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(54) Title: NONWOVEN FABRIC WITH LOW ICE ADHESION

(57) Abstract: The present disclosure provides a method to remove ice from a substrate with very low amounts of force needed to remove the ice. It has been found that certain nonwoven fabrics provide a relatively ice-phobic surface. The application of the nonwoven fabric to a substrate can provide a substrate wherein any accumulated ice is easily removed.



TITLE

Nonwoven Fabric With Low Ice Adhesion

FIELD OF THE DISCLOSURE

[01] The present disclosure is directed toward a method for removing a layer of accumulated ice from a surface.

BACKGROUND OF DISCLOSURE

[02] The accumulation of ice on surfaces is a major problem, especially in cold climates. The build-up of ice creates unsafe conditions and the resulting costs of the icing events can run into the billions of dollars.

[03] Ice formation can affect a broad range of structures and substrates, including airplanes, wind turbines, power transmission lines and towers, off-shore and marine structures, solar panels, automobiles and buildings. Many industries have set tolerances for ice accumulating on structures and should the amount of ice exceed the tolerances, the damage to the structure can be severe. In the case of power transmission lines and power transmission towers, accumulating ice can cause power outages due to the weight of the accumulated ice.

[04] The aviation industry has several well-known methods to deal with icing issues while an aircraft is on the ground and during flight. The methods used on the ground can include spraying a de-icing fluid on the surfaces to remove the ice and to delay the formation of new ice. Such methods require large amounts of de-icing fluids, which can be expensive and cause environmental concerns. During flight, several anti-icing methods can be used depending upon the type and size of the aircraft. While they are necessary, these in-flight systems can be expensive and require regular maintenance.

[05] There is a need for a system or process which would prevent the formation of ice from such structures. If ice formation cannot be completely prevented, then the system should reduce the adhesion of ice to the substrate which in turn would require less energy to remove the ice.

SUMMARY OF THE DISCLOSURE

[06] The present disclosure provides a method of removing ice from a substrate comprising the steps of:

- 1) providing a substrate that is free from ice;
- 2) applying to at least a portion of the substrate, a nonwoven fabric having a bending modulus, as determined by ASTM D790, of less than $3,500 \text{ kg/cm}^2$, a water contact angle of greater than 65°C and a surface tension of less than 50 dyne/cm ;
- 3) allowing ice to form on at least a portion of the applied nonwoven fabric; and
- 4) applying a force to the ice, to the substrate, to the nonwoven fabric or a combination thereof that is sufficient to separate the ice from the nonwoven fabric; wherein a layer of the nonwoven fabric has an average ice adhesion of less than 1.76 kg/cm^2 when a shear stress force is applied to ice on the nonwoven fabric according to the following test:
 - i) a layer of the nonwoven fabric is adhered to a horizontally situated aluminum plate;
 - ii) a cuvette is placed onto the layer of nonwoven fabric;
 - iii) $0.5 \text{ cubic centimeter}$ of water is placed into the cuvette so that the water contacts the nonwoven fabric, and the water is cooled to -20°C to form ice;
 - iv) a shear stress is applied to the cuvette in a direction that is parallel to the applied layer of nonwoven fabric.

DETAILED DESCRIPTION

[07] The features and advantages of the present disclosure will be more readily understood, by those of ordinary skill in the art from reading the following detailed description. It is to be appreciated that certain features of the disclosure, which are, for clarity, described above and below in the context of separate embodiments, may also be provided in combination in a single element. Conversely, various features of the disclosure that are, for brevity, described in the context of a single embodiment, may

also be provided separately or in any sub-combination. In addition, references to the singular may also include the plural (for example, "a" and "an" may refer to one or more) unless the context specifically states otherwise.

[08] The use of numerical values in the various ranges specified in this application, unless expressly indicated otherwise, are stated as approximations as though the minimum and maximum values within the stated ranges were both preceded by the word "about". In this manner, slight variations above and below the stated ranges can be used to achieve substantially the same results as values within the ranges. Also, the disclosure of these ranges is intended as a continuous range including each and every value between the minimum and maximum values.

[09] As used herein:

[10] The phrase "free from ice" means that a given area of a substrate or a substrate coated with the nonwoven fabric contains less than 10 percent of its area covered by ice. In other embodiments, the given area contains less than 5 percent ice, and, in still further embodiments, the given area contains less than 1 percent ice. In other embodiments, the substrate contains no ice. The area percentage of ice is based on the total area of the ice on the substrate divided by the total area of the substrate.

[11] The phrase "nonwoven fabric" means a structure produced by the bonding and/or interlocking of fibers, as accomplished by one or more treatment methods. Suitable treatment methods are mechanical, thermal, or solvent treatment.

[12] The phrase "average ice adhesion" is determined according to the following procedure;

- i) a layer of the nonwoven fabric is adhered to a horizontally situated aluminum plate;
- ii) a cuvette is placed onto the layer of nonwoven fabric;
- iii) 0.5 cubic centimeter of water is placed into the cuvette so that the water contacts the nonwoven fabric, and the water is cooled to -20°C to form ice;
- iv) a shear stress is applied to the -20°C ice in a direction that is parallel to the applied layer of nonwoven fabric;
- v) determining the applied force necessary to separate the ice from the nonwoven fabric;

- vi) repeating steps i) through v) at least 3 times and determining an average based on the repetitions.

The nonwoven fabric can be mounted to the aluminum plate by a variety of methods. For example, the nonwoven fabric can be adhered to the aluminum using an adhesive material, such as, an adhesive agent or double-sided tape, or it can be clamped to the aluminum plate or any other known method can be used. The method used to mount the plate is not important, however, it is important that the nonwoven fabric has little or no movement on the aluminum plate during the application of the shear stress. In some embodiments, steps i) through v) are repeated 5 times in order to determine the average ice adhesion. In other embodiments, the steps are repeated at least 8 times in order to determine the average ice adhesion.

[13] The present disclosure is related to a method for removing ice from a substrate. The method comprises the steps of;

- 1) providing a substrate that is free from ice;
- 2) applying to at least a portion of the substrate, a nonwoven fabric having a bending modulus, as determined by ASTM D790, of less than $3,500 \text{ kg/cm}^2$, a water contact angle of greater than 65°C and a surface tension of less than 50 dyne/cm ;
- 3) allowing ice to form on at least a portion of the applied nonwoven fabric; and
- 4) applying a force to the ice, to the substrate, to the nonwoven fabric or a combination thereof that is sufficient to separate the ice from the nonwoven fabric; wherein a layer of the nonwoven fabric has an average ice adhesion of less than 1.76 kg/cm^2 when a shear stress force is applied to ice on the nonwoven fabric according to the following test:
 - i) a layer of the nonwoven fabric is adhered to a horizontally situated aluminum plate;
 - ii) a cuvette is placed onto the layer of nonwoven fabric;
 - iii) $0.5 \text{ cubic centimeter}$ of water is placed into the cuvette so that the water contacts the nonwoven fabric, and the water is cooled to -20°C to form ice;

- iv) a shear stress is applied to the cuvette in a direction that is parallel to the applied layer of nonwoven fabric.

[14] It has been surprisingly found that certain nonwoven fabrics can have very low levels of adhesion to ice. One well-known brand of nonwoven material is provided by E.I. du Pont de Nemours and Company, Wilmington, Delaware as TYVEK[®] polyolefin. TYVEK[®] polyolefin is a nonwoven fabric and comes in many different grades, each of them having different properties depending on the final use. The desired properties can be varied by selection of the polyolefin, the nonwoven fabric formation process, and by using one or more of the different bonding techniques. In some embodiments, it has been found that relatively soft nonwoven fabrics, i.e., those nonwoven fabrics having a bending modulus, as determined by ASTM D790, of less than 3,500 kg/cm², also having a water contact angle of greater than 65° and a surface tension of less than 40 dyne/cm at 20°C can provide very low levels of adhesion to ice. In other embodiments, the bending modulus can be less than 3,000 kg/cm² or less than 2,500 kg/cm² or less than 2,000 kg/cm² or less than 1,750 kg/cm² or less than 1,500 kg/cm² or less than 1,250 kg/cm² or less than 1,000 kg/cm².

[15] In any of the above embodiments, the water contact angle of the nonwoven fabric is greater than 70°, or the water contact angle is greater than 75°. In any of the above embodiments, the water contact angle can be greater than 80°, or the water contact angle can be greater than 85°, or the water contact angle can be greater than 90°, or the water contact angle can be greater than 95°, or the water contact angle can be greater than 100°, or the water contact angle can be greater than 105°.

[16] In any of the above embodiments, the surface tension of the nonwoven fabric is less than 45 dyne/cm at 20°C, or the surface tension is less than 44 dyne/cm at 20°C, or the surface tension is less than 43 dyne/cm at 20°C or the surface tension is less than 42 dyne/cm at 20°C, or the surface tension is less than 41 dyne/cm at 20°C, or the surface tension is less than 40 dyne/cm at 20°C, or the surface tension is less than 39 dyne/cm at 20°C, or the surface tension is less than 38 dyne/cm at 20°C, or the surface tension is less than 37 dyne/cm at 20°C, or the surface tension is less than 36 dyne/cm at 20°C, or the surface tension is less than 35 dyne/cm at 20°C, or the surface tension is less than 34 dyne/cm at 20°C, or the surface tension is less than 33 dyne/cm at 20°C, or

the surface tension is less than 32 dyne/cm at 20°C, or the surface tension is less than 31 dyne/cm at 20°C, or the surface tension is less than 30 dyne/cm at 20°C. The surface tension is generally greater than about 5 dyne/cm at 20°C.

[17] In some embodiments, the nonwoven fabric is a point bonded polyethylene nonwoven fabric. TYVEK® 1460, 1422 and 1560 grades are particularly suited as point bonded nonwoven fabrics. Such point bonded grades can have two differently patterned sides of the nonwoven fabric. One side of the nonwoven fabric is the 'linen' side while the opposite side is the point bonded side. It has been found that the ice adhesion is greater on the point bonded side and is therefore important to place the linen side "up" or, in other words, the linen side should be facing away from the substrate. In contrast, area bonded TYVEK® grades, which have a bending modulus of greater than 3,500 kg/cm², do not provide the same ice release characteristics as the point bonded low bending modulus grades. Other types of nonwoven fabrics can also provide low levels of ice adhesion, provided that they conform to the criteria of having a bending modulus as determined by ASTM D790 of less than 3,500 kg/cm², a water contact angle of greater than 65° and a surface tension of less than 50 dyne/cm at 20°C. Other suitable nonwoven fabrics include, for example, point bonded polyethylene, point bonded polyolefin, needlefelt fluoropolymer, spunbond polypropylene, spunbond polyurethane and nonwoven blends of polypropylene, polyethylene and polyester fibers.

[18] To apply the nonwoven fabric to at least a portion of the substrate, the nonwoven fabric must be secured to a portion of the substrate that is free from ice. In some embodiments, the nonwoven fabric is applied using an adhesive agent. In other embodiments, the nonwoven fabric can be secured to the substrate by clamping, riveting, screwing, double sided adhesive tape or a combination thereof. The method of attachment is not particularly important provided that the securing method does not weaken the substrate, does not allow the nonwoven fabric to move or shift positions on the substrate or does not otherwise impede the working of the substrate. The method of application should also not change the bending modulus, the surface tension or the water contact angle of the nonwoven fabric.

[19] In some embodiments, the nonwoven fabric may be secured to at least a portion of the substrate using an adhesive agent. The layer of adhesive agent may be applied to the fabric, to the substrate or to both prior to the application of the nonwoven fabric to the substrate. The nonwoven fabric can then be applied to the substrate with the adhesive layer interposed between the nonwoven fabric and the substrate. If the nonwoven fabric has a linen side, then the adhesive agent is applied to the side opposite the linen side. In other embodiments, the adhesive agent can be applied to at least a portion of the substrate followed by the application of the nonwoven fabric to the applied layer of adhesive. Double sided tape can also be used to secure the nonwoven fabric to the substrate. Still other methods for securing the nonwoven fabric to the substrate are known and can be used.

[20] Optionally, an adhesive layer can be applied to the nonwoven fabric and then a release layer can be applied to the adhesive layer. The release layer allows the nonwoven fabric/adhesive structure to be produced at one location then packaged for storage and later use. The release layer should be easily removed from the adhesive layer and not affect the adhesive qualities of the layer. Suitable release layers are known in the art and any of them can be used. Used in this way, the disclosed method would further comprise the step of removing the release layer from the adhesive layer prior to the step of applying the nonwoven fabric to the substrate.

[21] The adhesive agent can be any of the known adhesive agents that are suitable to bond a nonwoven fabric to a substrate. In some embodiments, the adhesive agent can be, for example, epoxy adhesives, urethane adhesives, acrylate adhesives, methacrylate adhesives, cyanoacrylate adhesives, polyvinyl acetate adhesives or a combination thereof. In some embodiments, the adhesive agent can be solventborne, waterborne, hot-melt or pressure sensitive. Each adhesive should be tested for compatibility with the nonwoven fabric. Some nonwoven fabrics are not compatible with certain organic solvents that may be present in the adhesive agent. The manufacturer of each nonwoven fabric will generally provide information on testing the solvent compatibility with their particular nonwoven fabric. Since the adhesive agent and the nonwoven fabric will be in contact with one another for long periods of time, it is important that the adhesive and the nonwoven fabric are stable towards one another.

As an example, it is known that certain low molecular weight polybutyl acrylates used in pressure sensitive adhesives can cause wrinkling and distortion of some TYVEK® nonwovens if the adhesive coated TYVEK® is stored in locations where the temperatures are above 32°C. It is also known that high molecular weight polybutyl acrylates are compatible with some TYVEK® nonwovens at temperatures up to 100°C.

[22] The substrate that the nonwoven fabric can be applied to can be any substrate that is subject to unwanted ice accumulation. Such substrates can include, for example, airplane wings, airplane bodies, wind turbine blades, wind turbines, power transmission lines, power transmission towers, oil rigs, marine structures, marine vessels, bridges, vehicles, buildings, radio antennas, cell phone towers, solar panels, glass, automobile coatings, and food containers.

[23] Essentially, any structure where ice accumulation can cause damage due to the weight of the accumulated ice, damage due to falling ice, due to the disruption of airflow over the substrate or a combination thereof can be coated with the nonwoven fabric. In some embodiments, the nonwoven fabric can be applied to at least a portion of the substrate, for example, the leading edge of an airplane wing, the leading edge of a wind turbine blade. Once the nonwoven fabric is applied to the substrate, it should not impede the performance or functioning of the substrate as long as the nonwoven fabric remains intact. If the nonwoven fabric begins to tear or come loose, the damaged portion can be removed or the entire damaged piece can be removed and replaced it with new material. Many nonwoven fabrics, including TYVEK® nonwovens are very lightweight, have outstanding strength, are able to function at a wide range of temperatures, withstand many chemicals and have excellent UV resistance.

[24] The nonwoven fabric can be applied to the substrate when the substrate is free from ice. Once the nonwoven fabric has been applied, any ice formed on the nonwoven fabric can be removed by the application of a force to the substrate, to the nonwoven fabric, to the ice or to a combination thereof. The nonwoven fabric provides an average ice adhesion of less than 1.76 kg/cm² when a shear stress is applied to ice that is adhered to the nonwoven fabric.

[25] In various embodiments, the average ice adhesion is less than 1.41 kg/cm² (20 psi) or less than 1.33 kg/cm² (19 psi) or less than 1.26 kg/cm² (18 psi) or less than 1.20

kg/cm² (17 psi) or less than 1.12 kg/cm² (16 psi) or less than 1.05 kg/cm² (15 psi), or less than 0.98 kg/cm² (14 psi) or less than 0.91 kg/cm² (13 psi) or less than 0.84 kg/cm² (12 psi) or less than 0.77 kg/cm² (11 psi) or less than 0.70 kg/cm² (10 psi) or less than 0.63 kg/cm² (9 psi) or less than 0.56 kg/cm² (8 psi) or less than 0.49 kg/cm² (7 psi) or less than 0.42 kg/cm² (6 psi) or less than 0.35 kg/cm² (5 psi). In each embodiment, the force required to separate the ice from the nonwoven fabric is the shear stress as measured by the test outlined above.

[26] It has also been found that the application of a thin layer of a fluoropolymer to the nonwoven fabric can also be used to decrease the amount of force necessary to remove any accumulated ice from the surface of the nonwoven fabric. In some embodiments, the thin layer of fluoropolymer can be applied so that the fluoropolymer forms a film having a thickness in the range of from 10 nanometers to 50 micrometers. In other embodiments, the thickness of the fluoropolymer film is in the range of from 100 nanometers to 20 micrometers, and, in still further embodiments, the fluoropolymer thickness is in the range of from 1 to 10 micrometers.

[27] The fluoropolymer can be any fluorine containing polymer. Suitable examples of fluorine-containing monomers that can be used to produce the fluoropolymer can include, for example, homopolymers or copolymers of tetrafluoroethylene, hexafluoropropylene, perfluoro monoalkenes having in the range of from 2 to 20 carbon atoms, fluoroacrylates and fluoromethacrylates, vinylidene fluoride, vinyl fluoride, vinyl trifluoroacetate, vinyl pentafluoropropionate, vinyl heptafluorobutyrate, CAPSTONE[®] fluoro monomers, available from DuPont, Wilmington, Delaware or a combination thereof. In some embodiments, the fluoropolymer is a copolymer produced from tetrafluoroethylene and hexafluoropropylene.

[28] In some embodiments, the fluoropolymer can be dissolved in an appropriate solvent and the solution coated onto the nonwoven fabric. The solvent can then be allowed to dry or can be dried under forced conditions (i.e., heat and/or the application of a vacuum). The application method of the solution can be any of those that are known in the art, for example, spraying, rolling, brushing, flow coating, curtain coating, dipping, knife coating, or draw down coating. The fluoropolymer coating can be applied to the nonwoven fabric prior to the nonwoven fabric being applied to the substrate or the

fluoropolymer can be applied to the nonwoven fabric after the nonwoven fabric has been applied to the substrate.

[29] In other embodiments, the layer of fluoropolymer can be applied using atmospheric pressure plasma liquid deposition (APPLD) techniques. In this process, an aerosol of monomers is directed into a homogeneous atmospheric pressure plasma where the monomers are activated by the action of the ionized gas molecules or the substrate surface, i.e., the nonwoven fabric, can be activated by the action of the ionized gas molecules and the monomers contacting the activated surface are deposited as a thin conformal layer of polymer. In some embodiments, a primer layer is first applied to the nonwoven fabric prior to depositing the fluoropolymer film layer. Suitable primer layers can be, for example, homopolymers or copolymers of acrylate or methacrylate monomers having a long chain (12 to 20 carbon atoms) hydrophobic backbone, polyacrylates or polymethacrylates having in the range of from 2 to 10 ethylenically unsaturated double bonds, for example, propoxylated neopentyl glycol diacrylate, and polyhedral oligomeric silsesquioxane compounds that contains multiple methacrylate groups, for example, MA0735 Methacryl POSS[®] Cage Mixture, available from Hybrid Plastics, Inc., Hattiesburg, Mississippi. Following the formation of the primer layer, the fluoropolymer layer can then be applied to at least a portion of the primer layer. Suitable fluoromonomers can include, for example, any of those listed above. In some embodiments, polyunsaturated monomers are also used in order to produce crosslinked fluoropolymer layers. Suitable polyunsaturated monomers can include, for example, ditrimethylolpropane tetraacrylate, trimethylolpropane triacrylate, hexanediol diacrylate, pentaerythritol tetraacrylate or a combination thereof.

[30] The nonwoven fabric retains low levels of ice adhesion after many cycles. Even a nonwoven fabric that has been treated with a fluoropolymer continues to exhibit low levels of ice adhesion even after as many as 10 cycles. In order to test the adhesion after several cycles, the shear stress for removing ice from the nonwoven fabric was determined using the above mentioned test for determining the average ice adhesion value. For cycle number 2, the cuvettes were placed on the same spots that they were for the first test, or were placed as closely to the same spots as was possible and the average ice adhesion value was determined for cycle number 2. This process was

repeated for as many times as desired. In some embodiments, the ice adhesion values over 10 cycles were determined to have a statistically insignificant difference between each of the tests.

[31] The disclosure also relates to an article comprising the substrate, an adhesive layer applied to at least a portion of the substrate and the nonwoven fabric applied to at least a portion of the substrate, wherein the nonwoven fabric has a bending modulus, as determined by ASTM D790, of less than 50 kpsi (3,500 kg/cm²) and a water contact angle of greater than 65° and a surface tension of 50 dyne/cm. The substrate, the adhesive and the nonwoven fabric can be any of those that have been previously described.

EXAMPLES

[32] Unless otherwise specified, all ingredients are available from Sigma-Aldrich, St. Louis, Missouri.

[33] TYVEK® nonwoven fabrics, CAPSTONE® acrylates and FORAFAC™ 1051 fluoro alcohol are available from E.I. du Pont de Nemours and Company, Wilmington, Delaware.

[34] NUSIL™ R1009, silicone dispersion, is available from NuSil, Inc., Carpinteria, California.

[35] Daikin R-1633 fluoroacrylate is available from Daikin America, Inc., Orangeburg, New York.

[36] MA0735, Methacryl POSS® Cage Mixture, is available from Hybrid Plastics, Inc., Hattiesburg, Mississippi.

[37] SR9003, SR355 and SR257C acrylates are available from Sartomer, Exton, Pennsylvania.

[38] HEMA is 2-hydroxyethyl methacrylate.

[39] FC-75 and FC-40 fluorinated solvents are available from 3M, St. Paul, Minnesota.

[40] Ice Adhesion Testing

[41] The ice adhesion behavior of the surfaces was tested via the following method: the nonwoven fabric was first mounted on an aluminum plate via double sided tape. The nonwoven fabric-aluminum composite was mounted onto a cold stage (TE

Technology Inc, Model # CP 200 TT). Eight glass cuvettes (1 centimeter (cm) by 1 cm by 2.54 cm tall, available from VWR Inc,) were placed randomly on the nonwoven fabric and 0.5 cubic centimeter of deionized water was added to each cuvette. The cold stage was then programmed to -20°C at 1.5°C /min from room temperature. When the water had frozen and equilibrated to -20°C, the cuvettes were subjected to shearing using the circular head of a force gauge (Mark 10 Inc, Series 3) mounted on a syringe pump (Harvard Inc, model number 33) and moving towards the substrate at 0.029 millimeter/second. Shear stress was calculated by the shear force (reading on the force gauge) divided by cross sectional area of the ice in contact with the substrate (1 cm²). Care was taken to ensure optimal separation distance (1 mm) between the bottom portion of the force gauge and the substrate to minimize torque. The entire experiment was carried out under nitrogen circulation to normalize any humidity related effects. The reported ice adhesion is the average of the eight measured values.

[42] For the ice adhesion cycle tests, the ice adhesion measurements were performed at the same set of areas of the test substrate 10 times in succession.

[43] Surface tension measurements and contact angle measurements were made using Rame-Hart 250F1 Goniometer and DROP Image Advanced software. Two test liquids, deionized water and methylene iodide (available from Sigma Aldrich) were employed and an average of three values (tested at random locations along the sample). The surface tension was calculated according to the geometric mean method of S. Wu, *Polymer Interface and Adhesion*, 1982, by solving for γ_s^d and γ_s^p , the following quadratic equations in two variables:

$$\begin{aligned}(1 + \cos \theta_1)\gamma_1 &= 2[(\gamma_1^d \gamma_s^d)^{1/2} + (\gamma_1^p \gamma_s^p)^{1/2}] \\ (1 + \cos \theta_2)\gamma_2 &= 2[(\gamma_2^d \gamma_s^d)^{1/2} + (\gamma_2^p \gamma_s^p)^{1/2}]\end{aligned}$$

where θ = contact angle, γ = surface tension, superscripts d and p represent dispersion and polar components, and subscripts 1 and 2 represent deionized water and methylene iodide respectively. Published values of $\gamma_1^d = 21.8$ dyne/cm, $\gamma_1^p = 51$ dyne/cm, $\gamma_2^d = 49.5$ dyne/cm and $\gamma_2^p = 1.3$ dyne/cm were used

[44] Calendered TYVEK® samples

[45] Samples of certain nonwoven fabrics were treated by calendaring in order to provide samples having relatively similar water contact angles and surface tensions, but

increased bending moduli when compared to the non-calendered versions. In order to calender the sample fabrics, each 12.7cm by 20.32cm fabric sheet was passed through two steel calendering rolls at the specified pressures.

TABLE 1

Nonwoven	Average Thickness (μm)	Average Static water contact angle (degrees)	Average Static CH_2I_2 contact angle (degrees)	Average Bending Modulus (kg/cm^2)	Surface Tension (dyne/cm)	Average Ice Adhesion (kg/cm^2)
TYVEK [®] 1460B	186	107.97	38.2	1,276	43.8	0.33
TYVEK [®] 1422A	142	112.88	36.3	916	46.9	0.47
TYVEK [®] 1560B	169	105.3	43.1	962	39.9	0.60
TYVEK [®] M3563B	187	76.9	43.1	3,071	46.85	0.73
TEFLON [®] needlefelt	1393	131.45	102.1	974	8.29	0.657
HYTREL [®] NW (comparative)	788	115.86	0	5	61.4	8.41
TYVEK [®] 1560B calendered at 70 kg/cm^2 (comparative)	90	105.3	44.8	12,005	37.13	6.19
TYVEK [®] 1560B calendered at 140 kg/cm^2 (comparative)	69	101.3	57	21,533	38.9	5.84
TEFLON [®] needlefelt calendered at 70 kg/cm^2 (comparative)	575	116.1	104.9	4,545	7.68	4.27
TYVEK [®] 1056D (comparative)	165	71.22	59.4	4,042	36.42	4.80
TYVEK [®] 1059B (comparative)	146	117.08	57	4,127	33.83	5.15

TYVEK® 1055B (comparative)	101.33	108.65	37.8	5,470	44.3	6.01
TYVEK® 1073B (comparative)	156.7	119.82	54.2	5,146	37	5.37
NUSIL™ R1009 (comparative)	n/a	n/a	n/a	n/a	n/a	1.16

n/a - not applicable

[46] The ice adhesion for each of the fabrics in Table 1 was tested according to the ice adhesion test procedure given above. Each sample was tested at least 8 times and the results shown represent the average ice adhesion values for the test. A commercially available low ice adhesion product, NUSIL™ R1009, silicone dispersion, was used as a comparative. The NUSIL™ R1009 dispersion was prepared according to the manufacturer's instructions and applied to the aluminum plate at a thickness of 147.3 micrometers (5.8 mil). The results in Table 1 show that if the nonwoven fabric provides a water contact angle of greater than 65°, a bending modulus, as determined by ASTM-D790, of less than 3,500, and a surface tension of less than 50 dyne/cm, then the ice adhesion is less than 1.76 kg/cm².

[47] Nonwoven fabric coated with fluoropolymer using an atmospheric pressure plasma liquid deposition technique (APPLD)

[48] TYVEK® 1560B was modified by coating the fabric with a variety of fluororacrylates via an APPLD technique according to the following process; an aerosol of liquid monomer or monomer mixture was directed into homogenous atmospheric pressure plasma where it was activated by the action of ionized process gas molecules on the aerosol droplet surfaces. The surface of the substrate, TYVEK® 1560B, was also in contact with the plasma. Representative examples of devices used to generate such a plasma discharge include those disclosed in WO2001/59809, WO2002/28548, WO2005/110626 and US2005/0178330. The following process conditions were used: monomer feed rate 500 millimole/minute, web speed of 2.5 meters per minute, plasma power of 5 kilowatts, web tension of 10 Newtons and the helium gas consumption was 30 liters/minute. The nonwoven fabric was first coated using monomer mixture #1 (Table 2, all amounts are in parts by weight) to form a layer of a primer, which was then

followed by a fluoropolymer layer using monomer mixture #2 (Table 3, all amounts are in parts by weight).

TABLE 2

Primer layer				
Monomer Mixture #1	MA0735	SR9003	SR257	Total
7	0	100	0	100
8	0	100	0	100
9	0	50	50	100
10	10	40	50	100

TABLE 3

Fluoropolymer layer								
Monomer Mixture #2	Daikin - R1633	CAPSTONE® MA-62	CAPSTONE® AC-62	Poly HFPO	FORAFAC™ 1051	SR 355	HEMA	Total
6	0	0	35	35	25	5	0	100
7	35	0	35	0	25	5	0	100
8	45	0	50	0	0	5	0	100
9	45	50	0	0	0	5	0	100
10	0	0	70	0	0	0	30	100

PolyHFPO is polyhexafluoropropylene oxide

[49] Once the various polymer layers had been deposited, the values of ice adhesion were tested according to the procedure given above. Table 4 shows the primer layer/ fluoropolymer layer and the resulting values of ice adhesion.

TABLE 4

Sample	Primer layer	Fluoropolymer layer	Ice Adhesion (kg/cm ²)
1	7	6	0.77
2	7	7	1.10
3	7	8	0.72
4	7	9	0.86
5	7	10	1.70
6	8	6	0.85
7	8	7	0.73
8	8	8	0.94
9	8	9	0.90
10	8	10	0.93
11	9	6	0.76
12	9	7	0.79
13	9	8	0.80

14	9	9	0.89
15	9	10	1.01
16	10	6	0.87
17	10	7	0.88
18	10	8	1.28
19	10	9	0.86
20	10	10	0.76
NUSIL™ (comparative)	n/a	n/a	1.16

[50] Adhesion test over 10 cycles

[51] The ice adhesion of TYVEK® 1560B and a TYVEK® 1560B fabric coated with a layer of a fluoropolymer was tested against a commercially available product, NUSIL™ R1009 dispersion, using the cycle test described above.

[52] Nonwoven fabric coated with HFP fluoropolymer film

[53] A fluoropolymer of hexafluoropropylene (52.7 percent by weight) and tetrafluoroethylene (47.3 percent by weight) was prepared according to the process of US Patent Number 5,478,905. The prepared HFP fluoropolymer had a weight average molecular weight of 428,000, a number average molecular weight of 137,000, a melt flow index of 1.3 g/min at 297°C with a 5 kg weight and an inherent viscosity in FLUORINERT™ FC-75 of 0.54 cm³/g.

[54] A 2.5 weight percent solution of the HFP fluoropolymer in FLUORINERT™ FC-40 was coated via a drawdown technique onto TYVEK® 1422A nonwoven fabric, and then heated at 100°C for 10 minutes. The coated nonwoven fabric was then tested for ice adhesion using the previously mentioned procedure over a total of 10 cycles. NUSIL™ R1009 was tested as a comparison. The results of each cycle test are shown in Table 5.

TABLE 5

Cycle	Ice Adhesion (kg/cm ²)		
	TYVEK® 1560B	HFP fluoropolymer coated TYVEK® 1422A	NUSIL™ R1009 (comparative)
1	0.63	0.46	1.14
2	0.55	0.57	1.25
3	0.69	0.49	1.07
4	0.65	0.60	1.14

5	0.84	0.68	1.09
6	0.39	0.48	1.01
7	0.60	0.50	0.91
8	0.60	0.58	1.08
9	0.52	0.56	1.16
10	0.59	0.52	1.15

[55] The data in Table 5 shows that both the nonwoven fabric and a nonwoven fabric coated with a layer of a fluoropolymer can sustain low levels of ice adhesion even over multiple cycles.

CLAIMS

What is claimed is:

1. A method of removing ice from a substrate comprising the steps of:
 - 1) providing a substrate that is free from ice;
 - 2) applying to at least a portion of the substrate, a nonwoven fabric having a bending modulus, as determined by ASTM D790, of less than $3,500 \text{ kg/cm}^2$, a water contact angle of greater than 65°C and a surface tension of less than 50 dyne/cm ;
 - 3) allowing ice to form on at least a portion of the applied nonwoven fabric; and
 - 4) applying a force to the ice, to the substrate, to the nonwoven fabric or a combination thereof that is sufficient to separate the ice from the nonwoven fabric; wherein a layer of the nonwoven fabric has an average ice adhesion of less than 1.76 kg/cm^2 when a shear stress force is applied to ice on the nonwoven fabric according to the following test:
 - i) a layer of the nonwoven fabric is adhered to a horizontally situated aluminum plate;
 - ii) a cuvette is placed onto the layer of nonwoven fabric;
 - iii) $0.5 \text{ cubic centimeter}$ of water is placed into the cuvette so that the water contacts the nonwoven fabric, and the water is cooled to -20°C to form ice;
 - iv) a shear stress is applied to the cuvette in a direction that is parallel to the applied layer of nonwoven fabric.
2. The method of claim 1 wherein the nonwoven fabric is a point-bonded nonwoven fabric.
3. The method of claim 1 or 2 wherein the nonwoven fabric is point-bonded polyethylene, point bonded polyolefin, needlefelt fluoropolymer, spunbond

polypropylene, spunbond polyurethane or a nonwoven blend of polypropylene, polyethylene and polyester fibers.

4. The method of any one of claims 1, 2 or 3 wherein the step of applying the nonwoven fabric to at least a portion of the substrate comprises applying a layer of adhesive to at least a portion of the nonwoven fabric, the substrate or both.
5. The method of any one of claims 1, 2, 3 or 4 wherein the substrate is an airplane wing, airplane body, wind turbine blade, wind turbine, power transmission line, power transmission tower, oil rig, marine structure, marine vessel, bridge, vehicle, building, radio antenna, cell phone tower, solar panel, glass, automobile coatings, and food containers.
6. The method of any one of claims 1, 2, 3, 4 or 5 wherein an adhesive layer is applied to the nonwoven fabric or to the substrate prior to the application of the nonwoven fabric to the substrate.
7. The method of any one of claims 1, 2, 3, 4, 5 or 6 wherein the nonwoven fabric further comprises a layer of a fluoropolymer applied to at least a portion of the nonwoven fabric.
8. The method of any one of claims 1, 2, 3, 4, 5, 6 or 7 wherein the applied layer of nonwoven fabric has an average ice adhesion of less than 1.05 kg/cm^2 .
9. The method of any one of claims 1, 2, 3, 4, 5, 6, 7 or 8 wherein the applied layer of nonwoven fabric has an average ice adhesion of less than 0.70 kg/cm^2 .
10. An article comprising a substrate, an adhesive layer applied to at least a portion of the substrate surface and a nonwoven fabric applied to at least a portion of the adhesive layer, wherein the nonwoven fabric has a bending modulus, as determined by

ASTM D790, of less than 50 kpsi (3,515 Kg/cm²), a water contact angle of greater than 65° and a surface tension of 50 dyne/cm.

11. The article of claim 10 wherein the substrate is an airplane wing, airplane body, wind turbine blade, wind turbine, power transmission line, power transmission tower, oil rig, marine structure, marine vessel, bridge, vehicle, building, radio antenna, cell phone tower, solar panel, glass, automobile coatings, and food containers.

12. The article of claim 10 or 11 wherein the nonwoven fabric is a point-bonded polyethylene, a point bonded polyolefin, a needlefelt fluoropolymer, spunbond polypropylene, spunbond polyurethane or a nonwoven blend of polypropylene, polyethylene and polyester fibers.

13. The article of any one of claims 10, 11 or 12 wherein the nonwoven fabric further comprises a layer of a fluoropolymer on at least a portion of the nonwoven fabric.

14. The article of any one of claims 10, 11, 12 or 13 wherein the nonwoven fabric has an average ice adhesion of less than 1.76 kg/cm².

15. The article of any one of claims 10, 11, 12, 13 or 14 wherein the nonwoven fabric has an average ice adhesion of less than 1.41 kg/cm².

16. The article of any one of claims 10, 11, 12, 13, 14 or 15 wherein applied layer of nonwoven fabric has an average ice adhesion of less than 1.05 kg/cm².

INTERNATIONAL SEARCH REPORT

International application No

PCT/US2014/070289

A. CLASSIFICATION OF SUBJECT MATTER

INV. B64D15/16
ADD.

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)

B64D D04H B32B

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)

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 4 875 644 A (ADAMS LOWELL J [US] ET AL) 24 October 1989 (1989-10-24) column 15, lines 22-48; figure 8c -----	1,4-6, 10,11
A	US 2 567 804 A (DAVIES JOHN M) 11 September 1951 (1951-09-11) column 5, line 61 - column 6, line 36; figure 2 -----	1,4-6, 10,11
A	EP 2 333 025 A1 (GEN ELECTRIC [US]) 15 June 2011 (2011-06-15) abstract -----	1,10
A	WO 2007/149617 A1 (3M INNOVATIVE PROPERTIES CO [US]) 27 December 2007 (2007-12-27) paragraphs [0012] - [0020] ----- -/-	1,10



Further documents are listed in the continuation of Box C.



See patent family annex.

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

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"&" document member of the same patent family

Date of the actual completion of the international search

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C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 1 826 119 A2 (GOODRICH CORP [US]; ROHR INC [US]) 29 August 2007 (2007-08-29) paragraphs [0020] - [0022] -----	1-10

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/US2014/070289

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 4875644	A	24-10-1989	BR 8905218 A 15-05-1990
		CA 2000357 A1 14-04-1990	
		CN 1041734 A 02-05-1990	
		DE 68908069 D1 09-09-1993	
		DE 68908069 T2 18-11-1993	
		EP 0363923 A2 18-04-1990	
		ES 2044012 T3 01-01-1994	
		JP H02197498 A 06-08-1990	
		US 4875644 A 24-10-1989	

US 2567804	A	11-09-1951	NONE

EP 2333025	A1	15-06-2011	CA 2723156 A1 13-06-2011
		EP 2333025 A1 15-06-2011	
		JP 2011122156 A 23-06-2011	
		US 2011143148 A1 16-06-2011	

WO 2007149617	A1	27-12-2007	CN 101466481 A 24-06-2009
		CN 103894333 A 02-07-2014	
		EP 2051821 A1 29-04-2009	
		JP 5296675 B2 25-09-2013	
		JP 2009541033 A 26-11-2009	
		US 2007298216 A1 27-12-2007	
		WO 2007149617 A1 27-12-2007	

EP 1826119	A2	29-08-2007	EP 1826119 A2 29-08-2007
		EP 2330034 A2 08-06-2011	
		US 2007210073 A1 13-09-2007	
