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(71) Applicants: **COMMONWEALTH SCIENTIFIC AND INDUSTRIAL ORGANISATION** [AU/AU]; Limestone Avenue, Campbell, Australian Capital Territory 2612 (AU). **THE BOEING COMPANY** [US/US]; 7755 East Marginal Way South, Seattle, Washington 98108 (US).

(72) Inventors: **BATEMAN, Stuart Arthur**; Private Bag 10, Clayton South, Victoria 3169 (AU). **SIMONS, Ranya**; Private Bag 10, Clayton South, Victoria 3169 (AU). **LI, Sheng**; Private Bag 10, Clayton South, Victoria 3169 (AU). **RUSSELL, Lee**; Private Bag 10, Clayton South, Victoria 3169 (AU). **BILYK, Alexander**; Private Bag 10, Clayton South, Victoria 3169 (AU). **BERRY, Douglas Henry**; PO Box 3707, Seattle, Washington 98124 (US). **SEEBERGH, Jill Elisabeth**; PO Box 3707, Seattle, Washington 98124 (US).

(74) Agent: **FB RICE**; Level 14, 90 Collins Street, Melbourne, Victoria 3000 (AU).

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(54) Title: ICE ADHESION REDUCING PREPOLYMERS AND POLYMERS

(57) Abstract: The present disclosure relates to an FPOSS prepolymer which may be reacted with a reactive coating or a polyisocyanate and/ or one or more of a polysiloxane, a polyol, a polyamine and a reactive coating; an FPOSS polyisocyanate prepolymer which may be reacted with one or more of a polysiloxane, a polyol, a polyamine or a reactive coating; and an FPOSS siloxane prepolymer which may be reacted with a polyisocyanate and/or one or more of a polyol, a polyamine or a reactive coating to form cross-linked polymers 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 prepolymers and polymers and their use in coating surfaces.



ICE ADHESION REDUCING PREPOLYMERS AND POLYMERS**FIELD**

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

BACKGROUND

The everyday build-up of ice upon the surfaces of objects is a familiar
10 annoyance and 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 conditioning and signs
15 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
20 and dramatically reduce lift. Further, ice 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 may be
deiced before take-off by radiant heat energy or by application of a chemical spray
25 which melts the ice from the wings. Such deicing sprays are not an environmentally
preferred solution. The ritual of deicing 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
30 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 in order to rid the wing of its burden. It would be preferred, of course, to reduce the adhesion of ice in the first place.

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 do 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.

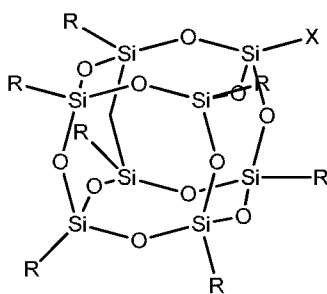
There is a need for a method which provides a durable surface with low ice adhesion properties and/or delayed freezing, which eliminates or at least reduces the continuous supply of air, chemicals or electrical power in order to reduce the amount of ice forming on a surface and/or the adhesion of ice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

SUMMARY

There is provided an FPOSS prepolymer which may be reacted with a reactive coating or a polyisocyanate and optionally one or more of a polysiloxane, a polyol, a polyamine and a reactive coating; an FPOSS polyisocyanate prepolymer which may be reacted with one or more of a polysiloxane, a polyol, a polyamine or a reactive coating; and an FPOSS siloxane prepolymer which may be reacted with a polyisocyanate and/or one or more of a polyol, a polyamine or a reactive coating to form an at least partially cross-linked polymer which is capable of reducing the adherence of ice to a surface or reducing the build-up of ice on a surface. There is also provided methods of producing the prepolymers and polymer and a method of coating objects such as vehicles, particularly aircraft, with the polymer. The polymer forms an ice reducing polymer coating when employed upon a surface of an object. Alternatively, the polymer may be used as a component of an existing coating to provide ice reducing properties to the coating. When coated upon a

surface, it is believed that the polymer disrupts bonding between ice and the polymer coated surface. Moreover, if ice does form, it is believed that the polymer disrupts the hydrogen bonding between the ice and the polymer coated surface, thereby diminishing the ability of the ice to adhere to the polymer surface. The ability of the polymer coating to adhere to surfaces and to reduce the formation of ice upon polymer coated surfaces, makes the polymer particularly useful for reducing the adherence of ice to surfaces or reducing the build-up of ice on surfaces of objects such as power lines, buildings, wind turbines, refrigeration units and aircraft or other vehicles.

In a first aspect, there is provided an FPOSS prepolymer of the formula (I):



(I)

in which X is a branched or unbranched side chain of 1 to 20 carbons comprising one or more functional groups selected from amino, hydroxy, epoxy, isocyanate, thiol, anhydride, ether, ester or ketone, wherein the functional groups are either present as end groups, or on one or more C atoms of the side chain;

R is independently selected from the group consisting of a polyisocyanate and optionally substituted C_{1-20} alkyl which may be optionally interrupted with O, C=O, N=C=O, CH(OH), CH_2OR^{11} , CH_2SR^{11} and $(CH_2)_m(CF_2)_nCF_3$ provided that at least one R is $(CH_2)_m(CF_2)_nCF_3$;

m is 1 to 20;

n is 0 to 20; and

R^{11} is H or optionally substituted C_{1-16} alkyl.

Prefrably X is $(CH_2)_2OC(O)NH(CH_2)_2OC(O)CH(NCO)(CH_2)_4NCO$ (lysine triisocyanate FPOSS), $(CH_2)_nOH$, $(CH_2)_nNH_2$, $(CH_2)_nCO_2CH_3$, $(CH_2)_nCO_2N((CH_2)_2OH)_2$, $(CH_2)_nOCH_2CH(OH)CH_2OH$, or optionally substituted

C₁₋₂₀ alkyl which may be optionally interrupted by O, CH₂O, Si, NH, NR¹¹, C=O, CH(OH), NH, CR(NCO), (CH₂)_n or CO₂.

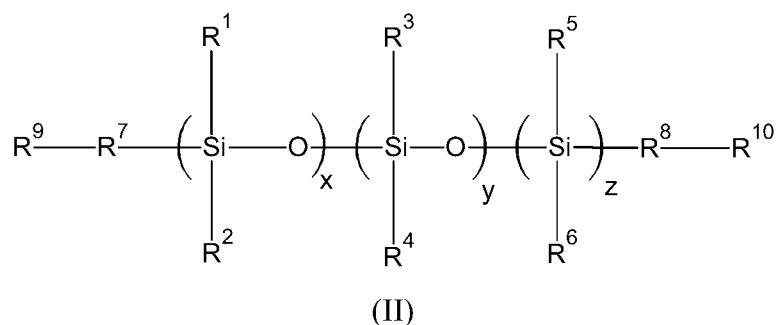
The FPOSS prepolymer can be used as an additive for an existing coating formulation (Figure 1 A) or used as an additive with polysiloxane/polyisocyanate based coating formulations (Figure 1B). Alternatively, the FPOSS prepolymer can be linked to a polyisocyanate (Figure 1C).

In a second aspect, there is provided an FPOSS polyisocyanate prepolymer of the formula (I) defined above in which X is (CH₂)_nOL, (CH₂)_nNHL or optionally substituted (CH₂)_mL which may be optionally interrupted with O, CH₂O, Si, NH, NR¹¹, C=O, CH(OH), NH, CR(NCO), (CH₂)_n or CO₂ in which L denotes the position at which a polyisocyanate is attached and R, m, n and R¹¹ are as defined in formula (I) above.

The FPOSS polyisocyanate prepolymer can form part of the isocyanate backbone of polymers and coatings. This embodiment is shown in Figure 1D.

The FPOSS prepolymer can also be linked to one or more polysiloxanes to form an FPOSS siloxane prepolymer. This embodiment is shown in Figures 2 and 3.

In a third aspect, there is provided an FPOSS siloxane prepolymer of the formula (II):



in which

R¹ to R⁶ are independently selected from the group consisting of H; optionally substituted C₁₋₁₆ alkyl optionally interrupted with a group selected from NR¹¹, C=O, C=C, S, CO₂, O and CH(NCO); OSiR¹²₃; (CH₂)_nOH; (CH₂)_nO(CH₂)_nOH; (CH₂)_n NR¹¹R¹²; (CH₂)_nNH(CH₂)_n NR¹¹R¹²; (CH₂)_nO(CH₂)_n NR¹¹R¹²; (CH₂)_nNCO; epoxy; (CH₂)_nFPOSS of formula (I), optionally substituted

C₁₋₁₆ alkylaryl; optionally substituted aryl; optionally substituted polyaryl; optionally substituted C₃₋₆cycloaliphatic; and optionally substituted C₃₋₆ heterocyclyl;

R⁷ and R⁸ are independently absent or independently selected from the group consisting of optionally substituted C₁₋₁₆ alkyl optionally interrupted with a group selected from NR¹¹, C=O, C=C, S, CO₂, O and CH(NCO); O; S; OSi(R¹³)₂; (CH₂)_n; (CH₂)_nNH; (CH₂)_nO; optionally substituted C₁₋₁₆ alkylaryl; optionally substituted aryl; optionally substituted polyaryl; optionally substituted C₃₋₆cycloaliphatic; and optionally substituted C₃₋₆ heterocyclyl;

R⁹ and R¹⁰ are independently selected from the group consisting of H, OH, NR¹¹R¹², optionally substituted C₁₋₁₆ alkyl, NCO, epoxy, Si(R¹³)₃ and FPOSS of formula (I);

R¹¹ and R¹² are independently selected from the group consisting of H and optionally substituted C₁₋₁₆ alkyl;

R¹³ is selected from the group consisting of optionally substituted C₁₋₁₆ alkyl, (CH₂)_nOH and (CH₂)_nNH₂;

n is 1 to 16;

x and z are independently selected from 1 to 1500; and

y is 0 to 1500,

with the proviso that at least one of R¹ to R⁶, R⁹ and R¹⁰ is the FPOSS

prepolymer of the formula (I) defined above in which

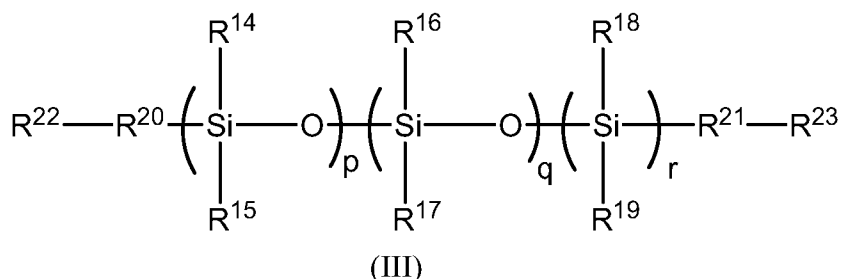
X is (CH₂)₂OC(O)NH(CH₂)₂OC(O)CH (NHCOY) (CH₂)₄NHCOY' (lysine triisocyanate linked siloxane), (CH₂)_nOY, (CH₂)_nNHY or optionally substituted (CH₂)_mY which may be optionally interrupted with O, CH₂O, Si, NH, NR¹¹, C=O, CH(OH), NH, CR(NCO), (CH₂)_n or CO₂;

Y and Y' denote positions at which the FPOSS prepolymer of formula (I) can be linked to the FPOSS siloxane prepolymer of formula (II) and R, m, n and R¹¹ are as defined in formula (I) above.

In a fourth aspect, there is provided a polymer comprising a cross-linked reaction product of the following:

(i) the FPOSS prepolymer of the formula (I) defined above and a reactive coating [Figure 1A];

(ii) the FPOSS prepolymer of the formula (I) defined above, a polyisocyanate and one or more of a polysiloxane of formula (III) [Figure 1B]:



in which

- R^{14} to R^{19} are independently selected from the group consisting of hydrogen; optionally substituted C_{1-16} alkyl optionally interrupted with a group selected from NR^{24} , $\text{C}=\text{O}$, $\text{C}=\text{C}$, S , CO_2 , O and $\text{CH}(\text{NCO})$; OSiR^{25}_3 ; $(\text{CH}_2)_n\text{OH}$;
 10 $(\text{CH}_2)_n\text{O}(\text{CH}_2)_n\text{OH}$; $(\text{CH}_2)_n\text{NR}^{24}\text{R}^{25}$; $(\text{CH}_2)_n\text{NH}(\text{CH}_2)_n\text{NR}^{24}\text{R}^{25}$; $(\text{CH}_2)_n\text{O}(\text{CH}_2)_n\text{NR}^{24}\text{R}^{25}$; $(\text{CH}_2)_n\text{NCO}$; 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^{20} and R^{21} are independently absent or independently selected from the
 15 group consisting of optionally substituted C_{1-16} alkyl optionally interrupted with a group selected from NR^{24} , $\text{C}=\text{O}$, $\text{C}=\text{C}$, S , CO_2 , O and $\text{CH}(\text{NCO})$; O ; S ; $\text{OSi}(\text{R}^{26})_2$; $(\text{CH}_2)_n$; $(\text{CH}_2)_n\text{NH}$; $(\text{CH}_2)_n\text{O}$; 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;
- 20 R^{22} and R^{23} are independently selected from the group consisting of H , OH , $\text{NR}^{11}\text{R}^{12}$, optionally substituted C_{1-16} alkyl, NCO , epoxy and $\text{Si}(\text{R}^{13})_3$;
- R^{24} and R^{25} are independently selected from the group consisting of H and optionally substituted C_{1-16} alkyl;
- R^{26} is selected from the group consisting of optionally substituted C_{1-16} alkyl,
 25 $(\text{CH}_2)_n\text{OH}$ and $(\text{CH}_2)_n\text{NH}_2$;
- n is 1 to 16;
- p and r are independently selected from 1 to 1500; and
- q is 0 to 1500,
- a polyol, a polyamine and a reactive coating;

- (iii) the FPOSS polyisocyanate prepolymer defined above, one or more of the polysiloxane of formula (III) defined above and optionally a polyol, a polyamine or a reactive coating [Figure 1C];
- (iv) a 1:2 – 14:15 ratio of the FPOSS polyisocyanate prepolymer defined above and a siloxane of the formula (III) defined above [Figure 1D];
- (v) the FPOSS siloxane prepolymer of the formula (II) defined above and a polyisocyanate and optionally one or more of a polyol, a polyamine or a reactive coating [Figures 2 and 3],
- with the provisos that:
- (a) when the siloxane of formula (II) or (III) reacts with a polyisocyanate, then at least one of R^1 to R^6 , R^9 and R^{10} or R^{14} to R^{18} and R^{22} and R^{23} must bear at least one OH or NH_2 or both;
- (b) when the siloxane of formula (II) or (III) 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} or R^{14} to R^{18} and R^{22} and R^{23} must bear at least one NCO; and
- (c) when the siloxane of formula (II) or (III) reacts with a reactive coating, then at least one of R^1 to R^6 , R^9 and R^{10} or R^{14} to R^{18} and R^{22} and R^{23} 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 coating.

The polymer is an ice reducing polymer which means that the polymer is capable of reducing the adherence of ice to a surface or reducing the build-up of ice on a surface and does not imply the total prevention of ice accretion on a surface.

In a fifth aspect, there is provided an ice reducing polymer comprising the polymer defined above.

In a sixth aspect, there is provided a polymer formulation comprising the polymer defined above, a solvent and an optional additive such as an extender, catalyst and/or cross-linking agent.

The polymer or polymer formulation may be in the form of a polymer coating or can be present as an additive to an existing coating. The polymer and the polymer coating are cross-linked. The cross-linking can be within the ice reducing

polymer coating layer as well as between the polymer coating and adjacent existing coatings.

In a sixth aspect, there is provided a method of producing the prepolymer and polymer defined above as described herein.

- 5 In a seventh aspect, there is provided an object comprising an external surface in which at least a portion of the external surface is coated with the polymer or polymer formulation defined above.

- In an eighth aspect, there is provided a method of imparting ice reducing properties to at least a portion of an external surface of an object comprising
10 applying a coating of the polymer or polymer formulation defined above onto the surface.

In a ninth aspect, there is provided an object comprising components with surfaces coated with the polymer or polymer formulation defined above.

DETAILED DESCRIPTION

- 15 The disclosure relates to the prepolymers, polymers and polymer formulations as defined above which provides an improved polymer coating which reduces the ability of ice to adhere and/or form upon a coated 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, stainless steel,
20 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 polymer coating also forms an effective ice reducer when used on a wide variety of materials other than the preferred aluminium, titanium or carbon
25 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 formulation to at least a portion of the surface of an object,
30 such as an aircraft, is also provided.

Definitions

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

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

- 5 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-butyne, 2-methyl-2-propynyl, 2-pentyne, 3-pentyne, 4-pentyne, 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 C₆, C₁₀, C₁₄ 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 C₃₋₆ cycloaliphatic is a non-aromatic cyclic group having from 3 to 6 carbon atoms and includes C₃₋₆ 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 C₃₋₆ 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.

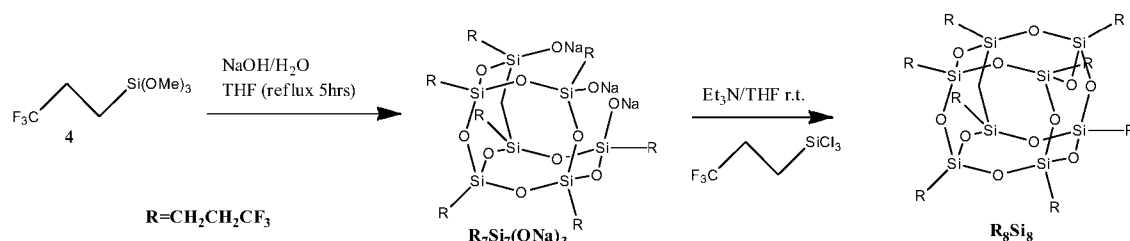
- 30 The term “optionally substituted” refers to a group which may or may not be further substituted with 1, 2, 3, 4 or more groups, preferably 1, 2 or 3, more preferably 1 or 2 groups selected from the group consisting of C₁₋₆ alkyl, C₂₋₆ alkenyl, C₂₋₆ alkynyl, C₃₋₈ cycloalkyl, hydroxyl, oxo, C₁₋₆ alkoxy, aryloxy, C₁₋₆ alkoxyaryl, halo, C₁₋₆ alkylhalo (such as CF₃ and CHF₂), C₁₋₆ alkoxyhalo (such as OCF₃ and OCHF₂), carboxyl, esters, cyano, nitro, amino, substituted amino, disubstituted amino, acyl, ketones, amides, aminoacyl, substituted amides,

disubstituted amides, thiol, alkylthio, thioxo, isocyanates, sulfates, sulfonates, sulfinyl, substituted sulfinyl, sulfonyl, substituted sulfonyl, sulfonylamides, substituted sulfonamides, disubstituted sulfonamides, aryl, C₁₋₆ alkyl, heterocycl and heteroaryl wherein each alkyl, alkenyl, alkynyl, cycloalkyl, aryl and heterocycl and groups containing them may be further optionally substituted. In one example, the optional substituents are selected from the group consisting of C₁₋₆ alkyl, hydroxyl, amino, substituted amino, disubstituted amino, isocyanate and C₁₋₆ alkoxy.

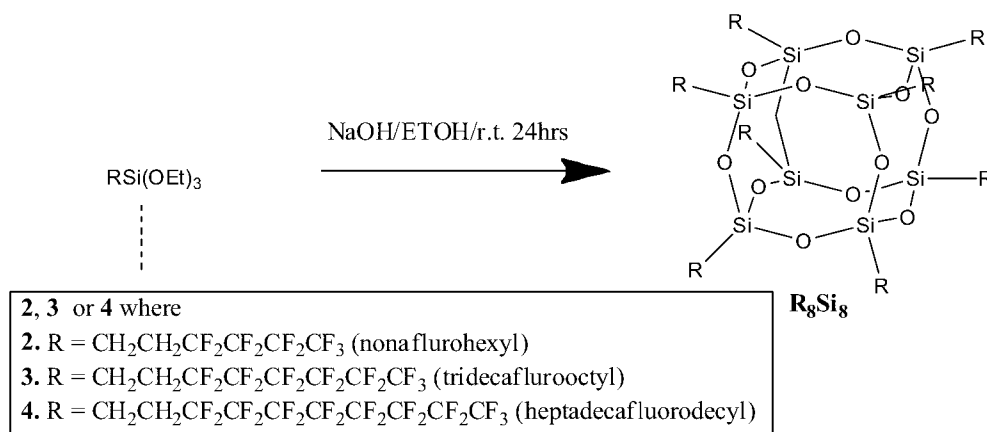
Formula (I)

The compound of formula (I) is also known as FPOSS (fluorinated polyhedral oligomeric silsequioxanes). It demonstrates both oleophobic and hydrophobic behaviour from its fluorinated side chains along with the capacity to impart nano-scale morphological features on a surface via its cage structure.

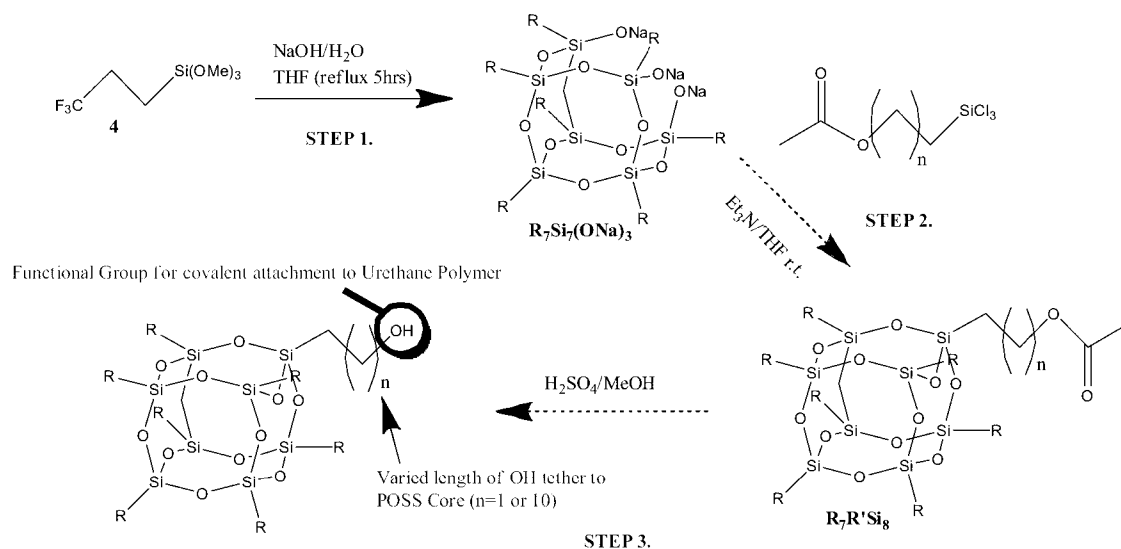
A variety of FPOSS compounds have been prepared, the synthesis methodology optimized, and the compounds purified and characterized for use as modifiers. The FPOSS derivatives include (i) tri-fluoropropyl POSS (TFP-POSS) (ii) tri-decafluoro(octyl)POSS (TDF(Octyl)POSS) and (iii) hydroxyl functional tri-fluoropropyl POSS (Hydroxy TFP POSS), Scheme 1 and 2.



Scheme 1 Synthesis of Tri-fluoropropyl POSS



Scheme 2: Synthesis of tri-decafluoro(octyl) POSS (compound 3)



5

R = $-\text{CH}_2\text{CH}_2\text{CF}_3$

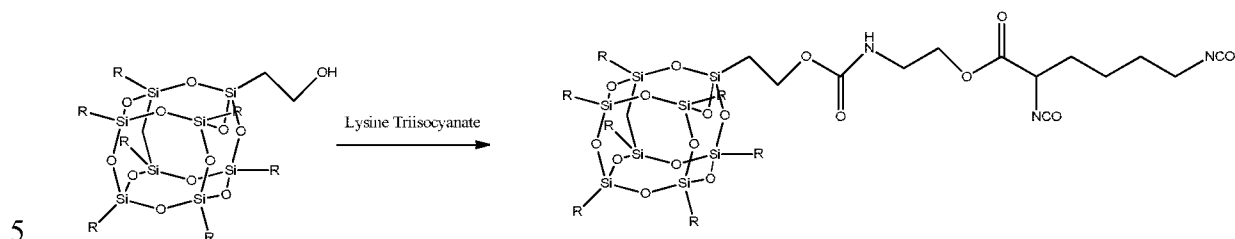
R' = alcohol functionalised arm

Scheme 3: Synthesis of (mono) hydroxyl functional trifluoropropyl POSS

10 An alternate route is to synthesise diisocyanate functional FPOSS as described above which can then be reacted with the polyol component of a polyurethane coating such as the Desothane[®] HS CA8000 series. Initial synthesis of these compounds (Scheme 4) has been successful, and Fourier transform infrared spectroscopy (FTIR) indicates that the diisocyanate group is available for further

15 reaction with the polyol component of the coating.

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Scheme 3: Synthesis of diisocyanate functional FPOSS

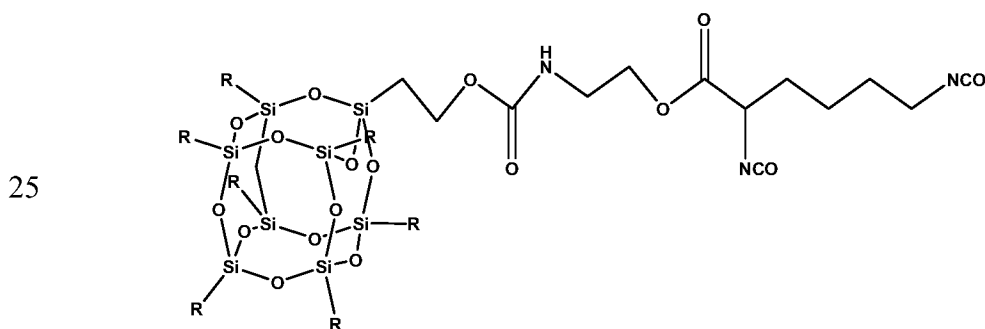
Formula (II) and (III)

The compound of formula (II) is an FPOSS siloxane prepolymer when at least one of R^1 to R^6 , R^9 and R^{10} is FPOSS.

10 In one example, the FPOSS siloxane prepolymer is the reaction product of about 15:14 to 2:1 polysiloxane (III): FPOSS polyisocyanate prepolymer. The resulting FPOSS siloxane prepolymer in turn can be reacted with a further polyisocyanate, polyol and/or polyamine. The further polyisocyanate, polyol and/or polyamine can be any polyisocyanate, polyol or polyamine described in herein or
 15 found in reactive coatings such as polyurethane coatings, for example, the Desothane[®] HS CA8000 series.

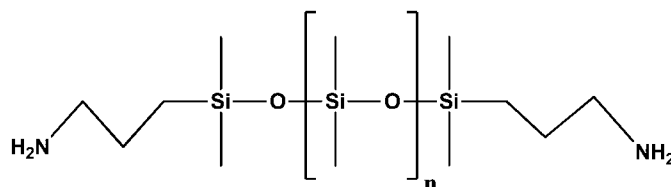
Alternatively, the FPOSS siloxane prepolymer can be used as an additive of up to 99% in an ice reducing polymer described in the applicant's co-pending application filed concurrently.

20 A representative example of a FPOSS siloxane prepolymer is a reaction product of the following:



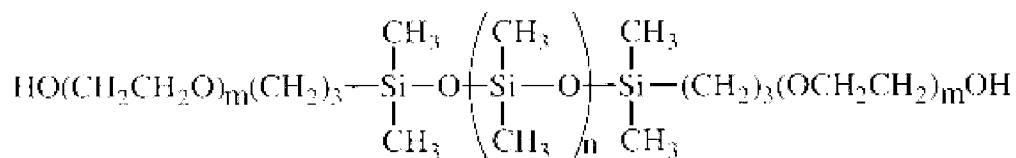
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and

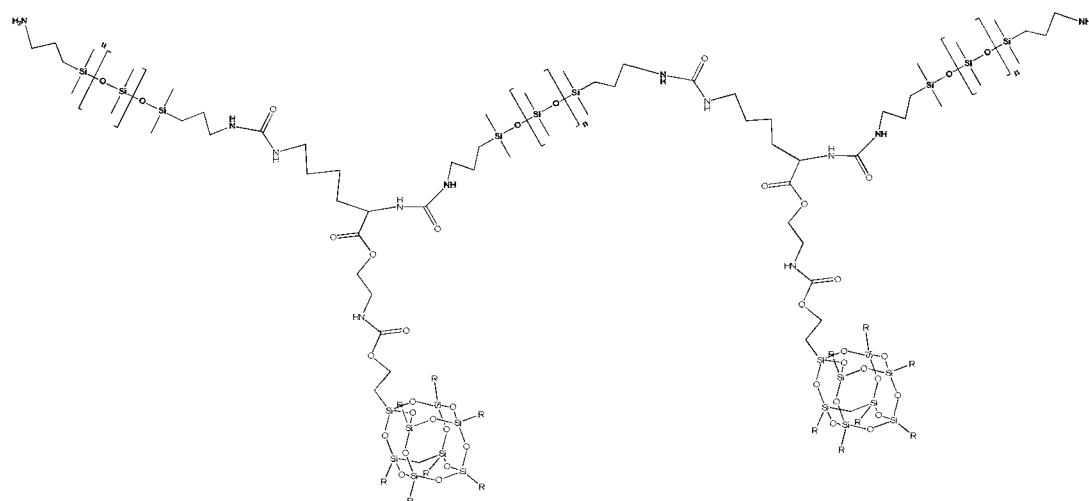


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or



to afford Figure 3.



10

Figure 3

Any reactive FPOSS siloxane prepolymers made using siloxanes of formula (II) or (III) may be used provided they are capable of reacting with polyisocyanate and/or a polyol, a polyamine or a reactive coating. Examples of reactive siloxanes include amino functional siloxanes, carbinol functional siloxanes, isocyanate functional siloxanes and epoxy functional siloxanes. Such siloxanes also contain at least one FPOSS as in formula (II). Alternatively, the siloxanes of formula (III) can be reacted with a source of FPOSS such as the polyisocyanate functional FPOSS shown above.

The compound of formula (II) is an amino functional siloxane when the terminal group on any one of R¹ to R⁶, R⁹ and R¹⁰ is NH₂, a carbinol functional

20

siloxane when the terminal group on any one of R^1 to R^6 , R^9 and R^{10} is OH, an isocyanate functional siloxane when at least one of R^1 to R^{10} bears at least one NCO or an epoxy functional siloxane when at least one of R^1 to R^6 , R^9 and R^{10} 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.

The compound of formula (III) is an amino functional siloxane when the terminal group on any one of R^{14} to R^{19} , R^{22} R^{23} is NH_2 , a carbinol functional siloxane when the terminal group on any one of R^{14} to R^{19} , R^{22} and R^{23} is OH, an isocyanate functional siloxane when at least one of R^{14} to R^{23} bears at least one NCO or an epoxy functional siloxane when at least one of R^{14} to R^{19} , R^{22} and R^{23} bears an epoxy. The integers p, q and r 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.

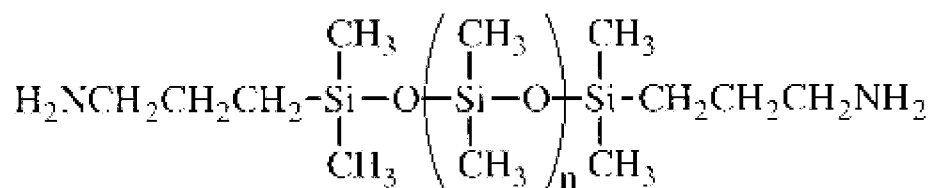
Amino functional siloxanes include those available from UCT Silanes such as PS510, PS512 and PS513 and those available from Gelest such as primary aminopropyl terminated siloxanes such as DMS-A11, DMS-A12, DMS-A15, DMS-A21, DMS-A31, DMS-A32, DMS-A35, secondary amino functional (N-ethylaminoisobutyl terminated PDMS) siloxanes such as DMS-A211, 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 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.

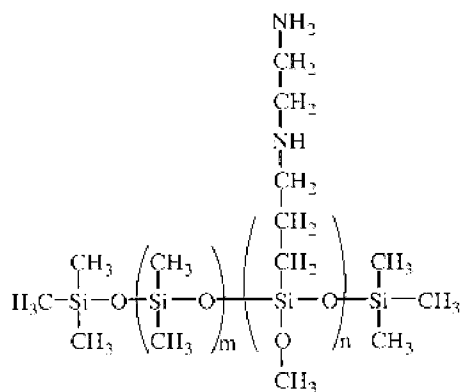
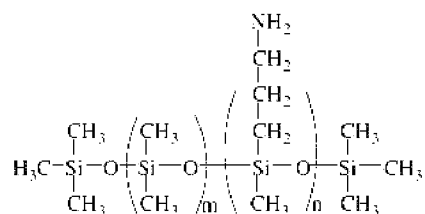
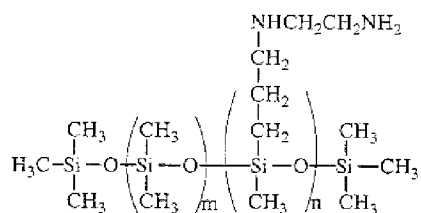
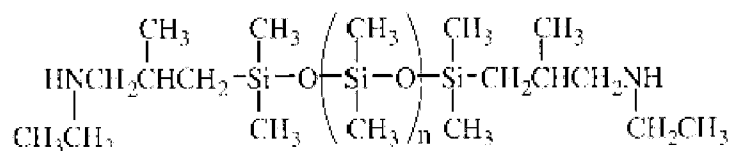
Epoxy functional siloxanes include those available from Gelest such as epoxypropoxypropyl terminated polydimethylsiloxanes including DMS-E range (09-21), epoxypropoxypropyl terminated polyphenylmethylsiloxanes such as PMS E-11, PMS E 15, monophenyl functional tris(epoxy terminated polydimethylsiloxane)

such as MCT-EP13, mono-(2,3-epoxy)propylether terminated polydimethylsiloxane such as MCR-E11, MCR-E21 and (epoxycyclohexylethylethylsiloxane) - dimethylsiloxane dipolymers such as ECMS-127, 227, 327, 924.

Representative examples of aminosiloxanes include the following:



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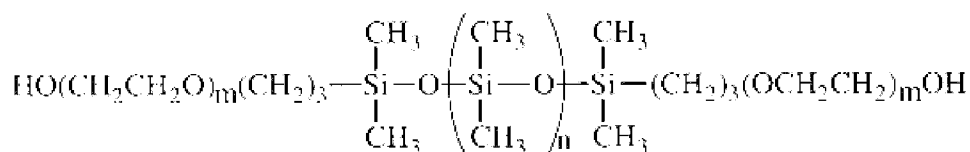
in which

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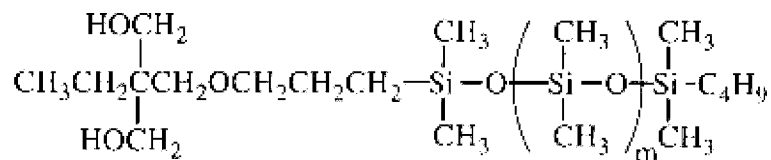
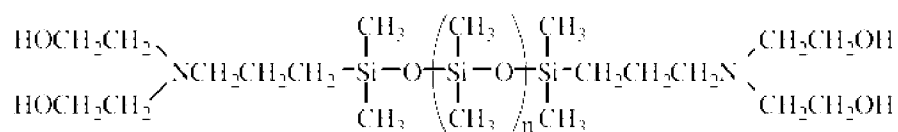
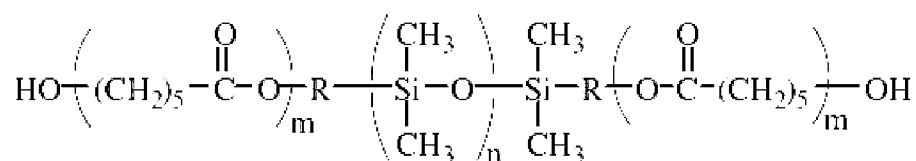
m is 1-1500; and

n is 1-1500.

Representative examples of carbinol siloxanes include the following:



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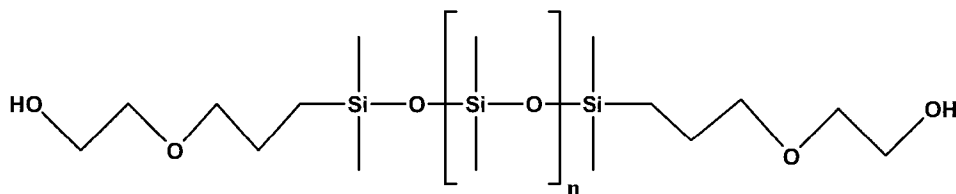
in which

m is 1-1500; and

n is 1-1500.

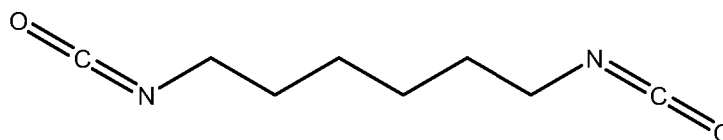
Representative examples of isocyanate siloxanes include the reaction product

15 of:



20

and



5

in which

n is 1-1500.

The compound of formula (II) or (III) 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.

10

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 ε-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.

30

Triisocyanates include 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

5 Desmodur[®] N 3300, which is the isocyanurate of hexamethylene diisocyanate, available from Bayer.

Polyisocyanates with higher functionality include but are not limited aliphatic polyisocyanates based on hexamethyldiisocyanate such as sold by Bayer under the Desmodur[®] N range, aliphatic polyisocyanates based on

10 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[®] VL and VK range, blocked polyisocyanates such as those sold under the Desmodur[®] BL

15 range and Basonet[®] isocyanate cross-linkers (Bayer).

Isocyanurate rings containing 3 or more isocyanate groups can also be used for example the isocyanurate ring of hexamethylene diisocyanate such as Desmodur[®] N-3300 and N-3390 from Bayer.

The polyisocyanates may be used in combination with other isocyanates.

20 In one example, the polyisocyanate is a triisocyanate such as lysine triisocyanate or polyisocyanates sold by Bayer under the Desmodur[®] 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

25 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.

30 Polyols that may be used include polyester polyols such as Desmophen, Baycoll[®] (Bayer); polyether polyols such as Desmophene[®] and Acclaim[®]; polyaspartics such as Desmophen[®] NH; polycarbonate polyols such as Desmophen[®]

C, as well as polymer cross-linkers such as poly(caprolactone) which contain multiple arms, as well as the polyol base component of Desothane[®] 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 EP, Invista), 1,6-diaminohexane, 2-methyl-1,5-pentane diamine (Dytek 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-amino trimethyl- δ -aminomethyl-cyclohexane, 2,4- and/or 2,6-hexahydrotoluylene 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[®] or Laromin[®] C260, BASF; Ancamine[®] 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[®] D-230, Jeffamine[®] D-400, Jeffamine[®] D- 2000, and Jeffamine[®] 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[®] T-403, Jeffamine[®] T-3000, Jeffamine[®] 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.

5 **Reactive Coating**

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

Surface

15 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
20 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
25 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
30 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;

5 (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
10 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
15 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 alkyl ketones for example, methyl ethyl ketone, methyl propyl ketone,
20 methyl amyl ketone, methyl isoamyl ketone and 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
25 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.

30 In one example, the polymer comprises or consists of the reaction product of the siloxane prepolymer of formula (II) 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.

In another example, the polymer comprises or consists of the reaction product of the isocyanate prepolymer of formula (I) and (i) a polysiloxane and optionally a polyol or a polyamine.

The polymer formulation comprises or consists of the polymer,, 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, 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 capable of reacting with the existing coating such as hydroxyl, isocyanate or amine.

The additives are present in an amount of 0-80% by weight such as 1-70% by weight or 5-60% by weight based on the total weight of the polymer.

Polymers

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

- (a) FPOSS siloxane prepolymer with at least one terminal amino group, polyisocyanate and optionally a catalyst, polyol or polyamine;
- (b) FPOSS siloxane prepolymer with at least one terminal hydroxy group, polyisocyanate and optionally a catalyst, polyol or polyamine;
- (c) FPOSS siloxane prepolymer with at least one terminal amino group or FPOSS siloxane prepolymer with at least one terminal hydroxy group, a reactive coating and optionally a catalyst, polyol or polyamine;
- (d) FPOSS siloxane prepolymer with at least one isocyanate, polysiloxane and optionally a catalyst, polyol or polyamine; and
- (e) FPOSS polyisocyanate prepolymer, polysiloxane and optionally a catalyst.

Polymer Formulation

The polymer formulation may be made by dissolving the compound of formula (I) or (II) 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) or (II). The polymer formulation is typically mixed for 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) or (II), the polyisocyanate and/or the polyol, polyamine, or the reactive coating.

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. The polymer formulation may also be suitably applied to painted surfaces 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 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 simply 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 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.

As a two component system, the compound of formula (I) or (II) may be dissolved in a solvent and the second component which is a polysiloxane (when formula I is used) or polyisocyanate (when formula II is used) 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.

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

5 Alternatively, the compound of formula (I) or (II) is mixed with a solution of the polysiloxane or 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 a cross-linked polymer,
10 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
15 as an appliqué by first depositing the 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
20 the solvent has evaporated. Secondary process could include operations such as masking, taping and application of additional layers of the polymer 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 cross-link and form almost as soon as the two parts are mixed and sprayed onto the
25 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 polymer 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 key advantage of a clear film coating is that it provides sufficient transparency to allow the coating
30 to be used with a pigmented topcoat. A key 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 – clear coat 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.

5 The polymer formulation can be applied anywhere between about about 1°C and about 45°C. Typically, the polymer coating is applied at ambient temperatures, preferably 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.

10 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 are provided by coating at least some portions of the outer surface of other objects such as missiles, ships, automobiles and wind turbines.

25 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 power lines.

Properties

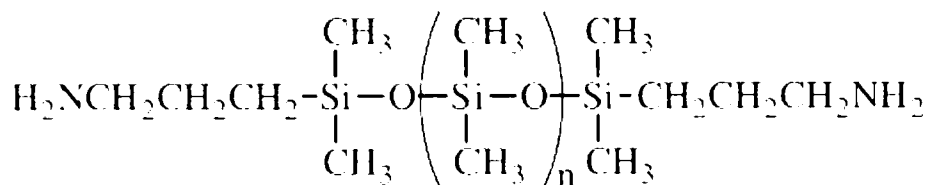
When the polymer used as an ice reducing coating on a surface, the coated surface can demonstrate a minimum average adhesion force of ≈ 5 N when subjected to the ice adhesion test, a pencil hardness value of up to 4H and a 60 degree glass value of up to 75.

EXAMPLES

The invention will now be described with reference to the following non-limiting examples.

The following abbreviations are used in the examples:

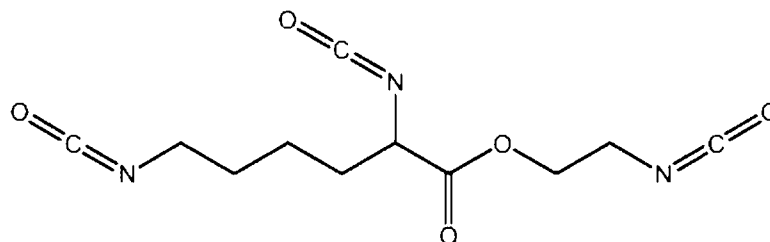
10 Amino siloxane: PS510, PS512, PS513, and DMS A12



n is 5-1500

15

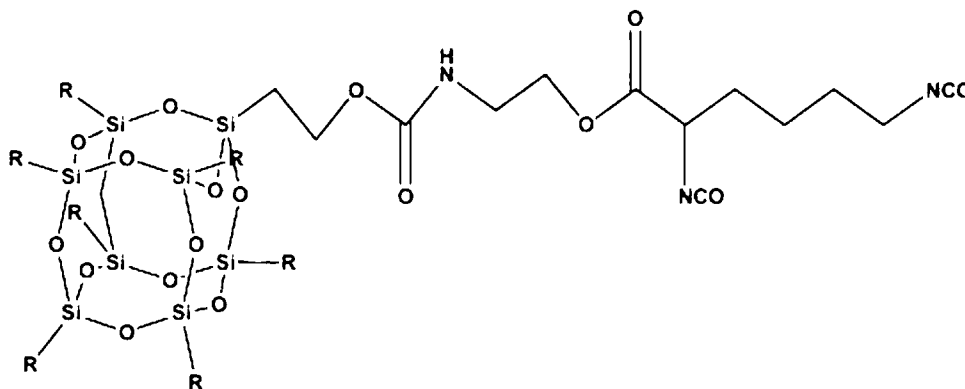
Lysine Triisocyanate



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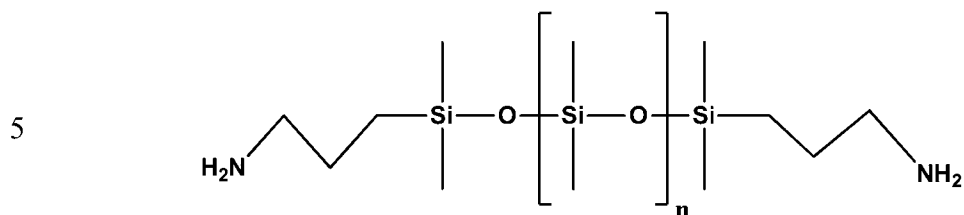
F-POSS-siloxane prepolymer prepared by reacting:

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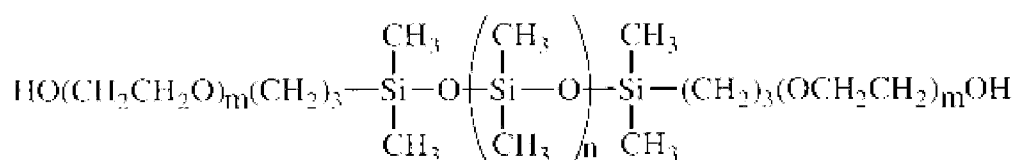


in which

R is as defined in formula (II) above; and



or



10

n is 5-1500; and

m is 1-20

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

- 15
1. Solvent MAK(2-heptanone, methylamyl ketone) was used in all formulations in the examples and makes up between 30-85% weight of total formulation.
 2. Mole ratio of 1:1 (reactive siloxane groups: isocyanate groups) used in all formulations.
 3. All formulations were applied onto aluminium panels which had previously
- 20
- been coated with primer and an existing clear coat (Desothane[®] HS Clear Topcoat CA 8000/B900A) via a spray gun and then cured at ambient conditions for 12-24 hours.

The FPOSS containing reactive siloxane prepolymer is mixed in a solvent such as ketone, alcohol or ester. The isocyanate component is then added to the

25

formulation and the solution mixed for 15-120 minutes prior to spray or brush application of the polymer coating on a surface.

Ice Adhesion Test Method

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 that is 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 surface. A pendulum attachment is 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 required to separate ice was recorded and the stress calculated. The mode of failure – cohesive or adhesive was also noted.

Table 1

Number	Siloxane		Isocyanate	% F-POSS siloxane prepolymer (Figure 3) (Mw 23,370)	Polyol/polyamine	Solvent
	Reactive group	Molecular weight				
Desothane HS Clear Topcoat CA 8000/ B900A (PPG)*	-	-	Desothane Activator [^]	-	Desothane Base ^{^^}	Proprietary mix of solvents including 2,6-dimethyl-4-heptanone, 4,6-dimethyl-2-heptanone, methyl amyl ketone , 2,4-pentanedione ethyl acetate, N-butyl acetate and 1,2,4-trimethyl benzene
1	-	-	Lysine triisocyanate	100%	-	2-heptanone
2	-	-	Desothane Activator [^]	2%	Desothane Base ^{^^}	2-heptanone
3	-	-	Desothane Activator [^]	5%	Desothane Base ^{^^}	2-heptanone
4	-	-	Desothane Activator [^]	10%	Desothane Base ^{^^}	2-heptanone
5	Amino (PS510)	2500	Lysine triisocyanate	4%	-	2-heptanone
6	Amino (PS510)	2500	Lysine triisocyanate	10%	-	2-heptanone
7	Amino (PS510)	2500	Desothane Activator [^]	4%	-	2-heptanone
8			Desothane Activator [^]	2%	Desothane Base ^{^^}	F-POSS-siloxane added as 50% solution in 2-heptanone (scaled up formulation)

*Comparative example

Note:

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

Surface Energy Testing Method

Surface Energy calculations are based on contact angle measurements complete using 'FIRST TEN ANGSTROMS' semi-automated video equipped
5 contact angle analyser. Diiodomethane (CH_2I_2) and water (H_2O) were employed as the reference solvents to calculate the dispersive and polar contributions to surface energy through the Young-Dupre relationship and Fowkes equation.

Gloss Test Method

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

10 Pencil Hardness Test Method

Pencil hardness is measured according to ASTM D3363.

Table 2

Example	Ice Adhesion- Tensile Force (N)	Ice Adhesion- Tensile Stress (kPa)	Failure Mode^{**}
Desothane HS CA 8000 B900A Clearcoat*	45 ± 14.3	176.7 ± 56.1	40% CF 60% AF
NuSil R1082*	11.6 ± 4.4	45.7 ± 17.1	100% AF
NuSil R2180*	16.5 ± 3.1	64.7 ± 12.3	100% AF
US6797795* (Example 1)	5.2 ± 2.6	20.3 ± 10.3	100% AF
US7910683* (Example 3)	10.4 ± 5.9	40.9 ± 23.1	100% AF
1	3.1 ± 3.5	12.3 ± 13.9	100%AF
2	26.1 ± 10.6	102.4 ± 41.5	90%AF; 10% CF
3	10.4 ± 3.2	40.9 ± 12.6	100%AF
4	21.6 ± 16.5	85.0 ± 64.8	85% AF, 15% CF
5	4.9 ± 3.4	19.3 ± 13.3	100%AF
6	5.6 ± 2.9	22 ± 11.2	100%AF
7	8.2 ± 2	32 ± 8	100%AF
8	17.5 ± 4.9	69 ± 19	99% AF, 1% CF

* Comparative example

** AF= adhesive failure, CF = Cohesive failure

Table 3

Example	H ₂ O Contact Angle (°)	CH ₂ I ₂ Contact Angle (°)	Surface ENERGY Dispersion (mJ/m ²)	Surface Energy Polar (mJ/m ²)	Gloss 20°	Gloss 60°	Pencil Hardness (Gauge)
Desothane HS CA 8000 B900A Clearcoat *	82.2	39.8	41.6	2.5	86	95	4H
NuSil R1082*	109.0	62.2	28.6	0	30	66	HB
NuSil R2180*	110.1	61.5	29.1	0	27	57	HB
US679779 5* (Example 1)	106.2	63.6	27.7	0.05	18	53	< 6B tacky
US791068 3* (Example 3)	127.8	104.4	7.5	0.03	44	68	< 6B tacky
1	108.2	74.5	21.3	0.23	35	69	H
2	103.7	69.2	24.4	0.43	38	69	4H
3	106.3	54.9	27	0.07	46	72	H
4	107.8	69.6	24.2	0.10	42	68	2H
5	103.3	63.3	28	0.22	48	73	4H
6	104.6	62.9	28.2	0.12	55	75	H
7	106.5	63.8	27.6	0	50	73	B
8	103.2	71.2	23.2	0.6	49	74	3H

* Comparative example

5 Cross-linked FPOSS containing polysiloxane prepolymer 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 thin final top layer or as a component of the current topcoat to provide a polymer coating with reduced ice adhesion. Two commercially available NuSil polysiloxane elastomer coatings, and two coating formulations disclosed in Example 1 of US6797795 and Example 3 of US7910683 which do not contain FPOSS all have ice adhesion tensile stress values of greater than 19 kPa.

The present polymer coatings demonstrate the following advantages:

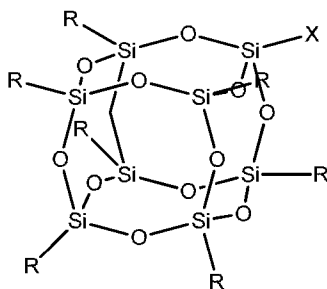
- (i) Reduced ice adhesion <19 kPa stress, or < 5 N force, which is less than previously published values for ice adhesion; and
- (ii) Pencil Hardness values above commercially available siloxane hardness materials such as those from NuSil and much higher than existing art such as US6797795.
- (iii) 60 degree gloss values up to 75, demonstrating higher gloss than commercially available siloxane coating materials such as NuSil; and
- (iv) Improved compatibility to existing polyurethane topcoat for aircraft application and the polymer coating formulation can be used as a component of the existing polyurethane topcoat.

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 spirit and scope of the invention.

CLAIMS

1. An FPOSS prepolymer of the formula (I):



(I)

5

in which X is a branched or unbranched side chain of 1 to 20 carbons comprising one or more functional groups selected from amino, hydroxy, epoxy, isocyanate, thiol, anhydride, ether, ester or ketone, wherein the functional groups are either present as end groups, or on one or more C atoms of the side chain;

- 10 R is independently selected from the group consisting of a polyisocyanate and optionally substituted C_{1-20} alkyl which may be optionally interrupted with O, C=O, N=C=O, CH(OH), CH_2OR^{11} , CH_2SR^{11} and $(CH_2)_m(CF_2)_nCF_3$ provided that at least one R is $(CH_2)_m(CF_2)_nCF_3$;

m is 1 to 20;

- 15 n is 0 to 20; and

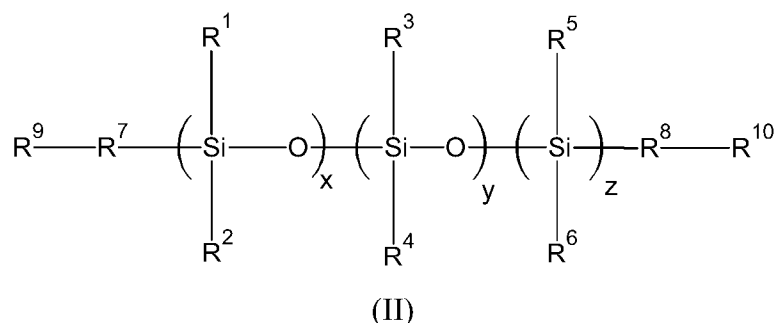
R^{11} is H or optionally substituted C_{1-16} alkyl.

2. The FPOSS prepolymer according to claim 1 in which X is $(CH_2)_2OC(O)NH(CH_2)_2OC(O)CH(NCO)(CH_2)_4NCO$ (lysine triisocyanate FPOSS), $(CH_2)_nOH$, $(CH_2)_nNH_2$, $(CH_2)_nCO_2CH_3$, $(CH_2)_nCO_2N((CH_2)_2OH)_2$, $(CH_2)_nOCH_2CH(OH)CH_2OH$, or optionally substituted C_{1-20} alkyl which may be optionally interrupted by O, CH_2O , Si, NH, NR^{11} , C=O, CH(OH), NH, CR(NCO), $CH_2)_n$ or CO_2 .
- 20

3. An FPOSS prepolymer of the formula (I) according to claim 1 in which X is $(CH_2)_nOL$, $(CH_2)_nNHL$ or optionally substituted $(CH_2)_mL$ which may be optionally interrupted with O, CH_2O , Si, NH, NR^{11} , C=O, CH(OH), NH, CR(NCO), $(CH_2)_n$ or
- 25

CO₂ in which L denotes the position at which a polyisocyanate is attached and R, m, n and R¹¹ are as defined in formula (I).

4. An FPOSS siloxane prepolymer of the formula (II):



in which

R¹ to R⁶ are independently selected from the group consisting of H;

optionally substituted C₁₋₁₆ alkyl optionally interrupted with a group selected from NR¹¹, C=O, C=C, S, CO₂, O and CH(NCO); OSiR¹²₃; (CH₂)_nOH;

10 (CH₂)_nO(CH₂)_nOH; (CH₂)_n NR¹¹R¹²; (CH₂)_nNH(CH₂)_n NR¹¹R¹²; (CH₂)_nO(CH₂)_n NR¹¹R¹²; (CH₂)_nNCO; epoxy; (CH₂)_nFPOSS of formula (I), optionally substituted C₁₋₁₆ alkylaryl; optionally substituted aryl; optionally substituted polyaryl; optionally substituted C₃₋₆ cycloaliphatic; and optionally substituted C₃₋₆ heterocyclyl;

R⁷ and R⁸ are independently absent or independently selected from the group
 15 consisting of optionally substituted C₁₋₁₆ alkyl optionally interrupted with a group selected from NR¹¹, C=O, C=C, S, CO₂, O and CH(NCO); O; S; OSi(R¹³)₂; (CH₂)_n; (CH₂)_nNH; (CH₂)_nO; optionally substituted C₁₋₁₆ alkylaryl; optionally substituted aryl; optionally substituted polyaryl; optionally substituted C₃₋₆ cycloaliphatic; and optionally substituted C₃₋₆ heterocyclyl;

20 R⁹ and R¹⁰ are independently selected from the group consisting of H, OH, NR¹¹R¹², optionally substituted C₁₋₁₆ alkyl, NCO, epoxy, Si(R¹³)₃ and FPOSS of formula (I);

R¹¹ and R¹² are independently selected from the group consisting of H and optionally substituted C₁₋₁₆ alkyl;

25 R¹³ is selected from the group consisting of optionally substituted C₁₋₁₆ alkyl, (CH₂)_nOH and (CH₂)_nNH₂;

n is 1 to 16;

x and z are independently selected from 1 to 1500; and

y is 0 to 1500,

with the proviso that at least one of R¹ to R⁶, R⁹ and R¹⁰ is the FPOSS prepolymer of the formula (I) according to claim 1 in which

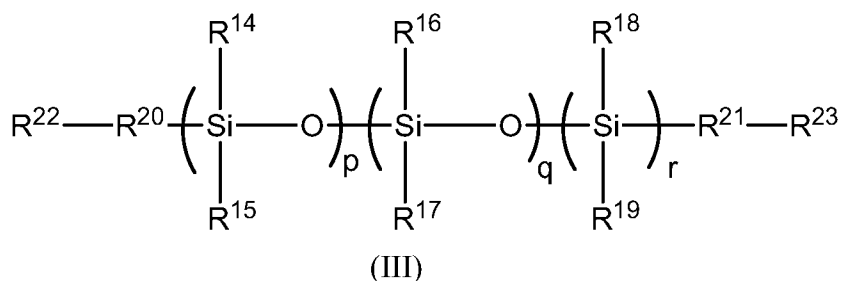
X is (CH₂)₂OC(O)NH(CH₂)₂OC(O)CH (NHCOY) (CH₂)₄NHCOY' (lysine triisocyanate linked siloxane), (CH₂)_nOY, (CH₂)_nNHY or optionally substituted (CH₂)_mY which may be optionally interrupted with O, CH₂O, Si, NH, NR¹¹, C=O, CH(OH), NH, CR(NCO), (CH₂)_n or CO₂;

Y and Y' denote positions at which the FPOSS prepolymer of formula (I) can be linked to the FPOSS siloxane prepolymer of formula (II) and R, m, n and R¹¹ are as defined in formula (I).

5. A polymer comprising a cross-linked reaction product of the following:

(i) the FPOSS prepolymer of the formula (I) according to claim 1 and a reactive coating;

(ii) the FPOSS prepolymer of the formula (I) according to claim 1, a polyisocyanate and one or more of a polysiloxane of formula (III):



in which

R¹⁴ to R¹⁹ are independently selected from the group consisting of hydrogen; optionally substituted C₁₋₁₆ alkyl optionally interrupted with a group selected from NR²⁴, C=O, C=C, S, CO₂, O and CH(NCO); OSiR²⁵₃; (CH₂)_nOH; (CH₂)_nO(CH₂)_nOH; (CH₂)_n NR²⁴R²⁵; (CH₂)_nNH(CH₂)_n NR²⁴R²⁵; (CH₂)_nO(CH₂)_n NR²⁴R²⁵; (CH₂)_nNCO; epoxy; optionally substituted C₁₋₁₆ alkylaryl; optionally substituted aryl; optionally substituted polyaryl; optionally substituted C₃₋₆ cycloaliphatic; and optionally substituted C₃₋₆ heterocyclyl;

R²⁰ and R²¹ are independently absent or independently selected from the group consisting of optionally substituted C₁₋₁₆ alkyl optionally interrupted with a group selected from NR²⁴, C=O, C=C, S, CO₂, O and CH(NCO); O; S; OSi(R²⁶)₂;

$(\text{CH}_2)_n$; $(\text{CH}_2)_n\text{NH}$; $(\text{CH}_2)_n\text{O}$; 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^{22} and R^{23} are independently selected from the group consisting of H, OH, $\text{NR}^{11}\text{R}^{12}$, optionally substituted C_{1-16} alkyl, NCO, epoxy and $\text{Si}(\text{R}^{13})_3$;

R^{24} and R^{25} are independently selected from the group consisting of H and optionally substituted C_{1-16} alkyl;

R^{26} is selected from the group consisting of optionally substituted C_{1-16} alkyl, $(\text{CH}_2)_n\text{OH}$ and $(\text{CH}_2)_n\text{NH}_2$;

n is 1 to 16;

p and r are independently selected from 1 to 1500; and

q is 0 to 1500,

a polyol, a polyamine and a reactive coating;

(iii) the FPOSS polyisocyanate prepolymer according to claim 3, one or more of the polysiloxane of formula (III) according to claim 5 and optionally a polyol, a polyamine or a reactive coating;

(iv) a 1:2 ratio of the FPOSS polyisocyanate prepolymer of claim 3, siloxane of the formula (III) according to claim 5; the FPOSS siloxane prepolymer of the formula (II) according to claim 4, a polyisocyanate and optionally a polyol, a polyamine or a reactive coating, with the provisos that:

(a) when the siloxane of formula (II) or (III) reacts with a polyisocyanate, then at least one of R^1 to R^6 , R^9 and R^{10} or R^{14} to R^{18} and R^{22} and R^{23} must bear at least one OH or NH_2 or both;

(b) when the siloxane of formula (II) or (III) 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} or R^{14} to R^{18} and R^{22} and R^{23} must bear at least one NCO; and

(c) when the siloxane of formula (II) or (III) 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} or R^{14} to R^{18} and R^{22} and R^{23} must bear at least one NCO to react with a polyol or polyamine present in the reactive coating.

6. The polymer according to claim 5 in which the polyisocyanate is a diisocyanate, triisocyanate, higher functionality isocyanate or a combination thereof.
7. The polymer according to claim 6 in which the triisocyanate is lysine triisocyanate or the polyisocyanate is sold by Bayer under the Desmodur[®] range.
- 5 8. The polymer according to claim 6 in which the polyisocyanate is present in an amount of 0.1-70% by weight based on the total weight of the polymer.
9. The polymer according to claim 5 in which the polyol or polyamine is a polyester polyol / polyamine, a polyether polyol / polyamine, a polycarbonate polyol / polyamine, an acrylic polyol / polyamine or a combination thereof.
- 10 10. The polymer according to claim 5 in which the polyamine is present in an amount of 0-99% by weight based on the total weight of the polymer.
11. The polymer according to claim 5 in which the reactive coating is a polyurethane, polyurea, polysilicone, polyester or epoxy coating, each of which contain a polyisocyanate and/or a polyol or polyamine.
- 15 12. An ice reducing polymer comprising the polymer according to claim 5.
13. A polymer formulation comprising the polymer according to claim 5, a solvent and an optional additive.
14. The polymer formulation according to claim 13 in which the solvent is selected from (a) an ester based solvent; (b) a ketone; (c) an aromatic; (d) an ether;
- 20 and (e) a halogenated solvent or a combination thereof.
15. The polymer formulation according to claim 14 in which the ester based solvent is 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
- 25 ketone solvent is selected from methyl ethyl ketone, methyl propyl ketone, methyl amyl ketone, methyl isoamyl ketone and methyl isobutyl ketone, acetone, pentanone, butanone and 2-heptanone.
16. The polymer formulation according to claim 13 in which the optional additive is a curing agent, cross-linking agent, catalyst, filler, pigment or other
- 30 colorant, reinforcement, thixotrope, accelerator, surfactant, plasticizer, extender, stabilizer, corrosion inhibitor, hindered amine light stabilizer, UV light absorber, antioxidant or a combination thereof.

17. A coating comprising the polymer according to claim 5 or the polymer formulation according to claim 13.
18. An object comprising an external surface in which at least a portion of the external surface is coated with the polymer according to claim 5 or the polymer formulation according to claim 13.
19. The object according to claim 18 in which the external surface coated with the polymer has an average adhesion force of <5 N when subject to the Ice Adhesion Test Method described herein.
20. 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 according to claim 5 or the polymer formulation according to claim 13 onto the surface.
21. An object comprising components with surfaces coated with the polymer according to claim 5 or the polymer formulation according to claim 13.

1/3

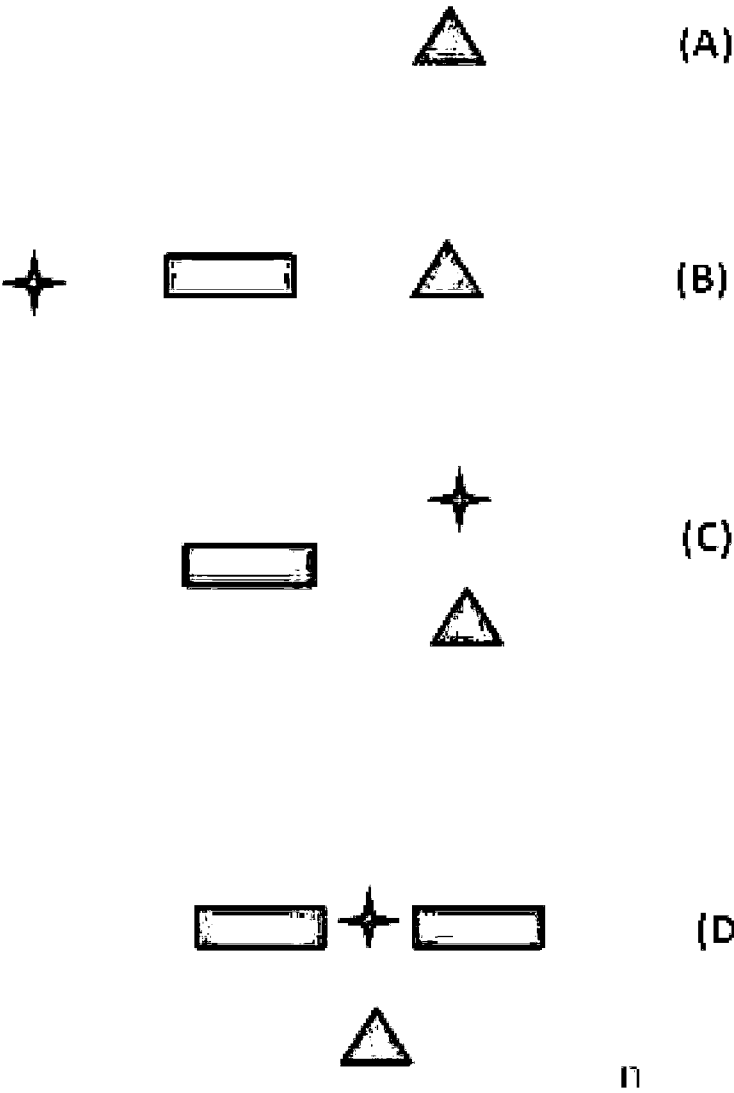


Figure 1

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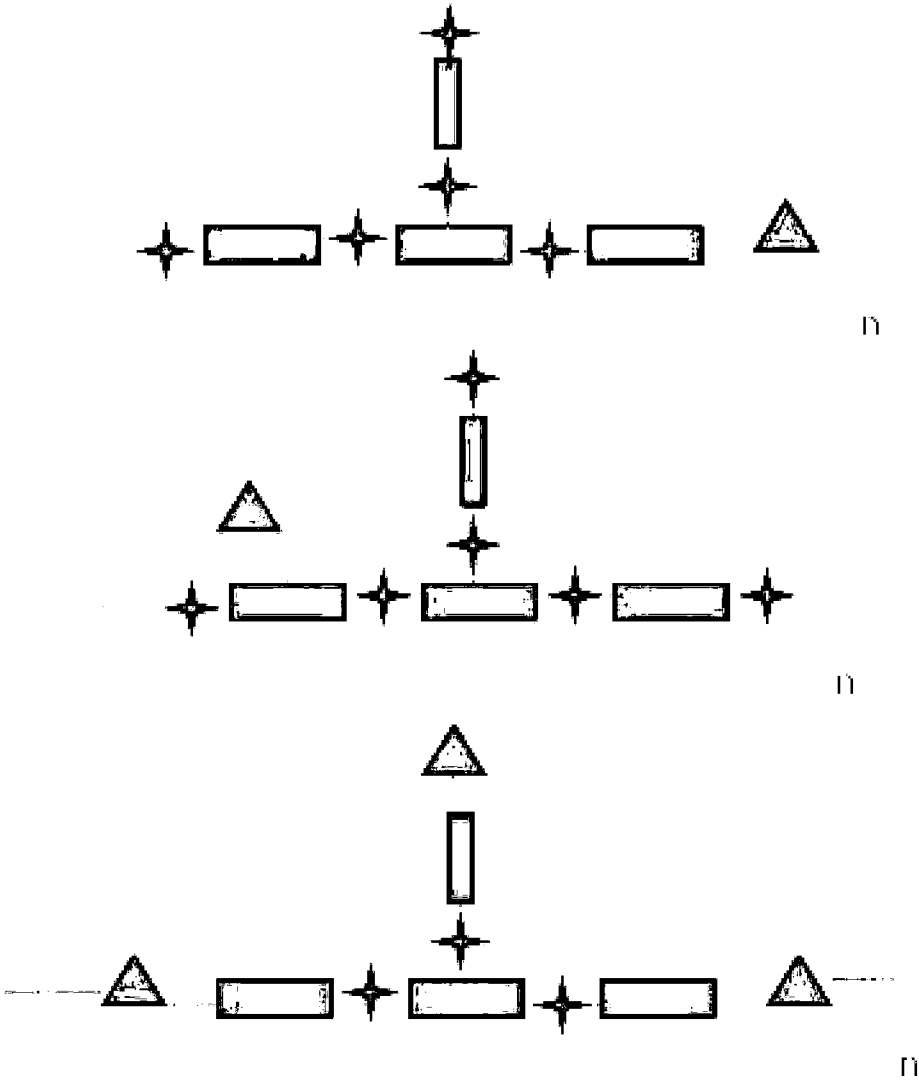


Figure 2

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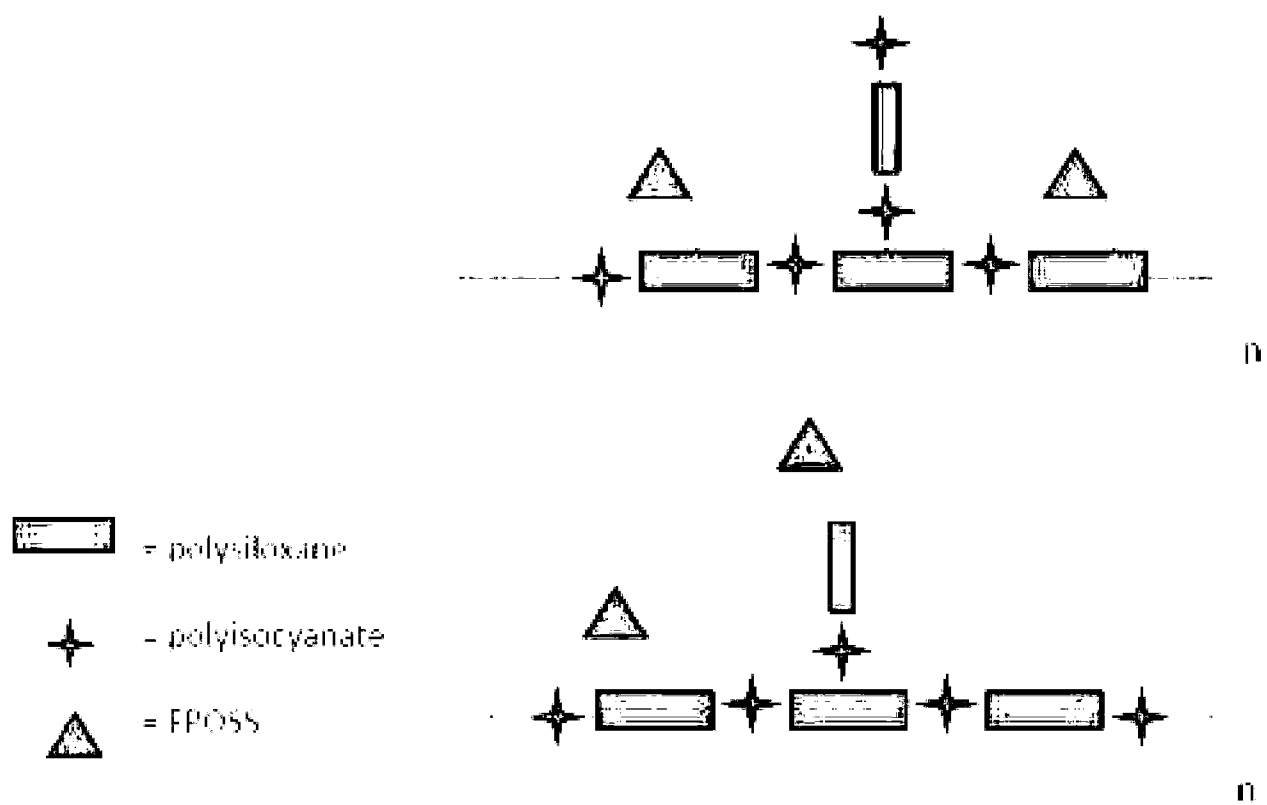


Figure 3

INTERNATIONAL SEARCH REPORT

International application No.
PCT/AU2015/000323

A. CLASSIFICATION OF SUBJECT MATTER

C07F 7/21 (2006.01) C08G 18/61 (2006.01) C08G 77/04 (2006.01) C09D 5/16 (2006.01) C09D 183/10 (2006.01)
C08F 220/22 (2006.01) C08F 283/12 (2006.01) B05D 5/00 (2006.01) C08L 83/10 (2006.01) C09K 3/18 (2006.01)

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

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

WPIAP, EPODOC, CAPLUS, WSCA, WPIDS, GOOGLE SCHOLAR, ESPACENET (Silsequioxane, FPOSS, POSS, Siloxane, Silicone, Siloxy, Isocyanate, Polyisocyanate, Desmodur, Desothane, Chemtura, Baxendon, Bayhydur, Cythane, Basonat, Polyol, Polyamine, Epoxy, Thiol, Anhydride, Ether, Ester, Ketone, Fluorine, Halogen, Urethane, Hydroxyl, Amino, Coat, Ice, Frost, Hydrophobic, Ice Reducing, Anti-icing and associated terms).

ESPACENET : Applicant / Inventor Name Search

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
	Documents are listed in the continuation of Box C	



Further documents are listed in the continuation of Box C



See patent family annex

* Special categories of cited documents:	
"A" document defining the general state of the art which is not considered to be of particular relevance	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"E" earlier application or patent but published on or after the international filing date	"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"O" document referring to an oral disclosure, use, exhibition or other means	"&" document member of the same patent family
"P" document published prior to the international filing date but later than the priority date claimed	

Date of the actual completion of the international search
29 October 2015

Date of mailing of the international search report
29 October 2015

Name and mailing address of the ISA/AU

AUSTRALIAN PATENT OFFICE
PO BOX 200, WODEN ACT 2606, AUSTRALIA
Email address: pct@ipaustalia.gov.au

Authorised officer

Balaji Rengarajan
AUSTRALIAN PATENT OFFICE
(ISO 9001 Quality Certified Service)
Telephone No. 0399359648

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

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

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:
the subject matter listed in Rule 39 on which, under Article 17(2)(a)(i), an international search is not required to be carried out, including
2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:
3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a)

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

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

See Supplemental Box for Details

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

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.
- ☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.
- ☐ No protest accompanied the payment of additional search fees.

INTERNATIONAL SEARCH REPORT		International application No.
C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		PCT/AU2015/000323
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2006/0167206 A1 (MAIER et al.) 27 July 2006 (See paras 0015-0121; Examples, paras 0123-0152; Claims)	1-21
X	CN 103468120 A (UNIV TIANJIN) 25 December 2013, English Translation retrieved from Google Patents database (See abstract; paras 0005-0007, paras 0010-0012, 0015-0017, 0021-0023; Examples 1-3; claims)	1-21
X	KANNAN, A. G. et al., "Fluoro-silsesquioxane-urethane Hybrid for Thin Film Applications", ACS Applied Materials and Interfaces, 2009, Vol. 1 (2), 336-347. (See abstract; page 337, para 4-column 2, para 2; page 338, scheme 1; page 342, Table 1; page 345, column 2, para 2-page 347, column 1, para 2)	1-21
X	CN 102757708 A (UNIV TIANJIN) 31 October 2012, English Translation retrieved from Google Patents database (See abstract; paras 0005-0009, 0016, 0019, 0022-0025; Examples 1-3, claims)	1-21
X	WO 2006/115799 A1 (UNIVERSITY OF CONNECTICUT) 02 November 2006 (See paras 0014-0032; 0044-0045, 0051; Schemes 1-6; claims)	1-21
X	MADHAVAN, K. et al., "Synthesis and Characterization of Polyurethane Hybrids: Influence of the Polydimethylsiloxane Linear Chain and Silsesquioxane Cubic Structure on the Thermal and Mechanical Properties of Polyurethane Hybrids", Journal of Applied Polymer Science, 2009, Vol. 113, pages 4052-4065. (See page 4053; column 1, last para-column 2, first para; page 4055, scheme 2; page 4059, scheme 4; 4057, column 1, last para; page 4058, column 2, para 2)	1-21
A	MEULER, A. J. et al., "Relationships Between Water Wettability and Ice Adhesion", ACS Appl. Mater. Interfaces, 2010, Vol. 2 (11), pages 3100-3110. (See the whole document)	1-21
<p>Form PCT/ISA/210 (fifth sheet) (July 2009)</p>		

Supplemental Box

Continuation of: Box III

This International Application does not comply with the requirements of unity of invention because it does not relate to one invention or to a group of inventions so linked as to form a single general inventive concept.

This Authority has found that there are different inventions based on the following features that separate the claims into distinct groups:

- Claims 5-21 (in-part) are directed to a polymer comprising a crosslinked reaction product of FPOSS prepolymer of formula I and a reactive coating. The feature of a polymer comprising a crosslinked reaction product of FPOSS prepolymer of formula I is specific to this claim.
- Claims 5-21 (in-part) are directed to a polymer comprising crosslinked reaction product of FPOSS prepolymer of Formula I, a polyisocyanate and one or more of polysiloxane of formula III, a polyol, a polyamine or a reactive coating. The feature of a polymer comprising crosslinked reaction product of FPOSS prepolymer of Formula I, a polyisocyanate and one or more of polysiloxane of formula III, a polyol, a polyamine or a reactive coating is specific to this claim.
- Claims 5-21 (in-part) are directed to a polymer comprising a crosslinked reaction product of FPOSS polyisocyanate prepolymer and one or more of polysiloxane of formula III. The feature of a polymer comprising a crosslinked reaction product of FPOSS polyisocyanate prepolymer and one or more of polysiloxane of formula III is specific to this claim.
- Claims 5-21 (in-part) are directed to a polymer comprising a crosslinked reaction product of FPOSS siloxane prepolymer of Formula II and a polyisocyanate. The feature of a polymer comprising a crosslinked reaction product of FPOSS siloxane prepolymer of Formula II and a polyisocyanate is specific to this claim.

PCT Rule 13.2, first sentence, states that unity of invention is only fulfilled when there is a technical relationship among the claimed inventions involving one or more of the same or corresponding special technical features. PCT Rule 13.2, second sentence, defines a special technical feature as a feature which makes a contribution over the prior art.

When there is no special technical feature common to all the claimed inventions there is no unity of invention.

In the above groups of claims, the identified features may have the potential to make a contribution over the prior art but are not common to all the claimed inventions and therefore cannot provide the required technical relationship. The only feature common to all of the claimed inventions and which provides a technical relationship among them is "a polymer comprising a crosslinked reaction product of FPOSS prepolymer of formula I".

However this feature does not make a contribution over the prior art because it is disclosed in:

D1: US 2006/0167206 A1 (MAIER) 27 July 2006

D2: CN 103468120 A (UNIV TIANJIN) 25 December 2013, English Translation retrieved from Google Patents database

D3: KANNAN, A. G. et al., "Fluoro-silsesquioxane-urethane Hybrid for Thin Film Applications", ACS Applied Materials and Interfaces, 2009, Vol. 1 (2), 336-347.

Therefore in the light of this document this common feature cannot be a special technical feature. Therefore there is no special technical feature common to all the claimed inventions and the requirements for unity of invention are consequently not satisfied *a posteriori*.

Furthermore, each of variation of substituents in Formula I, II and III result in wide ranges of FPOSS prepolymers, FPOSS siloxane prepolymers and polysiloxanes with huge structural variations. In addition, the combination of reactants and variations in Formula I (FPOSS prepolymers) / Formula II (FPOSS siloxane prepolymers) and Formula III (polysiloxanes) result in wide ranges of different crosslinked reactant products (polymers) with structural variations. Hence, the search is restricted to specific FPOSS prepolymer (Formula I), FPOSS siloxane prepolymer (Formula II) and polysiloxane of Formula III used for the preparation of crosslinked reaction products (polymers) as mentioned in the examples of the specification.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/AU2015/000323**Supplemental Box**

INTERNATIONAL SEARCH REPORT		International application No.	
Information on patent family members		PCT/AU2015/000323	
This Annex lists known patent family members relating to the patent documents cited in the above-mentioned international search report. The Australian Patent Office is in no way liable for these particulars which are merely given for the purpose of information.			
Patent Document/s Cited in Search Report		Patent Family Member/s	
Publication Number	Publication Date	Publication Number	Publication Date
US 2006/0167206 A1	27 July 2006	US 2006167206 A1	27 Jul 2006
		DE 10331483 A1	10 Feb 2005
		EP 1644429 A1	12 Apr 2006
		JP 2009513748 A	02 Apr 2009
		WO 2005007722 A1	27 Jan 2005
CN 103468120 A	25 December 2013	CN 103468120 A	25 Dec 2013
CN 102757708 A	31 October 2012	CN 102757708 A	31 Oct 2012
WO 2006/115799 A1	02 November 2006	WO 2006115799 A1	02 Nov 2006
		AU 2003254106 A1	16 Feb 2004
		AU 2003277332 A1	04 May 2004
		AU 2003277332 B2	12 Mar 2009
		AU 2003282572 A1	04 May 2004
		AU 2003282572 B2	09 Apr 2009
		AU 2003284088 A1	04 May 2004
		AU 2003300377 A1	04 May 2004
		AU 2003300377 B2	02 Apr 2009
		AU 2005294569 A1	20 Apr 2006
		AU 2006240293 A1	02 Nov 2006
		AU 2006240293 B2	24 Feb 2011
		AU 2010200568 A1	11 Mar 2010
		AU 2010200568 B2	02 Feb 2012
		AU 2010246481 A1	23 Dec 2010
		AU 2010246481 B2	16 Aug 2012
		CA 2501549 A1	22 Apr 2004
		CA 2501551 A1	22 Apr 2004
		CA 2501617 A1	22 Apr 2004
		CA 2501643 A1	22 Apr 2004
		CA 2583191 A1	20 Apr 2006
		CA 2605497 A1	02 Nov 2006
		EP 1554328 A2	20 Jul 2005
		EP 1554328 B1	23 Feb 2011
		EP 1558671 A1	03 Aug 2005

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Due to data integration issues this family listing may not include 10 digit Australian applications filed since May 2001.

Form PCT/ISA/210 (Family Annex)(July 2009)

INTERNATIONAL SEARCH REPORT		International application No.	
Information on patent family members		PCT/AU2015/000323	
This Annex lists known patent family members relating to the patent documents cited in the above-mentioned international search report. The Australian Patent Office is in no way liable for these particulars which are merely given for the purpose of information.			
Patent Document/s Cited in Search Report		Patent Family Member/s	
Publication Number	Publication Date	Publication Number	Publication Date
		EP 1558671 B1	16 Feb 2011
		EP 1560612 A2	10 Aug 2005
		EP 1560881 A1	10 Aug 2005
		EP 1560881 B1	23 Nov 2011
		EP 1824412 A2	29 Aug 2007
		EP 1874371 A2	09 Jan 2008
		EP 1874371 B1	27 May 2009
		EP 1907434 A1	09 Apr 2008
		EP 2260881 A2	15 Dec 2010
		EP 2260882 A2	15 Dec 2010
		EP 2311902 A2	20 Apr 2011
		JP 2006503171 A	26 Jan 2006
		JP 4530989 B2	25 Aug 2010
		JP 2006503172 A	26 Jan 2006
		JP 4530990 B2	25 Aug 2010
		JP 2006503170 A	26 Jan 2006
		JP 4960631 B2	27 Jun 2012
		JP 2008536628 A	11 Sep 2008
		JP 5255434 B2	07 Aug 2013
		JP 2008537010 A	11 Sep 2008
		JP 2011099121 A	19 May 2011
		US 2004024098 A1	05 Feb 2004
		US 7067606 B2	27 Jun 2006
		US 2004116641 A1	17 Jun 2004
		US 7091297 B2	15 Aug 2006
		US 2004122184 A1	24 Jun 2004
		US 7173096 B2	06 Feb 2007
		US 2004122174 A1	24 Jun 2004
		US 7208550 B2	24 Apr 2007
		US 2007135578 A1	14 Jun 2007
		US 7371799 B2	13 May 2008
		US 2005245719 A1	03 Nov 2005
		US 7524914 B2	28 Apr 2009
		US 2007142562 A1	21 Jun 2007
		US 7563848 B2	21 Jul 2009
		US 2009275704 A1	05 Nov 2009
Due to data integration issues this family listing may not include 10 digit Australian applications filed since May 2001.			

Due to data integration issues this family listing may not include 10 digit Australian applications filed since May 2001.

Form PCT/ISA/210 (Family Annex)(July 2009)

INTERNATIONAL SEARCH REPORT Information on patent family members		International application No. PCT/AU2015/000323	
This Annex lists known patent family members relating to the patent documents cited in the above-mentioned international search report. The Australian Patent Office is in no way liable for these particulars which are merely given for the purpose of information.			
Patent Document/s Cited in Search Report		Patent Family Member/s	
Publication Number	Publication Date	Publication Number	Publication Date
		US 7705098 B2	27 Apr 2010
		US 2005216074 A1	29 Sep 2005
		US 7794494 B2	14 Sep 2010
		US 2008249245 A1	09 Oct 2008
		US 7795350 B2	14 Sep 2010
		US 2010160522 A1	24 Jun 2010
		US 7906573 B2	15 Mar 2011
		US 2005251249 A1	10 Nov 2005
		US 7976936 B2	12 Jul 2011
		US 2011054591 A1	03 Mar 2011
		US 8784465 B2	22 Jul 2014
		US 2012253451 A1	04 Oct 2012
		US 9115245 B2	25 Aug 2015
		US 2005010275 A1	13 Jan 2005
		US 2009253842 A1	08 Oct 2009
		US 2010331954 A1	30 Dec 2010
		US 2011172753 A1	14 Jul 2011
		UY 27907 A1	28 Nov 2003
		WO 2004011525 A1	05 Feb 2004
		WO 2004032799 A2	22 Apr 2004
		WO 2004033515 A2	22 Apr 2004
		WO 2004033539 A1	22 Apr 2004
		WO 2004033553 A1	22 Apr 2004
		WO 2006041767 A2	20 Apr 2006
		WO 2006115847 A2	02 Nov 2006
End of Annex			
<p>Due to data integration issues this family listing may not include 10 digit Australian applications filed since May 2001.</p> <p>Form PCT/ISA/210 (Family Annex)(July 2009)</p>			