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(54) Title: COATING COMPOSITION FOR COATED SUBSTRATES AND METHODS OF MAKING THE SAME

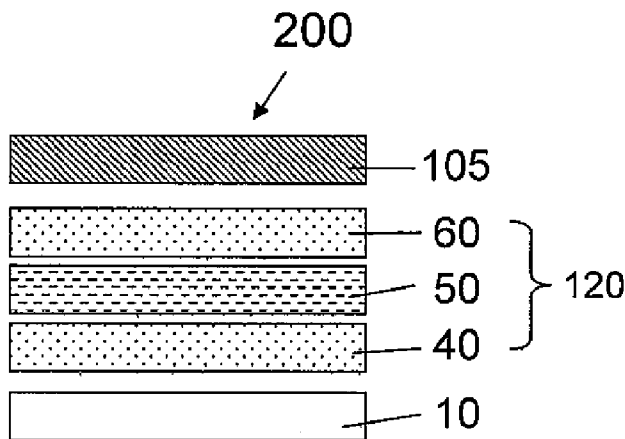


FIG. 2

(57) Abstract: A coating composition including a hydrophobic first aliphatic polyisocyanate, a second aliphatic polyisocyanate including a hydrophilic portion, a polyester polyol, a hydrophilic polyol, and a fluorinated polyol compound is disclosed. A coated substrate including a topcoat including the composition is also disclosed. Methods of forming the topcoat on a substrate are also disclosed.

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1 extreme weather conditions. As a result, coatings (e.g., organic and inorganic coatings) are employed to impart high electrical conductivity and other characteristics to the canopy.

SUMMARY

5 [0005] Aspects of embodiments of the present invention are directed toward a coating composition including a hydrophobic first aliphatic polyisocyanate, a second aliphatic polyisocyanate including a hydrophilic portion, a polyester polyol, a hydrophilic polyol, and a fluorinated polyol.

10 [0006] In some embodiments, the second aliphatic polyisocyanate further includes a hydrophobic portion. For example, the hydrophobic portion of the second aliphatic polyisocyanate includes an isophorone diisocyanate moiety or a derivative thereof. In some embodiments the hydrophilic portion of the second aliphatic polyisocyanate includes a polyether chain.

15 [0007] The second aliphatic polyisocyanate can include a polyether chain bonded to an isophorone diisocyanate trimer. In some embodiments, the hydrophobic first aliphatic polyisocyanate has an isocyanate functionality in a range of 3.0 to 4.2. The hydrophobic first aliphatic polyisocyanate can be one or more of a biuret-based polyisocyanate or an isocyanurate ring-based polyisocyanate. A weight ratio of the hydrophobic first aliphatic polyisocyanate to the second aliphatic polyisocyanate can be in a range of about 95:5 to 85:15. In some embodiments, the polyester polyol includes four hydroxyl groups.

20 [0008] In some embodiments, the polyester polyol is a polycaprolactone polyol and/or a polycaprolactone diol. The polyester polyol can include polycaprolactone having four polycaprolactone chains, and one of the four hydroxyl groups can be at a terminal end of each polycaprolactone chain. The coating composition can further include a polyester diol. In some embodiments, the polyester diol is a linear aliphatic diol having a first end including a hydroxyl group and a second end including a hydroxyl group.

25 [0009] The fluorinated polyol can include a backbone including alternating substituted or unsubstituted fluoroethylene and substituted or unsubstituted vinyl ether segments. In some embodiments, the coating composition includes a fluorinated alcohol including a perfluorinated carbon chain and a hydroxyl group. The fluorinated alcohol can further include a linking group between the perfluorinated carbon chain and the hydroxyl group. The coating composition can further include an anti-static agent including a hydroxyl group, a UV

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1 absorber including a hydroxyl group, a migratory UV absorber, a migratory UV stabilizer,
and/or a UV stabilizer including a hydroxyl group.

5 [0010] Embodiments of the present invention are also directed toward a coating formed
from the coating composition, and a coated substrate including a substrate and a topcoat
including the coating on the substrate. In some embodiments, the coated substrate further
includes an electrically conductive multilayer stack between the substrate and the coating.
The electrically conductive multilayer stack can include first and second metal oxide layers
including titanium oxide. The first metal oxide layer can include a first region, a second
10 region on the first region, and a third region on the second region, the first region and the
third region each having a higher oxygen concentration than that of the second region. The
electrically conductive multilayer stack can further include a metal layer between the first and
second metal oxide layers. In some embodiments, the metal layer includes gold.

15 BRIEF DESCRIPTION OF THE DRAWINGS

[0011] These and other features and advantages of the present invention will be better
understood by reference to the following detailed description when considered in conjunction
with the accompanying drawings, in which:

20 [0012] FIG. 1 is an exploded, cross-sectional view of a coated substrate including a
coating formed from a coating composition according to an embodiment of the invention;

[0013] FIG. 2 is an exploded, cross-sectional view of a coated substrate according to
another embodiment of the invention;

25 [0014] FIG. 3 is an exploded, cross-sectional view of a portion of an electrically
conductive multilayer stack according to an embodiment of the invention;

[0015] FIG. 4 is an exploded, cross-sectional view of a portion of an electrically
conductive multilayer stack according to an embodiment of the invention;

30 [0016] FIG. 5 is an exploded, cross-sectional view of an electrically conductive
multilayer stack according to an embodiment of the invention;

[0017] FIG. 6 is an exploded, cross-sectional view of a coated substrate according to
another embodiment of the invention;

35 [0018] FIG. 7 is an exploded, cross-sectional view of a coated substrate according to
another embodiment of the invention; and

[0019] FIG. 8 is an exploded, cross-sectional view of a coated substrate according to
another embodiment of the invention.

1 [0020] FIG. 9 is a graph comparing the light transmittance versus wavelength of light of a multilayer stack including a titanium oxide/Au/titanium oxide stack according to an embodiment of the present invention to a multilayer stack including AZO/Au/AZO and a multilayer stack including ITO/Au/ITO.

5 [0021] FIG. 10 is a schematic side view of the arrangement used in the Four Point Bend Test.

[0022] FIG. 11 is a schematic top view of a portion of the arrangement used in the Four Point Bend Test.

10 [0023] FIG. 12 is a graph comparing the results of the Four Point Bend Test for a multilayer stack including a titanium oxide/Au/titanium oxide stack according to an embodiment of the present invention to a multilayer stack including AZO/Au/AZO, a multilayer stack including ITO/Au/ITO and a multilayer stack including ITO/Ag/ITO.

15 DETAILED DESCRIPTION

[0024] In the following description and in the claims, various layers are described as being "on," "over," or "positioned over" one or more additional layers. This language simply denotes the relative positions of the layers. Thus, in some embodiments, two layers are literally right next to each other, while in other embodiments, the same two layers are separated by one or more additional layer(s). In each case, one of the two layers is considered to be "on," "over," or "positioned over" the other layer. Also, "on" or "over" can mean "below." For example, a layer that is "on" or "over" another layer can also be

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[0025] As used herein, the term "coated substrate" or "coated transparency" refers to a substrate or transparency that has been protected (e.g., coated) with one or more layer(s) on the substrate. The substrate or transparency can be made of glass or plastic, coated or uncoated, and can form a window or a windshield of a car, aircraft, boat, building, or any other suitable vehicle or structure.

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[0026] Aspects of embodiments of the present invention are directed toward a coating that is tough, durable and weather resistant, yet is still pliable and flexible. For example, aspects of embodiments of the present invention are directed toward a coating composition capable of forming a coating providing p-static charge dissipation and having good weatherability and good resistance to acid rain, chemicals (e.g., solvents), salt-fog, abrasion and rain erosion. According to embodiments of the invention, the coating can be formed

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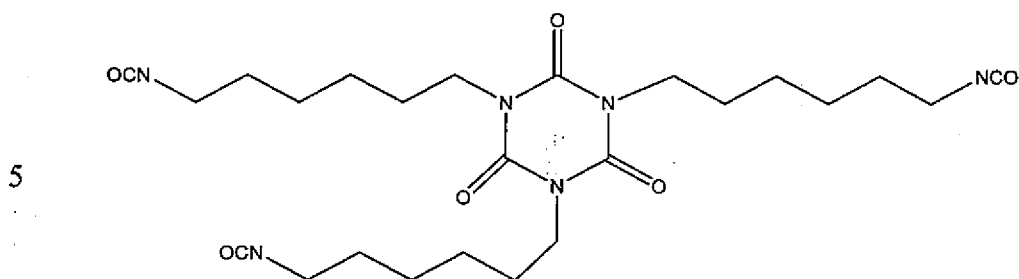
1 from a coating composition including a hydrophobic first aliphatic polyisocyanate, a second
aliphatic polyisocyanate including a hydrophilic portion, a polyester polyol, a fluorinated
polyol and a fluorinated alcohol. The coating composition can be reacted to form a coating
including a polyurethane polymer. Thus, as described herein, the coating can include the
5 various components of the coating composition in their reacted or unreacted forms, for
example, the hydrophobic first aliphatic isocyanate and polyester polyol can be included in
the coating in their reacted forms (e.g., as monomers in a urethane or carbamate polymer
linkage).

10 [0027] A variety of isocyanates and polyisocyanates (such as difunctional,
polyfunctional, aromatic, aliphatic, monomeric and oligomeric isocyanates) can be used in
coating compositions for forming polyurethane coatings. Aliphatic isocyanates have good
hydrolytic stability and UV resistance. Non-limiting examples of monomeric aliphatic
15 diisocyanates include hexamethylene diisocyanate, methylene bis-(4-cyclohexylisocyanate),
and isophorone diisocyanate. Monomeric aliphatic diisocyanates can be used to prepare
polyisocyanate adducts, prepolymers and thermoplastic polyurethanes ("TPUs"). For
example, monomeric aliphatic diisocyanates can be used to prepare biuret-based
polyisocyanates (e.g., polyisocyanates including the $-(HN-CO-)_2N-$ functional group),
20 isocyanurate ring-based polyisocyanates (e.g., isophorone diisocyanate trimers), and other
oligomers of polyisocyanates. More specifically, hexamethylene diisocyanate (HDI) can be
used to prepare the HDI-based biuret shown in Structure 1 below or the HDI-based trimer
including an isocyanurate ring shown in Structure 2 below. Isophorone diisocyanate (IPDI)
25 can be used to prepare the IPDI-based trimer shown in Structure 3 below, which is an
isocyanurate ring-based polyisocyanate. HDI trimers including an isocyanurate ring have
much lower viscosity than HDI-based biurets. IPDI trimers have lower reactivity than HDI
trimers.

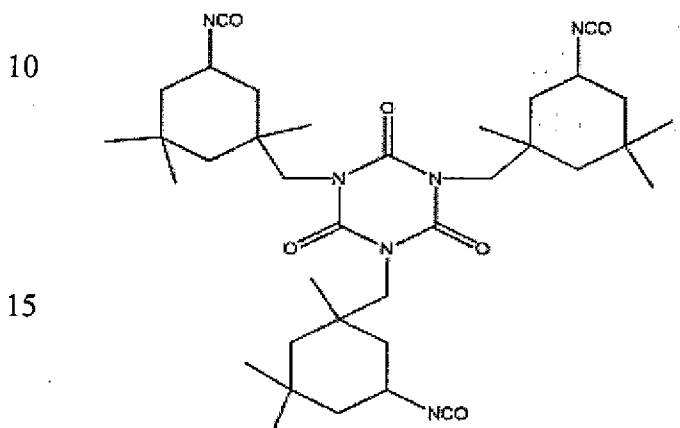
30 [Structure 1]



1 [Structure 2]



10 [Structure 3]



[0028] According to embodiments of the present invention, the first aliphatic polyisocyanate can be one or more of a biuret-based polyisocyanate, an isocyanurate ring-based polyisocyanate, or an isophorone diisocyanate oligomer. For example, the first aliphatic polyisocyanate can include one or more of the HDI-based biuret shown in Structure 1 above (or a derivative thereof), the HDI-based trimer including an isocyanurate ring shown in Structure 2 above (or a derivative thereof), or the IPDI-based trimer shown in Structure 3 above (or a derivative thereof). Non-limiting commercially available examples of the first aliphatic polyisocyanate (or mixtures including the first aliphatic polyisocyanate) include methylene bis-(4-cyclohexylisocyanate) (e.g., DESMODUR® W), methylene 1,6-hexamethylene diisocyanate-based polyisocyanates (e.g., DESMODUR® N-75, DESMODUR® N-100, DESMODUR® N-3200, DESMODUR® N-3300, DESMODUR® N-3600, and DESMODUR® N-3790) and isophorone diisocyanate-based polyisocyanates (e.g., DESMODUR® Z-4470) (each available from Bayer Material Science). DESMODUR® is a registered trademark of Bayer Material Science, Leverkusen, Germany. Some of the foregoing examples include an aliphatic polyisocyanate dispersed in (or diluted with) a solvent, which reduces the viscosity of the polyisocyanate, thereby improving ease of handling the first aliphatic polyisocyanate.

1 [0029] The first aliphatic isocyanate can have a functionality of 3 or more (e.g., have 3 or
more isocyanate functional groups). In some embodiments, the first aliphatic polyisocyanate
has an isocyanate functionality in a range of 3.0 to 4.2. For example, the first aliphatic
polyisocyanate can have an isocyanate functionality of about 3.2, 3.5, 3.8 or 4.1. In some
5 embodiments, for example, the first aliphatic polyisocyanate can have an isocyanate
functionality of about 3.8

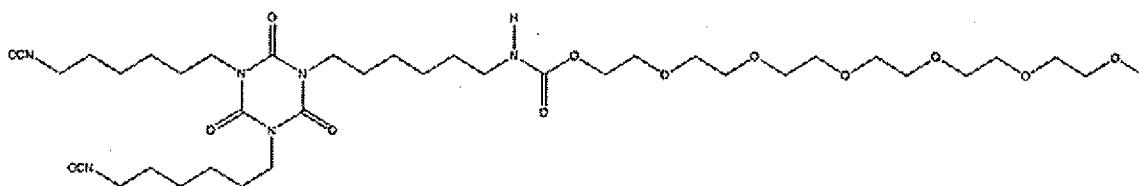
[0030] According to embodiments of the present invention, a coating composition
including the first aliphatic polyisocyanate described herein (e.g., an HDI biuret-based
10 polyisocyanate) is capable of forming an elastic coating (or film) having good low
temperature flexibility, thereby providing resistance to rain erosion that is not achieved with
other polyisocyanates. The coating may also have good weatherability and mechanical
strength. Some examples of the coating composition including an HDI biuret-based
polyisocyanate formed a coating having good durability, but reduced resistance to rain
15 erosion. Some examples of the coating composition including an isocyanurate ring-based
polyisocyanate (e.g., an HDI trimer-based polyisocyanate) formed a coating having good
resistance to rain erosion, but reduced chemical (e.g., solvent) resistance. Some examples of
the coating composition including an isocyanurate ring-based polyisocyanate formed a
20 coating having a relatively short tack-free time and good chemical resistance, but, due to the
high T_g of the isocyanurate ring-based polyisocyanate (~ 60 °C), the resultant coating was
rigid and had poor resistance to rain erosion. In comparison, the T_g of some HDI biuret-
based polyisocyanates (e.g., DESMODUR® N-75 and DESMODUR® N-100) is about -60
25 °C.

[0031] According to embodiments of the invention, the coating composition further
includes a second aliphatic polyisocyanate including a hydrophilic portion. The hydrophilic
portion of the second aliphatic polyisocyanate can include a polyether chain. In some
30 embodiments, the second aliphatic polyisocyanate further includes a hydrophobic portion.
The hydrophobic portion of the second aliphatic isocyanate can include an isophorone
diisocyanate moiety or a derivative thereof. Non-limiting, commercially available examples
of the second aliphatic polyisocyanate (or mixtures including the second aliphatic
polyisocyanate) include polyether modified HDI trimer-based polyisocyanates (e.g.,
35 BAYHYDUR® 302 and BAYHYDUR® 303), polyether modified HDI allophonate-based
polyisocyanates (e.g., BAYHYDUR® 304, and/or BAYHYDUR® 305), isophorone
diisocyanate-based hydrophilically modified aliphatic polyisocyanate (e.g., polyether

1 modified isophorone diisocyanate trimer, such as BAYHYDUR® 2150BA and/or
BAYHYDUR® 401-70), ionic aminosulfonic acid modified HDI polyisocyanates (e.g.,
BAYHYDUR® XP2547, BAYHYDUR® XP2487/1, and/or BAYHYDUR® XP 2655)
5 (each available from Bayer Material Science). BAYHYDUR® is a registered trademark of
Bayer Material Science. The second aliphatic polyisocyanate can have a functionality of 2 or
more (e.g., 2 or more isocyanate functional groups).

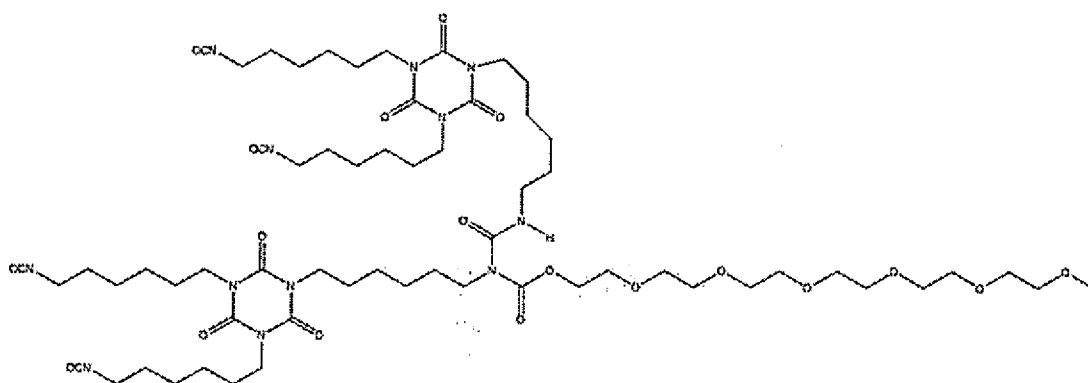
[0032] An example of a polyether modified HDI trimer-based polyisocyanate (non-ionic)
is shown as Structure 4 below, which is hydrophilic and readily dispersible in water.
10 Examples of the coating composition including a polyether modified HDI trimer-based
polyisocyanate (non-ionic) as the second aliphatic polyisocyanate formed coatings having
enhanced anti-static properties, but the coatings exhibited reduced integrity against certain
tests such as the humidity test and 50/50 - water/IPA test, which are described in more detail
15 below. Accordingly, while these polyisocyanates may be used as the second aliphatic
polyisocyanate, other polyisocyanates may provide better coating integrity.

[Structure 4]



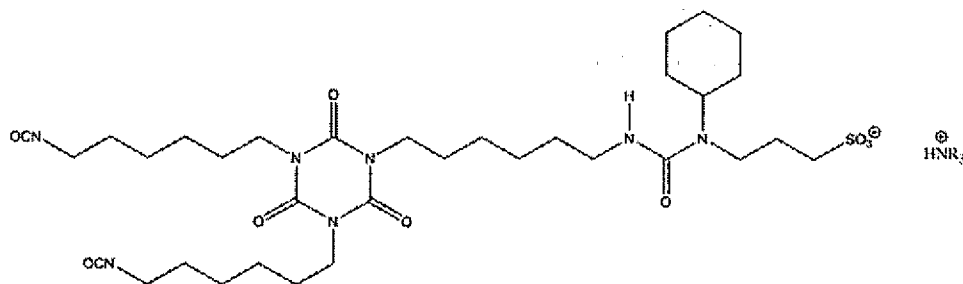
[0033] An example of a polyether modified HDI allophanate-based polyisocyanate is
shown as Structure 5 below, which is more hydrophobic than the polyether modified HDI
25 trimer-based polyisocyanates (non-ionic) described above, and has higher NCO functionality.
Examples of the coating composition including a polyether modified HDI allophanate-based
polyisocyanate as the second aliphatic polyisocyanate formed coatings having enhanced film
durability and resistance, but the coatings exhibited reduced static charge dissipation,
30 particularly at -40 °F. Accordingly, while these polyisocyanates may be used as the second
aliphatic polyisocyanate, other polyisocyanates may provide better charge dissipation.

[Structure 5]



[0034] An example of an ionic aminosulfonic acid modified HDI polyisocyanate is shown as Structure 6 below, which has high NCO functionality. Ionic aminosulfonic acid modified HDI polyisocyanates (CAPS) are commercially available from Bayer Material Science as BAYHYDUR® XP2547, BAYHYDUR® XP2487/1, and BAYHYDUR® XP 2655. Examples of the coating composition including an ionic aminosulfonic acid modified HDI polyisocyanate as the second aliphatic polyisocyanate formed coatings having good chemical (e.g., solvent) resistance, but the coatings exhibited minimal improvement in anti-static properties. Accordingly, while these polyisocyanates may be used as the second aliphatic polyisocyanate, other polyisocyanates may provide better anti-static properties.

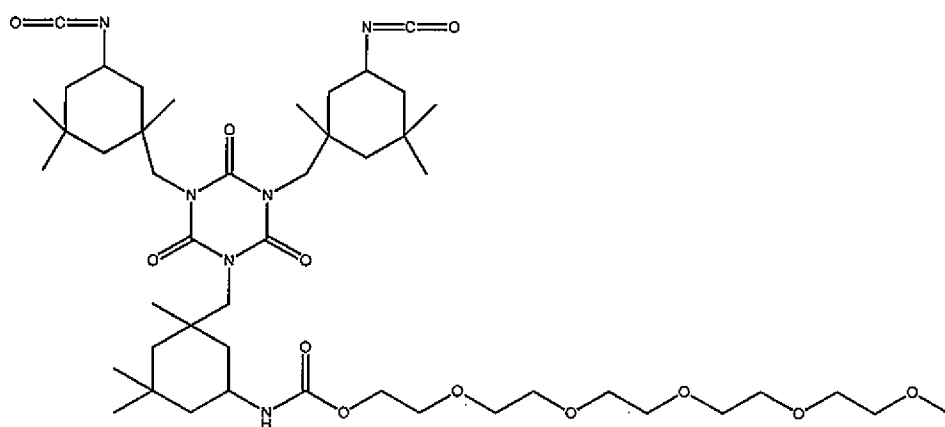
[Structure 6]



[0035] In some embodiments, the second aliphatic polyisocyanate includes a polyether modified IPDI trimer, which includes a polyether chain bonded to an isophorone diisocyanate trimer. An example of a polyether modified IPDI trimer-based polyisocyanate is shown as Structure 7 below. Examples of the coating composition including a polyether modified IPDI trimer-based polyisocyanate as the second aliphatic polyisocyanate unexpectedly formed coatings having good film integrity as well as good static charge dissipation properties. A commercial example of a polyether modified IPDI trimer-based polyisocyanate is BAYHYDUR® 401-70, which has a T_g of about 30 °C, forms coatings having an improved time to tack-free (i.e., a shorter time to become tack-free), reduced surface tackiness, and

1 enhanced anti-static properties. However, when excessive amounts of polyether modified
IPDI trimer-based polyisocyanate are included in the coating composition as the second
aliphatic isocyanate, the coating formed from the coating composition exhibits reduced
resistance to rain erosion, increased sensitivity to humidity, and reduced Bayer abrasion
5 resistance. Accordingly, in some embodiments, a weight ratio of the hydrophobic first
aliphatic polyisocyanate to the second aliphatic polyisocyanate is in a range of 95:5 to 85:15,
such as, for example, a ratio of 95:5, 92:8, 90:10, 87:13 or 85:15.

[Structure 7]



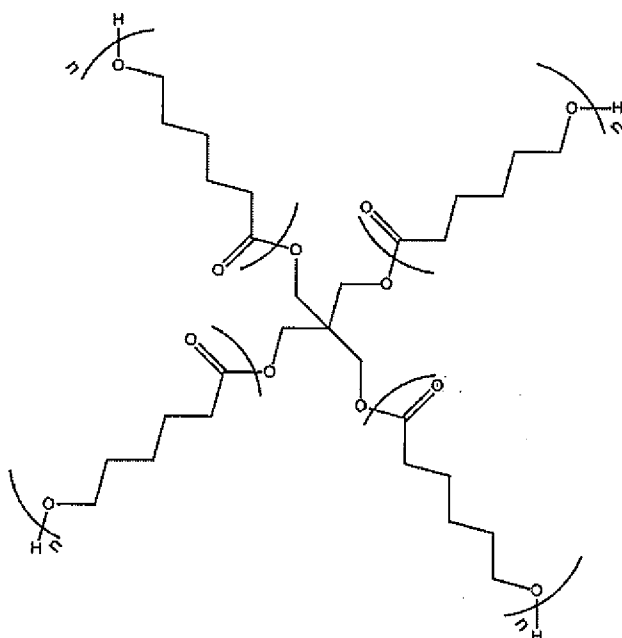
[0036] In some embodiments, the coating composition further includes a polyester
polyol. For example, the polyester polyol can be an aliphatic compound having 2 to 4
hydroxyl groups or a mixture of aliphatic compounds having an average of 2 to 4 hydroxyl
groups. The polyester polyol can provide crosslinking and resiliency to a coating formed
from the coating composition. Non-limiting examples of the polyester polyol include
25 polycaprolactone polyols and diols. For example, the polyester polyol can be a
polycaprolactone polyol, polycaprolactone diol, or mixture thereof having a weight average
molecular weight in a range of 300 to 5,000 g/mole, for example, 500 to 1,500 g/mol, and in
some embodiments, about 1,000 g/mol.

[0037] Polycaprolactone polyols and diols can be prepared using ring-opening
30 polymerization under mild conditions resulting in well-controlled polymerization resulting in
no or few byproducts (e.g., water). Polycaprolactone polyols and diols prepared using ring-
opening polymerization have low acid values, highly defined functionality, low
polydispersity indexes and can be prepared with very high reproducibility. Polycaprolactone
35 polyols and diols can also be prepared with low levels of impurities, are non-toxic and
biodegradable, and have high flexibility at low-temperatures, good hydrolytic stability, good
tear strength, consistent reactivity and low viscosity (as compared to other polyols). The high

1 flexibility and good tear strength of polycaprolactone polyols and diols can impart resiliency
to a coating formed from a coating composition including a polycaprolactone polyol and/or
polycaprolactone diol. Coatings having improved resiliency exhibit enhanced Bayer abrasion
(described in more detail below) and rain erosion resistance properties. Additionally, the low
5 viscosity of polycaprolactone polyols and diols is beneficial for coating compositions having
a high solids content. In some embodiments, the polyester polyol includes a
polycaprolactone polyol, a polycaprolactone diol or a mixture thereof.

[0038] In some embodiments, the polyester polyol is a polycaprolactone polyol including
10 four hydroxyl groups. For example, the polyester polyol may be a polycaprolactone polyol
including four polycaprolactone chains. In some embodiments, each of the polycaprolactone
chains includes one of the four hydroxyl groups at a terminal end of the polycaprolactone
chain. An example of the polyester polyol (e.g., a polycaprolactone polyol) is shown as
15 Structure 8 below. In the polyester polyol shown as Structure 8, n may be in a range of 1 to
6, such as in a range of 2 to 4. For example, in the polyester polyol shown as Structure 8, n
may have an average value of 2. When the polyester polyol is a polycaprolactone polyol
including four polycaprolactone chains including one hydroxyl group at a terminal end of
20 each polycaprolactone chain, the coating composition may form a coating having enhanced
crosslink density, which in turn improves the resistance of the coating to salt-fog and SO₂,
chemicals (e.g., solvents), and inorganic acids (e.g., sulfuric acid and nitric acid).
Additionally, the resultant coating may still have suitable flexibility due to the presence of the
caprolactone units (e.g., 1 to 6 units of caprolactone) in each of the four chains.

[Structure 8]

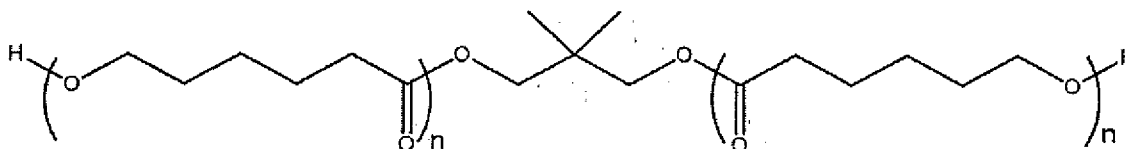


[0039] In some embodiments, the polyester polyol is a polyester diol. The polyester diol may be a linear aliphatic diol having a first end including a hydroxyl group and a second end including another primary hydroxyl group. The primary hydroxyl groups may be connected by a polycaprolactone backbone. An example of the polyester polyol (e.g., a polycaprolactone diol) is shown as Structure 9 below. In the polyester diol shown as Structure 9, n may be in a range of 1 to 8, such as in a range of 2 to 6. For example, in the polyester polyol shown as Structure 9, n may have an average value of 4.

[0040] When the coating composition includes a polyester polyol, such as a polycaprolactone diol, a coating formed from the coating composition has enhanced resiliency. For example, the relatively long polycaprolactone backbone between the hydroxyl groups may provide the coating with enhanced resiliency. Example embodiments of the coating prepared without the polyester diol, but including another polyester polyol, exhibited resistance to Bayer abrasion (described in more detail below) after 600 strokes of about 3 to 4%, while example embodiments of the coating prepared with the polyester diol exhibited resistance to Bayer abrasion of less than 1% after 600 strokes. Including the polyester diol in the coating composition in excess increases the tackiness of coatings formed from the coating composition and reduces the chemical (e.g., solvent) resistance of the coating. Accordingly, in some embodiments, the polyester polyol and the polyester diol are present in the coating composition at a weight ratio of 95:5 to 50:50, for example at a weight ratio 75:25. Non-limiting, commercially available examples of the polyester polyol and the polyester diol

1 include Capa™ 2101, Capa™ 3031, Capa™ 3041 and Capa™ 4101, each of which are available from Perstop Group, Perstop, Sweden.

[Structure 9]



10 [0041] In some embodiments, the coating composition further includes a fluorinated alcohol. For example, the fluorinated alcohol can have one reactive functional group (e.g., a hydroxyl group). By having one reactive group, the fluorinated alcohol can be a migratory fluorinated compound capable of migrating to a surface of the coating composition during formation (e.g., reaction or curing) of the coating. While the extent of the migration of the first fluorinated compound (e.g., the migratory fluorinated compound) is not fully known, based on the acid resistance of the coating formed from the composition and the observed contact angle of water on the coating, it is believed that at least some of the fluorinated alcohol (e.g., the migratory fluorinated compound) migrates to the surface of the coating composition (e.g., the surface of a coating formed from the coating composition).

15 [0042] It is believed that the migration of the fluorinated alcohol to the surface of the coating composition (or the surface of the coating) improves the surface hydrophobicity of the resultant coating and enhances resistance of the coating to acid rain and humidity. In some embodiments, the fluorinated alcohol has a relatively low molecular weight to improve migration of the fluorinated alcohol. For example, the fluorinated alcohol may have a weight average molecular weight in a range of about 300 g/mole to about 400 g/mole, such as a weight average molecular weight of about 364 g/mole. The fluorinated alcohol can include a perfluorinated carbon chain and a hydroxyl group. The fluorinated alcohol can also include a linking group between the perfluorinated carbon chain and the hydroxyl group. Non-limiting examples of the linking group include alkylene groups, such as ethylene, propylene and vinylene groups, and sulfonamide groups.

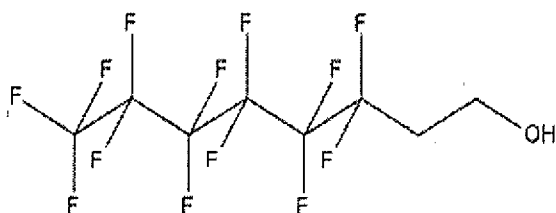
20 [0043] According to embodiments of the invention, a coating formed from the coating composition can include the fluorinated alcohol at a surface of the coating. By including the fluorinated alcohol at a surface of the coating, the hydrophobicity and acid resistance of the surface of the coating are increased, thereby increasing the corrosion resistance of the coating. The presence of the fluorinated alcohol at a surface of the coating composition (or

the coating) also increases the corrosion resistance of a coated substrate including the coating composition, for example, as a coating. The fluorinated alcohol may be included in the coating composition in an amount in a range of about 0.1 wt% to about 5 wt%, for example, 1 wt%, based on the total weight of the solids content of the coating composition.

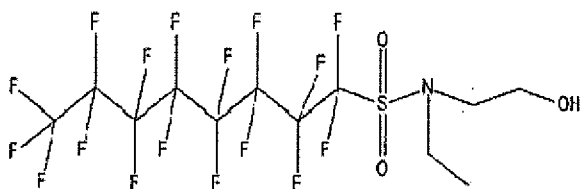
[0044] In some embodiments, the fluorinated alcohol is a partially fluorinated compound including a hydroxyl group. For example, in certain portions of the compound, most or all of the hydrogen atoms can be replaced with fluorine atoms, while other portions of the compound can include hydrogen bonded to carbon. In other embodiments, the fluorinated alcohol is a perfluorinated compound including a perfluorinated carbon backbone and a hydroxyl group. As would be understood by those of ordinary skill in the art, a "perfluorinated" compound (or chain) is a compound (or chain) in which all hydrogen atoms bonded to carbon atoms are replaced with fluorine atoms. The fluorinated alcohol can have a carbon backbone having 1 to 20 carbon atoms.

[0045] Non-limiting examples of the fluorinated alcohol include perfluorinated or partially fluorinated aliphatic compounds. For example, commercially available perfluorinated aliphatic compounds and/or solutions of perfluorinated aliphatic compounds such as, for example, N-ethyl-N-(2-hydroxyethyl)perfluorooctylsulphonamide (e.g., FLUORAD™ FC-10; available from 3M Company, St. Paul, Minnesota); and 3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluoro-1-octanol (e.g., CAPSTONE™ 62-AL), and perfluoroalkyl-1-ethanol (e.g., ZONYL® BA) (each available from E.I. du Pont de Nemours and Company, Wilmington, Delaware) can be used. ZONYL® is a registered trademark of E.I. du Pont de Nemours and Company. Examples of the fluorinated alcohol include Structures 10 and 11 below

[Structure 10]



[Structure 11]



1 [0046] In some embodiments, the coating composition further includes a fluorinated
polyol. The fluorinated polyol can be a compound having a carbon backbone with 1 to 20
carbon atoms, and two or more reactive groups, such as hydroxyl groups. That is, the
fluorinated polyol can be multifunctional. For example, the fluorinated polyol can be
5 bifunctional, such as a compound having two or more hydroxyl groups. As a result of having
two or more reactive functional groups, the fluorinated polyol can react to form a three-
dimensional network. In contrast to the fluorinated alcohol, the majority of the fluorinated
polyol does not migrate to a surface of the coating composition (or a surface of a coating
10 formed from the composition) and instead is distributed across the thickness of the coating
composition or coating (e.g., is distributed throughout the bulk material of the coating
composition, or the bulk material of a coating formed from the coating composition). The
fluorinated polyol improves the bulk hydrophobicity of a coating formed from the coating
15 composition, thereby improving the acid rain resistance of the coating. Existing coatings
(e.g., topcoats), such as FX-446 (available from PPG Industries Inc.), provide some acid rain
resistance, but coatings according to embodiments of the present invention including the
fluorinated polyol (or a reacted fluorinated polyol) in the bulk of the coating provide
improved acid rain resistance compared to existing coatings.

20 [0047] Inclusion of the fluorinated polyol causes the coating composition to form a three-
dimensional polymer network. Specifically, the two or more reactive functional groups (e.g.,
hydroxyl groups) of the fluorinated polyol each react with other polymer molecules to form
the three-dimensional network structure. The rigidity of the three-dimensional polymer
25 network formed with the fluorinated polyol affects the resiliency of a coating formed from
the coating composition. Similarly, other components of the coating composition, such as
non-fluorinated polyols (e.g., the aliphatic polyester polyols), can also form part of the three-
dimensional network and contribute to the resiliency of a coating formed from the
composition. As an example, the rigidity of the three-dimensional network of the
30 composition is influenced, in part, by the number of reactive functional groups (e.g., hydroxyl
groups) contained in the fluorinated polyol. Thus, the number of reactive functional groups
of the fluorinated polyol will affect the resiliency of a coating formed from the coating
composition. Similarly, the number of reactive functional groups (e.g., hydroxyl groups)
35 included in the non-fluorinated polyol (e.g., the polyester polyol) will also affect the
resiliency of a coating formed from the coating composition.

1 [0048] In general, greater crosslink density (which is directly related to the number of
reactive functional groups (e.g., hydroxyl groups) included in each of the components of the
composition) leads to greater rigidity, improved chemical and solvent resistance, and
5 decreased abrasion resistance. The resiliency of a coating formed from the coating
composition is also influenced by the molecular weight, and size and type of the backbone of
the fluorinated and non-fluorinated compounds in the coating composition. When the
composition includes compounds that have more rigid backbone structures, the composition
will also be more rigid, while compounds that have relatively more flexible backbone
10 structures will produce a composition that has relatively more resiliency. For a given polyol,
increasing the molecular weight of the polyol generally results in a compound that forms
coatings having greater resiliency, as compared to the corresponding lower molecular weight
polyols.

15 [0049] Accordingly, the desired resiliency of the composition can be achieved by
appropriately selecting the number of reactive functional groups (e.g., hydroxyl groups) and
molecular weights of the fluorinated compounds or the non-fluorinated compounds. For
example, a fluorinated polyol having a fluorinated carbon backbone and two reactive
functional groups (e.g., two hydroxyl groups) will form a three-dimensional network that is
20 more flexible than the three-dimensional network formed by a fluorinated polyol having
similar chemical composition, the same (or substantially the same) molecular weight, and a
fluorinated carbon backbone and three reactive groups (e.g., three hydroxyl groups).
Similarly, a fluorinated polyol having three reactive functional groups (e.g., three hydroxyl
25 groups) will form a three-dimensional network that is more flexible than the three-
dimensional network formed by a fluorinated polyol having the same (or substantially the
same) chemical structure, the same (or substantially the same) molecular weight, a
fluorinated carbon backbone, but four reactive groups (e.g., four hydroxyl groups).
Increasing the flexibility of the three-dimensional network resulting from use of a fluorinated
30 polyol having two hydroxyl groups increases the resiliency of a coating formed from the
coating composition. Thus, in some embodiments, the coating composition (or coating)
includes a bifunctional fluorinated polyol (e.g., a compound having two hydroxyl groups),
such coating compositions produce coatings having increased resiliency over coatings
35 produced from coating compositions including trifunctional or tetrafunctional fluorinated
polyols (e.g., compounds having three or four hydroxyl groups, respectively). The above-
described principles are also applicable to other components of the coating composition, such

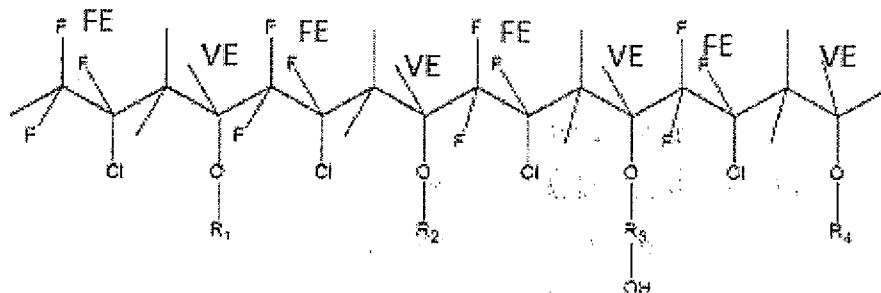
1 as the non-fluorinated compounds. For example, desirable resiliency of the coating) can be achieved using an appropriate mixture of non-fluorinated di-functional and tetra-functional polyester polyols in the coating composition.

5 [0050] Non-limiting examples of the fluorinated polyol include fluoropolymers and fluoropolymer precursors, examples of which include, but are not limited to, commercially available pure resins and/or solutions of fluoropolymers and/or fluoropolymer precursors such as LUMIFLON® LF 600X, LUMIFLON® LF 9716, LUMIFLON® LF 9721, LUMIFLON®-910LM and LUMIFLON® LF 916F (available from AGC Chemicals Inc.,
10 Exton, Pennsylvania); FLUOROLINK® D10-H, FLUOROLINK® E10-H, FLUOROLINK® D, FOMBLIN® ETX, FOMBLIN® MF-402 and FLUOROBASE Z-1030 (each available Solvay Solexis, Inc.); and POLYFOX® PF-656 and POLYFOX® PF-7002 (available from Omnova Solutions, Fairlawn, Ohio). LUMIFLON® is a registered trademark of Asahi Glass Co., Ltd., FLUOROLINK® is a registered trademark of Solvay Solexis, Inc., FOMBLIN®
15 is a registered trademark of Solvay-Fluorati Holding S.P.A., Corporation and POLYFOX® is a registered trademark of Ampac Fine Chemicals LLC.

20 [0051] Of the foregoing examples of the fluorinated polyol, LUMIFLON®-910LM, which is a fluoroethylene vinyl ether, exhibited the best compatibility with the other components of the coating composition. LUMIFLON®-910LM was compatible with the other components of the coating composition throughout a wide range of amounts. The alternating fluoroethylene and vinyl ether segments of LUMIFLON®-910LM provide the resultant coating with good weatherability. For example, the fluoroethylene segments may
25 enhance durability and hydrophobicity of the resultant coating. Accordingly, in some embodiments, the fluorinated polyol includes a backbone including alternating substituted or unsubstituted fluoroethylene and substituted or unsubstituted vinyl ether segments. An example of the fluorinated polyol is shown as Structure 12 below, in which "FE" indicates a repeating fluoroethylene unit and "VE" indicates a repeating vinyl ether unit. In Structure 12,
30 R₁ may provide transparency, gloss and hardness; R₂ may provide flexibility; R₃ may provide crosslinking ability; and R₄ may provide adhesion.

35

1 [Structure 12]



10 [0052] The fluorinated polyol can be included in the coating composition in an amount in a range of about 5 wt% to about 35 wt%, such as in a range of about 15 wt% to about 25 wt%, based on the total weight of the solids in the coating composition. In some

15 embodiments, the fluorinated polyol is present in an amount of about 20 wt% based on the total weight of the solids in the coating composition. At 5 wt% and 10 wt% of the fluorinated polyol, there was some improvement in the acid resistance of the resultant coating. At 15 wt% and 20 wt% of the fluorinated polyol, the resultant coating exhibited substantially

20 enhanced resistance to sulfuric acid and nitric acid (e.g., a 50:50 mixture of sulfuric acid and nitric acid) as compared to existing coatings, such as FX-446. The resultant coating also exhibited improved surface tackiness and steam, humidity and QUV resistance as compared to existing coatings, such as FX-446. Unexpectedly, the fluorinated polyol did not noticeably

25 reduce the anti-static properties of the coating. However, the fluorinated polyol does reduce the Bayer abrasion resistance of the resultant coating. For example, one example of the coating composition including 20 wt% of the fluorinated polyol (based on the total weight of the solids in the coating composition) formed a coating that exhibited a change in haze of 3.5-

3.0% after 600 strokes of the Bayer abrasion test (described in more detail below), while an example of the coating composition that did not include the fluorinated polyol exhibited a change in haze of about 1% after 600 strokes of the Bayer abrasion test.

30 [0053] The coating composition described herein can be formed by mixing (or blending) a Part A mixture (e.g., a base component) with a Part B mixture (e.g., a curing component). For example, the Part A mixture and the Part B mixture can be mixed together and cured to form a durable composition (or coating) which is highly weatherable, abrasion resistant, acid resistant and resistant to chemicals or solvents. After mixing the Part A mixture and the Part

35 B mixture, the resultant coating composition can be air dried for a time period in a range of 1.5 to 2 hours and then cured at about 200 °F for a time period of about 5 hours to form a

1 coating. For example, the coating composition (or coating) can form a polyurethane coating having anti-static properties.

5 [0054] The Part A mixture and Part B mixture may be mixed to achieve a ratio of reactive isocyanate groups to reactive hydroxyl groups (e.g., an NCO to OH ratio) in a range of 1.05 to 1.5, such as a ratio of about 1.3. An NCO to OH ratio of about 1.05 resulted in a coating exhibiting good abrasion resistance, but compromised QUV resistance (described in more detail below). An NCO to OH ratio of about 1.3 resulted in a coating exhibiting good abrasion resistance, good QUV resistance, and good resistance to rain erosion. An NCO to OH ratio of about 1.4 resulted in a coating exhibiting good QUV resistance, but lower abrasion resistance and inferior resistance to rain erosion, as compared to the coating formed from the coating composition having an NCO to OH ratio of about 1.3. An NCO to OH ratio of about 1.5 resulted in a coating composition having a short pot life, poor surface flow and poor cosmetics.

15 [0055] The Part A mixture can include, for example, any or all of the polyester polyol (e.g., the first and/or second polyester polyol), the fluorinated polyol, the hydrophilic polyol and the fluorinated alcohol. The Part A mixture can further include additives, such as, for example, a migratory ultraviolet light (UV) absorber, a reactive UV absorber including a hydroxyl group, a migratory UV stabilizer, a reactive UV stabilizer including a hydroxyl group, an antistatic agent (e.g., a conductive compound); an antioxidant, a catalyst, a flow control agent and/or a solvent. However, the Part A mixture need not contain each of these components. The Part A mixture can include additional additives as well.

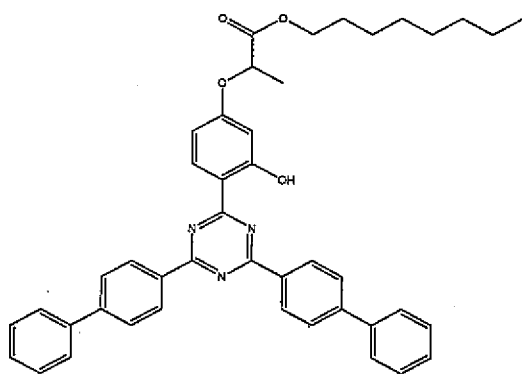
25 [0056] A migratory UV absorber and/or a reactive UV absorber may be included in the coating composition to absorb UVA and UVB radiation incident to the resultant coating. UV absorbers increase the resistance of the resultant coating to yellowing and/or degradation, and improve long term outdoor durability of the coating. The migratory UV absorber and reactive UV absorber can be based upon any suitable UV absorber. The migratory UV absorber does not include a reactive functional group (e.g., a hydroxyl group) and migrates to a surface of the coating composition (or coating) during the formation (e.g., curing) of the coating composition (or coating). By including the migratory UV absorber, the coating includes a higher concentration of UV absorber at the surface of the composition than a coating not including a migratory UV absorber. Having a higher concentration of UV absorber at the surface of the composition (or coating) improves the lifetime of the coating made from the composition. However, it is desirable to also have UV absorber in the bulk of

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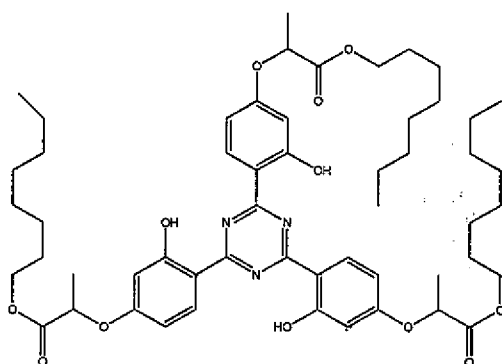
1 the composition, as having UV absorbers both at the surface of the composition and in the
bulk of the composition will extend the lifetime of a coating made from the composition as
compared to a coating made from a composition that only includes UV absorber at the
surface.

5 [0057] Additionally, if the compounds migrate to a surface of the composition too
quickly, the composition may form haze. For example, UV absorbers that do not include a
hydroxyl group (e.g., a reactive hydroxyl group) may migrate to the surface of the coating too
quickly resulting in haze. Accordingly, in some embodiments, the coating composition
10 includes the migratory UV absorber only in small amounts (e.g., in a range of about 0.5 wt%
to about 0.75 wt% based on the total weight of the solids of the coating composition), if at all.
Examples of migratory UV absorbers are shown as Structures 13-17 below.

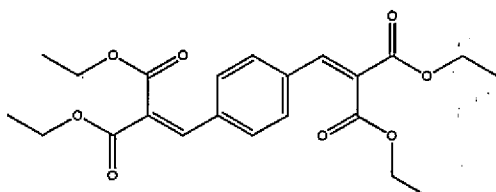
[Structure 13]



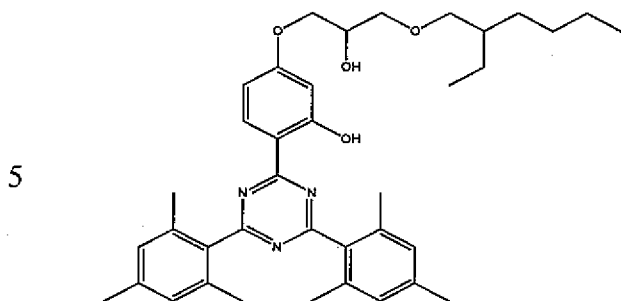
[Structure 14]



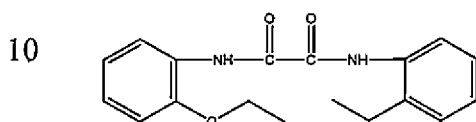
[Structure 15]



1 [Structure 16]

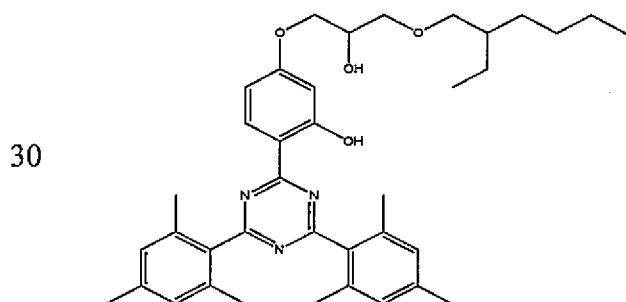


10 [Structure 17]



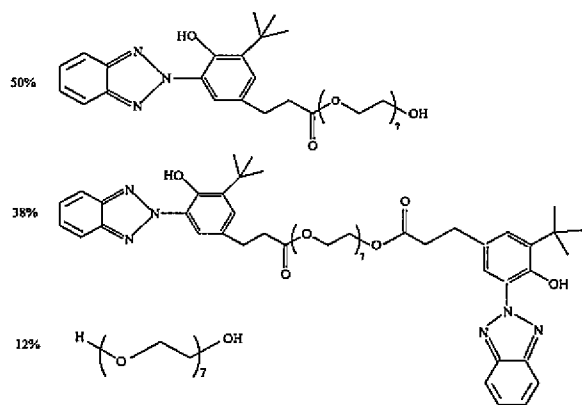
[0058] A coating composition according to embodiments of the present invention can include reactive UV absorber as well as, or instead of, the migratory UV absorber. The reactive UV absorber can include one or more reactive functional groups, such as a hydroxyl group. By including the reactive groups, a majority of the reactive UV absorber does not migrate to the surface of the coating composition or the resultant coating and instead is distributed across the thickness of the coating composition or resultant coating (e.g., is distributed throughout the bulk of the coating composition or the resultant coating). Additionally, if the reactive UV absorber is multifunctional, it may contribute to the three-dimensional polymer network formed on reaction of the components of the composition. A non-limiting example of the reactive UV absorber is shown as Structure 18 below, and an example of a commercially available mixture of a migratory UV absorber and a reactive UV absorber is shown as Structure 19 below.

15 [Structure 18]



35

[Structure 19]



TINUVIN 1130

[0059] Non-limiting commercially available examples of the migratory UV absorber and reactive UV absorber include propanoic acid,2-[4-[4,6-bis([1,1'-biphenyl]-4-yl)-1,3,5-triazin-2-yl]-3-hydroxyphenoxy]-,isooctyl ester (e.g., TINUVIN® 479), β -[3-(2-H-benzotriazole-2-yl)-4-hydroxy-5-t-butylphenyl]-propionic acid-poly(ethylene glycol) 300 ester, *bis*{ β -[3-(2-H-benzotriazole-2-yl)-4-hydroxy-5-t-butylphenyl]-propionic acid}-poly(ethylene glycol) 300 ester (e.g., TINUVIN® 1130), TINUVIN® 477 and 2-[4-[(2-hydroxy-3-(2'-ethyl)hexyl)oxy]-2-hydroxyphenyl]-4,6-*bis*(2,4-dimethylphenyl)-1,3,5-triazine (e.g., TINUVIN® 405) (each available from BASF Resins); and p-phenylenebis(methylenemalonic acid)tetraethyl ester (e.g., HOSTAVIN® B-CAP), 2-ethyl,2'-ethoxy-oxalanilide (e.g., HOSTAVIN® VSU), and propanedioic acid,2-[(4-methoxyphenyl)methylene]-,1,3-dimethylester (e.g., HOSTAVIN® PR-25) (each available from Clariant International Ltd.). TINUVIN® is a registered trademark of Ciba Specialty Chemical Corporation. HOSTAVIN® is a registered trademark of Hoechst GMBH Corporation.

[0060] Example coatings formed from coating compositions including the UV absorber according to Structure 18 exhibited no discernible sign of haze formation. It is believed that the presence of the hydroxyl group of the foregoing reactive UV absorbers prevented (or reduced) the migration of the UV absorbers to the surface of the coating by reacting with isocyanate functional groups to form urethane linkages and becoming part of the three-dimensional network, thereby preventing (or reducing) the formation of haze. TINUVIN® 1130 includes both a reactive UV absorber and a migratory UV absorber and, therefore, may cause haze in the coating when used in excess. The migratory UV absorber may be included in the coating composition in a small amount without causing haze in the resultant coating. For example, the migratory UV absorber shown as Structure 13 can be included in the coating composition in an amount in a range of about 0.5 wt% to about 0.75 wt% based on

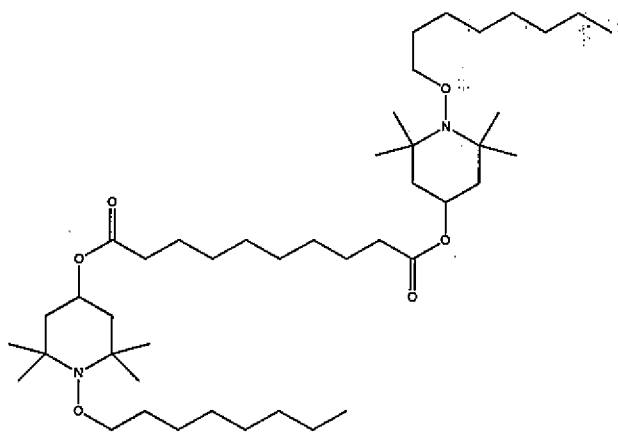
1 the total weight of the solids of the coating composition without causing noticeable haze in
the resultant coating, while also enhancing the QUV resistance of the resultant coating. It is
believed that the migratory UV absorber shown as Structure 13 will be present at a higher
concentration at the surface of the resultant coating than in the bulk material of the coating,
5 thereby providing additional protection against UV light. Some UV absorbers, such as
HOSTAVIN® B-CAP, exhibited poor solubility as a result of poor compatibility with the
other components of the coating composition.

[0061] The migratory UV stabilizer and reactive UV stabilizer can be based upon any
10 suitable UV stabilizer, such as any suitable free radical scavenger, that has been modified to
be reactive or migratory. The migratory UV stabilizer and reactive UV stabilizer reduce
degradation of the coating by UV light by scavenging free radicals formed by the dissociation
of chemical bonds as a result of UV light absorption. The migratory UV stabilizer does not
15 include a reactive functional group (e.g., a hydroxyl group) and migrates to the surface of the
coating during the formation (e.g., curing) of the coating. By including the migratory UV
stabilizer, the coating includes a higher concentration of the UV stabilizer at the surface of
the coating than does a coating not including a migratory UV stabilizer. Having a higher
concentration of UV stabilizer at the surface of the coating improves the lifetime of the
20 coating, and hence improves the lifetime of a coating formed from the coating composition.

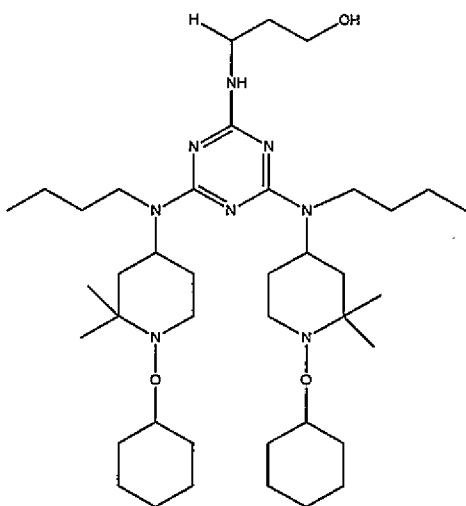
[0062] However, it is desirable to also have UV stabilizers in the bulk of the coating, as
having UV stabilizers both at the surface of the coating and in the bulk of the coating will
extend the lifetime of the coating as compared to a coating that only includes UV stabilizers
25 at the surface. Additionally, if the compounds migrate to a surface of the coating too quickly,
the coating may develop a haze. Accordingly, a composition according to embodiments of
the present invention can include the reactive UV stabilizer, the migratory UV stabilizer or
both. The reactive UV stabilizer can include one or more reactive functional groups, such as
a hydroxyl group. By including the reactive groups, a majority of the reactive UV stabilizer
30 does not migrate to a surface of the coating and instead remains in the interior of the coating
(e.g., in the bulk material of the coating) due to reaction of the reactive functional groups
with other components of the coating composition. Additionally, if the reactive UV stabilizer
is multifunctional, it may contribute to the formation of the three-dimensional network. Non-
35 limiting commercially available examples of the UV stabilizer include propanedioic acid [(4-
methoxyphenyl)-methylene]-bis(1,2,2,6,6-pentamethyl-4-piperidiny)ester (e.g.,
HOSTAVIN® PR-31 available from Clariant International Ltd.), Sanduvor 3055 (available

1 from Clariant International Ltd.) and commercially available hindered aminoether light
stabilizers such as TINUVIN® 123, TINUVIN® 292, TINUVIN® 326, TINUVIN® 328,
TINUVIN® 765, TINUVIN® 900, TINUVIN® 900 and TINUVIN® 152 (each available
5 from BASF Resins). TINUVIN® is a registered trademark of Ciba Specialty Chemical
Corporation. HOSTAVIN® is a registered trademark Hoechst GMBH Corporation.
Examples of reactive UV stabilizers and migratory UV stabilizers are shown as Structures
20-29. Example coatings formed from examples of coating compositions including the UV
10 stabilizer according to Structure 21 exhibited no discernible sign of haze formation.

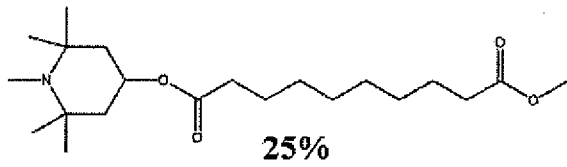
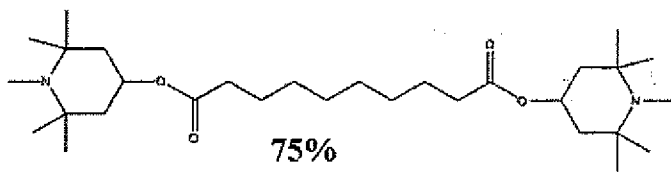
[Structure 20]



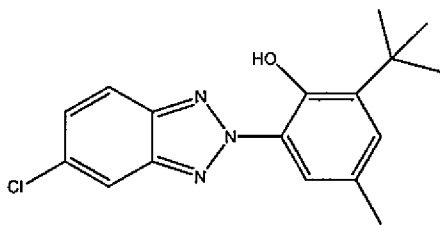
[Structure 21]



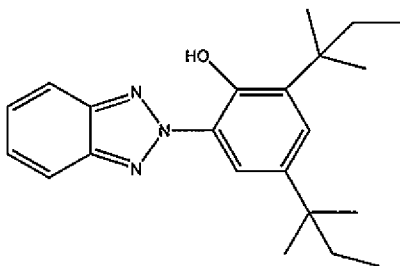
1 [Structure 22]



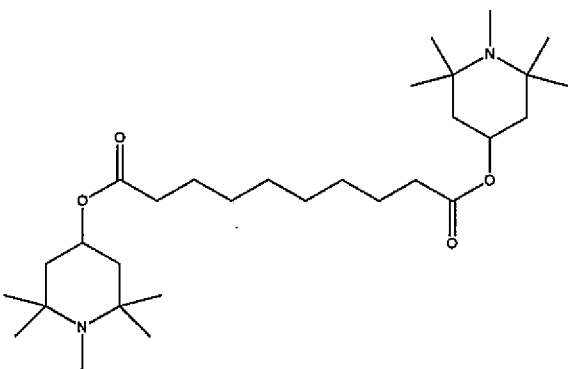
10 [Structure 23]



[Structure 24]

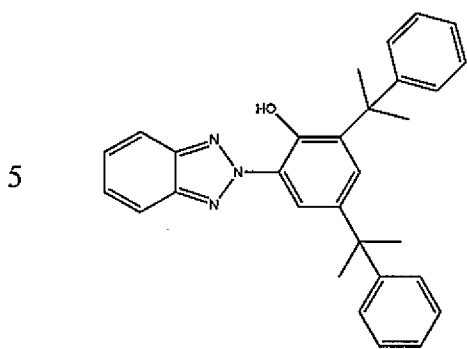


[Structure 25]

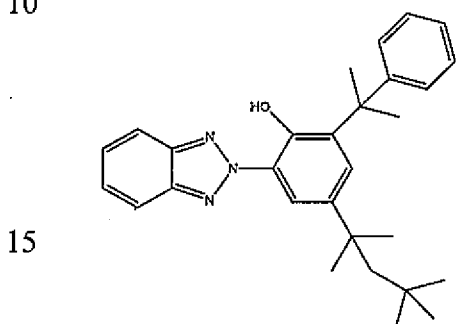


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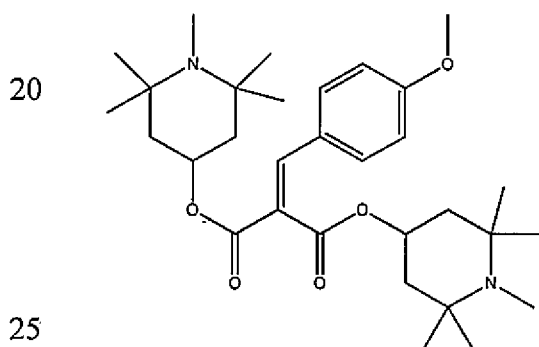
1 [Structure 26]



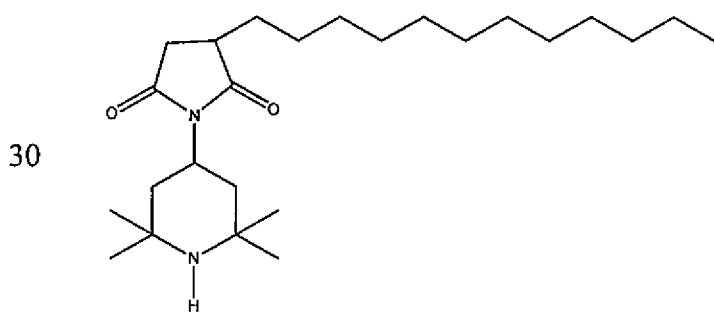
10 [Structure 27]



[Structure 28]



[Structure 29]



[0063] The Part A mixture can include anti-static agents (e.g., conductive compounds, such as conductive metal oxides, quaternary ammonium salts, inherently conductive polymers, and/or other suitable conductive agents), such as those described in U.S. Patent Application Publication No. 2010/0025533 and U.S. Patent Application Publication No.

1 2010/0028684, the entire contents of which are incorporated herein by reference. Non-
limiting commercially available examples of the anti-static agents include Antistat SD100
(available from E.I. du Pont de Nemours and Company), EA Antistat (available from Wells
Plastics Ltd), and MAXOMER® AS-1018/75DC (available from PCC Chemax, Inc.).
5 MAXOMER® is a registered trademark of PCC Chemax, Inc.

[0064] The anti-static agents (e.g., conductive compounds) can be used to reduce the
electrical resistance (e.g., sheet resistance) of the resultant coating to levels acceptable for P-
static dissipation, which should be maintained even at low temperatures (e.g., -40 °F). The
10 hydrophilic polyisocyanates discussed above can act as a conductive compound.
Alternatively or additionally, a hydrophilic polyol may be included in the coating
composition.

[0065] For example, the coating described herein can have a sheet resistance such that
15 electric charge (e.g., P-static) can pass through the coating to another layer (e.g., an
electrically conductive stack), which can then dissipate or drain the charge. If the resistance
of the coating is too high, the amount of electric charge that can pass through the coating is
reduced, and the conductive layer will not provide acceptable levels of P-static dissipation.
In some embodiments, a primer layer (e.g., a polyacrylate primer) may be included between
20 the coating and the conductive layer (e.g., the electrically conductive stack). Although the
primer layer may have a high sheet resistance (e.g., higher than that of the coating), charge
may still pass through the coating and the primer layer to the conductive layer if the primer
layer is sufficiently thin. Thus, if a primer layer is included it should be made sufficiently
25 thin to allow enough electric charge to pass through the coating and the primer layer to the
conductive layer to provide P-static dissipation.

[0066] The general electrical resistance of the polyurethane topcoats are more than or
equal to $10^{12} \Omega/\square$ to independently dissipate the static charge. The sheet resistance of the
30 coatings described herein varies depending upon the sheet resistance of the material on which
the coating is formed. For example, if the coating is on a dielectric layer (e.g.,
polycarbonate), the sheet resistance of the coating may be about 10^9 ohms per square, even if
a thin primer layer is included between the coating and the dielectric layer. If the coating is
on a conductive layer (e.g., a titanium oxide/Au/titanium oxide stack), the sheet resistance of
35 the coating may be 10^7 ohms per square.

[0067] Hydrophilic polyisocyanates, such as those described above, improve conductivity
in the coatings. Additionally, as described above, hydrophobic polyisocyanates provide

1 coatings with durability. Thus, as described above, through the combination of hydrophobic
and hydrophilic polyisocyanates (e.g., hydrophobic/hydrophilic HDI and IPDI based
polyisocyanates), a coating having a good balance of hardness, resiliency, surface tackiness,
and conductivity can be obtained.

5 [0068] According to some embodiments, the coating composition may further include a
hydrophilic polyol (e.g., a reactive anti-static resin), such as hydrophilic polyol having a
functionality of more than 2. The p-static properties of a coating can be significantly
improved by introduction of the hydrophilic polyol. The hydrophilic polyol can be any
10 suitable hydrophilic polymer having salt moieties and pendant reactive hydroxyl groups. One
non-limiting example of a suitable hydrophilic polyol is Superstat 463, which is
commercially available from Advanced Materials & Coating Specialties, Azusa, California.
The hydrophilic polyol reacts with the polyisocyanates and becomes part of the three
15 dimensional network. A clear coating is then formed with no discernible sign of migration of
the hydrophilic polyol to the surface of the coating. It is believed that the conductivity is
achieved by moisture absorption in the coating, but the hydrophilic polyol appears to have
some inherent conductivity.

20 [0069] A coating having an electrical resistance of $10^5 \Omega/\square$ (on polycarbonate) and good
optics is formed when the combined amount of the polyester polyol and the hydrophilic
polyol includes 50 wt% of Superstat 463. Such a coating has good performance in p-static
tests, even at -40°F . The hydrophilic polyol (e.g., Superstat 463) may be included in the
coating composition in an amount in a range of about 5 wt% to about 30 wt% based on the
25 total weight of the solids of the coating composition. When the hydrophilic polyol (e.g.,
Superstat 463) is included in the coating composition in an amount that is outside of the
foregoing range (e.g., is higher than 30 wt%), the resultant coating may have high surface
tackiness and may be susceptible to moisture attack when exposed to humidity. The surface
tackiness can be reduced by the addition of BYK 3700 (a polydimethylsiloxane resin with
30 pendant hydroxyl groups), incorporation of ethylene glycol or trimethylol propane (TMP),
and/or partial replacement of N-75 with IPDI trimer. None of these improvements in surface
tackiness yielded a coating having good weatherability, but some of the coatings did exhibit
good abrasion resistance.

35 [0070] Useful anti-static coatings were formulated by reducing the hydrophilic polyol
(e.g., Superstat 463) content down to a range of 14 wt% to 26 wt%. A typical two-part
polyurethane coating has a resistance of more than 10^{12} ohms/sq. and is dielectric. By

1 addition of 14 to 24 wt% Superstat 463 (depending upon the other components of the coating
composition), the resistance is reduced to between the range of 10^8 to 10^9 ohms/sq. on
polycarbonate and 10^7 to 10^8 ohms/sq. on a conductive layer, such as a stack including
5 titanium oxide/Au/titanium oxide, a stack including AZO/Au/AZO, an ITO layer, a Au layer,
an Al layer, and the like. It has repeatedly been demonstrated, by the results of specification
tests, that a combination of conductive layer/primer/topcoat can readily dissipate p-static
charge even at temperatures as low as -40°F .

10 [0071] Superstat 463 can enhance the conductivity of the coating. Superstat 463 is
compatible with all components of the coating composition and gives a coating with high
transparency, low haze, good surface flow, and superior cosmetics. Interestingly, without the
presence of Superstat 463, the coating composition may exhibit poor film-forming properties.
Therefore, Superstat may be beneficial in enhancing the compatibility among the
15 hydrophilic/hydrophobic components of the coating composition.

[0072] The Part A mixture can further include a catalyst, a flow control agent and
solvents as is known in the art. Selection of a suitable catalyst, flow control agent and
solvent is within the skill of those of ordinary skill in the art and, therefore, further discussion
of those components will be omitted.

20 [0073] The Part B mixture (e.g., curing component) can include the isocyanate as
described above. The curing component can further include cure accelerators, cure
retardants, plasticizers, additives, and/or fillers. However, like the Part A mixture, the Part B
mixture need not contain each of these components. The Part B can include additional
25 additives as well. Selection of suitable cure accelerators, cure retardants, plasticizers,
additives, and fillers is within the skill of those of ordinary skill in the art and, therefore,
further discussion of those components will be omitted.

30 [0074] According to embodiments of the present invention, the coating composition
includes at least one solvent. The solvent(s) may be added to the Part A mixture, the Part B
mixture, or both the Part A mixture and the Part B mixture. The solvent(s) reduce the
viscosity of the coating composition to make it flow-coatable. The integrity and appearance
of the resultant coating can be affected by the nature of the solvents used, even though the
solvents are not a permanent component of the cured coating. The evaporation rate of the
35 solvent (or solvent mixture) can be adjusted so that evaporation takes place quickly during
the initial drying (e.g., after flow coating) to prevent excessive flow, but slowly enough to
give sufficient leveling and adhesion. The solvent(s) used can be non-reactive with

1 isocyanates and non-aggressive against the substrate and/or coated surfaces, so that no (or
little) attack takes place during the flow coating and/or air-drying process. The solvent(s)
could also influence the rate of isocyanate-hydroxyl reactions, for example during the
air-drying period, depending on the extent of hydrogen bonding and dipole moment character
5 of the solvent.

[0075] Non-limiting examples of the solvent include isobutyl acetate, 2,6-dimethyl-4-
heptanol, butoxy ethyl acetate, isobutyl acetate, 2-butoxyethyl acetate, diisobutyl ketone,
dipropylene glycol dimethyl ether, and propylene glycol dimethyl ether. In some
10 embodiments, the solvent includes diacetone alcohol (DAA). DAA has a slow evaporation
rate and good flow properties. DAA effectively dissolves all (or most) of the components of
the coating composition to give a clear, homogeneous solution. DAA has a tertiary hydroxyl
group, but the reactivity of the tertiary hydroxyl with isocyanate is much lower than the
hydroxyls of the other components of the coating composition, and since DAA begins to
15 evaporate during the air-drying period, the reaction of DAA with the polyisocyanates is
negligible.

[0076] The solvent may also be used to adjust the solids content of the coating
composition. It may be beneficial to maximize the thickness of the resultant coating for
20 improved performance in the rain erosion test. At 70% solids content the coating
composition is too viscous for successful flow coating application with existing equipment.
At a solids content of 65%, the coating composition forms a coating that is free from
cosmetic defects, has good surface quality, and provides good performance in the rain erosion
test. A coating composition having a 65% solids content applied to a production F-22 test
25 canopy by a two component mixer (e.g., a mixer, such as the DL 2 mixer, available from
Liquid Control Ltd., Wellingborough, England) formed a coating having good surface
quality. Offcuts from the test canopy had no apparent damage after 44 minutes of rain
erosion testing at 550 mph.

[0077] As described above, the coating composition can be used to form a coating. For
example, a coated substrate 100 (e.g., a coated transparency) is shown in FIG. 1. As can be
seen in the embodiment shown in FIG. 1, the coated transparency includes a substrate 10, and
a coating 105 (e.g., a topcoat) on the substrate 10. In this embodiment, the coating 105
35 includes the coating described herein. The coated substrate can be used as a windshield,
window, or canopy of an aircraft, but the present invention is not limited thereto. For
example, the coated substrate can also be used as a window or windshield of a car, aircraft,

1 boat, building, or any other suitable vehicle or structure. In the case of a modern aircraft canopy, the substrate is typically an organic resin, such as polycarbonate or polyacrylate.

5 [0078] In the embodiment shown in FIG. 1, the coating 105 (e.g., the topcoat or top layer) is in direct physical contact with the substrate 10. However, it is understood that the present invention is not limited to this configuration, and there can be one or more intervening layers or features between the substrate and the coating. In FIG. 1, the coating 105 is the outer most layer of the multilayer stack 200, and includes the above-described coating, which is a tough, durable and weather resistant material, such as polyurethane, yet is sufficiently pliable and flexible to prevent crack formation due to thermal stress. As described above, the coating composition, and therefore the coating, can include conductive compounds to provide anti-static properties, and the coating can be conductive to help dissipate static charge and other electromagnetic forces. For example, the coating can have antistatic properties to allow static charge to be dissipated to underlying conductive layer(s), if present. In some embodiments, the coating includes other additives such as those described in U.S. Patent Application Publication No. 2010/0025533 and U.S. Patent Application Publication No. 2010/0028684 (e.g., conductive metal oxides, quaternary ammonium salts, inherently conductive polymers, and/or other suitable conductive agents).

20 [0079] As described above, the coated substrate 100 of FIG. 1 can include additional layers or features not shown in FIG. 1. For example, the coated substrate can further include an electrically conductive multilayer stack. The electrically conductive multilayer stack can include first and second metal oxide layers including titanium oxide, the first metal oxide layer including a first region (e.g., a first sub-layer), a second region (e.g., a second sub-layer) on the first region, and a third region (e.g., a third sub-layer) on the second region, the first region and the third region each having a higher oxygen concentration than that of the second region, and a metal layer (such as a metal layer including gold (Au)) between the first and second metal oxide layers. The first metal oxide layer can be positioned over the transparency, and the metal layer can be positioned between the first metal oxide layer and the second metal oxide layer. As used herein, the term "titanium oxide" refers to any compound containing only Ti and O as the constituent elements. Some non-limiting examples of suitable titanium oxides include TiO_2 , TiO , Ti_2O_3 , Ti_3O , Ti_2O , and derivatives or variations thereof.

35 [0080] A coated substrate (e.g., a coated transparency) including the electrically conductive multilayer stack is shown in FIG. 2. As can be seen in the embodiment of FIG. 2,

1 the coated substrate 200 includes a substrate 10 or transparency (such as an aircraft canopy),
and an electrically conductive multilayer stack 120. The electrically conductive multilayer
stack includes a first metal oxide layer 40 including titanium oxide adjacent to a metal layer
50, and a second metal oxide layer 60 including titanium oxide adjacent to the metal layer 50.
5 Each of the first and second metal oxide layers and the metal layer can be positioned on or
over an adjacent layer in the order shown. One or more of the first metal oxide layer 40 and
the second metal oxide layer 60 can include various regions (or sub-layers) as described in
more detail below. The coated transparency can also include additional layers (not shown in
10 FIGS. 1 or 2), such as tie, base, and topcoat layers, as desired. For example, although the
coating 105 according to embodiments of the present invention can be used as a topcoat, in
some embodiments, the coating may be used as a base coat or other coating with one or more
additional layers on top of the coating 105.

15 [0081] At least one of the first metal oxide layer and the second metal oxide layer
includes a first region, a second region on the first region, and a third region on the second
region. The first region and the third region each have a higher oxygen concentration than
that of the second region. For example, an embodiment in which the first metal oxide layer
40 includes a first region 40a, a second region 40b, and a third region 40c is shown in FIG. 3.
20 As can be seen in the embodiment in FIG. 3, the second region 40b is on the third region 40c,
and the first region 40a is on the second region 40b. Alternatively, the second region 40b can
be on the first region 40a, and the third region 40c can be on the second region 40b.
However, it is understood that the first, second and third regions 40a, b and c can be
25 positioned in any order relative to each other, and are not limited to the positions and order
described here and depicted in the drawings.

[0082] FIG. 4 shows another embodiment in which the second metal oxide layer 60
includes a first region 60a, a second region 60b, and a third region 60c. As can be seen in the
embodiment in FIG. 4, the second region 60b is on the third region 60c, and the first region
30 60a is on the second region 60b. Alternatively, the second region 60b can be on the first
region 60a, and the third region 60c can be on the second region 60b. FIG. 5 shows another
embodiment in which each of the first metal oxide layer 40 and the second metal oxide layer
60 include a first region, a second region, and a third region. The first region and the third
35 region each have a higher oxygen concentration than that of the second region.

[0083] According to embodiments of the present invention, a method of manufacturing
an electrically conductive multilayer stack includes: forming a first metal oxide layer

1 including titanium oxide; forming a metal layer on the first metal oxide layer; and forming a
second metal oxide layer including titanium oxide on the metal layer, at least one of the
forming the first metal oxide layer and the forming the second metal oxide layer including
forming a first region, a second region and a third region, the first region and the third region
5 each having a higher oxygen concentration than the second region. The metal oxide layers
can be prepared using any suitable process capable of producing a metal oxide layer
including a first region, a second region and a third region, the first region and the third
region each having a higher oxygen concentration than the second region. For example, the
10 metal oxide layers can be prepared using physical vapor deposition, atomic layer deposition,
and chemical vapor deposition (e.g., plasma enhanced chemical vapor deposition).
Additionally, the first region, second region and third region can be formed after the
deposition of the corresponding metal oxide layer. For example, the metal oxide layer can be
15 deposited first and then subjected to a post deposition treatment to create the first region,
second region and/or third region.

[0084] In some embodiments, at least one of the first metal oxide layer or the second
metal oxide layer is formed by varying a flow rate of oxygen during formation. The metal
oxide layers can be formed by any suitable process, such as, for example, a physical vapor
20 deposition process such as sputtering. The sputtering can include, for example, sputtering
from a titanium metal target or TiO₂ target, but the present invention is not limited thereto. In
some embodiments, both of the first metal oxide layer and the second metal oxide layer are
formed by varying the flow rate of oxygen during formation (e.g., while sputtering). By
25 varying the flow rate of oxygen during formation, the oxygen concentration of the metal
oxide layer can be varied, thereby forming an oxygen concentration gradient in the formed
layer. The different oxygen concentrations in the gradient forming the first, second and third
regions of the first metal oxide layer or the second metal oxide layer.

[0085] For example, varying the flow rate of oxygen while sputtering can include flowing
30 oxygen at a first oxygen flow rate, then flowing oxygen at a second oxygen flow rate, and
then flowing oxygen at a third oxygen flow rate. In some embodiments, a ratio of the first
oxygen flow rate to the second oxygen flow rate is in a range of about 10:1 to about 25:1, and
a ratio of the third oxygen flow rate to the second oxygen flow rate is in a range of about 10:1
35 to about 25:1. By varying the oxygen flow rate during formation, the first or second metal
oxide layer is formed with first, second and third regions, each region having a different
oxygen concentration. Additionally, as described in more detail below, varying the oxygen

1 flow rate can also vary the surface roughness of the first region, the second region, and the
third region, thereby varying the surface area of each. For example, forming a region of
titanium oxide while flowing oxygen at a higher flow rate results in an increased surface area
(or surface energy) as compared to forming a region of titanium oxide while flowing oxygen
5 at a lower flow rate. The increased surface area of a region of titanium oxide formed at
higher oxygen flow rate can be observed using transmission electron microscopy (TEM),
under which the region of titanium oxide will exhibit a wavier cross-section as compared to a
region of titanium oxide formed at a lower flow rate of oxygen, which will exhibit a smoother
10 cross-section under TEM.

[0086] In some embodiments, varying the flow rate of oxygen during formation (e.g.,
while sputtering) further includes flowing a first inert gas at a first inert gas flow rate, then
flowing a second inert gas at a second inert gas flow rate, and then flowing a third inert gas at
15 a third inert gas flow rate. For example, a ratio of the first oxygen flow rate to the first inert
gas flow rate can be in a range of about 0.8:2.2 to about 1:1.8, a ratio of the second oxygen
flow rate to the second inert gas flow rate can be in a range of about 1:29 to about 2:25, and a
ratio of the third oxygen flow rate to the third inert gas flow rate can be in a range of about
0.8:2.2 to about 1:1.8. By flowing inert gases at the foregoing flow rates, the oxygen
20 concentration of the first region, the second region, or the third region can be further
controlled.

[0087] In some embodiments, flowing inert gas at the first inert gas flow rate is
performed simultaneously with flowing oxygen at the first oxygen flow rate, flowing inert
25 gas at the second inert gas flow rate is performed simultaneously with flowing oxygen at the
second oxygen flow rate, and flowing inert gas at the third inert gas flow rate is performed
simultaneously with flowing oxygen at the third oxygen flow rate. The first, second and third
inert gases can be the same or different. In some embodiments, each of the first inert gas,
second inert gas and the third inert gas are all the same (e.g., Ar).

[0088] The duration of the deposition process will depend upon the deposition process
being used and the characteristics of the electrically conductive multilayer stack, such as the
size of the substrate (e.g., the area) on which the electrically conductive multilayer stack is
being deposited and the thickness of each of the various layers of the electrically conductive
35 multilayer stack. For example, the duration of the sputtering process will depend upon the
size of the target, the power applied to the target, and because the target can move, the
number of passes that the target makes over the substrate. The substrate can also move

1 during the deposition process. In consideration of the above-described variables, the deposition process can be carried out for a period of time sufficient to form the first region, the second region, and/or the third region to an appropriate thickness.

5 [0089] For example, the first region can have a thickness in a range of about 0.5 to about 6 nm, such as in a range of about 2 to about 6 nm. Similarly, the third region can have a thickness in a range of about 0.5 to about 6 nm, such as in a range of about 2 to about 6 nm. The second region can have a thickness in a range of about 3 to about 8 nm. Additionally, a ratio of the thickness of the first region to that of the second region can be in a range of about 10 0.0625:1 to about 1:1, such as in a range of about 0.25:1 to about 1:1. Similarly, a ratio of the thickness of the third region to that of the second region can be in a range of about 0.0625:1 to about 1:1, such as in a range of about 0.25:1 to about 1:1.

15 [0090] As described above, the second region can have a lower oxygen concentration than that of each of the first region and the third region. For example, as set forth above, the second region can be formed by flowing oxygen at a lower flow rate (i.e., lower relative to the oxygen flow rates for either the first region or the third region) during formation. As a result of the second region having a lower oxygen concentration than that of each of the first region and the third region, the second region has improved light transmission properties as compared to the first region and the third region. Consequently, metal oxide layers including 20 first, second and third regions have improved light transmission properties as compared to metal oxide layers that only include a first region and/or a third region.

25 [0091] Additionally, by having a higher oxygen concentration than the second region (e.g., by being formed at a higher oxygen flow rate than that of the second layer), each of the first region and the third region has greater surface roughness than the second region (e.g., the region of lower oxygen concentration). The increased oxygen concentration, and hence increased surface roughness and increased surface area (or surface energy), of the first region and the third region, relative to the second region, improves the adhesion of the metal oxide layer to the substrate or other layers (non-limiting examples of which include metal layers, tie 30 layers, base layers, topcoat layers or the like). For example, metal oxide layers including first and third regions, with higher surface roughness than the second region, have improved adhesion to the substrate as compared to metal oxide layers including only a second region 35 (e.g., a region of relatively lower oxygen concentration). Consequently, the multi-region metal oxide layer described above achieves greater adhesion to at least some of the components of the coated transparency than can be achieved by a metal oxide layer that only

1 includes the second region. Thus, the multi-region metal oxide layer described above has improved adhesion and light transmission properties as compared to metal oxide layers that have only a single region (i.e., a single oxygen concentration) or that do not vary the oxygen concentration as described here.

5 **[0092]** In some embodiments, the coated substrate (e.g., coated transparency) provides the functionality required of a modern stealth aircraft canopy. For example, in some embodiments, the electrically conductive multilayer stack 120 has a sheet resistance suitable for radar attenuation. More specifically, one or more of the first and second metal oxide layers and the metal layer can be electrically conductive and have a sheet resistance suitable for radar attenuation. When positioned over a transparency or substrate, such as an aircraft canopy, an electrically conductive multilayer stack having a sheet resistance suitable for radar attenuation can prevent or reduce the buildup of static charge on the coated transparency by draining or dissipating the static charge, and it can provide radar attenuation functionality to the coated transparency.

15 **[0093]** Additionally, some embodiments of the electrically conductive multilayer stack are transparent and, for example, have a visible light transmittance of at least about 61%. In some embodiments, for example, the electrically conductive multilayer stack can have a visible light transmittance in a range of about 61% to about 67%. More specifically, the coating one or more of the first and second metal oxide layers of the electrically conductive multilayer stack can be transparent and/or anti-reflective. Consequently, a coated transparency or substrate, such as an aircraft canopy, including a coating made from the coating composition and the electrically conductive multilayer stack can be transparent and, for example, have a visible light transmittance of at least about 61%. In some embodiments, the visible light transmittance of the coated substrate is above 65% (e.g., in a range of about 65% to about 67%).

20 **[0094]** In some embodiments, the electrically conductive multilayer stack includes first and second metal oxide layers including titanium oxide, which, according to embodiments of the invention, has a higher refractive index than certain other transparent conductive metal oxides, such as indium tin oxide ITO and AZO. As a result of its higher refractive index, a titanium oxide layer does not need to be made as thick as a corresponding ITO or AZO layer in order to achieve roughly the same anti-reflective properties. By making the metal oxide layer thinner, the flexibility of the metal oxide layer, as measured by strain elongation, can be improved over previous coatings including ITO or AZO, as described in more detail below.

1 Although an AZO layer generally has higher flexibility than a titanium oxide layer of the
same thickness, the metal oxide layers including titanium oxide of embodiments of the
present invention can be ultra-thin and therefore, have a higher flexibility than the thicker
AZO layers of previous coatings. As such, an electrically conductive multilayer stack
5 including ultra-thin titanium oxide according to embodiments of the present invention can be
more flexible than previous electrically conductive multilayer stacks including thicker layers
of ITO or AZO. For example, the improved flexibility of the ultra-thin metal oxide layers
including titanium oxide can improve the overall flexibility of a coating including those
10 layers. Additionally, titanium oxide films, such as those included in embodiments of the
present invention have good light transmittance in the visible light region (e.g., ~85%), a high
refractive index (e.g., ~2.1). Titanium oxide also has better environmental stability (e.g.,
chemical stability, such as resistance to corrosion induced by water or acid) and mechanical
15 durability than other metal oxides.

16 [0095] Because of the relatively higher refractive index of titanium oxide, a titanium
oxide layer can be made thinner than other metal oxide layers such as ITO and AZO and still
result in an acceptable amount of destructive interference in the visible light reflected by the
first and second metal oxide layers and the metal layer, thereby resulting in an acceptable
20 amount of visible light that is reflected (and consequently an acceptable amount of visible
light that is transmitted). Although the anti-reflective properties and visible light
transmittance of anti-reflective coatings (such as ITO, AZO and titanium oxide) depend on
the relative refractive index of the anti-reflective coating, those properties also depend on the
25 thickness of the anti-reflective coating. Anti-reflective coatings that have a thickness equal to
one quarter of the wavelength of visible light (e.g., light having a wavelength of about 400
nm to about 750 nm, or about 550 nm), depending upon the refractive index of the metal
oxide, produce destructive interference in the reflected visible light, thereby canceling the
reflected visible light and increasing the amount of transmitted visible light. That is, when
30 the thickness of the anti-reflective coating is equal to one quarter of the wavelength of the
visible light, the visible light reflected by the anti-reflective coating (i.e., the metal oxide
layer) will be out of phase with the visible light reflected by the metal layer, and the visible
light reflected from the anti-reflective coating and the metal layer will be canceled as a result
35 of destructive interference. Consequently, the light that would have been reflected by the
anti-reflective coating (i.e., the metal oxide layer) and the metal layer is instead transmitted
through the anti-reflective coating and the metal layer. Because ITO has to be made ultra-

1 thin to pass the below-described four point bend test, the thicknesses of previous ITO layers
were substantially less than one quarter of the wavelength of visible light, thereby limiting
the amount of destructive interference produced by those ITO layers and reducing the amount
of visible light transmitted. In contrast to the ultra-thin ITO layers, the presently described
5 first and second metal oxide layers, which can include titanium oxide, can be made thinner
and still provide acceptable anti-reflective properties. Also, since the titanium oxide layers
are made thinner, they are more flexible and can more easily pass the four point bend test. As
such, an electrically conductive multilayer stack according to embodiments of the present
10 invention provides suitable anti-reflective properties and visible light transmittance.

[0096] In some embodiments, the first metal oxide layer has a thickness in a range of
about 4 to about 20 nm, such as about 5 to about 15 nm, about 8 to about 15 nm, or about 10
to about 15 nm. Additionally, in some embodiments, the second metal oxide layer has a
15 thickness in a range of about 4 to about 20 nm, such as about 5 to about 15 nm, about 8 to
about 15 nm, or about 10 to about 15 nm. An electrically conductive multilayer stack
according to embodiments of the present invention can include metal oxide layers having the
above-described thicknesses and still pass the four point bend test. In contrast, an electrically
conductive multilayer stack including an ITO metal oxide layer would typically need to have
20 an ITO layer having a thickness of greater than 20 nm to have suitable anti-reflective
properties, and would lack the flexibility necessary to pass the below-described four point
bend test. Because an electrically conductive multilayer stack including titanium oxide metal
oxide layers of embodiments of the present invention are more flexible than, for example, a
25 comparable electrically conductive multilayer stack including ITO metal oxide layers, the
electrically conductive stacks of embodiments of the present invention are more flexible, and
hence more durable (i.e., have superior mechanical properties), than certain previous
multilayer stacks.

[0097] The present inventors have also discovered that electrically conductive multilayer
30 stacks according to some embodiments of the present invention, e.g., electrically conductive
multilayer stacks including metal layers including gold, exhibit better corrosion resistance
and durability than certain previous coatings. Because gold is less susceptible to corrosion
than certain other metals, such as silver, electrically conductive multilayer stacks including
35 gold layers are less susceptible to corrosion than certain previous coatings (e.g., those
including silver layers). Consequently, electrically conductive multilayer stacks including
gold metal layers are less likely to suffer from degradation of electrical (e.g., sheet resistance)

1 and optical properties (e.g., visible light transmittance), resulting in improved durability of coated transparencies including such multilayer stacks.

5 [0098] In some exemplary embodiments, the electrically conductive multilayer stack includes a first metal oxide layer 40 including titanium oxide, a metal layer 50 including gold, and a second metal layer 60 including titanium oxide. The first metal oxide layer 40 is positioned over a transparency 10, the metal layer 50 is positioned over the first metal oxide layer 40, and the second metal oxide layer 60 is positioned over the metal layer 50. For instance, the metal layer can have a thickness in a range of about 5 to about 20 nm. 10 Additionally, in some embodiments, the metal layer consists essentially of gold. As used herein and in the claims that follow, the term "consisting essentially of gold" and "consisting essentially of" means that the metal layer primarily contains gold, but can contain other substances that do not affect the corrosion resistance, sheet resistance and/or radar attenuation properties of the gold. For instance, a metal layer consisting essentially of gold would be 15 substantially free, or even completely free, of silver (Ag). As used herein, the term "substantially" is used as a term of approximation and not a term of degree, such that the term "substantially free" means that the material being discussed is present in the coating composition (or coating), if at all, as an incidental impurity. As used herein, the term 20 "completely free" means that the material is not present in the coating composition (or coating) at all.

25 [0099] Because gold is less susceptible to corrosion than, for example, silver, a coated transparency including an electrically conductive multilayer stack including a metal layer including gold does not require additional protective organic layers, such as a barrier layer, to protect the metal layer from oxidation. For example, a coated transparency according to some embodiments of the present invention includes an electrically conductive multilayer stack including a first metal oxide layer including titanium oxide (e.g., first metal oxide layer 30 40), a metal layer including gold (e.g., metal layer 50), and a second metal oxide layer including titanium oxide (e.g., second metal oxide layer 60), with the proviso that the coated transparency does not include a barrier layer. As a result, such electrically conductive multilayer stacks can be less complicated and less costly to produce than certain previous stacks (i.e., because it does not require additional protective organic layers, such as a barrier 35 layer, to protect the metal layer from oxidation). By eliminating the barrier layer, the coated transparencies of some embodiments of the present invention can be produced in fewer steps

1 and with fewer materials than certain previous transparencies, thereby reducing cost and increasing efficiency of production.

5 [00100] Nonetheless, some embodiments of the coated transparency of the present invention can include one or more additional layer(s), such as those set forth below. For example, in some embodiments, the coated transparency further includes a topcoat (e.g., a
10 conductive top layer including a conductive metal oxide, a quaternary ammonium salt, an inherently conductive polymer, and/or other suitable conductive agent), a base layer(s) (e.g., a layer including a material selected from polyepoxides, polyacrylates, polyurethanes, polysiloxanes, and combinations thereof), and/or a tie layer(s) (e.g., an acrylic polymer and/or mixture of polymers), such as those described in U.S. Patent Application Publication No. 2010/0025533 and U.S. Patent Application Publication No. 2010/0028684, the entire contents of which are herein incorporated by reference.

15 [00101] For example, another embodiment of the present invention is shown in FIG. 6. According to this embodiment, a coated substrate 300 includes a substrate 10 (e.g., a transparency), a polymeric base layer 30, an electrically conductive multilayer stack 120, and a coating 105 (e.g., a topcoat or top layer) as described herein. Each of the layers of the coated transparency can be positioned on or over an adjacent feature (or layer) in the order
20 shown in FIG. 6. Although not shown, the coated transparency can also include an adhesion promoter (e.g., an adhesion promoter layer), such as 3-aminopropyltriethoxysilane, between the substrate and the subsequent layers. The substrate and electrically conductive multilayer stack are similar to those described above with reference to FIGS. 1 and 2.

25 [00102] The polymeric base layer 30 can be selected to adhere well to the material of the substrate (e.g., polycarbonate and polyacrylate). For example, the base layer can cover imperfections of the substrate and promote adhesion of the substrate to another layer, such as the coating 105 or the first metal oxide layer 40. That is, the base layer 30 couples the substrate 10 to the coating 105 or the electrically conductive multilayer stack 120, and should
30 be capable of bonding thereto. When used in a windshield, window or canopy of an aircraft, the base layer should not adversely affect the impact resistance of the substrate. Additionally, when the based layer directly contacts the first metal oxide layer of the electrically conductive stack, the base layer should be hard enough to support the ceramic metal oxide
35 antireflective coating (e.g., the first metal oxide layer).

[00103] In some embodiments of the invention, the base layer 30 includes a material selected from polyepoxides, polyacrylates, polyurethanes, polysiloxanes, and combinations

1 thereof. A polysiloxane base layer can be particularly useful as a result of its inorganic
composition and hardness. As such, the base layer 30 can include a polymeric and/or
oligomeric silane, among other species. For example, a coating composition can be prepared
5 from a combination of monomeric silanes and silane terminated polymers that are hydrolyzed
in a mixture of water and acid to form silanols, which are condensed to a precondensate state
after being formed. When the coating composition is applied to a surface and cured, the
precondensate, which includes the silanols, reacts to form siloxane linkages, thereby forming
an exemplary polysiloxane base layer 30. Alternatively, the base layer 30 can include any
10 suitable polyepoxide, polyacrylate, or polyurethane. For example, the base layer 30 can
include a thermally-curable polyacrylate coated with the above-described polysiloxane.

[00104] A soft tie coat can also be positioned between the base layer and the substrate.
When present, the tie coat dissipates the shrinkage stress that results from the addition of the
15 other layers (e.g., the base layer and the electrically conductive multilayer stack 120), and the
tie coat accommodates the dimensional change of the substrate due to extreme thermal
exposure. For example, FIG. 7 shows a coated substrate 400 including a substrate 10 (i.e., a
transparency), a base layer 30, an electrically conductive multilayer stack 120, and a coating
105 (e.g., a topcoat), as described above. The coated transparency further includes a tie layer
20 20 between the substrate 10 and the base layer 30.

[00105] In the case where the substrate is a polyacrylate, polycarbonate, or similar organic
resin, the tie layer 20 can be an acrylic polymer or mixture of polymers, for example an
acrylic polymer made of one or more alkyl acrylates and/or methacrylates. Optionally, the tie
25 layer can also include one or more additional adhesion promoters, such as additional
monomers. The layer can be applied to the substrate by gravity coating or another suitable
application technique. In gravity coating, a polymeric solution of the tie layer polymer(s) or
precursor monomers is prepared, and the solution is applied to the canopy in the center and
30 along a longitudinal axis that extends along the entire length of the canopy. The polymeric
solution is then discharged from a nozzle and poured over the canopy at the top, allowing the
solution to flow down both sides and thereby coat the surface of the canopy. The solution is
applied slowly from one end to another along the longitudinal axis of the canopy, until the
entire canopy is coated with a tie layer. The coating thickness can be controlled by, for
35 example, controlling the viscosity of the polymeric solution. The liquid coating can be
applied by multiple passes to ensure a consistent layer is formed across the canopy. Any

1 excess drips off the canopy are collected at the bottom, through a gutter, where they can be properly disposed of and/or re-used.

5 [00106] In another embodiment, multiple streams of the polymeric solution are directed to impinge on the canopy. The solution streams are ejected through one or more nozzles or other outlets at a constant flow rate. By keeping the flow rate of the polymeric solution constant, the thickness of the coating can be controlled. In addition to the flow rate, the thickness of the coating also depends on the viscosity of the polymeric solution. Increasing the viscosity of the polymeric solution increases the thickness of the coating. In some
10 embodiments, the viscosity of the polymeric solution is in a range of about 2 to about 200 centipoise. Once the canopy is coated with the tie layer material(s), it is air dried under atmospheric conditions and ambient temperatures, and then cured using heat or ultraviolet light.

15 [00107] After the tie layer 20 is applied to the substrate 10 and cured, the base layer 30 is applied by gravity coating or a process similar to that described above. The substrate, including the tie layer 20 and the base layer 30, is then allowed to air dry under ambient conditions, and is then cured.

20 [00108] The first metal oxide layer 40 is applied to the base layer 30 by any suitable process, such as, for example, sputtering. In one exemplary embodiment, the first metal oxide layer is formed using a magnetron sputtering process in which a high voltage plasma discharge causes atoms to be ejected from a target, such as a titanium metal or TiO₂ target. The metal or metal oxide then strike the base layer and form a thin, transparent layer of metal
25 oxide. Since the coating is formed on an atomic scale, it is possible to produce uniform layers of films. For titanium oxide, the metal oxide layer 40 can be applied at a relatively moderate temperature, i.e. from about 100 °F to about 200 °F. The substrate, including the tie layer 20 and the base layer 30, is heated to a temperature within that range, and a sufficiently thick layer is deposited thereon. Additionally, as described above, forming the
30 first metal oxide layer or the second metal oxide layer can include varying the flow rate of oxygen while sputtering. The target can move during the sputtering process and the target can make multiple passes over the substrate.

35 [00109] In an exemplary embodiment, the titanium oxide film is formed using pulsed DC magnetron sputtering in an argon and O₂ gas mixture at a temperature of about 100 to about 200 °F.

1 [00110] Once the first metal oxide layer 40 is applied, the metal layer 50 is applied using a
physical vapor deposition or sputtering process as described above. For gold, the deposition
process can be carried out at a temperature of about 100 °F to about 200 °F. After the metal
layer 50 is deposited, the second metal oxide layer 60 is then applied, using a process similar
5 to that described above with respect to the first metal oxide layer 40.

[00111] After the electrically conductive multilayer stack 120 is formed, a topcoat can be
formed thereon. For example, as shown in FIGS. 2, 6 and 7, the coating 105 can be formed
directly on the second metal oxide layer 60 to provide a coating 105 (e.g., a topcoat) that is in
10 direct physical contact with the second metal oxide layer 60.

[00112] Alternatively, the coated substrate can include a tie layer (e.g., a conductive tie
layer) between the electrically conductive stack and the coating (or topcoat), as shown in
FIG. 8. According to the embodiment shown in FIG. 8, the coated transparency includes a
15 substrate 10 (e.g., a transparency); a tie layer 20, a base layer 30, an electrically conductive
multilayer stack 120, and a coating 105, as described above. The coated transparency further
includes a tie layer 70 (e.g., a topcoat tie layer) between the coating 105 and the electrically
conductive multilayer stack 120. In one embodiment, the tie layer 70 includes a polymeric
resin that is compatible with the coating 105 and optionally includes an organosiloxane
20 compound, which can interact with and bond to the second metal oxide layer 60 of the
electrically conductive multilayer stack 120. The coating 105 can be made of a durable,
weather resistant polymer, such as polyurethane. For example, the tie layer 70 can be a tie
layer (e.g., an acrylic polymer and/or mixture of polymers) such as those described in U.S.
25 Patent Application Publication No. 2010/0025533 and U.S. Patent Application Publication
No. 2010/0028684.

[00113] The following examples are presented for illustrative purposes only and are not to
be viewed as limiting the scope of the present invention. Unless otherwise indicated, all parts
and percentages in the following examples, as well as throughout the specification, are by
30 weight.

Example 1

[00114] A polycarbonate canopy for an F-22A jet aircraft was lightly abraded to increase
its surface roughness and surface area for receiving a primer (3-aminopropyltriethoxy silane,
35 an adhesion promoter). The primer was gravity coated onto the canopy. Next, a polymeric
solution (FX-430, produced by PPG Industries, Inc.) was applied to the canopy by flow
coating. The polymeric solution was poured from the top of the canopy and from one end to

1 another, allowing the solution to flow down and coat the canopy by gravity flow. Excess
polymeric solution was allowed to flow down into a dripping pan and was collected for
proper disposal.

5 [00115] After the entire outer surface of the canopy had been coated, it was cured in a
heated oven at about 230 °F for about 5 hours. After the coating was cured, the canopy was
abraded to increase its surface area for receiving the next coating layer and then cleaned with
isopropanol (IPA). A silane basecoat was then applied by flow coating, followed by a layer
of a base coat (FX-419, produced by PPG Industries, Inc.). The coated canopy was then
10 cured in a preheated oven at a temperature of about 190 °F for about 2 hours. After curing,
the canopy was thoroughly cleaned to remove dust particles and particulates that may have
accumulated on the surface.

15 [00116] The cleaned canopy was then placed in a vacuum chamber. The pressure in the
vacuum chamber was reduced and the substrate in the chamber was heated to about 100 to
about 200 °F. Two metal oxide layers and one metal layer were deposited on the coated
canopy at an elevated temperature (e.g., about 100 to about 200 °F) using magnetron
sputtering. First, a layer of titanium oxide was formed by sputtering a TiO₂ target using a
pulsed DC power supply with 300 kHz frequency. A first region of the titanium oxide was
20 formed by simultaneously flowing oxygen and inert gas at a ratio of about 1:2 while
sputtering for a time period of about 5-10 minutes. A second region of the titanium oxide
was formed by simultaneously flowing oxygen and inert gas at a ratio of 1:29 while
sputtering for a time period of about 5-10 minutes. A third region of the titanium oxide was
25 formed by simultaneously flowing oxygen and inert gas at a ratio of about 1:2 while
sputtering for a time period of 5-10 minutes. During sputtering, both the canopy and the
target moved.

30 [00117] Then, a gold layer was deposited onto the canopy at the same temperature. After
the layer of gold was formed, a second layer of titanium oxide was deposited on top of the
gold layer at a temperature of about 100 to about 200 °F in a manner similar to that described
above with respect to the first layer of titanium oxide. The canopy was then removed from
the chamber and cleaned to remove any contaminants that might have adhered to the surface.
A topcoat (FX-446, produced by PPG Industries, Inc.; FX-469, also produced by PPG
35 Industries, Inc. may also be used) was then applied to the second metal oxide layer (i.e., the
second titanium oxide layer) and cured.

Comparative Example 1

1 [00118] A polycarbonate coupon was lightly abraded to increase its surface roughness and
surface area for receiving a primer (3-aminopropyltriethoxy silane, an adhesion promoter).
The primer was gravity coated onto the coupon. Next, a polymeric solution (FX-430,
5 produced by PPG Industries, Inc.) was applied to the coupon by flow coating. The
polymeric solution was poured from the top of the coupon and from one end to another,
allowing the solution to flow down and coat the coupon by gravity flow. Excess polymeric
solution was allowed to flow down into a dripping pan and was collected for proper disposal.

10 [00119] After the entire outer surface of the coupon has been coated, it was cured in a
heated oven at about 230 °F for about 5 hours. After the coating was cured, the coupon was
abraded to increase its surface area for receiving the next coating layer and then cleaned with
isopropanol (IPA). A silane basecoat was then applied by flow coating, followed by a layer
of a base coat (FX-419, produced by PPG Industries, Inc.). The coated coupon was then
15 cured in a preheated oven at a temperature of about 190 °F for about 2 hours. After curing,
the coupon was thoroughly cleaned to remove dust particles and particulates that may have
accumulated on the surface.

20 [00120] The cleaned coupon was then placed in a vacuum chamber. The pressure in the
vacuum chamber was reduced and the substrate in the chamber was heated to about 100 to
about 200 °F. Two metal oxide layers and one metal layer were deposited on the coated
coupon at an elevated temperature (e.g., about 100 to about 200 °F) using magnetron
sputtering. First, a layer of AZO was formed, and then a gold layer was deposited onto the
coupon at the same temperature. After a layer of gold was formed, a second layer of AZO
25 was deposited on top of the gold layer at a temperature of about 100 to about 200 °F. The
coupon was then removed from the chamber and then cleaned to remove any contaminants
that might have adhered to the surface.

30 [00121] A topcoat (FX-446, produced by PPG Industries, Inc.; FX-469, also produced by
PPG Industries, Inc. may also be used) was then applied to the second metal oxide layer (i.e.,
second AZO layer) and cured. The following test procedures were then performed on the
coated transparencies of Example 1 and Comparative Example 1.

Haze and Luminous Transmittance Tests

35 [00122] A 3 inch by 12 inch coupon prepared according to Example 1 and a 3 inch by 12
inch coupon prepared according to Comparative Example 1 were each tested according to
ASTM D1003 using a Haze-Gard Plus instrument. Haze measures the clearness and
transparency of the film (the film should not be translucent and diffuse light), while luminous

1 or visible light transmittance indicates the amount of visible light transmitted through the
sample. The coupon according to Example 1 exhibited a visible light transmittance of 61-
67% and a haze of 1.24%, while the coupon according to Comparative Example 1 exhibited a
5 visible light transmittance of 67% and a haze of 2.66%. According to the test results, the
coupon according to Example 1 meets the visible light transmittance and haze values required
for aircraft canopy, windshield and windows, which are 58% or above and 10% or below,
respectively.

Bayer Abrasion Test

10 [00123] The abrasion resistance of a 2 inch by 2 inch coupon prepared according to
Example 1 was tested according to ASTM F735 for 300 cycles and 600 cycles. Prior to the
Bayer abrasion test, the coupon exhibited a visible light transmittance of 61-67% and a haze
of 1.24%, as determined by the above-described haze and luminous transmittance test. After
15 300 cycles of the Bayer Abrasion test, the coupon exhibited a visible light transmittance of
61-67% and haze of 1.24%, as determined by the above-described haze test. After 600 cycles
of the Bayer Abrasion test, the coupon exhibited a visible light transmittance of 61-67% and
haze of 1.45%, as determined by the above-described haze test. According to the test results,
the visible light transmittance and haze of the coupon were not significantly altered by the
20 Bayer abrasion test.

Humidity Test

25 [00124] A 3 inch by 12 inch coupon prepared according to Example 1, was exposed to
100% condensing humidity at 122 °F (50 °C). The haze and visible light transmittance
(VLT) were then measured after 3 weeks, 4 weeks, and then 5 weeks of exposure. The
results of the humidity test are shown in Table 1 below, along with remarks regarding the
quality of the coupon following the exposure.

Humidity and Solar Radiation (QUV) Test

30 [00125] A 3 inch by 12 inch coupon prepared according to Example 1, was exposed to
cycles of 8 hours of ultraviolet (UV) radiation at 158 °F (70 °C) followed by exposure to
condensation for 4 hours at 122 °F (50 °C). The haze and visible light transmittance (VLT)
were then measured after the cycles had been repeated for a total of 3 weeks, 4 weeks, and
then 5 weeks. The results of the QUV test are shown in Table 1 below, along with remarks
35 regarding the quality of the coupon following the exposure.

Table 1.

Number of weeks	QUV			Humidity		
	Haze (%)	VLT (%)	Remarks	Haze (%)	VLT (%)	Remarks
3	2.4	64.7	Good	1.6	64.4	Good
4	2.56	64.5	Good	1.88	64.1	Good
5	2.51	64.5	Good	2.40	64.0	Good

[00126] As can be seen in Table 1 above, the coupon prepared according to Example 1 exhibited good performance after 5 weeks of the QUV test, and the coupon only exhibited some water damage after 5 weeks of the Humidity test. Even after 5 weeks of either test, the coupon exhibited acceptable haze and visible light transmittance, and would be expected to exhibit acceptable haze and visible light transmittance even after 12 weeks of exposure to the QUV test or the Humidity test.

[00127] The above Humidity and QUV tests were also performed for different time periods on coupons prepared according to Example 1 and Comparative Example 1, except that the coupons did not include the topcoat, to evaluate the effects of the Humidity and QUV tests directly on the metal oxide layers. The results of these tests, including remarks regarding the quality of the coating, are presented in Table 2 below. As can be seen in Table 2 below, even without the topcoat, the coupon prepared according to Example 1 (i.e., the coupon including a titanium oxide/Au/titanium oxide electrically conductive stack) performed better than the coupon prepared according to Comparative Example 1 (i.e., the coupon including an AZO/Au/AZO stack).

Table 2.

	Number of days of exposure	QUV			Humidity		
		Haze (%)	VLT(%)	Remarks	Haze (%)	VLT (%)	Remarks
Comparative Example 1	2	2.4	66.5	Good	2.2	66.3	Good
	6	3.8	66.4	Light corrosion	4.9	66.1	Heavy corrosion

	14	9.84	65.87	Heavy corrosion	5.19	65.7	Heavy corrosion; AZO removed
Example 1	14	1.56	61.5	Good	1.72	61.5	Good
	21	8.05	60.7	Bad	1.55	61.5	Good
	28					61.2	Good
	35					61.3	Good
	39					60.9	Good
	42					61.3	Good

Accelerated Steam Test

[00128] A 2 inch by 2 inch coupon prepared according to Example 1, except that the coupon did not include a topcoat, and a 2 inch by 2 inch coupon prepared according to Comparative Example 1, except that the coupon did not include a topcoat, were each placed just above boiling water in an enclosed chamber. This test was carried out to observe the accelerated effect of directly exposing the bare metal oxide layer to steam. The results of the test after 6 hours, 15-16 hours, 21-22 hours, and 33-34 hours, including remarks regarding the quality of the coating, are shown in Table 3 below. The total thickness range for each stack is shown in Table 3.

Table 3.

Coating	6 hours	15-16 hours	21-22 hours	VLT and Haze after 33-34 hours		
AZO/Au/AZO (AZO thickness of 25-40 nm)	Light corrosion	Heavy corrosion	Heavy corrosion	64.7%	7.53%	Bad
AZO/Au/AZO (AZO thickness of 50-80 nm)	Light corrosion	Heavy corrosion	Heavy corrosion	67.7%	7.02%	Bad
Titanium oxide/Au/titanium oxide (titanium oxide thickness of	Good	Good	Good	60	1.67	Good

1	2-5 nm)						
5	Titanium oxide/Au/titanium oxide (titanium oxide thickness of 5-7 nm)	Good	Good	Good	60.4	1.5	Good
10	Titanium oxide/Au/titanium oxide (titanium oxide thickness of 18-25 nm)	Good	Good	Good	60.9	1.88	Good

Rain Erosion Test

[00129] A 1 inch by 1 inch coupon prepared according to Example 1 and a 1 inch by 1 inch coupon prepared according to Comparative Example 1 were each exposed to simulated rainfall at a wind speed of 550 miles per hour (mph) at the University of Dayton Research Institute (UDRI). The coupons were inspected for degradation of the coating after 1 minute, 11 minutes and 22 minutes of exposure to the simulated rainfall. The results of the test are shown below in Table 4.

Table 4.

	1 minute	11 minutes	22 minutes
25 Comparative Example 1	100%	97%	93%
Example 1	100%	100%	100%

50/50 Test

[00130] A coupon was prepared according to Example 1. An area of the coupon of about 3 inches by 2.5 inches was marked off with tacky tape. A mixture of 50 percent isopropanol and 50 percent water was applied to the surface of the coupon. The coupon was then left in a semi-open container to evaporate overnight. After about 12-14 hours, the coupon was inspected for fisheye, delamination, or distortion of the surface. No changes to the coupon were observed. Additionally, the light transmittance and haze of the coupon was measured before and after the 50/50 test, and no change in the light transmittance or haze was observed.

Acid Test

[00131] A coupon was prepared according to Example 1 and a coupon was prepared according to Comparative Example 1, except that neither coupon included a topcoat. Both coupons were tested for acid resistance. A solution was prepared by mixing 5 g of 96.3% sulfuric acid and 5 g of 65% nitric acid (the remaining 35% being water) to provide a solution having a Normality of 2.25 and a pH of 0. Several drops of the solution were placed on the bare metal oxide surface of each coupon (i.e., titanium oxide of Example 1, and AZO of Comparative Example 1) to form a drop having a diameter of about 1 cm. A watch glass was then placed over the drop and the coupon and watch glass were sealed with tacky tape to prevent evaporation. After 15 minutes the tacky tape and watch glass were removed and the metal oxide layer was examined. The AZO layer of the coupon prepared according to Comparative Example 1 was completely removed. The titanium oxide layer of the coupon prepared according to Example 1 exhibited virtually no change after exposure to the acid. As such, titanium oxide exhibited substantially higher acid resistance than AZO.

Comparative Example 2 - ITO/Au/ITO

[00132] A first ITO layer was prepared using a pulsed DC magnetron sputtering system in an Ar and O₂ gas mixture at a temperature of about 100 to about 200 °F. An ITO ceramic target including about 90 at.% In₂O₃ and 10 at.% Sn₂O₄ was used. A gold layer was deposited on the first ITO layer using a DC magnetron sputtering system at a temperature of about 100 to about 200 °F using an Ar gas atmosphere. A second ITO layer was formed over the gold layer using a pulsed DC magnetron sputtering system in an Ar and O₂ gas mixture at a temperature of about 100 to about 200 °F.

Comparative Example 3 - ITO/Ag/ITO

[00133] A first ITO layer was prepared using a pulsed DC magnetron sputtering system in an Ar and O₂ gas mixture at a temperature of about 100 to about 200 °F. An ITO ceramic target including about 90 at.% In₂O₃ and 10 at.% Sn₂O₄ was used. A silver layer was deposited on the first ITO layer using a DC magnetron sputtering system at room temperature using an Ar gas atmosphere. A second ITO layer was formed over the silver layer using a pulsed DC magnetron sputtering system in an Ar and O₂ gas mixture at room temperature.

[00134] FIG. 9 is a graph showing light transmittance versus wavelength of light of a multilayer titanium oxide/Au/titanium oxide stack according to an embodiment of the present invention as compared to an AZO/Au/AZO stack according to Comparative Example 1 and

1 an ITO/Au/ITO stack according to Comparative Example 2. The results are also shown below in Table 5.

Table 5.

Sample	Light transmittance (%)
Titanium oxide/Au/titanium oxide	65.49
AZO/Au/AZO	66.70
ITO/Au/ITO	67.31

Four Point Bend Test

[00135] Coatings including multilayer stacks prepared according to Example 1, Comparative Example 1, Comparative Example 2, and Comparative Example 3 were subjected to the four point bend test to measure the change in electrical resistance ($\Delta R/R$) of each multilayer stack as a function of the uniaxial tensile elongation of the multilayer stack. For example, a coupon according to Example 1 was prepared for the four point bend test as follows. A first basecoat was applied on a substrate 10 (i.e., a transparency) 2 inches wide, 12 inches in length, and 0.75 inches thick. Then, an electrically conductive multilayer stack 120 including titanium oxide/Au/titanium oxide was deposited on the substrate 10 in a vacuum chamber. A conductive tape (one inch wide) was then vertically applied over the electrically conductive multilayer stack to provide application sites for the bus-bars 170, as shown in FIGS. 10 and 11. The remaining portion of the electrically conductive multilayer stack (8.5 inches in length) was coated with a primer and a topcoat. No organic coating was applied over the conductive tape. Two flexible metallic conductive bus-bars 170 were applied over the conductive tape as shown in FIGS. 10 and 11, and the bus-bus resistance of the coupon was recorded.

[00136] Next, a strain gage resistor (not shown) obtained from Vishay Precision Group, Inc. was mounted on the center section of the substrate, on the side opposite to the bus-bars. The strain gage was used to determine the tensile elongation (flexibility) of the coating layers. A tensile load was applied to the substrate using a united tensile testing system. Four bending bars 160, shown in FIG. 10, applied the tensile load. The bending bars 160 on the side opposite to the bus-bars were spaced about 4 inches apart. The electrical bus-bus resistance was monitored throughout the test. If the resistance of the substrate exceeded 20%

1 above the original value, the tensile strain of the coupon was recorded. The four point bend
 test was then repeated, as described-above, for coupons prepared according to Comparative
 Example 1 (i.e., a coupon including an AZO/Au/AZO stack), Comparative Example 2 (i.e., a
 coupon including an ITO/Au/ITO stack), and Comparative Example 3 (i.e., a coupon
 5 including an ITO/Ag/ITO stack).

[00137] Some of the results of the above-described four point bend test are shown in FIG.
 12, which is a graph of the change in electrical resistance ($\Delta R/R$) versus strain of the
 multilayer stack prepared according to Example 1 (titanium oxide/Au/titanium oxide). A
 10 summary of the results of the four point bend test is also shown below in Table 6.

Table 6.

Sample	Four Point Bend Test Results: Uniaxial Tensile Elongation (%)
Example 1 (2" × 12" coupon)	Greater than 7.9%
Comparative Example 1 (2" × 12" coupon)	about 6.4%
Comparative Example 2 (2" × 12" coupon)	about 4%
Comparative Example 3 (2" × 12" coupon)	about 2%

25 [00138] As can be seen in FIG. 12 and Table 6, Example 1 performed better in the four
 point bend test than Comparative Example 1, and substantially better than either Comparative
 Example 2 or Comparative Example 3. Specifically, according to the above-described four
 point bend test, Example 1, which includes a titanium oxide/Au/titanium oxide multilayer
 stack according to an exemplary embodiment of the present invention, exhibited a greater
 30 than 50% increase in uniaxial tensile elongation over Comparative Example 2, which
 includes an ITO/Au/ITO multilayer stack. Here, the flexibility of Example 1 exceeded the
 capabilities of the equipment used for the test. Due to the limitations of the equipment used
 for the four point bend test, the maximum uniaxial tensile elongation that could be measured
 35 for Example 1 was 7.9%. However, as can be seen in FIG. 12, the coupon prepared
 according to Example 1 would be expected to exhibit a uniaxial tensile elongation greater
 than 7.9%, if measured using equipment having increased capabilities. In contrast,

1 Comparative Example 2 exhibited a maximum of about 4% uniaxial tensile elongation. Additionally, according to the above-described four point bend test, Example 1 exhibited a
5 greater than 200% increase in uniaxial tensile elongation over Comparative Example 3, which includes an ITO/Ag/ITO multilayer stack. That is, as described above, Example 1 would be expected to exhibit a maximum uniaxial tensile elongation of greater than 7.9%, while Comparative Example 3 exhibited about 2% maximum uniaxial tensile elongation. The relatively lower flexibility of the ITO/Ag/ITO stack of Comparative Example 3 is due, in part, to the Ag layer, a portion of which oxidizes to silver oxide, which is relatively brittle.
10 However, even when the Ag layer is replaced with a Au layer, a coating including the corresponding electrically conductive multilayer stack of Comparative Example 2, only exhibits a strain elongation of about 4%. Accordingly, a coating including an electrically conductive multilayer stack according to an exemplary embodiment of the present invention performed substantially better in the above-described four point bend test than Comparative
15 Examples 2 and 3.

TEM ANALYSIS

[00139] A titanium oxide/Au/titanium oxide electrically conductive multilayer stack prepared according to Example 1 was analyzed using a transmission electron microscope
20 (TEM). The thickness of the layer was determined by TEM analysis to be about 11-12 nm. Additionally, to investigate the effect of oxygen concentration on the thickness of the titanium oxide layers, two titanium oxide layers were formed directly on silicon substrates, each layer having a uniform oxygen concentration, and analyzed using TEM. The only
25 difference in the formation of these two titanium oxide layers was the flow rate of oxygen during the formation of the titanium oxide layers by sputtering from a TiO₂ target. The change in oxygen flow rate was compensated for by a corresponding change in the flow rate of the inert gas. As could be seen by TEM, the thickness of the titanium oxide layer could be reduced by as much as one half by reducing the flow rate of oxygen. In particular, the high
30 oxygen content titanium oxide layer had a thickness of about one half the thickness of the low oxygen content titanium oxide layer. Thus, if all other conditions are kept the same (e.g., sputtering time, power applied, target size, etc.) varying the oxygen flow rate while forming the titanium oxide layer will result in a variation in the thickness of the resultant titanium
35 oxide layer.

Light Transmittance and Adhesion vs. Oxygen Flow Rate

1 [00140] Using the above-described light transmittance test, the light transmittance was
 studied for various titanium oxide layers formed using several different oxygen flow rates
 while sputtering. Additionally, those same samples were tested for cross-hatch adhesion
 according to ASTM D3359. The results of the light transmittance and cross-hatch adhesion
 5 tests are shown below in Table 7.

Table 7.

Gas Flow Rate Ar/O ₂ (sccm)	Light Transmittance (%)	Adhesion
200/100	50	100
260/40	58	0
270/30	61	0
280/20	63	0
290/10	68	0

15 [00141] Although various embodiments of the invention have been described, additional
 modifications and variations will be apparent to those skilled in the art. For example, the
 coated substrate can have additional tie layers or primers, conductive tie layers, alternate
 thicknesses, additional components, etc. Also, as the individual layers included in the coated
 substrate are formed, they can be cleaned before the next adjacent layer is deposited. For
 20 example, the substrate can be cleaned with a solvent such as acetone, and then dried to
 remove any surface water, which could cause premature crosslinking of the polysiloxane of
 the base layer 30. The invention is not limited to the embodiments specifically disclosed, and
 the coated transparency, its layers, and compositions may be modified without departing from
 25 the invention, which is limited only by the appended claims and equivalents thereof.
 Throughout the text and claims, the word "about" is used as a term of approximation, not as a
 term of degree, and reflects the penumbra of variation associated with measurement,
 significant figures, and interchangeability, all as understood by a person having ordinary skill
 30 in the art to which this invention pertains. Additionally, throughout this disclosure and the
 accompanying claims, it is understood that even those ranges that may not use the term
 "about" to describe the high and low values are also implicitly modified by that term, unless
 otherwise specified.

1 WHAT IS CLAIMED IS:

1. A coating composition comprising:
a hydrophobic first aliphatic polyisocyanate;
5 a second aliphatic polyisocyanate comprising a hydrophilic portion;
a polyester polyol;
a hydrophilic polyol; and
a fluorinated polyol.

10 2. The coating composition of claim 1, wherein the second aliphatic polyisocyanate further comprises a hydrophobic portion.

15 3. The coating composition of claim 2, wherein the hydrophobic portion of the second aliphatic polyisocyanate comprises an isophorone diisocyanate moiety or a derivative thereof.

20 4. The coating composition of claim 1, wherein the hydrophilic portion of the second aliphatic polyisocyanate comprises a polyether chain.

25 5. The coating composition of claim 1, wherein the second aliphatic polyisocyanate comprises a polyether chain bonded to an isophorone diisocyanate trimer.

6. The coating composition of claim 1, wherein the hydrophobic first aliphatic polyisocyanate has an isocyanate functionality in a range of 3.0 to 4.2.

30 7. The coating composition of claim 1, wherein the hydrophobic first aliphatic polyisocyanate is selected from the group consisting of biuret-based polyisocyanates, isocyanurate ring-based polyisocyanates, and combinations thereof.

35 8. The coating composition of claim 1, wherein a weight ratio of the hydrophobic first aliphatic polyisocyanate to the second aliphatic polyisocyanate is in a range of about 95:5 to about 85:15.

1 9. The coating composition of claim 1, wherein the polyester polyol comprises four hydroxyl groups.

5 10. The coating composition of claim 1, wherein the polyester polyol is a polycaprolactone polyol and/or a polycaprolactone diol.

10 11. The coating composition of claim 9, wherein the polyester polyol comprises polycaprolactone having four polycaprolactone chains, and one of the four hydroxyl groups is at a terminal end of each polycaprolactone chain.

 12. The coating composition of claim 1, further comprising a polyester diol.

15 13. The coating composition of claim 12, wherein the polyester diol is a linear aliphatic diol having a first end comprising a hydroxyl group and a second end comprising a hydroxyl group.

20 14. The coating composition of claim 1, wherein the fluorinated polyol comprises a backbone comprising alternating substituted or unsubstituted fluoroethylene and substituted or unsubstituted vinyl ether segments.

25 15. The coating composition of claim 1, further comprising a fluorinated alcohol comprising a perfluorinated carbon chain and a hydroxyl group.

 16. The coating composition of claim 15, wherein the fluorinated alcohol further comprises a linking group between the perfluorinated carbon chain and the hydroxyl group.

30 17. The coating composition of claim 1, further comprising an anti-static agent comprising a hydroxyl group, a UV absorber comprising a hydroxyl group, a migratory UV absorber, a migratory UV stabilizer, or a UV stabilizer comprising a hydroxyl group.

35 18. A coating formed from the coating composition of claim 1.

 19. A coated substrate comprising:

1 a substrate, and
the coating of claim 18 on the substrate.

5 20. The coated substrate of claim 19, further comprising:
an electrically conductive multilayer stack between the substrate and the coating, the
electrically conductive multilayer stack comprising:

10 first and second metal oxide layers comprising titanium oxide, the first metal
oxide layer comprising a first region, a second region on the first region, and a third region on
the second region, the first region and the third region each having a higher oxygen
concentration than that of the second region; and

a metal layer between the first and second metal oxide layers.

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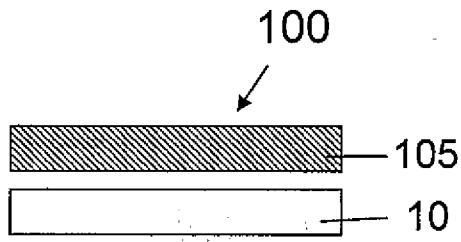


FIG. 1

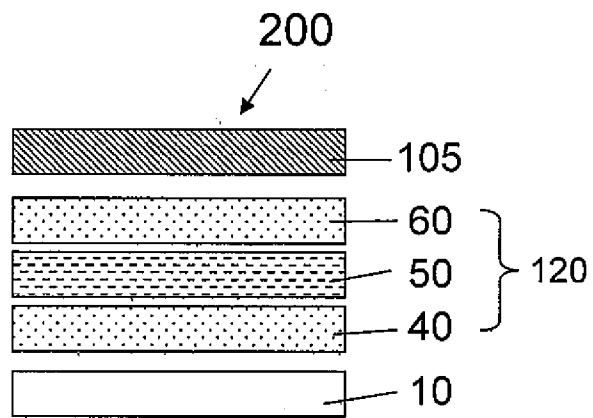


FIG. 2

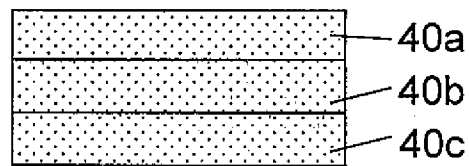


FIG. 3

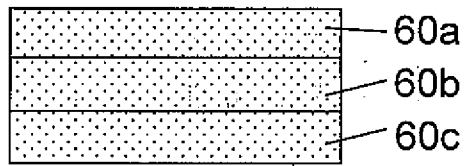


FIG. 4

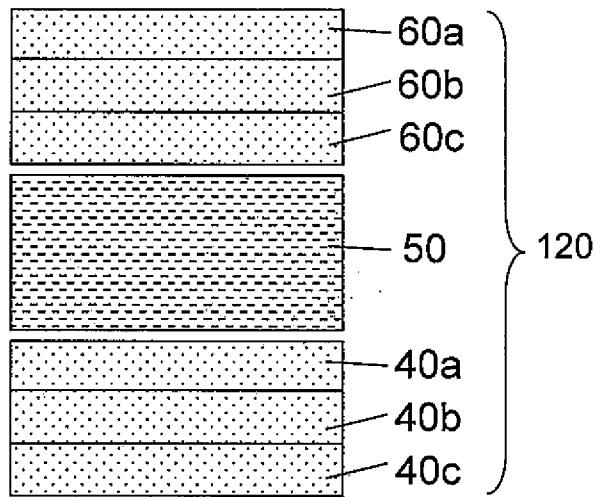


FIG. 5

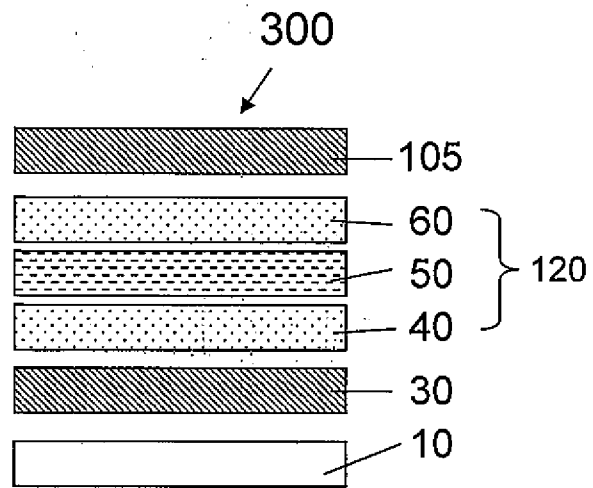


FIG. 6

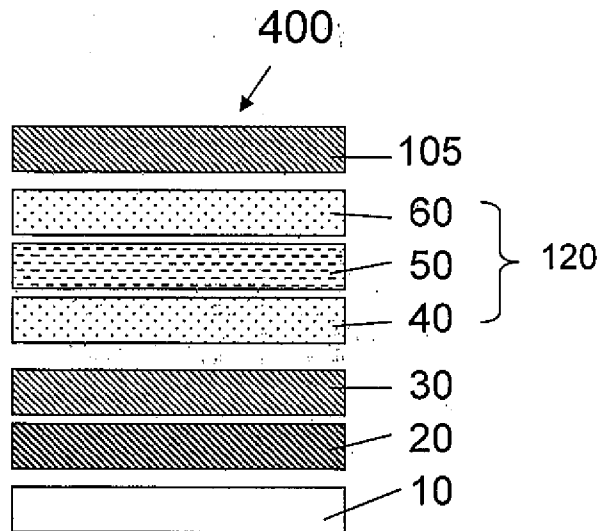


FIG. 7

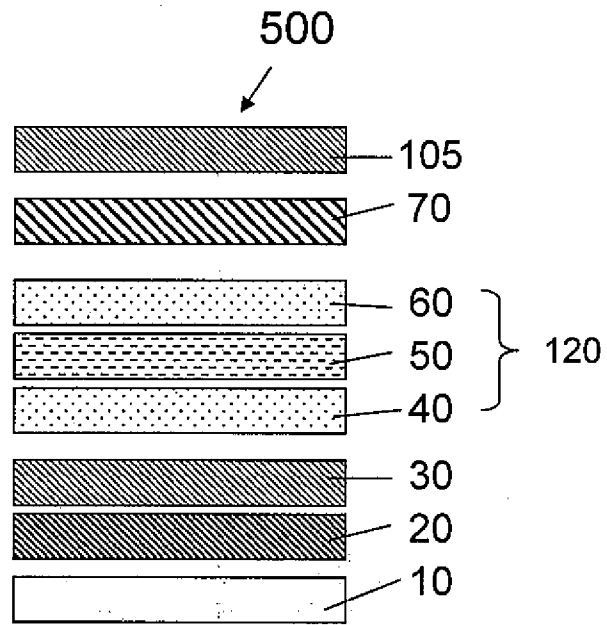


FIG. 8

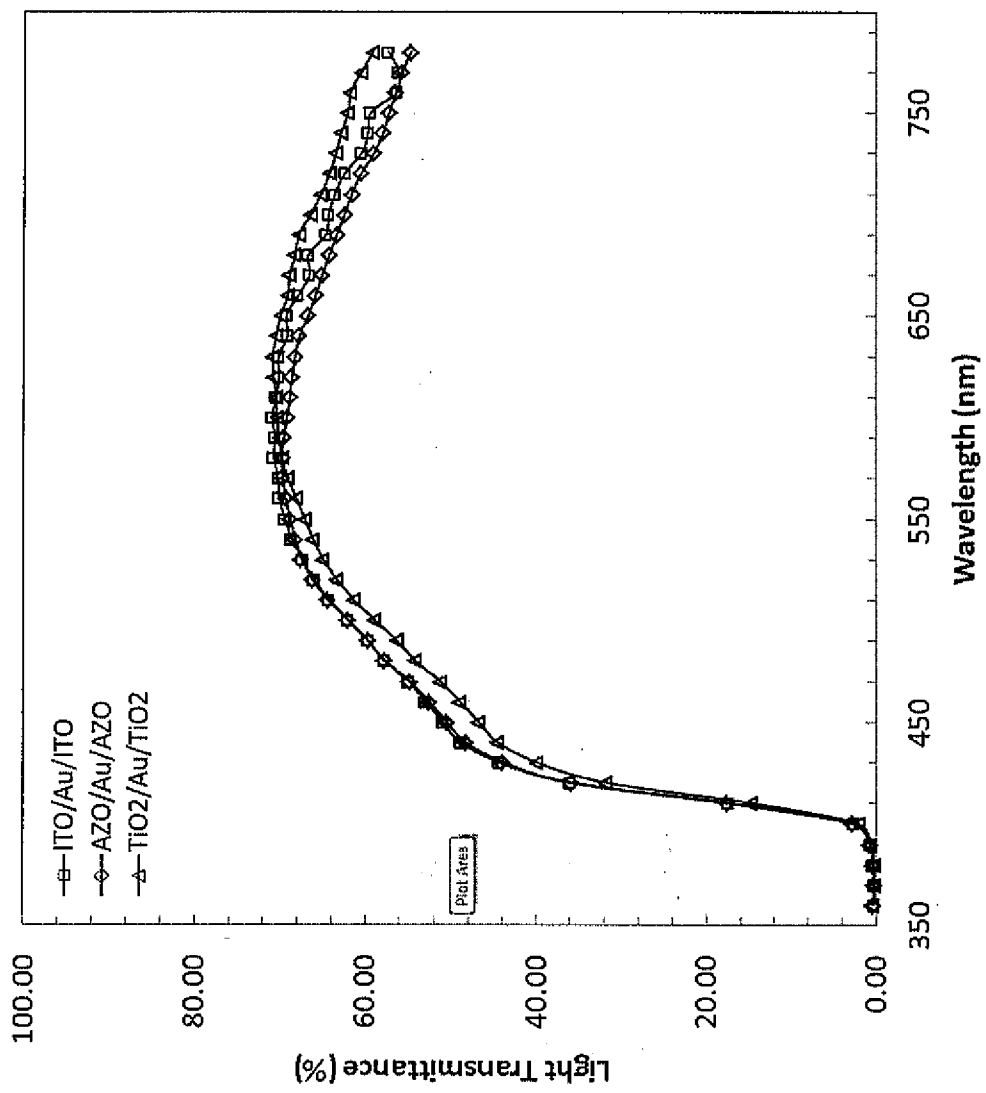


FIG. 9

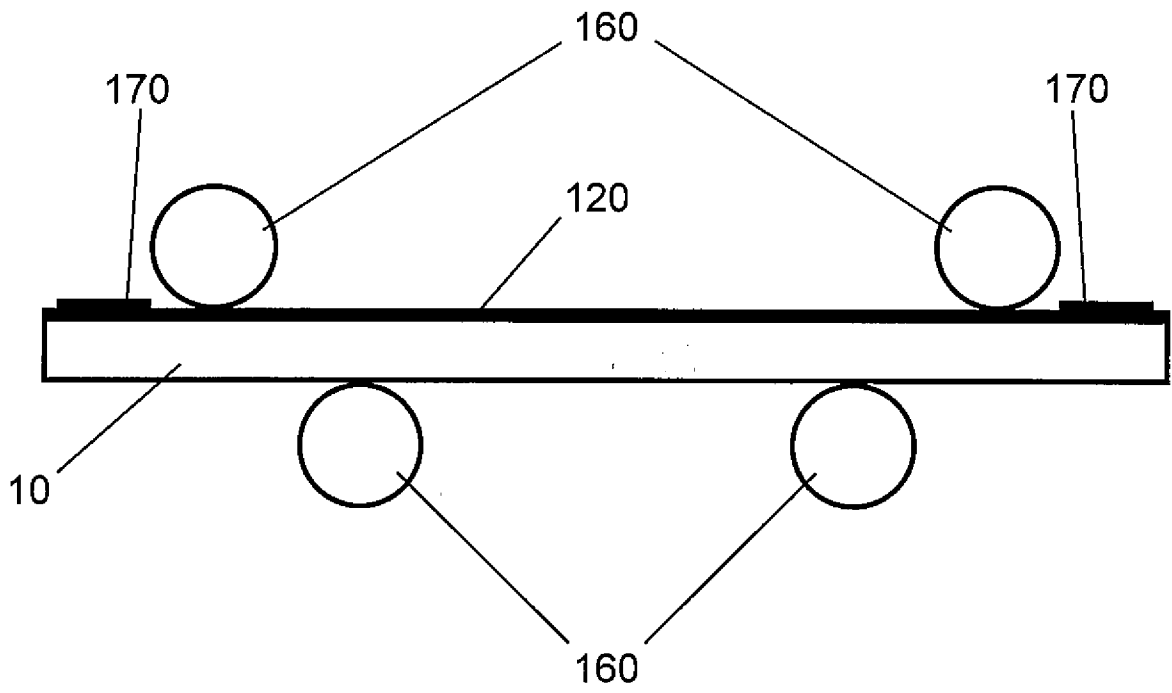


FIG. 10

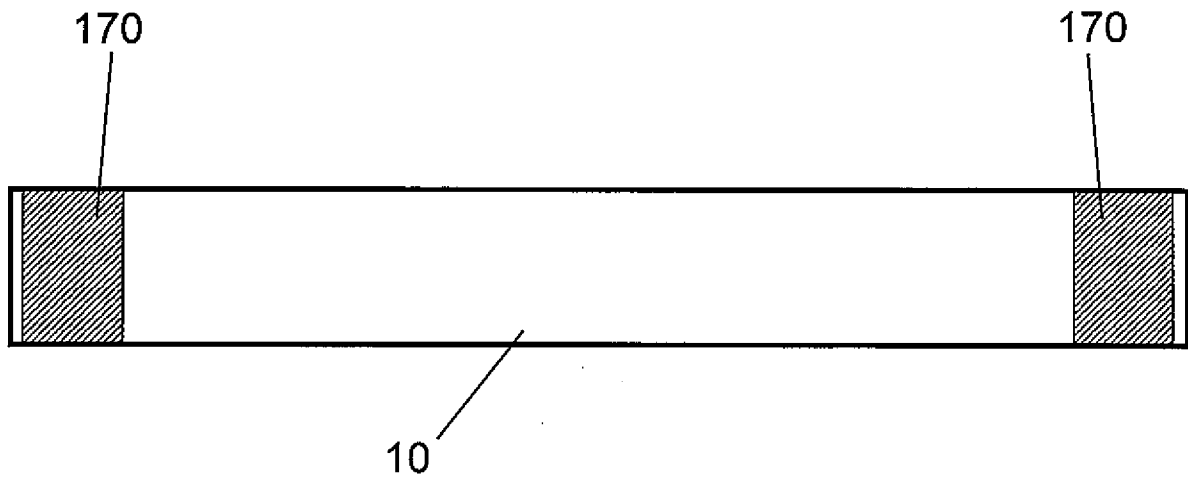


FIG. 11

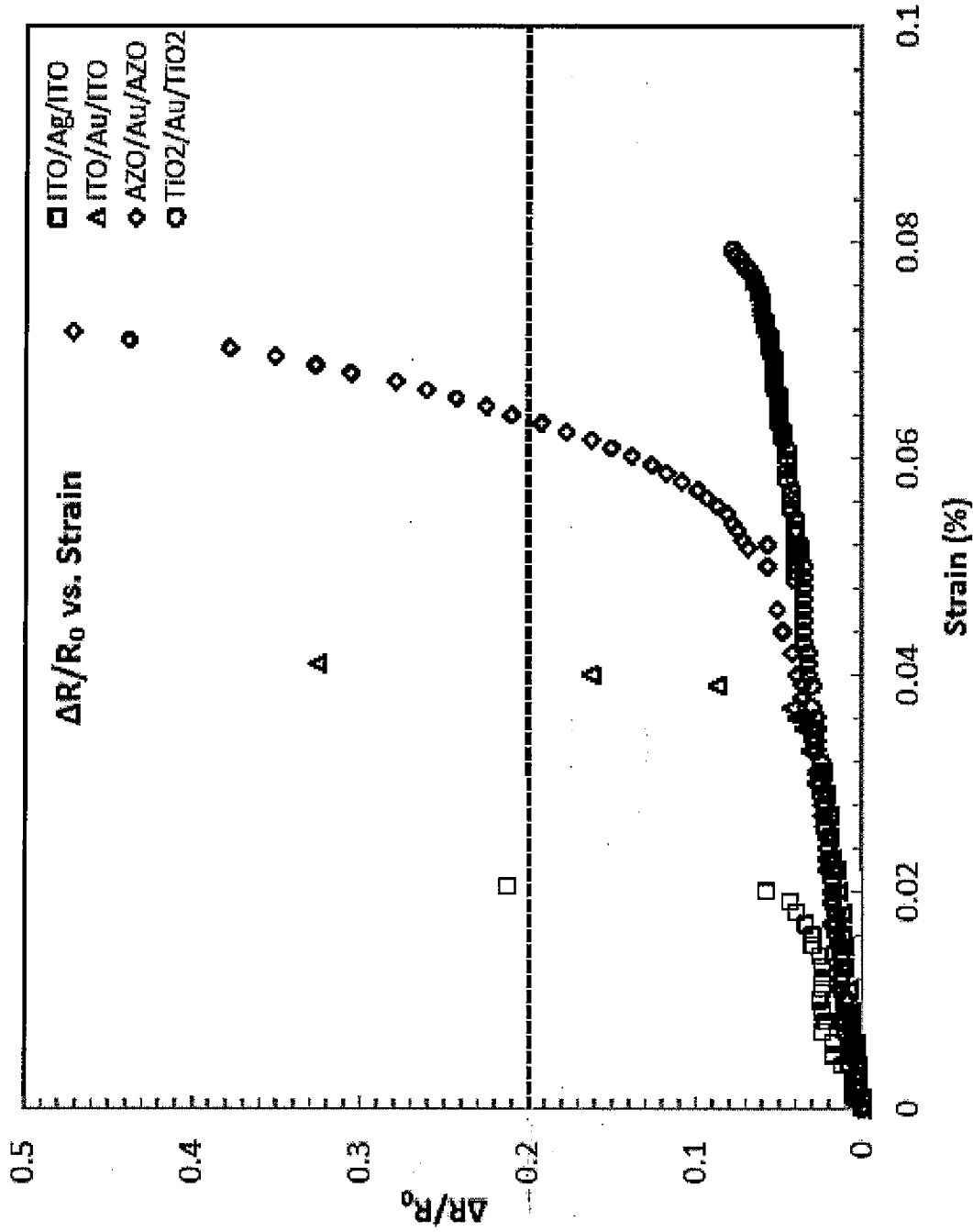


FIG. 12

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2014/011255

A. CLASSIFICATION OF SUBJECT MATTER
 INV. C09D175/04 B32B27/40 B64D47/00 C08G18/50 C08G18/72
 C08G18/75 C08G18/40
 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)
 C09D B32B B64D C08G

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.
X	WO 98/44015 A1 (PILKINGTON AEROSPACE INC [US]) 8 October 1998 (1998-10-08)	1-20
Y	page 35; claim 1; examples 18-20	1-20
X	US 2004/192835 A1 (STEIDL NORBERT [DE] ET AL) 30 September 2004 (2004-09-30)	1-20
Y	paragraph [0050]; example 2	
Y	US 2012/328859 A1 (UPRETY KRISHNA [US] ET AL) 27 December 2012 (2012-12-27)	1-20
	paragraphs [0057] - [0060]; claims 1-18; example 1	
A	US 2006/051592 A1 (RAWLINGS DIANE C [US] ET AL) 9 March 2006 (2006-03-09)	1-20
	paragraphs [0022], [0048]	

Further documents are listed in the continuation of Box C.

See patent family annex.

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- "&" document member of the same patent family

Date of the actual completion of the international search 17 April 2014	Date of mailing of the international search report 29/04/2014
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Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Authorized officer Scheuer, Sylvie
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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No PCT/US2014/011255

Patent document cited in search report	Publication date	Patent family member(s)	Publication date	
WO 9844015	A1	08-10-1998	AU 6579998 A	22-10-1998
			BR 9808436 A	23-05-2000
			EP 0970135 A1	12-01-2000
			US 6001923 A	14-12-1999
			WO 9844015 A1	08-10-1998
			ZA 9802529 A	30-09-1998

US 2004192835	A1	30-09-2004	AT 318292 T	15-03-2006
			DE 10208567 A1	11-09-2003
			DK 1478707 T3	03-07-2006
			EP 1478707 A1	24-11-2004
			ES 2254910 T3	16-06-2006
			PT 1478707 E	30-06-2006
			US 2004192835 A1	30-09-2004
			WO 03072667 A1	04-09-2003

US 2012328859	A1	27-12-2012	NONE	

US 2006051592	A1	09-03-2006	AT 552107 T	15-04-2012
			EP 1767344 A2	28-03-2007
			ES 2382784 T3	13-06-2012
			JP 5041773 B2	03-10-2012
			JP 2007083721 A	05-04-2007
			US 2006051592 A1	09-03-2006
