to adhere to the surface of an object, in particular aircraft or other vehicles, methods of producing the polymers and their use in coating surfaces.



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**ICE ADHESION REDUCING POLYMERS****FIELD**

5 The present disclosure relates to polymers capable of mitigating the effects of ice build-up on surfaces of objects by reducing the ability of ice to adhere to the surface of an object, in particular aircraft or other vehicles, methods of producing the polymers and their use in coating surfaces.

**BACKGROUND**

10 The everyday build-up of ice upon the surfaces of objects is a familiar annoyance, and quite often a safety hazard. The layers of ice that form on highways, driveways, and walkways make transportation difficult. The masses of ice that accumulate within or upon industrial, agricultural, or other mechanical equipment make operation of the equipment difficult or impossible. The weight of ice on power lines, buildings, wind turbines, refrigeration units, air  
15 conditioning and signs often impairs those structures.

Build-up of ice upon the wings and components of an aircraft is of particular concern. The lift generated by the wings, and thus the ability of the aircraft to become and remain airborne, is dependent on the shape of the wings. Even a small accumulation of ice upon the surface of the wings can significantly increase drag and dramatically reduce lift. Further, ice  
20 build-up along control surfaces of the aircraft can impede the movement of those surfaces.

There are a large variety of techniques used to control the build-up of ice upon the wings and other surfaces of aircraft. For instance, the aircraft are deiced before takeoff by radiant heat energy or by application of a chemical spray which melts the ice from the wings. Such deicing sprays are not an environmentally preferred solution. The requirement of deicing  
25 is well known to airline passengers traveling through cold environments.

Another method of deicing aircraft on the ground or in the air includes providing flexible pneumatic coverings (bladders) along the leading edges of the wings, and supplying bursts of air or fluid to expand the flexible coverings to break away any overlying ice. Similarly, bleeding air from the aircraft engine and routing the heated air to the surface of the

wing heats the wing and melts the ice. Ice may also be removed from the wing by providing mechanical energy to the wing, such as through the use of electrically actuated thumpers, which causes the wing to vibrate, fracturing any accumulated ice or by the use of electric blankets.

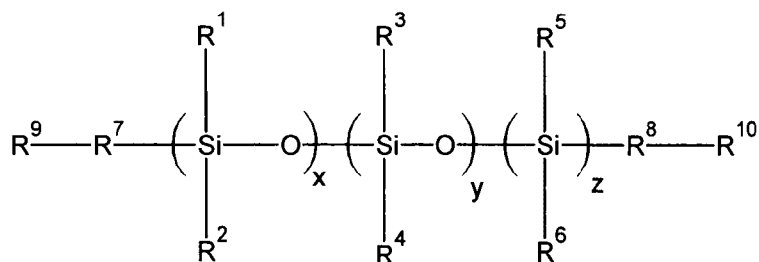
Although the previously mentioned methods of ice removal are generally effective, they require the continuous supply of air, chemicals, or electrical power. It would be preferred, of course, to reduce the adhesion of ice in the first place or at least, reduce the build-up of ice on surface.

One might expect that known non-stick coatings would be able to reduce ice from adhering to the surfaces which they coat. It has been found that aluminium surfaces coated with a polytetrafluoroethylene material show a reduction in adhesion (aluminium 1576 kPa, Teflon™ 238 kPa), but not as much as might be expected. Further, upon repeated freezing, the favourable properties exhibited by polytetrafluoroethylene and similar coatings can degrade, resulting in a coating with little or no anti-icing capacity.

There is a need for a method which provides a durable surface with low ice adhesion properties and/or delayed freezing which eliminates or at least reduces the continuous supply of air, chemicals or electrical power in order to reduce the amount of ice forming on a surface and/or the adhesion of ice to the surface.

## SUMMARY

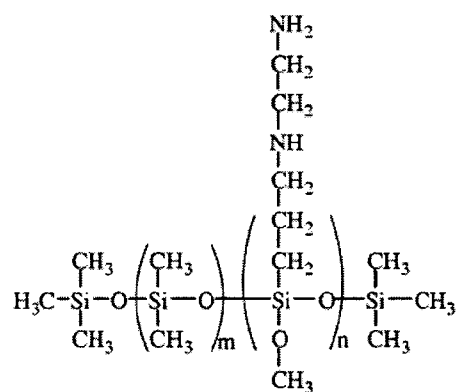
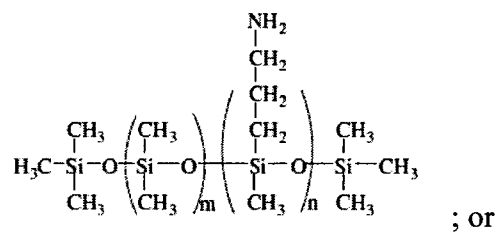
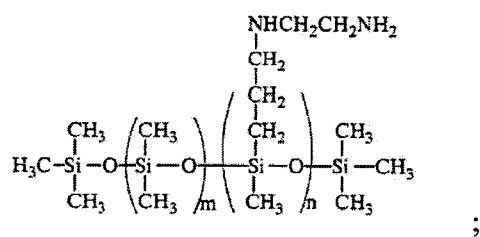
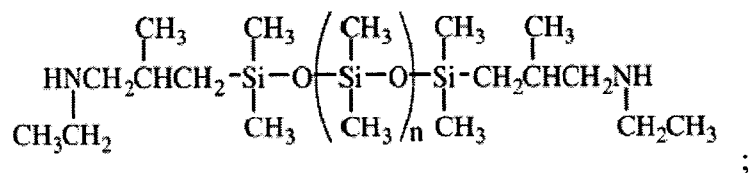
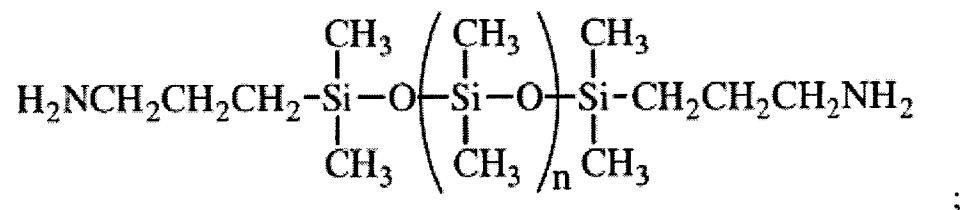
In one embodiment, there is provided an ice adhesion reducing polymer having an ice adhesion tensile force of less than 5 Newtons. The ice reducing polymer includes a cross-linked reaction product of the following siloxane:



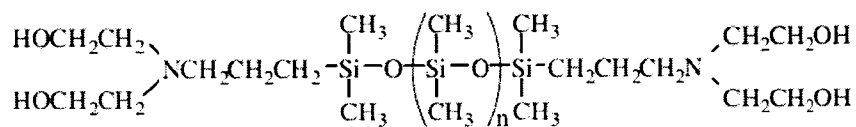
(I)

$R^1$  to  $R^6$  are independently selected from the group consisting of H; optionally substituted  $C_{1-16}$ alkyl optionally interrupted with a group selected from  $NR^{11}$ ,  $C=O$ ,  $C=C$ , S,  $CO_2$ , O, and  $CH(NCO)$ ;  $OSiR^{12}_3$ ;  $(CH_2)_pOH$ ;  $(CH_2)_pO(CH_2)_pOH$ ;  $(CH_2)_pNR^{11}R^{12}$ ;  $(CH_2)_pNH(CH_2)_pNR^{11}R^{12}$ ;  $(CH_2)_pO(CH_2)_pNR^{11}R^{12}$ ;  $(CH_2)_pNCO$ ; epoxy; optionally substituted  $C_{1-16}$ alkylaryl; optionally substituted aryl; optionally substituted polyaryl; optionally substituted  $C_{3-6}$ cycloaliphatic; and optionally substituted  $C_{3-6}$ heterocyclyl.  $R^7$  and  $R^8$  are independently absent or independently selected from the group consisting of optionally substituted  $C_{1-16}$ alkyl optionally interrupted with a group selected from  $NR^{11}$ ,  $C=O$ ,  $C=C$ , S,  $CO_2$ , O, and  $CH(NCO)$ ; O; S;  $OSi(R^{13})_2$ ;  $(CH_2)_p$ ;  $(CH_2)_pNH$ ;  $(CH_2)_pO$ ; optionally substituted  $C_{1-16}$ alkylaryl; optionally substituted aryl; optionally substituted polyaryl; optionally substituted  $C_{3-6}$ cycloaliphatic; and optionally substituted  $C_{3-6}$ heterocyclyl.  $R^9$  and  $R^{10}$  are independently selected from the group consisting of H, OH,  $NR^{11}R^{12}$ , optionally substituted  $C_{1-16}$ alkyl, NCO, epoxy and  $Si(R^{13})_3$ , and  $R^{11}$  and  $R^{12}$  are independently selected from the group consisting of H and optionally substituted  $C_{1-16}$ alkyl.  $R^{13}$  is selected from the group consisting of optionally substituted  $C_{1-16}$ alkyl,  $(CH_2)_pOH$ , and  $(CH_2)_pNH_2$ , p is 1 to 16, z is 1 and x is selected from 1 to 1500. y is 0 to 1500, and when at least one of  $R^1$  to  $R^6$ ,  $R^9$  and  $R^{10}$  bears an  $NH_2$  group then the siloxane of formula (I) has a molecular weight of between about 2500 and about 27000 Daltons and when at least one of  $R^1$  to  $R^6$ ,  $R^9$  and  $R^{10}$  bears an OH group the siloxane of formula (I) has a molecular weight of between about 5000 and about 10000 Daltons, and (i) a polyisocyanate and one or more of a polyol, a polyamine and a reactive coating, or (ii) any one of a polyisocyanate, a polyol, a polyamine or a reactive coating, with the provisos that: (a) when the compound of formula (I) reacts with a polyisocyanate, then at least one of  $R^1$  to  $R^6$ ,  $R^9$  and  $R^{10}$  must bear at least one OH or  $NH_2$  or both, (b) when the compound of formula (I) reacts with a polyol, a polyamine or a reactive coating, then at least one of  $R^1$  to  $R^6$ ,  $R^9$  and  $R^{10}$  must bear at least one NCO; (c) when the compound of formula (I) reacts with a reactive coating, then at least one of  $R^1$  to  $R^6$ ,  $R^9$  and  $R^{10}$  must bear at least one OH or  $NH_2$  or both to react with a polyisocyanate present in the coating or at least one of  $R^1$  to  $R^6$ ,  $R^9$  and  $R^{10}$  must bear at least one NCO to react with a polyol or polyamine present in the coating, and (d) when present, the amount of polyol/polyamine is in the range of from 5 to 30% by weight based on the total weight of the polymer.

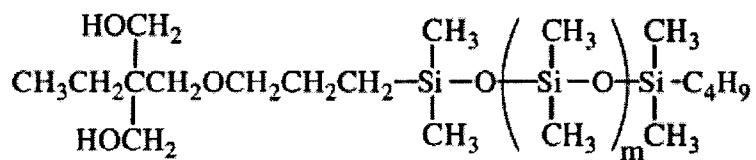
The compound of formula (I) may be selected from the following:



in which m is 1-1500, and n is 1-1500; or

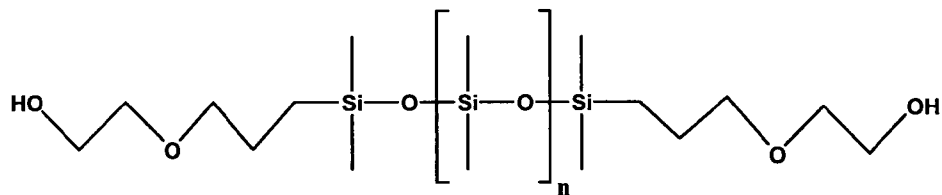


; or



in which m is 1-1500, and n is 1-1500 or the reaction product of:

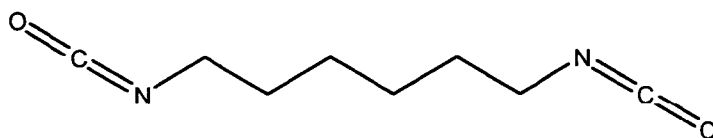
5



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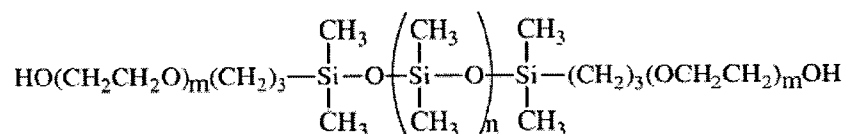
and

10



in which n is 1-1500.

In another embodiment, there is provided an ice reducing polymer having an ice adhesion tensile force of less than 5 Newtons, comprising a cross-linked reaction product of the following carbinol siloxane:



5 in which m is 1-1500; and n is 1-1500, wherein the siloxane has a molecular weight of between about 5000 and 10000 Daltons; and a polyisocyanate.

The compound of formula (I) may be present in an amount of 1-99% by weight based on the total weight of the polymer.

10 The polyisocyanate may be a diisocyanate, triisocyanate or higher functionality isocyanate.

The triisocyanate may be lysine triisocyanate or the polyisocyanate may be under the Desmodur® range.

The polyisocyanate may be present in an amount of 0.1-70% by weight based on the total weight of the polymer.

15 The polyol or polyamine may be selected from a polyester polyol/polyamine, a polyether polyol/polyamine, a polycarbonate polyol/polyamine, an acrylic polyol/polyamine or a combination thereof.

The polyol or polyamine may be present in an amount of 0-99% by weight based on the total weight of the polymer.

20 The reactive coating may be selected from a polyurethane, polyurea, polysilicone, polyester or epoxy coating each of which contain a polyisocyanate and/or a polyol or polyamine.

In another embodiment, there is provided an object comprising an external surface in which at least a portion of the external surface is coated with a polymer as described above.

25 The external surface coated with the polymer may have an average adhesion force of <5 N when subject to an Ice Adhesion Test Method described herein.

In another embodiment, there is provided a method of imparting ice adhesion reducing properties to at least a portion of an external surface of an object including applying a coating of a polymer as described above onto the surface.

In another embodiment, there is provided an object including components with surfaces  
5 coated with a polymer as described above.

In another embodiment, there is provided a coating including a polymer as described above.

In another embodiment, there is provided a polymer formulation including a polymer as described above, a solvent, and an optional additive.

10 The solvent may be selected from (a) an ester based solvent; (b) a ketone; (c) an aromatic; (d) an ether; (e) a halogenated solvent, or a combination thereof.

The solvent may be a ketone.

The ketone may be selected from the group consisting of methyl ethyl ketone, methyl propyl ketone, methyl amyl ketone, methyl isoamyl ketone, methyl isobutyl ketone, acetone,  
15 pentanone, butanone, 2-heptanone, or combinations thereof.

The ester based solvent may be selected from alkyl propionate, alkoxypropionate, alkyl alkoxypropionate, alkyl acetate, alkyl alkoxyacetate, ethyl acetate, propyl acetate, isopropyl acetate, butyl acetate, isobutyl acetate, tertiary butyl acetate and glycol ether acetate; or the ketone solvent is selected from methyl ethyl ketone, methyl propyl ketone, methyl amyl ketone,  
20 methyl isoamyl ketone, methyl isobutyl ketone, acetone, pentanone, butanone and 2-heptanone.

The optional additive may be selected from a curing agent, cross-linking agent, catalyst, filler, pigment or other colorant, reinforcement, thixotrope, accelerator, surfactant, plasticizer, extender, stabilizer, corrosion inhibitor, hindered amine light stabilizer, UV light absorber, antioxidant and a combination thereof.

25 In another embodiment, there is provided a coating including the polymer formulation as described above.

A method of producing the polymer may include reacting the compound of formula (I) with (i) a polyisocyanate and one or more of a polyol, a polyamine or a reactive coating or (ii) a polyisocyanate, a polyol, a polyamine or a reactive coating. When at least one of  $R^1$  to  $R^6$ ,  $R^9$   
30 and  $R^{10}$  bears an  $NH_2$  group then the siloxane of formula (I) has a molecular weight of between about 2500 and about 27000 Daltons and when at least one of  $R^1$  to  $R^6$ ,  $R^9$  and  $R^{10}$  bears an OH

group the siloxane of formula (I) has a molecular weight of between about 5000 and about 10000 Daltons, and with the provisos that: (a) when the compound of formula (I) reacts with a polyisocyanate, then at least one of  $R^1$  to  $R^6$ ,  $R^9$  and  $R^{10}$  must bear at least one OH or  $NH_2$  or both, (b) when the compound of formula (I) reacts with a polyol, a polyamine or a reactive coating, then at least one of  $R^1$  to  $R^6$ ,  $R^9$  and  $R^{10}$  must bear at least one NCO; and (c) when the compound of formula (I) reacts with a reactive coating, then at least one of  $R^1$  to  $R^6$ ,  $R^9$  and  $R^{10}$  must bear at least one OH or  $NH_2$  or both to react with a polyisocyanate present in the reactive coating or at least one of  $R^1$  to  $R^6$ ,  $R^9$  and  $R^{10}$  must bear at least one NCO to react with a polyol or polyamine present in the reactive coating.

In another embodiment, there is provided an object comprising an external surface in which at least a portion of the external surface is coated with the polymer formulation as described above.

The external surface coated with the polymer may have an average adhesion force of  $<5$  N when subject to the Ice Adhesion Test Method described herein.

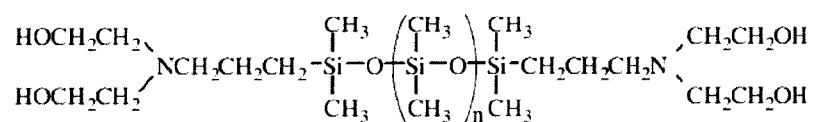
In another embodiment, there is provided a method of imparting ice adhesion reducing properties to at least a portion of an external surface of an object comprising applying a coating of the polymer formulation as described above onto the surface.

In another embodiment, there is provided an object including components with surfaces coated with the polymer formulation as described above.

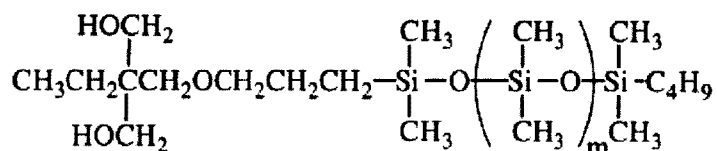
## DETAILED DESCRIPTION

The disclosure relates to the polymer or polymer formulation as defined above which provides an improved polymer coating which reduces the ability of ice to adhere and/or form upon a surface. The polymer coating is particularly effective when applied to a surface of an object. For example, coated or uncoated metal,

6



; or

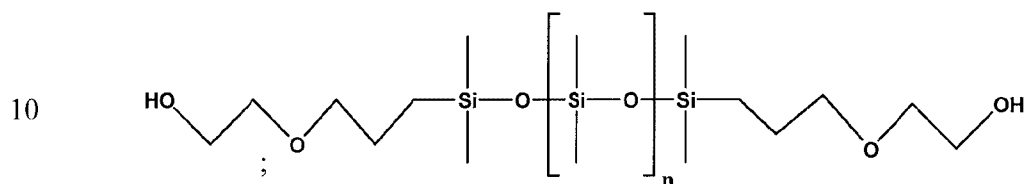


in which

5

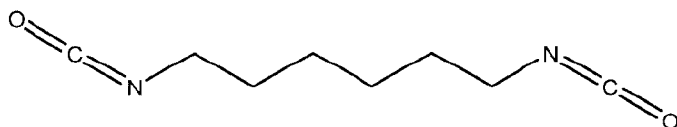
m is **1-1500**, andn is **1-1500** or

the reaction product of:



10

and



15

in which n is **1-1500**.

The compound of formula (I) may be present in an amount of **1-99%** by weight based on the total weight of the polymer.

20

The polyisocyanate may be a diisocyanate, triisocyanate or higher functionality isocyanate.

The triisocyanate may be lysine triisocyanate or the polyisocyanate is sold by Bayer under the Desmodur<sup>®</sup> range.

The polyisocyanate may be present in an amount of **0.1-70%** by weight based on the total weight of the polymer.

The polyol or polyamine may be selected from a polyester polyol/polyamine, a polyether polyol/polyamine, a polycarbonate polyol/polyamine, an acrylic polyol/polymine or  
5 a combination thereof.

The polyol or polyamine may be present in an amount of **0-99%** by weight based on the total weight of the polymer.

The reactive coating may be selected from a polyurethane, polyurea, polysilicone, polyester or epoxy coating each of which contain a polyisocyanate and/or a polyol or  
10 polyamine.

In another embodiment, there is provided an object comprising an external surface in which at least a portion of the external surface is coated with the polymer as described above.

The external surface coated with the polymer may have an average adhesion force of **<5** N when subject to the Ice Adhesion Test Method described herein.

15 In another embodiment, there is provided a method of imparting ice reducing properties to at least a portion of an external surface of an object including applying a coating of the polymer according to any of the methods described above.

In another embodiment, there is provided an object including components with surfaces coated with the polymer according to any of the methods described above.

20 In another embodiment, there is provided a coating including the polymer as described above.

In another embodiment, there is provided a polymer formulation including the polymer as described above, a solvent, and an optional additive.

The solvent may be selected from (a) an ester based solvent; (b) a ketone; (c) an aromatic; (d) an ether; (e) a halogenated solvent, or a combination thereof.  
25

The solvent may be a ketone.

The ketone may be selected from the group consisting of methyl ethyl ketone, methyl propyl ketone, methyl amyl ketone, methyl isoamyl ketone, methyl isobutyl ketone, acetone, pentanone, butanone, 2-heptanone, or combinations thereof.

The ester based solvent may be selected from alkyl propionate, alkoxypropionate, alkyl alkoxypropionate, alkyl acetate, alkyl alkoxyacetate, ethyl acetate, propyl acetate, isopropyl acetate, butyl acetate, isobutyl acetate, tertiary butyl acetate and glycol ether acetate; or the ketone solvent is selected from methyl ethyl ketone, methyl propyl ketone, methyl amyl ketone, methyl isoamyl ketone, methyl isobutyl ketone, acetone, pentanone, butanone and 2-heptanone.

The optional additive may be selected from a curing agent, cross-linking agent, catalyst, filler, pigment or other colorant, reinforcement, thixotrope, accelerator, surfactant, plasticizer, extender, stabilizer, corrosion inhibitor, hindered amine light stabilizer, UV light absorber, antioxidant or a combination thereof.

In another embodiment, there is provided a coating including the polymer formulation as described above.

A method of producing the polymer may include reacting the compound of formula (I) with (i) a polyisocyanate and one or more of a polyol, a polyamine or a reactive coating or (ii) a polyisocyanate, a polyol, a polyamine or a reactive coating,

wherein when at least one of  $R^1$  to  $R^6$ ,  $R^9$  and  $R^{10}$  bears an  $NH_2$  group then the siloxane of formula (I) has a molecular weight of between about **2500** and **27000** Daltons and when at least one of  $R^1$  to  $R^6$ ,  $R^9$  and  $R^{10}$  bears an OH group the siloxane of formula (I) has a molecular weight of between about **5000** and **10000** Daltons, and

with the provisos that:

(a) when the compound of formula (I) reacts with a polyisocyanate, then at least one of  $R^1$  to  $R^6$ ,  $R^9$  and  $R^{10}$  must bear at least one OH or  $NH_2$  or both,

(b) when the compound of formula (I) reacts with a polyol, a polyamine or a reactive coating, then at least one of  $R^1$  to  $R^6$ ,  $R^9$  and  $R^{10}$  must bear at least one NCO; and

(c) when the compound of formula (I) reacts with a reactive coating, then at least one of  $R^1$  to  $R^6$ ,  $R^9$  and  $R^{10}$  must bear at least one OH or  $NH_2$  or both to react with a polyisocyanate present in the reactive coating or at least one of  $R^1$  to  $R^6$ ,  $R^9$  and  $R^{10}$  must bear at least one NCO to react with a polyol or polyamine present in the reactive coating.

In another embodiment, there is provided an object comprising an external surface in which at least a portion of the external surface is coated with the polymer formulation as described above.

5 The external surface coated with the polymer may have an average adhesion force of <5 N when subject to the Ice Adhesion Test Method described herein.

In another embodiment, there is provided a method of imparting ice reducing properties to at least a portion of an external surface of an object comprising applying a coating of the polymer formulation as described above onto the surface.

10 In another embodiment, there is provided an object including components with surfaces coated with the prepolymer formulation as described above.

## DETAILED DESCRIPTION

The disclosure relates to the polymer or polymer formulation as defined above which provides an improved polymer coating which reduces the ability of ice to adhere and/or form  
15 upon a surface. The polymer coating is particularly effective when applied to a surface of an object. For example, coated or uncoated metal, including aerospace alloys of aluminium, steel, or titanium or to coated or uncoated resin composites having glass, ceramic, or carbon fiber reinforcement and is particularly useful for reducing the formation of ice upon the control or aerodynamic lifting surfaces of aircraft or space vehicles. The coating also forms an effective  
20 ice reducer when used on a wide variety of materials other than the preferred aluminium, titanium or carbon composite, such as glass and polymeric materials.

In use, the polymer formulation could be applied to the surface, especially to an aircraft, to retain its functionality under a variety of environmental conditions, such as those typically encountered by commercial or military aircraft. A method of applying the polymer  
25 formulation to at least a portion of the surface of an object, such as an aircraft, is also provided.

The polymer may be a reaction product of the compound of formula (I), the polyisocyanate and one or more of the polyol, the polyamine and the reactive coating. In this embodiment, the compound of formula (I) and the polyisocyanate can be mixed with a solvent

and sprayed on a coated or uncoated surface of an object. A polyol and/or polyamine can optionally be added as shown in Scheme 1 below.

*Solvent + reactive polysiloxane + polyisocyanate + polyol/polyamine (optional)*

*Reactive siloxane is amine and/or hydroxy functional*

5

### **Scheme 1**

Alternatively, the compound of formula (I) and the polyol or polyamine can be mixed with a solvent and sprayed on a coated or uncoated surface of an object. The polyisocyanate can then be added as shown in Scheme 2 below.

*Solvent + reactive polysiloxane + polyol/polyamine + polyisocyanate (optional)*

10

*Reactive siloxane is isocyanate functional*

### **Scheme 2**

The polymer may also be a reaction product of the compound of formula (I) and the polyisocyanate provided that at least one of R<sup>1</sup> to R<sup>6</sup>, R<sup>9</sup> and R<sup>10</sup> bear at least one OH or NH<sub>2</sub> or both.

15

Alternatively, the polymer may be a reaction product of the compound of formula (I) and the polyol, the polyamine or coating provided that at least one of R<sup>1</sup> to R<sup>6</sup>, R<sup>9</sup> and R<sup>10</sup> bear at least one NCO.

20

The compound of formula (I) may also be added to a reactive coating provided that at least one of R<sup>1</sup> to R<sup>6</sup>, R<sup>9</sup> and R<sup>10</sup> bear at least one OH or NH<sub>2</sub> or both to react with a polyisocyanate present in the reactive coating or at least one of R<sup>1</sup> to R<sup>6</sup>, R<sup>9</sup> and R<sup>10</sup> bear at least one NCO to react with a polyol or polyamine present in the reactive coating. In this embodiment a polyisocyanate and/or polyol or polyamine can also be added as shown in Scheme 3 below.

*Reactive coating + reactive polysiloxane + polyisocyanate/ polyol/polyamine (optional)*

25

*Reactive coating may be an existing paint formulation such as polyurethane, polyurea or epoxy coatings*

### **Scheme 3**

**Definitions**

The alkyls may be linear or branched, saturated or unsaturated, substituted or unsubstituted and contain **1** to **16** carbon atoms.

5 Examples of saturated alkyls include methyl, ethyl, propyl, isopropyl, butyl, isobutyl, sec-butyl, tert-butyl, pentyl, neopentyl, hexyl and the like.

Examples of unsaturated alkyls include alkenyls such as vinyl, **1**-propenyl, **1**- and **2**-butenyl, **2**-methyl-**2**-propenyl and the like or alkynyls such as ethynyl, **1**-propynyl, **1**- and **2**-butynyl, **2**-methyl-**2**-propynyl, **2**-pentynyl, **3**-pentynyl, **4**-pentynyl, **2**-hexynyl, **3**-hexynyl, **4**-hexynyl, **5**-hexynyl and the like.

10 Unless the context requires otherwise, the term “alkyl” also encompasses alkyl groups containing one less hydrogen atom such that the group is attached via two positions i.e. divalent.

The aryls may be  $C_6$ ,  $C_{10}$ ,  $C_{14}$  aryls selected from phenyl, naphthyl and tetrahydronaphthyl.

15 The alkylaryls may be linear or branched, saturated or unsaturated, substituted or unsubstituted such as benzyl.

The polyaryls are two or more aryls linked by at least one carbon-carbon bond and may be selected from biphenyl and terphenyl. The polyaryls may be linear or branched, substituted or unsubstituted.

20 The  $C_{3-6}$  cycloaliphatic is a non-aromatic cyclic group having from **3** to **6** carbon atoms and includes  $C_{3-6}$ cycloalkyls such as cyclopropyl, cyclobutyl, cyclopentyl and cyclohexyl. It will be understood that cycloalkyl groups may be saturated such as cyclohexyl or unsaturated such as cyclohexenyl.

25 The  $C_{3-6}$  heterocyclyls may be saturated or unsaturated, substituted or unsubstituted and include saturated or unsaturated **3-6** membered rings having heteroatoms selected from O, N and S.

The term “optionally substituted” refers to a group which may or may not be further substituted with **1**, **2**, **3**, **4** or more groups, preferably **1**, **2** or **3**, more preferably **1** or **2** groups selected from the group consisting of  $C_{1-6}$  alkyl,  $C_{2-6}$  alkenyl,  $C_{2-6}$  alkynyl,  $C_{3-8}$  cycloalkyl,

hydroxyl, oxo, C<sub>1-6</sub> alkoxy, aryloxy, C<sub>1-6</sub> alkoxyaryl, halo, C<sub>1-6</sub> alkylhalo (such as CF<sub>3</sub> and CHF<sub>2</sub>), C<sub>1-6</sub> alkoxyhalo (such as OCF<sub>3</sub> and OCHF<sub>2</sub>), carboxyl, esters, cyano, nitro, amino, substituted amino, di-substituted amino, acyl, ketones, amides, aminoacyl, substituted amides, di-substituted amides, thiol, alkylthio, thioxo, isocyanates, sulfates, sulfonates, sulfinyl, substituted sulfinyl, sulfonyl, substituted sulfonyl, sulfonylamides, substituted sulfonamides, di-substituted sulfonamides, aryl, C<sub>1-6</sub> alkyl, heterocyclyl and heteroaryl wherein each alkyl, alkenyl, alkynyl, cycloalkyl, aryl and heterocyclyl and groups containing them may be further optionally substituted. In one example, the optional substituents are selected from the group consisting of C<sub>1-6</sub> alkyl, hydroxyl, amino, substituted amino, di-substituted amino, isocyanate and C<sub>1-6</sub> alkoxy.

### Formula (I)

Any reactive siloxanes of formula (I) may be used provided they are capable of reacting with a polyisocyanate and/or a polyol, a polyamine or a coating. Examples of reactive siloxanes, include amino functional siloxanes, carbinol functional siloxanes, isocyanate functional siloxanes and epoxy functional siloxanes.

The compound of formula (I) is an amino functional siloxane when the terminal group on any one of R<sup>1</sup> to R<sup>6</sup>, R<sup>9</sup> and R<sup>10</sup> is NH<sub>2</sub>, a carbinol functional siloxane when the terminal group on any one of R<sup>1</sup> to R<sup>6</sup>, R<sup>9</sup> and R<sup>10</sup> is OH, an isocyanate functional siloxane when at least one of R<sup>1</sup> to R<sup>10</sup> bears at least one NCO or an epoxy functional siloxane when at least one of R<sup>1</sup> to R<sup>6</sup>, R<sup>9</sup> and R<sup>10</sup> bears an epoxy. The integers x y and z are selected so that the molecular weight of formula (I) is in the range of **200 to 500,000**, **500 to 100,000** or **500 to 50,000**.

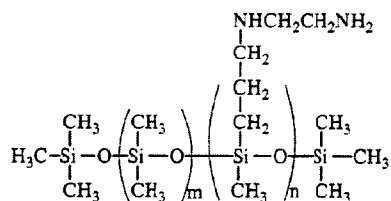
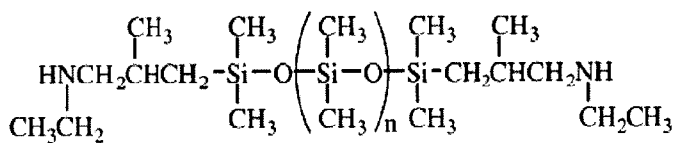
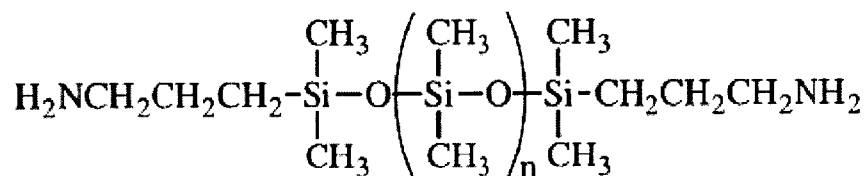
Amino functional siloxanes include, but are not limited to, those available from UCT Silanes such as PS**510**, PS**512** and PS**513** and those available from Gelest such as primary aminopropyl terminated siloxanes such as DMS-A**11**, DMS-A**12**, DMS-A**15**, DMS-A**21**, DMS-A**31**, DMS-A**32**, DMS-A**35**, secondary amino functional (N-ethylaminoisobutyl terminated PDMS) siloxanes such as DMS-A**211**, **214**, aminopropylmethylsiloxane - dimethylsiloxane copolymers such as AMS-**132**, AMS-**152**, AMS-**162**, AMS-**163**, AMS-**191**, AMS-**1203**, aminoethylaminopropylmethylsiloxane - dimethylsiloxane copolymers such as

AMS-233, AMS-2202, aminoethylaminoisobutylmethylsiloxane - dimethylsiloxane copolymers such as AMS-242 and ATM-1112, ATM-1322.

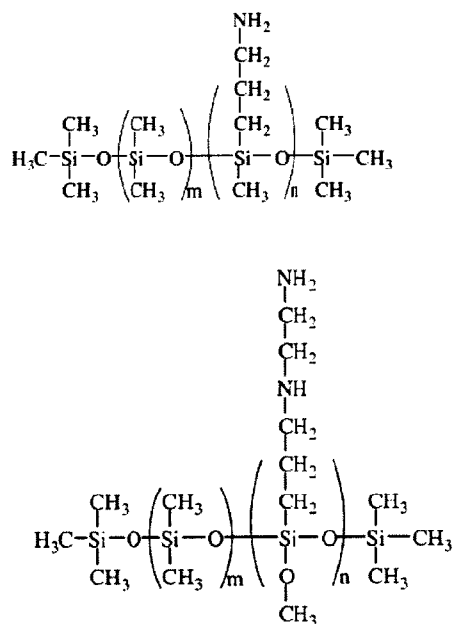
Carbinol functional siloxanes include, but are not limited to those available from Gelest such as carbinol (hydroxyl) terminated polydimethylsiloxanes DMS-C15, DMS-C16, DMS-C21, DMS-C23, DMS-C25, DBL-C31, DBL-C32, [bis(hydroxyethyl)amine] terminated polydimethylsiloxanes such as DMS-CA21 and (carbinol functional)methylsiloxane-dimethylsiloxane copolymers such as CMS-221, CMS-222, CMS-832, CMS-626.

Epoxy functional siloxanes include, but are not limited to, those available from Gelest such as epoxypropoxypropyl terminated polydimethylsiloxanes including DMS-E range (09-21), epoxypropoxypropyl terminated polyphenylmethylsiloxanes such as PMS E-11, PMS E15, monophenyl functional tris(epoxy terminated polydimethylsiloxane) such as MCT-EP13, mono-(2,3-epoxy)propylether terminated polydimethylsiloxane such as MCR-E11, MCR-E21 and (epoxycyclohexylethyleethylsiloxane) - dimethylsiloxane copolymers such as ECMS-127, 227, 327, 924.

Representative examples of aminosiloxanes include the following:



14



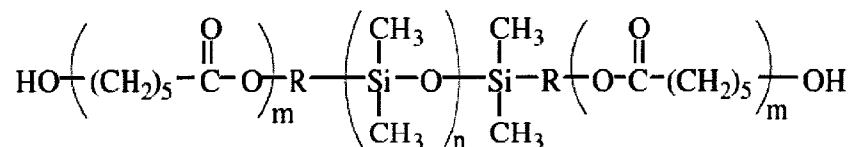
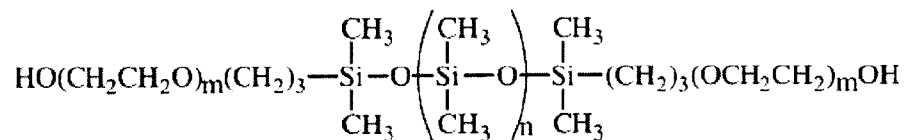
in which

m is **1-1500**; and

5

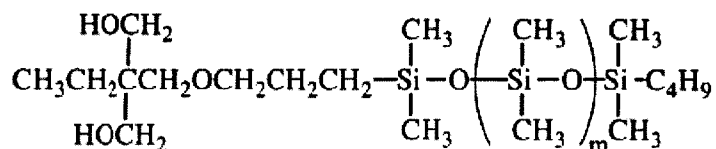
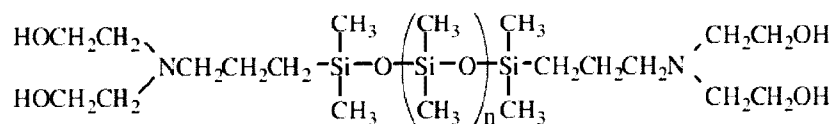
n is **1-1500**.

Representative examples of carbinol siloxanes include the following:



10

15

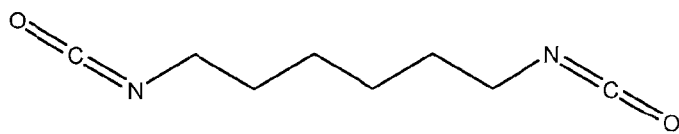
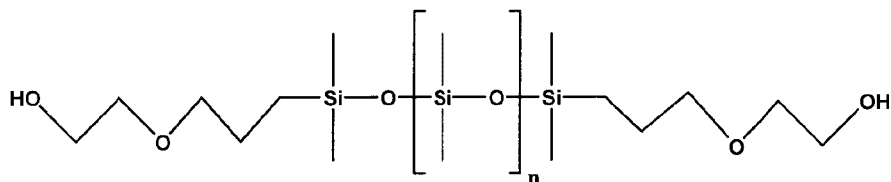


in which

m is **1-1500**; and

n is **1-1500**.

Representative examples of isocyanate siloxanes include the reaction product of:



in which

n is 1-1500.

The compound of formula (I) may be present in an amount of **1-99%** by weight, **10-80%** by weight or **20-60%** by weight based on the total weight of the polymer.

20

### Polyisocyanates

Suitable polyisocyanates include any isocyanate typically used to form cross-linked coatings. The polyisocyanate may be a masked isocyanate which are compounds in which the isocyanate group or groups are generated usually by heating at **100** to **200°C**. Masked isocyanates include those supplied by Chemtura Baxendon and the Bayhydur® range from Bayer. Blocking groups used to make masked isocyanates include  $\epsilon$ -caprolactone, methylethylketoxime, **3,5**-dimethylpyrazole and diethyl malonate. The polyisocyanates may include diisocyanates, triisocyanates and higher functionality isocyanates.

Diisocyanates include but are not limited to **1,5**-naphthalene diisocyanate, **4,4**-diphenyl-methane diisocyanate, tetra-alkyl-diphenyl methane diisocyanate, **1,3**-phenylene diisocyanate, **1,4**-phenylene diisocyanate, butane-**1,4**-diisocyanate, hexamethylene **1,6**-diisocyanate, **2,2,4**-trimethylhexamethylene **1,6**-diisocyanate, **2,4,4**-trimethyl-hexamethylene **1,6**-diisocyanate, cyclohexane-**1,4**-diisocyanate, xylilene diisocyanate, dicyclohexyl-methane-**4,4'**-diisocyanate, methyl-cyclohexane diisocyanate, **1,4**-tetramethylene diisocyanate, hexamethylene diisocyanate, **1,3**-trimethylene diisocyanate, metaxylene diisocyanate, decamethylene **1,10**-diisocyanate, cyclohexylene **1,2**-diisocyanate, cyclohexylene **1,4**-diisocyanate, 1-methyl cyclohexane **2,4**-diisocyanate, **2,4**-toluene diisocyanate, hexamethylene-**1,6**-diisocyanate, heptamethylene-**1,7**-diisocyanate, **1,3**-cyclopentene diisocyanate and **1,3**-cyclohexane diisocyanate.

Triisocyanates include but are not limited to trimers of isophorone diisocyanate, triisocyanato nonane, triphenylmethane triisocyanate, **1,3,5**-benzene triisocyanate, **2,4,6**-toluene triisocyanate, lysine triisocyanate, an adduct of trimethylol and tetramethyl xylene diisocyanate sold under the name Cythane® **3160** by Cytec Industries, and Desmodur® N **3300**, which is the isocyanurate of hexamethylene diisocyanate, available from Bayer.

Polyisocyanates with higher functionality include but are not limited to aliphatic polyisocyanates based on hexamethyldiisocyanate such as sold by Bayer under the Desmodur® N range, aliphatic polyisocyanate based on isophorondiisocyanate such as sold by Bayer under the Desmodur® Z range, aromatic polyisocyanates based on toluene diisocyanate such as sold by Bayer under the Desmodur® L range, aromatic polyisocyanates based on

methylenediphenyldiisocyanate such as sold by Bayer under the Desmodur<sup>®</sup> VL and VK range, blocked polyisocyanates such as those sold under the Desmodur<sup>®</sup> BL range and Basonat<sup>®</sup> isocyanate cross-linkers (Bayer).

Isocyanurate rings containing 3 or more isocyanates groups can also be used; for example the isocyanurate ring of hexamethylene diisocyanate such as Desmodur<sup>®</sup> N-3300 and N-3390 from Bayer.

The polyisocyanate may be used in combination with other isocyanates.

In one example, the polyisocyanate is a triisocyanate such as lysine triisocyanate or polyisocyanates sold by Bayer under the Desmodur<sup>®</sup> range.

The polyisocyanate may be present in an amount of 0.1-70% by weight, 0.5-50% by weight or 1-30% by weight based on the total weight of the polymer.

#### **Polyol or polyamine**

Suitable polyols or polyamines include those typically used to form cross-linked coatings such as polyester polyols/polyamines, polyether polyols/polyamines, polycarbonate polyols/polyamines and acrylic polyols/polyamines. A mixture of polyols/polyamines can be used in formulating the polymer.

Polyols that may be used include polyester polyols such as Desmophen<sup>®</sup>, Baycoll<sup>®</sup> (Bayer); polyether polyols such as Desmophene<sup>®</sup> and Acclaim<sup>®</sup>; polyaspartics such as Desmophen<sup>®</sup> NH; polycarbonate polyols such as Desmophen<sup>®</sup> C, as well as polymer cross-linkers such as poly(caprolactone) which contain multiple arms, as well as the polyol base component of Desothane<sup>®</sup> HS Clear Topcoat CA 8000/B900A (PPG Aerospace).

Suitable polyamines include but are not limited to primary amines and mixtures thereof including polyamines having at least two functional groups such as di-, tri- or higher functional polyamines and mixtures thereof. The polyamine may be aromatic or aliphatic, such as cycloaliphatic.

Examples of suitable aliphatic polyamines include but are not limited to ethylene diamine, 1,2-diaminopropane, 1,4-diaminobutane, 1,3-diaminopentane (Dytek<sup>®</sup> EP, Invista), 1,6-diaminohexane, 2-methyl-1,5-pentane diamine (Dytek<sup>®</sup> A, Invista), 2,5- diamino-2,5-dimethylhexane, 2,2,4- and/or 2,4,4-trimethyl-1,6-diamino-hexane, 1,11-diaminoundecane,

1,12-diaminododecane, 1,3- and/or 1,4-cyclohexane diamine, 1-aminotrimethyl- $\delta$ -aminomethyl-cyclohexane, 2,4- and/or 2,6-hexahydrotolulene diamine, 2,4'-diaminodicyclohexyl methane, 4,4'-diaminodicyclohexyl methane (PACM-20, Air Products) and 3,3'-dialkyl 4,4'-diaminodicyclohexyl methanes such as 3,3'-dimethyl-4,4'-diaminodicyclohexyl methane (Dimethyl Dicykan<sup>®</sup> or or Laromin<sup>®</sup> C260, BASF; Ancamine<sup>®</sup> 2049, Air Products) and 3,3'-diethyl-4,4'-diaminodicyclohexyl methane), 2,4- and/or 2,6-diaminotoluene and 2,4'- and/or 4,4'-diaminodiphenyl methane, or mixtures thereof. Other suitable amines include but are not limited to 3-(cyclohexylamine) propylamine, 3,3'-[1,4-butanediylbis]-1-propanamine and diamino functional polyetheramines having aliphatically bound primary amino groups, examples of which include Jeffamine<sup>®</sup> D-230, Jeffamine<sup>®</sup> D-400, Jeffamine<sup>®</sup> D-2000, and Jeffamine<sup>®</sup> D-4000 available from Huntsman Corporation.

In certain examples, the polyamine is a triamine. Examples of suitable triamines include dipropylene triamine, bis(hexamethylene) triamine and triamino functional polyetherpolyamines having aliphatically bound primary amino groups (Jeffamine<sup>®</sup> T-403, Jeffamine<sup>®</sup> T-3000, Jeffamine<sup>®</sup> T-5000 from Huntsman Corporation.)

In other examples, the amine can be a tetraamine or other higher functional amine.

The molecular weight of the polyol/polyamine may be in the range of 46-10000, 46-1000 or 46-100.

The polyol/polyamine may be present in an amount of 0-99% by weight, 0-50% by weight or 5-30% by weight based on the total weight of the polymer.

### Reactive Coating

The reactive coating may be any coating containing a polyisocyanate and/or a polyol or polyamine. Examples include polyurethane, polyurea, polysilicone, polyester or epoxy coatings which contain a polyisocyanate and/or a polyol or polyamine. Polyol containing coatings also include coatings containing hydroxyl polyesters. Specific examples include polyurethane coatings containing polyols such as Desothane<sup>®</sup> HS Clear Topcoat CA 8000/B900A available from PPG Aerospace or Eclipse<sup>®</sup> ECL-G-2 or Eclipse<sup>®</sup> ECL-G-7 or Aerodur 3002 Clear coat from AkzoNobel Aerospace Coatings.

### Surface

The surface on which the polymer coating is applied on may be an uncoated surface of an object or an object having an existing coating. The existing coating may be one or more layers of a coating selected from primers, conversion coatings, topcoats etc. The polymer coating may be applied on an object painted with a topcoat. Alternatively, the polymer may be mixed into a topcoat and applied on an object having a primer, a conversion coating or other coating. In the latter instance, the polymer forms part of the topcoat. Preferably, the existing coating or the topcoat is a polyurethane, polyurea, polysilicone, polyester or epoxy coating.

### Solvents

The solvent used in the polymer formulation may be a single solvent or a combination of two or more solvents. Preferably the solvent is an organic solvent. Suitable organic solvents or solvent combinations include but are not limited to:

(a) ester based solvents such as alkyl propionate, alkoxypropionate, alkyl alkoxypropionate, alkyl acetate, alkyl alkoxyacetate, ethyl acetate, propyl acetate, isopropyl acetate, butyl acetate, isobutyl acetate, tertiary butyl acetate and glycol ether acetates;

(b) ketones such as alkyl ketones for example, methyl ethyl ketone, methyl propyl ketone, methyl amyl ketone, methyl isoamyl ketone and methyl isobutyl ketone, acetone, pentanone, butanone and 2-heptanone;

(c) aromatics such as toluene and xylene;

(d) ethers such as glycol diethers, for example, the di-Ci-s alkyl ethers of glycols such as diethers of ethylene glycol, diethylene glycol, triethylene glycol, tetraethylene glycol, polyethylene glycol, propylene glycol, dipropylene glycol, tripropylene glycol and polypropylene glycol including but not limited to diethylene glycol dimethylether, dipropylene glycol dimethyl ether or methyl butylether of diethylene glycol such as those marketed by Dow under the trade name Downanol E-series and P-series glycolethers; and cyclic ethers such as tetrahydrofuran; and

(e) halogenated solvents such as dichloromethane and tetrachloroethylene.

In view of the toxicity and negative environmental impact of halogenated solvents, it will be understood that they should be used within the constraints of environmental, health and

safety regulations. Preferred solvents are ester based solvents such as alkyl propionate, alkoxypropionate, alkyl alkoxypropionate, alkyl acetate, alkyl alkoxyacetate, ethyl acetate, propyl acetate, isopropyl acetate, butyl acetate, isobutyl acetate, tertiary butyl acetate and glycol ether acetates; ketone solvents such as alkyl ketones for example, methyl ethyl ketone, methyl propyl ketone, methyl amyl ketone, methyl isoamyl ketone, methyl isobutyl ketone, acetone, pentanone, butanone and 2-heptanone.

### Additives

The polymer formulation can additionally include a variety of optional additives that are somewhat dependent on the particular application of the coating such as curing agents, cross-linking agents, catalysts, fillers, pigments or other colorants, reinforcements, thixotropes, accelerators, surfactants, plasticizers, extenders, stabilizers, corrosion inhibitors, hindered amine light stabilizers, UV light absorbers and antioxidants. Preferable additives may include extenders, catalysts and cross-linking agents.

In one example, the polymer comprises or consists of the reaction product of the compound of formula (I) and (i) a reactive coating and optionally a polyisocyanate and/or a polyol or polyamine or (ii) a polyisocyanate and optionally a polyol or a polyamine or (iii) a polyol or polyamine and optionally a polyisocyanate. The polymer formulation comprises or consists of the polymer, together with a solvent, an optional extender, an optional catalyst or an optional cross-linking agent.

Examples of extenders include pot-life extenders such as 2,4-pentanedione and alkyl acetoacetate.

Examples of catalysts include metal catalysts such as dibutyltin dilaurate (DBTD), stannous octoate, lead carbonate, lead octoate, ferric acetylacetonate and alkali-metal salts.

Examples of cross-linking agents include multifunctional polymers such as star shaped or multi-armed polymers with functionality such as hydroxyl, isocyanate or amine capable of reacting with the existing coating.

The additives may be present in an amount of 0-10% by weight based on the total weight of the polymer.

**Polymers**

Exemplary polymers include those which are reaction products of the following combinations:

- (a) Aminosiloxanes, polyisocyanate and optionally a catalyst, polyol or polyamine;
- 5 (b) Carbinolsiloxane, polyisocyanate and optionally a catalyst, polyol or polyamine;
- (c) Isocyanate siloxane and a polyol or polyamine or a coating containing a polyol or polyamine; and
- (d) Aminosiloxane or carbinolsiloxane and a reactive coating containing polyisocyanate.

**Polymer Formulation**

- 10 The polymer formulation may be made by dissolving the compound of formula (I) in an organic solvent such as a ketone for example 2-heptanone (MAK) prior to reaction with a polyisocyanate and/or a polyol, a polyamine or a reactive coating. The polyisocyanate and/or polyol or polyamine may also be dissolved in ketone, ether or ester based organic solvents prior to reaction with compound of formula (I). The polymer formulation is typically mixed for
- 15 15-120 minutes prior to applying on a surface.

The polymer formulation may optionally include the additives described above, in particular extenders, catalysts and/or cross-linking agents. A catalyst such as dibutyltin dilaurate may be required for the reaction between the compound of formula (I), the polyisocyanate and/or the polyol, the polyamine or the reactive coating.

**20 Uses**

- The polymer formulation may be applied as a continuous coating upon a wide variety of surfaces, particularly metal surfaces such as aluminium, stainless steel or titanium, or to composite surfaces such as resin matrices of carbon, glass fibers, or plastics and the like. The polymer formulation may also be applied to coated surfaces and as such independent of the
- 25 base material of the surface.

The polymer formulation may be applied to a surface of an object in a number of ways. For instance, it may be applied to a surface by spraying the polymer formulation upon a surface. As a one component spray, a formulation of the polymer in a solvent is sprayed onto a surface to be coated. In the event a catalyst is required, the polymer formulation and solvent

would be mixed with the catalyst prior to use. The resultant formulation may have a finite pot life and would have to be sprayed soon after the catalyst is mixed or during the pot life of the mixture.

5 As a two or more component system, the compound of formula (I) is dissolved in a solvent and the second component which is a polyisocyanate and optionally the polyol or the polyamine dissolved separately in a solvent. Alternatively a reactive coating is used in place of the second component. The two mixtures are combined in a common spray nozzle and mixed while being sprayed onto a dry surface to form a polymer coating on the surface of an object.

10 Once the polymer has been allowed to sufficiently cross-link and the solvent evaporates, a film of polymer is left behind.

Alternatively, the compound of formula (I) is mixed with a solution of the polyisocyanate and optionally the polyol, the polyamine or the reactive coating at a mixing nozzle of a spray gun and ejected onto the surface or mixed in a pot, transferred to a spray gun and ejected onto the surface prior to reaching the pot life of the mixture. This process results in  
15 a crosslinked polymer, which begins to cure within a few minutes and subsequently forms a cross-linked film.

Other methods of application can also be used such as those commonly known to those in the art such as by brush, roller, dip, droplet impact, printing, such as screen printing, or via a pre-packaged aerosol. The formulation may be applied as an appliqué by first depositing the  
20 formulation, as described above, upon a relief surface. When dry, the polymer coating may be removed from the relief surface and used in an appliqué process to adhere the coating onto a subsequent surface.

In a one component spray, the polymer is capable of being handled or walked upon as soon as the polymer has been allowed to sufficiently cross-link and the solvent has evaporated.  
25 Secondary process could include operations such as masking, taping and application of additional layers of the coating. Use of a heat source, such as hot air or infrared lamps, will accelerate the solvent removal and the cross-linking reaction. In the two component system, the polymer starts to crosslink and form almost as soon as the two parts are mixed and sprayed

onto the surface. Again use of hot air or heat lamps will facilitate solvent removal and cross-linking to leave behind a polymer coating in the form of a film.

The coating may be in the form of a clear coating film and may be applied onto a wide variety of surfaces, including painted surfaces. A potential advantage of a clear film coating is that it provides sufficient transparency to allow the coating to be used over a pigmented (coloured) topcoat for example in the formation of basecoat – clearcoat coatings known to those in the art. Alternatively, the polymer coating may be pigmented by mixture of one or more of the reaction components with a suitable pigment in a colloid mill. The clear coating or pigmented coating may then be used as a paint.

The polymer formulation can be applied anywhere between about 1°C and about 45°C. Typically, the polymer formulation is applied at ambient temperatures between about 15°C and 35°C. The polymer formulation may be applied to form a single layer or as multiple layers to achieve a desired thickness.

The polymer formulation may be applied as a continuous coating upon a wide variety of object surfaces, particularly metal surfaces such as aluminium, stainless steel or titanium, or to composite surfaces such as resin matrices of carbon or glass fibers, plastics and the like. The polymer may also be applied to coated surfaces and as such independent of the base material used in object. The polymer coating may be used to reduce the amount of ice forming on a surface and/or the adhesion of ice to the object's surface, for example upon the lift, stabilizing, and control surfaces of an aircraft. In this instance the entire surface of an aircraft may be coated with the polymer or just the lift, stabilizing, and/or control surfaces or other selected surfaces may be coated. Reduction of ice formation is of critical importance because even a slight build-up of ice upon the wings or other lift surfaces of the aircraft can cause dramatic alterations in the aerodynamic performance of the lift surfaces. Similarly, control surfaces of the aircraft must remain free of ice build-up which could block the movement and impair the operation of those control surfaces. Additionally, reduction of ice formation reduces the overall weight of the aircraft, thereby improving performance, and fuel efficiency. Similar advantages may be provided by coating at least some portions of the outer surface of other objects such as missiles, ships, automobiles and wind turbines.

The usefulness of the polymer is not limited to metal surfaces. The polymer finds use as a coating on any of a wide variety of surfaces such as carbon composites, and even wood or asphalt, a number of which may be applications unrelated to aircraft such as wind turbines, air conditioners, refrigeration units, buildings, signs and powerlines.

## 5 Properties

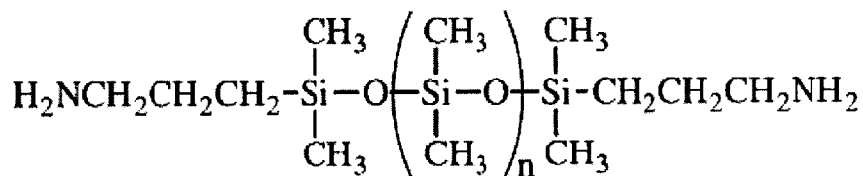
When the polymer used as an ice reducing coating on a surface, the coated surface can demonstrate a minimum average adhesion force of < 5N when subjected to the ice adhesion test, a pencil hardness value of up to 4H and a 60 degree glass value of up to 83.

## EXAMPLES

- 10 Embodiments will now be described with reference to the following non-limiting examples.

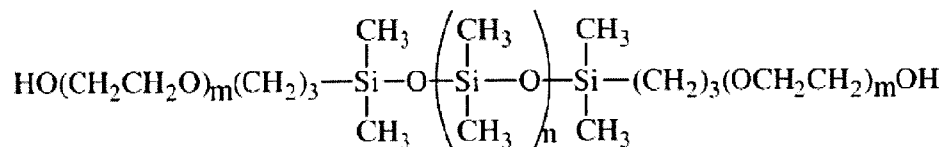
The following abbreviations are used in the examples:

Amino siloxane: PS510, PS512, PS513, and DMS-A12



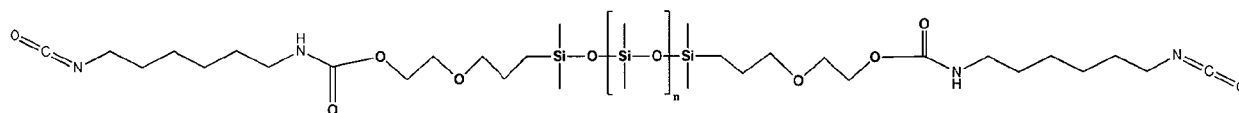
- 15 n is 5-1500

Carbinol Siloxane: DMS-C16, 15, 21, 22 and 23



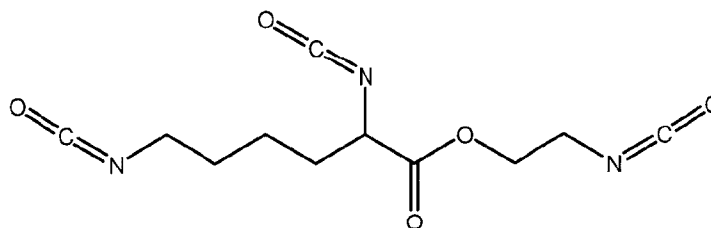
m is 1-10 and n is 5-1500

Isocyanate functional siloxane:



5

Lysine Triisocyanate



10

Desothane<sup>®</sup> HS CA **8000B** Activator from PPG Aerospace containing polyisocyanate in solvent

DESMODUR **N3390** a HDI trimer in n-butylacetate available from Bayer with a NCO content of **19.6%**

15 **N75** an aliphatic polyisocyanate (HDI biuret) in n-butylacetate available from Bayer with a NCO content of **16.5%**

Desothane<sup>®</sup> HS CA **8000/ B900A** base from PPG Aerospace containing polyol, polycaprolactone cross-linker (4-arm) solvents and styrenic acyclic polymer

The details of the polymer formulations are set out in Table **1** below with reference to the following:

20

1. Mole ratio of **1:1** (reactive siloxane groups: isocyanate/ polyol groups) used in all formulations.
2. Reaction is between a reactive siloxane and an isocyanate (except example **17** and **18** which is between isocyanate-functional siloxane and a polyol).
- 25 3. Examples **13-16** are hybrid polyurea-urethane siloxane coatings containing reactive siloxane, polyol and isocyanate.
4. All formulations were applied onto aluminium (Alclad **2024-T3**) panels which had previously been coated with primer and an existing clear coat (Desothane<sup>®</sup> HS Clear

Topcoat CA **8000/B900A**) via a spray gun and then cured at ambient conditions for **12-24** hours.

5 The reactive siloxane is mixed in an organic solvent such as ketone, ether or ester. The isocyanate component is then added to the formulation (and any catalyst, polyol, or polyamine as appropriate) and the solution mixed for **20-120** minutes prior to spray or brush application of the coating on a surface.

#### **Ice Adhesion Test Method**

10 Ice adhesion was measured using an Instron Universal Testing Machine (model **5565**) fitted with a **100** N load cell. Tests were carried out at a speed of **0.5** mm/min inside an environmental chamber maintained at **-20°C** and located within the Instron. The polymer coating was applied to aluminium coupons and water (ultra-pure Milli-Q resistivity value of **18.2** MΩ.cm @ **25°C**; ≤5 ppb) filled cylindrical columns were frozen at **-20°C** onto the coating surface. A pendulum attachment was fitted to the Instron and the ice columns and a tensile force was applied to dislodge the ice columns from the coated specimens. The tensile force  
15 required to separate the ice was recorded and the stress calculated. The mode of failure – cohesive or adhesive was also noted.

**Table 1**

| Example                                                           | Siloxane                                 |                                                                                     | Isocyanate                          | Polyol/<br>polyamine            | Catalyst           | %<br>Siloxane<br>(of solids<br>content) | Solvent                                                                                                                                                                                                                                  |
|-------------------------------------------------------------------|------------------------------------------|-------------------------------------------------------------------------------------|-------------------------------------|---------------------------------|--------------------|-----------------------------------------|------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
|                                                                   | Reactive<br>group                        | Molecular<br>weight                                                                 |                                     |                                 |                    |                                         |                                                                                                                                                                                                                                          |
| Desothane HS<br>Clear Topcoat<br>CA 8000/<br>B900A Clear<br>Coat* | -                                        | -                                                                                   | Desothane<br>Activator <sup>^</sup> | Desothane<br>Base <sup>^^</sup> | -                  | -                                       | Proprietary mix<br>of solvents<br>including 2,6-<br>dimethyl-4-<br>heptanone,<br>4,6-dimethyl-2-<br>heptanone,<br>methyl amyl<br>ketone ,<br>2,4-pentanedione<br>ethyl acetate,<br>N-butyl acetate<br>and 1,2,4-<br>trimethyl<br>benzene |
| US6797795*<br>(Example 1)                                         | Amino<br>(PS510)                         | 5000<br>(2 x PS510<br>linked with<br>fumaryl<br>chloride)                           | 2,4-toluene<br>diisocyanate         | -                               | -                  | 100                                     | dichloromethane                                                                                                                                                                                                                          |
| US7910683*<br>(Example 3)                                         | Amino<br>(PS510)                         | 5000 (2 x<br>PS510 linked<br>with fumaryl<br>chloride and<br>4,4'-<br>oxydianiline) | 2,4-toluene<br>diisocyanate         | -                               | -                  | 100                                     | dichloromethane                                                                                                                                                                                                                          |
| 1                                                                 | Amino<br>(PS510,<br>from UCT<br>Silanes) | 2500                                                                                | Lysine<br>triisocyanate             | -                               | -                  | 100                                     | 2-heptanone                                                                                                                                                                                                                              |
| 2                                                                 | Amino<br>(PS510:<br>DMSA12<br>95:5)      | 2500 (95%)<br>900-100<br>(5%)                                                       | Lysine<br>triisocyanate             | -                               | -                  | 100                                     | 2-heptanone                                                                                                                                                                                                                              |
| 3                                                                 | Amino<br>(PS512,<br>UCT<br>Silanes)      | 25,000                                                                              | Lysine<br>triisocyanate             | -                               | -                  | 100                                     | 2-heptanone                                                                                                                                                                                                                              |
| 4                                                                 | Amino<br>(PS513,<br>UCT<br>Silanes)      | 27,000                                                                              | Lysine<br>triisocyanate             | -                               | -                  | 100                                     | 2-heptanone                                                                                                                                                                                                                              |
| 5                                                                 | Carbinol<br>(DMS-C16 ,<br>from Gelest)   | 700                                                                                 | Desothane<br>Activator <sup>^</sup> | -                               | 0.075 wt%<br>DBTD* | 100                                     | 2-heptanone                                                                                                                                                                                                                              |

|    |                                   |        |                                                     |                                         |                   |     |             |
|----|-----------------------------------|--------|-----------------------------------------------------|-----------------------------------------|-------------------|-----|-------------|
| 6  | Carbinol<br>(DMS-C15)             | 1000   | Desothane<br>Activator <sup>^</sup>                 | -                                       | 0.075 wt%<br>DBTD | 100 | 2-heptanone |
| 7  | Carbinol<br>(DMS-C21)             | 5000   | Desothane<br>Activator <sup>^</sup>                 | -                                       | 0.075 wt%<br>DBTD | 100 | 2-heptanone |
| 8  | Carbinol<br>(DMS-C23)             | 10,000 | Desothane<br>Activator <sup>^</sup>                 | -                                       | 0.075 wt%<br>DBTD | 100 | 2-heptanone |
| 9  | Amino<br>(PS510)                  | 2500   | Desothane<br>Activator <sup>^</sup>                 | -                                       | -                 | 100 | 2-heptanone |
| 10 | Amino<br>(PS510)                  | 2500   | Desmodur<br>N3390<br>(Polyisocyanate<br>from Bayer) | -                                       | -                 | 100 | 2-heptanone |
| 11 | Amino<br>(PS510)                  | 2500   | Desmodur N75<br>(Polyisocyanate<br>from Bayer)      | -                                       | -                 | 100 | 2-heptanone |
| 12 | Carbinol<br>(DMS-C23)             | 10,000 | Desmodur<br>N3390<br>(Polyisocyanate<br>from Bayer) | -                                       | 0.075 wt%<br>DBTD | 100 | 2-heptanone |
| 13 | Amino<br>(PS510)                  | 2500   | Lysine<br>triisocyanate                             | Desothane<br>Base <sup>^^</sup>         | -                 | 46  | 2-heptanone |
| 14 | Amino<br>(PS510)                  | 2500   | Desothane<br>Activator                              | Desothane<br>Base <sup>^^</sup>         | -                 | 6.1 | 2-heptanone |
| 15 | Amino<br>(PS510)                  | 2500   | Desmodur N75                                        | polycaprolact<br>one (Mw<br>900)        |                   | 20  | 2-heptanone |
| 16 | Amino<br>(PS510)                  | 2500   | Desmodur N75<br>(Polyisocyanate<br>from Bayer)      | 65%<br>polycaprolact<br>one (Mw<br>900) |                   | 35  | 2-heptanone |
| 17 | Isocyanate<br>(made in-<br>house) | 1000   | -                                                   | Desothane<br>base <sup>^^</sup>         |                   | 100 | 2-heptanone |

|    |                               |        |                        |                                 |                    |     |                                                               |
|----|-------------------------------|--------|------------------------|---------------------------------|--------------------|-----|---------------------------------------------------------------|
| 18 | Isocyanate<br>(made in-house) | 5000   | -                      | Desothane<br>base <sup>^^</sup> |                    | 100 | 2-heptanone                                                   |
| 19 | Carbinol<br>(DMS-C23)         | 10,000 | Desothane<br>Activator | Desothane<br>base <sup>^^</sup> | 0.075 wt%<br>DBTD  | 5   | 33.3% 2-heptanone<br>43.3% pentanone<br>23.3% butanone        |
| 20 | Carbinol<br>(DMS-C23)         | 10,000 | Desothane<br>Activator | Desothane<br>base <sup>^^</sup> | 0.075 wt%<br>DBTD  | 10  | 33.3% 2-heptanone<br>43.3% pentanone<br>23.3% butanone        |
| 21 | Carbinol<br>(DMS-C23)         | 10,000 | Desothane<br>Activator | Desothane<br>base <sup>^^</sup> | 0.075 wt%<br>DBTD  | 20  | 33.3% 2-heptanone<br>43.3% pentanone<br>23.3% butanone        |
| 22 | Carbinol<br>(DMS-C23)         | 10,000 | Desothane<br>Activator | Desothane<br>base <sup>^^</sup> | 0.075 wt%<br>DBTD  | 30  | 33.3% 2-heptanone<br>43.3% pentanone<br>23.3% butanone        |
| 23 | Carbinol<br>(DMS-C23)         | 10,000 | Desothane<br>Activator | Desothane<br>base <sup>^^</sup> | 0.075 wt%<br>DBTD  | 40  | 33.3% 2-heptanone<br>43.3% pentanone<br>23.3% butanone        |
| 24 | Amino<br>(PSS10)              | 2500   | Desothane<br>Activator | -                               | -                  | 100 | 40% 2-heptanone<br>60% 2-pentanone                            |
| 25 | Carbinol<br>(DMS-C23)         | 10,000 | Desothane<br>Activator | -                               | 0.0208 wt%<br>DBTD | 100 | 33.33% 2-heptanone<br>43.33% 2-pentanone<br>23.33% 2-butanone |
| 26 | Carbinol<br>(DMS-C15)         | 1,000  | Desothane<br>Activator | -                               | 0.0208 wt%<br>DBTD | 100 | 33.33% 2-heptanone<br>43.33% 2-pentanone<br>23.33% 2-butanone |
| 27 | Carbinol<br>(DMS-C23)         | 10,000 | Desothane<br>Activator | Desothane<br>base <sup>^^</sup> | 0.0156 wt%<br>DBTD | 30  | 33.3% 2-heptanone<br>43.3% pentanone<br>23.3% butanone        |

\*Comparative Example

<sup>^</sup>DBTD – dibutyl tin dilaurate added based on resin weight

<sup>^</sup>Desothane HS Activator: Activator CA 8000B (PPG Aerospace)

<sup>^^</sup>Desothane HS Clear Topcoat CA 8000/ B900A Base: Base CA 8000/ B900A (PPG Aerospace)

**Table 2**

| <b>Example</b>                        | <b>Ice Adhesion- Tensile Force (N)</b> | <b>Ice Adhesion- Tensile Stress (kPa)</b> | <b>Failure Mode**</b>    |
|---------------------------------------|----------------------------------------|-------------------------------------------|--------------------------|
| Desothane HS CA 8000 B900A Clearcoat* | <b>45 ± 14.3</b>                       | <b>176.7 ± 56.1</b>                       | <b>40% CF<br/>60% AF</b> |
| NuSil R1082*                          | <b>11.6 ± 4.4</b>                      | <b>45.7 ± 17.1</b>                        | <b>100% AF</b>           |
| NuSil R2180*                          | <b>16.5 ± 3.1</b>                      | <b>64.7 ± 12.3</b>                        | <b>100% AF</b>           |
| US6797795*<br>(Example 1)             | <b>5.2 ± 2.6</b>                       | <b>20.3 ± 10.3</b>                        | <b>100% AF</b>           |
| US7910683*<br>(Example 3)             | <b>10.4 ± 5.9</b>                      | <b>40.9 ± 23.1</b>                        | <b>100% AF</b>           |
| <b>1</b>                              | <b>3.4 ± 1.1</b>                       | <b>13.4 ± 4.4</b>                         | <b>100% AF</b>           |
| <b>2</b>                              | <b>5.2 ± 0.3</b>                       | <b>20.3 ± 1.1</b>                         | <b>100% AF</b>           |
| <b>3</b>                              | <b>1.1 ± 0.1</b>                       | <b>4.4 ± 0.5</b>                          | <b>100% AF</b>           |
| <b>4</b>                              | <b>3.6 ± 3.1</b>                       | <b>14.2 ± 12.1</b>                        | <b>100% AF</b>           |
| <b>5</b>                              | <b>47.3 ± 15.5</b>                     | <b>185.8 ± 60.9</b>                       | <b>30% CF<br/>70% AF</b> |
| <b>6</b>                              | <b>36.7 ± 3.1</b>                      | <b>144.7 ± 12.1</b>                       | <b>30% CF<br/>70% AF</b> |
| <b>7</b>                              | <b>6.8 ± 35.6</b>                      | <b>26.7 ± 22.1</b>                        | <b>100% AF</b>           |
| <b>8</b>                              | <b>0.7 ± 0.1</b>                       | <b>2.6 ± 0.5</b>                          | <b>100% AF</b>           |
| <b>9</b>                              | <b>3.7 ± 3.1</b>                       | <b>14.5 ± 12.0</b>                        | <b>100% AF</b>           |
| <b>10</b>                             | <b>4.8 ± 2.4</b>                       | <b>18.9 ± 9.3</b>                         | <b>100% AF</b>           |
| <b>11</b>                             | <b>4.4 ± 3.5</b>                       | <b>17.2 ± 13.7</b>                        | <b>100% AF</b>           |
| <b>12</b>                             | <b>3.2 ± 3.1</b>                       | <b>12.8 ± 12.2</b>                        | <b>100% AF</b>           |
| <b>13</b>                             | <b>2.0 ± 0.5</b>                       | <b>7.9 ± 1.6</b>                          | <b>100% AF</b>           |
| <b>14</b>                             | <b>14.4 ± 4.0</b>                      | <b>56.6 ± 15.8</b>                        | <b>100% AF</b>           |

|    |             |              |                  |
|----|-------------|--------------|------------------|
| 15 | 26.7 ± 11.4 | 104.8 ± 44.6 | 100% AF          |
| 16 | 22.0 ± 9.2  | 86.5 ± 36.1  | 100% AF          |
| 17 | 36.1 ± 16.4 | 142 ± 64.5   | 44% CF<br>56% AF |
| 18 | 24.1 ± 9.1  | 94.6 ± 35.6  | 15% CF<br>85% AF |
| 19 | 21.1 ± 5.6  | 82.8 ± 22    | 31% CF<br>69% AF |
| 20 | 14.9 ± 5.6  | 58.5 ± 21.9  | 13% CF<br>87% AF |
| 21 | 5.0 ± 1.3   | 19.7 ± 5.0   | 100% AF          |
| 22 | 5.6 ± 2.7   | 21.9 ± 10.7  | 100% AF          |
| 23 | 6.3 ± 4.6   | 24.6 ± 18.0  | 100% AF          |
| 24 | 4.5 ± 3.7   | 18 ± 15      | 100% AF          |
| 25 | 0.9 ± 0     | 3.3 ± 0.2    | 100% AF          |
| 26 | 23.8 ± 3.1  | 93 ± 12      | 24% CF<br>76% AF |
| 27 | 9.9 ± 1.8   | 39 ± 7       | 100% AF          |

\* Comparative example

\*\* AF= adhesive failure, CF = Cohesive failure

Table 3

| Example                                        | H <sub>2</sub> O<br>Contact<br>Angle (°) | CH <sub>2</sub> I <sub>2</sub><br>Contact<br>Angle (°) | Surface<br>Energy<br>Dispersion<br>(mJ/m <sup>2</sup> ) | Surface<br>Energy<br>Polar<br>(mJ/m <sup>2</sup> ) | Gloss<br>20° | Gloss<br>60° | Pencil<br>Hardness<br>(Gauge) |
|------------------------------------------------|------------------------------------------|--------------------------------------------------------|---------------------------------------------------------|----------------------------------------------------|--------------|--------------|-------------------------------|
| Desothane<br>HS CA 8000<br>B900A<br>Clearcoat* | 82.2                                     | 39.8                                                   | 41.6                                                    | 2.5                                                | 86           | 95           | 4H                            |
| NuSil<br>R1082*                                | 109.0                                    | 62.2                                                   | 28.6                                                    | 0                                                  | 30           | 66           | HB                            |
| NuSil<br>R2180*                                | 110.1                                    | 61.5                                                   | 29.1                                                    | 0                                                  | 27           | 57           | HB                            |

|                               |       |       |       |      |    |    |               |
|-------------------------------|-------|-------|-------|------|----|----|---------------|
| US6797795<br>*<br>(Example 1) | 106.2 | 63.6  | 27.7  | 0.05 | 18 | 53 | < 6B<br>tacky |
| US7910683<br>*<br>(Example 3) | 127.8 | 104.4 | 7.5   | 0.03 | 44 | 68 | < 6B<br>tacky |
| 1                             | 104.3 | 60.8  | 29.6  | 0.08 | 47 | 77 | 2H            |
| 2                             | 104.9 | 61.1  | 29.3  | 0.06 | 58 | 75 | 2H            |
| 3                             | 116.6 | 62.4  | 28.4  | 0.46 | 35 | 68 | 4H            |
| 4                             | 116.4 | 64.3  | 27.3  | 0.35 | 51 | 72 | 2H            |
| 5                             | 102.9 | 73.5  | 21.9  | 0.8  | 60 | 79 | 3H            |
| 6                             | 104.6 | 72.0  | 22.8  | 0.48 | 56 | 82 | 2H            |
| 7                             | 109.5 | 65.9  | 26.4  | 0    | 41 | 70 | 4H            |
| 8                             | 111.4 | 64.1  | 27.4  | 0.04 | 51 | 71 | 4H            |
| 9                             | 106.5 | 65.5  | 26.6  | 0.08 | 29 | 67 | 4H            |
| 10                            | 104.4 | 62.7  | 28.3  | 0.12 | 56 | 76 | HB            |
| 11                            | 106.0 | 63.9  | 27.6  | 0.07 | 62 | 79 | 4H            |
| 12                            | 106.9 | 62.4  | 28.5  | 0.02 | 58 | 80 | B             |
| 13                            | 104.4 | 50.7  | 27.7  | 0.15 | 58 | 78 | 4B            |
| 14                            | 102.2 | 65.4  | 26.7  | 0.41 | 59 | 81 | B             |
| 15                            | 100.5 | 75.7  | 20.7  | 1.42 | 67 | 83 | 4H            |
| 16                            | 100.5 | 67.5  | 25.4  | 0.76 | 34 | 75 | HB            |
| 17                            | 103   | 64.7  | 26.12 | 0.37 | 47 | 74 | 2H            |
| 18                            | 103.3 | 67.5  | 27.11 | 0.27 | 51 | 75 | 4H            |
| 19                            | 102.8 | 82.5  | 17    | 1.6  | 55 | 76 | 4H            |
| 20                            | 104.7 | 82.4  | 17.1  | 1.02 | 55 | 73 | F             |
| 21                            | 108.4 | 65.7  | 26.5  | 0    | 50 | 72 | 4H            |
| 22                            | 110.6 | 66.9  | 25.8  | 0    | 49 | 72 | 4H            |
| 23                            | 114.9 | 63.3  | 27.9  | 0.3  | 39 | 70 | F             |
| 24                            | 108.8 | 64.8  | 21.7  | 0    | 49 | 71 | B             |

|    |       |      |      |     |    |    |   |
|----|-------|------|------|-----|----|----|---|
| 25 | 111.4 | 64.6 | 27.2 | 0   | 53 | 74 | B |
| 26 | 105.2 | 73.6 | 21.9 | 0.5 | 52 | 75 | B |
| 27 | 112.5 | 66.9 | 25.8 | 0   | 40 | 70 | B |

\*Comparative Example

### Surface Energy Testing Method

Surface Energy calculations were based on contact angle measurements complete using  
 5 'FIRST TEN ANGSTROMS' semi-automated video equipped contact angle analyser. Diiodomethane ( $\text{CH}_2\text{I}_2$ ) and water ( $\text{H}_2\text{O}$ ) were employed as the reference solvents to calculate the dispersion and polar contributions to surface energy through the Young-Dupre relationship and Fowkes equation.

### Gloss Test Method

10 Gloss was measured on a Byk-Gardner micro-TRI gloss meter at **20** and **60°**.

### Pencil Hardness Test Method

Pencil hardness was measured according to ASTM D3363.

Cross-linked polysiloxane based on urea and urethane cross-linked chemistry was found to be compatible with current aircraft polyurethane topcoat and can be used alone as a  
 15 thin final top layer or as a component of the current topcoat to provide a coating with reduced ice adhesion. Very low ice adhesion was found on such a coating surface (Tensile Force and Tensile Stress in Table 2) and represents a significant decrease compared to a commonly used aerospace topcoat (Desothane<sup>®</sup> HS). Two commercially available NuSil polysiloxane elastomer coatings, and two coating formulations disclosed in Example 1 of US6797795 and  
 20 Example 3 of US7910683 were also analysed and all have ice adhesion tensile values of greater than 19 kPa. Table 3 also demonstrates that compared to US6797795 and US6809169, there is (i) improved and proven cross-linked structure as demonstrated by pencil hardness values up to 4H (Table 2); (ii) 60 degree gloss values up to 83 (Table 3); (iii) improved compatibility to existing polyurethane topcoat for aircraft application and the coating  
 25 formulation can be used as a component of the existing polyurethane topcoat; and (iv) durability including chemical resistance as demonstrated by increased hardness and the present

coatings could not be redissolved in solvent (MEK) compared to the prior art coatings described in US **6797795** and US**6809169**.

As shown in Table 3, use of a superhydrophobic coating (water contact angle greater than **150°** and roll-off angle **< 10°**) is not required in order to achieve very low ice adhesion values. As shown in Table 3, the present coatings have very low polar surface energy and this may in part explain the low ice adhesion. However, the NuSil polysiloxane elastomer coatings also have low polar surface energies so there are additional morphological, chemical, or physical interactions that will determine ice adhesion.

The present coatings may provide the following advantages:

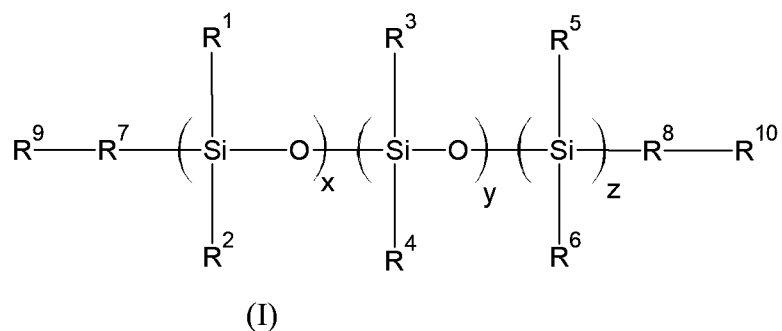
- (i) Reduced ice adhesion **<19** kPa tensile stress, or **< 5** N tensile force, which is less than previously published values for ice adhesion;
- (ii) Pencil hardness values up to **4H** which are similar to current conventional hardness values for polyurethane based aerospace coatings such as Desothane and higher than commercially available siloxane coatings such as NuSil;
- (iii) **60** degree gloss values up to **83**, demonstrating higher gloss than commercially available siloxane coating materials such as NuSil;
- (iv) Improved compatibility to existing polyurethane topcoat for aircraft application and the coating formulation can be used as a component of the existing polyurethane topcoat;
- (v) Durability including chemical resistance compared with existing art such as US**6797795**.

In the claims which follow and in the preceding description, except where the context requires otherwise due to express language or necessary implication, the word “comprise” or variations such as “comprises” or “comprising” is used in an inclusive sense, i.e. to specify the presence of the stated features but not to preclude the presence or addition of further features in various examples.

It will be understood to persons skilled in the art that many modifications may be made without departing from the teachings of the disclosure.

EMBODIMENTS IN WHICH AN EXCLUSIVE PROPERTY OR PRIVILEGE IS CLAIMED  
ARE DEFINED AS FOLLOWS:

1. An ice adhesion reducing polymer having an ice adhesion tensile force of less than  
5 Newtons, comprising a cross-linked reaction product of the following siloxane:



in which

R<sup>1</sup> to R<sup>6</sup> are independently selected from the group consisting of H; optionally substituted C<sub>1-16</sub>alkyl optionally interrupted with a group selected from NR<sup>11</sup>, C=O, C=C, S, CO<sub>2</sub>, O, and CH(NCO); OSiR<sup>12</sup><sub>3</sub>; (CH<sub>2</sub>)<sub>p</sub>OH; (CH<sub>2</sub>)<sub>p</sub>O(CH<sub>2</sub>)<sub>p</sub>OH; (CH<sub>2</sub>)<sub>p</sub>NR<sup>11</sup>R<sup>12</sup>; (CH<sub>2</sub>)<sub>p</sub>NH(CH<sub>2</sub>)<sub>p</sub>NR<sup>11</sup>R<sup>12</sup>; (CH<sub>2</sub>)<sub>p</sub>O(CH<sub>2</sub>)<sub>p</sub>NR<sup>11</sup>R<sup>12</sup>; (CH<sub>2</sub>)<sub>p</sub>NCO; epoxy; optionally substituted C<sub>1-16</sub>alkylaryl; optionally substituted aryl; optionally substituted polyaryl; optionally substituted C<sub>3-6</sub>cycloaliphatic; and optionally substituted C<sub>3-6</sub>heterocyclyl;

R<sup>7</sup> and R<sup>8</sup> are independently absent or independently selected from the group consisting of optionally substituted C<sub>1-16</sub>alkyl optionally interrupted with a group selected from NR<sup>11</sup>, C=O, C=C, S, CO<sub>2</sub>, O, and CH(NCO); O; S; OSi(R<sup>13</sup>)<sub>2</sub>; (CH<sub>2</sub>)<sub>p</sub>; (CH<sub>2</sub>)<sub>p</sub>NH; (CH<sub>2</sub>)<sub>p</sub>O; optionally substituted C<sub>1-16</sub>alkylaryl; optionally substituted aryl; optionally substituted polyaryl; optionally substituted C<sub>3-6</sub>cycloaliphatic; and optionally substituted C<sub>3-6</sub>heterocyclyl;

$R^9$  and  $R^{10}$  are independently selected from the group consisting of H, OH,  $NR^{11}R^{12}$ , optionally substituted  $C_{1-16}$ alkyl, NCO, epoxy and  $Si(R^{13})_3$ ;

$R^{11}$  and  $R^{12}$  are independently selected from the group consisting of H and optionally substituted  $C_{1-16}$ alkyl;

$R^{13}$  is selected from the group consisting of optionally substituted  $C_{1-16}$ alkyl,  $(CH_2)_pOH$ , and  $(CH_2)_pNH_2$ ;

p is 1 to 16;

z is 1;

x is selected from 1 to 1500; and

y is 0 to 1500; and

when at least one of  $R^1$  to  $R^6$ ,  $R^9$  and  $R^{10}$  bears an  $NH_2$  group then the siloxane of formula (I) has a molecular weight of between about 2500 and about 27000 Daltons and when at least one of  $R^1$  to  $R^6$ ,  $R^9$  and  $R^{10}$  bears an OH group the siloxane of formula (I) has a molecular weight of between about 5000 and about 10000 Daltons; and

(i) a polyisocyanate and one or more of a polyol, a polyamine and a reactive coating, or

(ii) any one of a polyisocyanate, a polyol, a polyamine or a reactive coating;

with the provisos that:

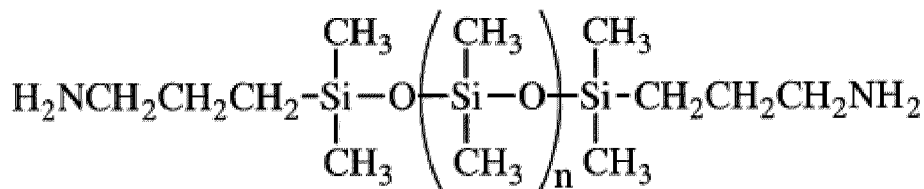
(a) when the compound of formula (I) reacts with a polyisocyanate, then at least one of R<sup>1</sup> to R<sup>6</sup>, R<sup>9</sup> and R<sup>10</sup> must bear at least one OH or NH<sub>2</sub> or both;

(b) when the compound of formula (I) reacts with a polyol, a polyamine or a reactive coating, then at least one of R<sup>1</sup> to R<sup>6</sup>, R<sup>9</sup> and R<sup>10</sup> must bear at least one NCO;

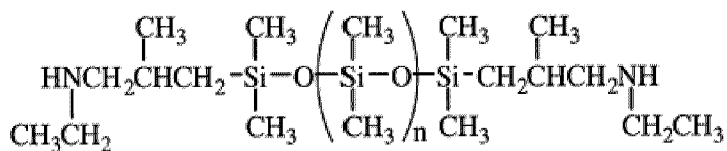
(c) when the compound of formula (I) reacts with a reactive coating, then at least one of R<sup>1</sup> to R<sup>6</sup>, R<sup>9</sup> and R<sup>10</sup> must bear at least one OH or NH<sub>2</sub> or both to react with a polyisocyanate present in the coating or at least one of R<sup>1</sup> to R<sup>6</sup>, R<sup>9</sup> and R<sup>10</sup> must bear at least one NCO to react with a polyol or polyamine present in the coating; and

(d) when present, the amount of polyol/polyamine is in the range of from 5 to 30% by weight based on the total weight of the polymer.

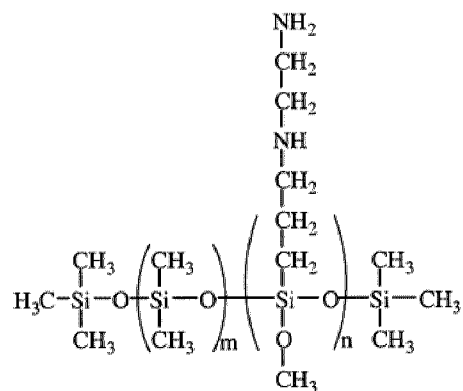
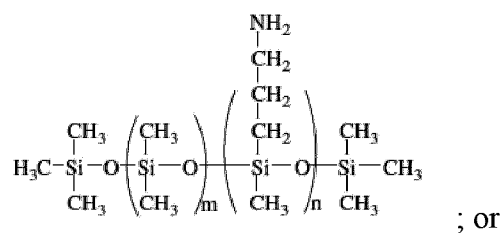
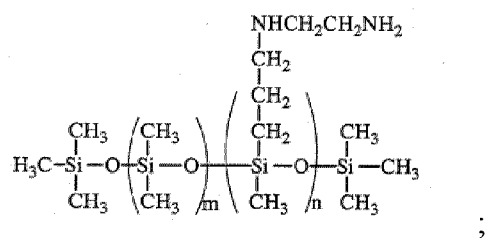
2. The polymer according to claim 1 in which the compound of formula (I) is selected from the following:



;



;

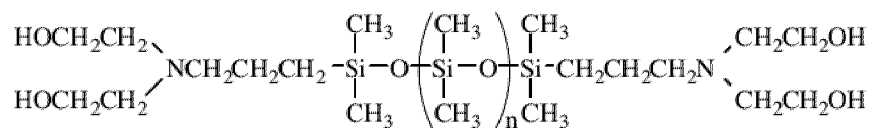


in which

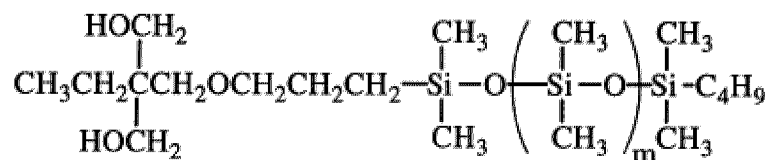
5

m is 1-1500; and

n is 1-1500; or



; or

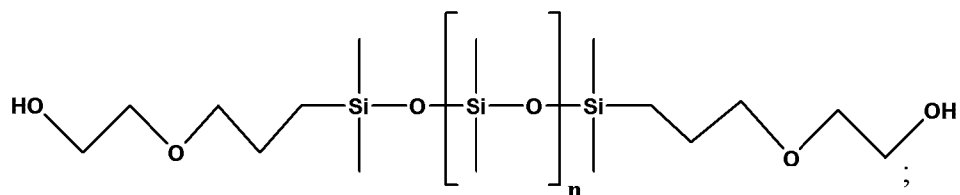


in which

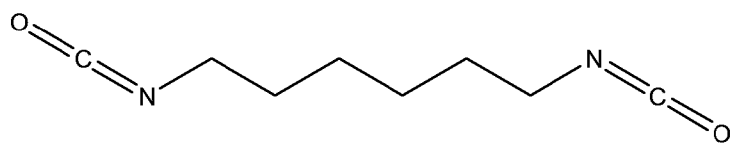
m is 1-1500; and

n is 1-1500; or

the reaction product of:



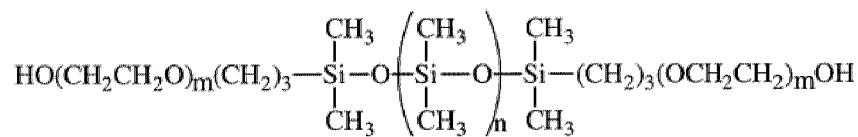
and



in which

n is 1-1500.

3. An ice reducing polymer having an ice adhesion tensile force of less than 5 Newtons, comprising a cross-linked reaction product of the following carbinol siloxane:



in which

m is 1-1500; and

n is 1-1500,

wherein the siloxane has a molecular weight of between about 5000 and 10000 Daltons; and a polyisocyanate.

5

4. The polymer according to claim 1 in which the compound of formula (I) is present in an amount of 1-99% by weight based on the total weight of the polymer.

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5. The polymer according to claim 1 or 3 in which the polyisocyanate is a diisocyanate, triisocyanate or higher functionality isocyanate.

6. The polymer according to claim 5 in which the triisocyanate is lysine triisocyanate or the polyisocyanate is under the Desmodur<sup>®</sup> range.

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7. The polymer according to claim 1 or 3 in which the polyisocyanate is present in an amount of 0.1-70% by weight based on the total weight of the polymer.

20

8. The polymer according to claim 1 in which the polyol or polyamine is selected from a polyester polyol/polyamine, a polyether polyol/polyamine, a polycarbonate polyol/polyamine, an acrylic polyol/polyamine or a combination thereof.

9. The polymer according to claim 1 in which the polyol or polyamine is present in an amount of 0-99% by weight based on the total weight of the polymer.

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10. The polymer according to claim 1 in which the reactive coating is selected from a polyurethane, polyurea, polysilicone, polyester or epoxy coating each of which contain a polyisocyanate and/or a polyol or polyamine.

11. An object comprising an external surface in which at least a portion of the external surface is coated with the polymer according to any one of claims 1-10.
- 5 12. The object according to claim 11 in which the external surface coated with the polymer has an average adhesion force of <5 N when subject to an Ice Adhesion Test Method measured using an Instron Universal Testing Machine, model 5565, fitted with a 100 N load cell, wherein tests are carried out at a speed of 0.5 mm/min inside an environmental chamber that is maintained at -20°C and located within the Instron, the method comprising applying the polymer coating to aluminium coupons; freezing water-filled cylindrical  
10 columns at -20°C onto the surface, the water having an ultra-pure Milli-Q resistivity value of 18.2 MΩ·cm at 25°C, ≤5 ppb; fitting a pendulum attachment to the Instron and the ice columns; applying a tensile force to dislodge the ice columns from the coated specimens; and calculating the average adhesion force.
- 15 13. A method of imparting ice adhesion reducing properties to at least a portion of an external surface of an object comprising applying a coating of the polymer according to any one of claims 1-10 onto the surface.
- 20 14. An object comprising components with surfaces coated with the polymer according to any one of claims 1-10.
15. A coating comprising the polymer according to any one of claims 1-10.
- 25 16. A polymer formulation comprising the polymer according to any one of claims 1-10, a solvent, and an optional additive.
17. The polymer formulation according to claim 16 in which the solvent is selected from (a) an ester based solvent; (b) a ketone; (c) an aromatic; (d) an ether; (e) a halogenated solvent, or a combination thereof.

18. The polymer formulation according to claim 17, in which the solvent is a ketone.
19. The polymer formulation according to claim 17, wherein the ketone is selected from the  
5 group consisting of methyl ethyl ketone, methyl propyl ketone, methyl amyl ketone, methyl isoamyl ketone, methyl isobutyl ketone, acetone, pentanone, butanone, 2-heptanone, and combinations thereof.
20. The polymer formulation according to claim 17 in which the ester based solvent is selected  
10 from alkyl propionate, alkoxypropionate, alkyl alkoxypropionate, alkyl acetate, alkyl alkoxyacetate, ethyl acetate, propyl acetate, isopropyl acetate, butyl acetate, isobutyl acetate, tertiary butyl acetate and glycol ether acetate; or the ketone solvent is selected from methyl ethyl ketone, methyl propyl ketone, methyl amyl ketone, methyl isoamyl ketone, methyl isobutyl ketone, acetone, pentanone, butanone and 2-heptanone.
21. The polymer formulation according to any one of claims 16-20 in which the optional  
15 additive is selected from a curing agent, cross-linking agent, catalyst, filler, pigment or other colorant, reinforcement, thixotrope, accelerator, surfactant, plasticizer, extender, stabilizer, corrosion inhibitor, hindered amine light stabilizer, UV light absorber, antioxidant or a combination thereof.
22. A coating comprising the polymer formulation according to any one of claims 16-21.
23. A method of producing the polymer according to claim 1 comprising reacting the compound  
25 of formula (I) with (i) a polyisocyanate and one or more of a polyol, a polyamine or a reactive coating or (ii) a polyisocyanate, a polyol, a polyamine or a reactive coating,

wherein when at least one of  $R^1$  to  $R^6$ ,  $R^9$  and  $R^{10}$  bears an  $NH_2$  group then the siloxane of formula (I) has a molecular weight of between about 2500 and about

27000 Daltons and when at least one of R<sup>1</sup> to R<sup>6</sup>, R<sup>9</sup> and R<sup>10</sup> bears an OH group the siloxane of formula (I) has a molecular weight of between about 5000 and about 10000 Daltons; and

5 with the provisos that:

(a) when the compound of formula (I) reacts with a polyisocyanate, then at least one of R<sup>1</sup> to R<sup>6</sup>, R<sup>9</sup> and R<sup>10</sup> must bear at least one OH or NH<sub>2</sub> or both;

10 (b) when the compound of formula (I) reacts with a polyol, a polyamine or a reactive coating, then at least one of R<sup>1</sup> to R<sup>6</sup>, R<sup>9</sup> and R<sup>10</sup> must bear at least one NCO; and

(c) when the compound of formula (I) reacts with a reactive coating, then at least one of R<sup>1</sup> to R<sup>6</sup>, R<sup>9</sup> and R<sup>10</sup> must bear at least one OH or NH<sub>2</sub> or both to react with a polyisocyanate present in the reactive coating or at least one of R<sup>1</sup> to R<sup>6</sup>, R<sup>9</sup> and R<sup>10</sup> must bear at least one NCO to react with a polyol or polyamine present in the reactive coating.

24. An object comprising an external surface in which at least a portion of the external surface is coated with the polymer formulation according to any one of claims 16-21.

20

25. The object according to claim 24 in which the external surface coated with the polymer has an average adhesion force of <5 N when subject to an Ice Adhesion Test Method measured using an Instron Universal Testing Machine, model 5565, fitted with a 100 N load cell, wherein tests are carried out at a speed of 0.5 mm/min inside an environmental chamber that is maintained at -20°C and located within the Instron, the method comprising applying the polymer coating to aluminium coupons; freezing water-filled cylindrical columns at -20°C onto the surface, the water having an ultra-pure Milli-Q resistivity value of 18.2 MΩ·cm at 25°C, ≤5 ppb; fitting a pendulum attachment to the Instron and the ice

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columns; applying a tensile force to dislodge the ice columns from the coated specimens; and calculating the average adhesion force.

26. A method of imparting ice adhesion reducing properties to at least a portion of an external surface of an object comprising applying a coating of the polymer formulation according to any one of claims 16-21 onto the surface.
27. An object comprising components with surfaces coated with the polymer formulation according to any one of claims 16-21.