Title: COMPOSITIONS AND METHODS OF PROMOTING ADHESION BETWEEN A SUBSTRATE AND A POLYUREA/POLYURETHANE COATING

Abstract: The present invention is directed to compositions comprising polyurea an adhesion promoter wherein the adhesion promoter comprises an adduct of an aminosilane and a material chosen from an acrylate, a methacrylate, a lactone, and mixtures thereof. The present invention is also directed to methods of applying the compositions to improve the adhesion of a polyurea or polyurea and polyurethane coating to a substrate.
COMPOSITIONS AND METHODS OF PROMOTING ADHESION BETWEEN A SUBSTRATE AND A POLYUREA/POLYURETHANE COATING

CROSS-REFERENCE TO RELATED APPLICATIONS

[0001] This patent application is a Continuation-In-Part (CIP) of patent applications having Serial Nos. 11/211,188 and 11/460,439, filed on August 25, 2005 and July 27, 2006, respectively, hereby incorporated by reference in their entirety.

FIELD OF THE INVENTION

[0002] The present invention is directed to compositions comprising an adhesion promoter wherein the adhesion promoter comprises an adduct of an aminosilane and a material chosen from an acrylate, a methacrylate, a lactone and mixtures thereof. The present invention is also directed to methods of applying the compositions to improve the adhesion of a polyurea or polyurea and polyurethane coating to a substrate.

BACKGROUND

[0003] Coating compositions are used in a wide variety of industries. Such industries may include but are not limited to landcraft such as cars, trucks, sport utility vehicles, motorcycles; watercraft such as boats, ships and submarines; aircraft such as airplanes and helicopters; industrial such as commercial equipment and structures including walls and roofs; construction such as construction vehicles and structures including walls and roofs; military such as military vehicles, for example tanks and humvees, and military structures including walls and roofs, military equipment such as ammunition cases and battery enclosures; and the like. In these industries, considerable efforts have been expended to develop coating compositions with improved properties. Coatings are used to protect various components against damage due to corrosion, abrasion, impact, chemicals, ultraviolet light, flame and heat, and other environmental exposure. Coatings may also be used for ballistic
and blast mitigation purposes. Additionally, coatings such as those imparting color and/or high gloss can be used as decorative coatings.

Certain polyurea and polyurethane coatings have been known to have deficiencies that inhibit their effectiveness in providing adequate protection to the substrate or in improving properties of the substrate. For example, polyurea and polyurethane coatings may exhibit poor adhesion to various substrates or various coatings applied to the substrates. It can be difficult to formulate coating compositions that can adequately adhere to various substrates like metal and plastic, particularly when these substrates have an existing coating layer.

Accordingly, it is desirable to provide compositions to improve the adhesion between polyurea/polyurethane coatings and the uncoated or coated substrate to which they may be applied.

**SUMMARY OF THE INVENTION**

The present invention is directed to a coating composition comprising polyurea formed from a reaction mixture comprising isocyanate and amine wherein the ratio of equivalents of isocyanate groups to equivalents of amine groups is greater than 1 and the isocyanate and the amine can be applied to a substrate at a volume mixing ratio of 1:1; and an adduct of an aminosilane and a material chosen from (meth)acrylate, lactone and mixtures thereof.

The present invention is also directed to an adhesion promoting composition comprising an adduct of aminosilane and a material chosen from (meth)acrylate, lactone and mixtures thereof.

The present invention is also directed to a composition for improving adhesion between a substrate and a polyurea coating comprising an adduct of aminosilane and a material chosen from (meth)acrylate, a lactone and mixtures thereof.

The present invention is also directed to a method of improving adhesion between a coating composition comprising polyurea and a substrate
comprising, applying to at least a portion of the substrate a coating composition or an adhesion promoting composition of the present invention.

[00010] The present invention is further directed to a coated article comprising a substrate and a coating layer formed by the coating composition of the present invention, deposited on at least a portion of the substrate.

[00011] The present invention is also directed to a method of improving adhesion between two coating layers comprising providing a substrate having a clear coat composition deposited thereon; applying an adhesion promoting composition of the present invention over at least a portion of the coated substrate; and applying over the adhesion promoting composition a coating composition comprising polyurea.

**DETAILED DESCRIPTION OF THE INVENTION**

[00012] The present invention is directed to compositions comprising an adduct of an aminosilane and a material chosen from an acrylate, a methacrylate, a lactone and mixtures thereof, and methods of applying the compositions to improve the adhesion of a polyurea or polyurethane and polyurethane coating to a substrate. In an embodiment, the adduct of the invention is present in a coating composition comprising polyurea or polyurethane and polyurethane. In another embodiment, the adduct of the present invention is present in an adhesion promoting composition.

[00013] In the coating composition of the present invention, the polyurea or polyurethane may be formed by the reaction product of isocyanate and amine. The ratio of equivalents of isocyanate groups to equivalents of amine groups is greater than 1 and the isocyanate and the amine reaction product may be applied to a substrate at a volume mixing ratio of 1:1.

[00014] As used herein, the term "polyurea" includes the reaction product of an an isocyanate and an amine as described herein. It will be appreciated by those skilled in the art, that polyurethane can be formed as a byproduct in the production of polyurea. Thus, the term "polyurea" as used herein includes polyurea and/or polyurethane. Also, as used herein, the term
"isocyanate" includes unblocked compounds capable of forming a covalent bond with a reactive group such as a hydroxyl or amine functional group. In alternate non-limiting embodiments, the isocyanate of the present invention can be monofunctional containing one isocyanate functional group (NCO) or the isocyanate of the present invention can be polyfunctional containing two or more isocyanate functional groups (NCOs).

[00015] Suitable isocyanates for use in the present invention are numerous and can vary widely. Such isocyanates can include those that are known in the art. Non-limiting examples of suitable isocyanates can include monomeric and/or polymeric isocyanates. The polyisocyanates can be selected from monomers, prepolymers, oligomers, or blends thereof. In an embodiment, the polyisocyanate can be C₂-C₂O linear, branched, cyclic, aromatic, or blends thereof.

[00016] Suitable isocyanates for use in the present invention may include but are not limited to isophorone diisocyanate (IPDI), which is 3,3,5-trimethyl-5-isocyanatomethyl cyclohexyl isocyanate; hydrogenated materials such as cyclohexylene diisocyanate, 4,4′-methylenedicyclohexyl diisocyanate (H₁₂MDI); mixed aralkyl diisocyanates such as tetramethyloxyl diisocyanates, OCN-C(CH₃)₂-C₆H₄C(CH₃)₂-NCO; polymethylene isocyanates such as 1,4-tetramethylene diisocyanate, 1,5-pentamethylene diisocyanate, 1,6-hexamethylene diisocyanate (HMDI), 1,7-heptamethylene diisocyanate, 2,2,4- and 2,4,4-trimethylhexamethylene diisocyanate, 1,10-decamethylene diisocyanate and 2-methyl-1,5-pentamethylene diisocyanate; and mixtures thereof.

[00017] Non-limiting examples of aromatic isocyanates for use in the present invention may include but are not limited to phenylene diisocyanate, toluene diisocyanate (TDI), xylene diisocyanate, 1,5-naphthalene diisocyanate, chlorophenylene 2,4-diisocyanate, bitoluene diisocyanate, dianisidine diisocyanate, toldine diisocyanate, alkylated benzene diisocyanates, methylene-interrupted aromatic diisocyanates such as methylenediphenyl diisocyanate, 4,4′-isomer (MDI) including alkylated
analogs such as 3,3’-dimethyl-4,4’-diphenylmethane diisocyanate, polymeric methylenediphenyl diisocyanate; and mixtures thereof.

[00018] In a non-limiting embodiment, polyisocyanate monomer may be used. It is believed that the use of a polyisocyanate monomer (i.e., residual-free monomer from the preparation of prepolymer) may decrease the viscosity of the polyurea composition thereby improving its flowability, and may provide improved adhesion of the polyurea coating to a previously applied coating and/or to an uncoated substrate. In alternate embodiments of the present invention, at least 1 percent by weight, or at least 2 percent by weight, or at least 4 percent by weight of the isocyanate component comprises at least one polyisocyanate monomer. In a further embodiment of the invention, isocyanate can include oligomeric polyisocyanate such as but not limited to dimers, trimers, and polymeric oligomers, and modified polyisocyanates such as but not limited to carbodiimides and uretone-imines; and mixtures thereof.

[00019] In a further embodiment of the invention, the isocyanate can include oligomeric polyisocyanates such as but not limited to dimmers, such as the uretdione of 1,6-hexamethylene diisocyanate; trimers, such as the biuret and isocyanurate of 1,6-hexamethylenediisocyanate and the isocyanurate of isophorone diisocyanate; polymeric oligomers; and mixtures thereof. Modified polyisocyanates may also be used, such as but not limited to carbodiimides and uretone-imine, and mixtures thereof. Suitable oligomeric polyisocyanates may include, without limitation, those available under the designation DESMODUR from Bayer Corporation of Pittsburgh, PA such as DESMODUR N 3200, DESMODUR N 3300, DESMODUR N 3400, DESMODUR XP 2410, and DESMODUR XP 2580.

[00020] As used herein, "prepolymer" means polyisocyanate which is pre-reacted with polyamine or other isocyanate reactive group such as polyl. Suitable polyisocyanates include those previously disclosed herein. Suitable polyamines may be numerous and selected from a wide variety known in the art. Non-limiting examples of suitable polyamines may include but are not limited to primary and secondary amines, and mixtures thereof. In an embodiment, the primary and secondary amines may include those disclosed
In another embodiment, polyamines comprising tertiary amine functionality may be used provided that the amine further comprises at least two primary and/or secondary amino groups. Suitable polyols may be numerous and selected from a wide variety known in the art. Non-limiting examples of suitable polyols may include but are not limited to polyether polyols, polyester polyols, polycaprolactone polyols, polycarbonate polyols, polyurethane polyols, polyvinyl alcohols, polymers containing hydroxy functional acrylates, polymers containing hydroxy functional methacrylates, polymers containing allyl alcohols and mixtures thereof.

Suitable amines for use in the present invention can be selected from a wide variety of known amines such as primary and secondary amines, and mixtures thereof. In alternate embodiments, the amine may include monoamines, or polyamines having at least two functional groups such as di-, tri-, or higher functional amines; and mixtures thereof. In further embodiments, the amine may be aromatic or aliphatic such as cycloaliphatic, or mixtures thereof. Non-limiting examples of suitable amines may include aliphatic polyamines such as but not limited to ethylamine, isomeric propylamines, butylamines, pentylamines, hexylamines, cyclohexylamine, ethylene diamine, 1,2-diaminopropane, 1,4-diaminobutane, 1,3-diaminopentane, 1,6-diaminohexane, 2-methyl-1,5-pentane diamine, 2,5-diamino-2,5-dimethylhexane, 2,2,4- and/or 2,4,4-trimethyl-1,6-diamino-hexane, 1,1,1-diaminoundecane, 1,2-diaminododecane, 1,3- and/or 1,4-cyclohexane diamine, 1-amino-3,3,5-trimethyl-5-aminomethyl-cyclohexane, 2,4- and/or 2,6-hexahydrotoluylene diamine, 2,4'- and/or 4,4'-diamino-dicyclohexyl methane and 3,3'-dialkyl4,4'-diamino-dicyclohexyl methanes (such as 3,3'-dimethyl-4,4'-diamino-dicyclohexyl methane and 3,3'-diethyl-4,4'-diamino-dicyclohexyl methane), 2,4- and/or 2,6-diaminotoluene and 2,4'- and/or 4,4'-diaminodiphenyl methane, or mixtures thereof.

Non-limiting examples of secondary amines can include monoacrylate and polyacrylate and methacrylate modified amines as well as acrylate or methacrylate modified monoamines or polyamines. Such acrylate or methacrylate modified amines may comprise aliphatic amines. Non-limiting
examples of suitable aliphatic polyamines may include those disclosed herein. Non-limiting examples of secondary amines may include polyaspartic esters which can include derivatives of compounds such as maleic acid, fumaric acid esters, aliphatic polyamines and the like; and mixtures thereof. In an embodiment, the polyaspartic ester may include the derivative of diethyl maleate and 1,5-diamino-2-methylpentaine, which is available commercially from Bayer Corporation of Pittsburgh, PA under the trade name DESMOPHEN NH1 220. In another embodiment of the present invention, the secondary amine may include an N-alkyl substituted aliphatic amine, such as a cycloaliphatic diamine, which is available commercially from Huntsman Corporation (Houston, TX) under the designation of JEFFLINK, including but not limited to JEFFLINK 754, and from Dorf-Ketal Chemicals, LLC under the designation CLEARLINK 1000.

In another embodiment, the amine can include an amine-functional resin. Suitable amine-functional resins can be selected from a wide variety known in the art and can include those having relatively low viscosity. In a non-limiting embodiment, the amine-functional resin may be an ester of an organic acid, for example, an aspartic ester-based amine-functional reactive resin that is compatible with isocyanate.

In a non-limiting embodiment, the amine may include high molecular weight amine, such as but not limited to polyoxyalkyleneamine. The polyoxyalkyleneamines may comprise two or more primary or secondary amino groups attached to a backbone derived, for example, from propylene oxide, ethylene oxide, butylene oxide or mixtures thereof. Non-limiting examples of such amines may include those available under the designation JEFFAMINE from Huntsman Corporation. In an embodiment, such amines may have a molecular weight ranging from 200 to 7500, such as but not limited to JEFFAMINE D-230, D-400, D-2000, HK-511, ED-600, ED-900, ED-2003, T-403, T-3000, T-5000, SD-231, SD-401, SD-2001 and ST-404.

In another embodiment, the amine for use in the present invention can include the reaction product of primary amine with monoepoxide to produce secondary amine and reactive hydroxyl group.
[00026] In a further embodiment, the amine may be a mixture of primary and secondary amines wherein the primary amine may be present in an amount of from 20 to 80 percent by weight or from 20 to 50 percent by weight, with the balance being secondary amine. In other embodiments, the primary amines present in the composition may have a molecular weight greater than 200, and the secondary amines present may include diamine having molecular weight of at least 190, or from 210 to 230.

[00027] In a further embodiment, the amine component may include no primary amine.

[00028] In another embodiment, the amine may include at least one secondary amine which may be present in an amount of from 20 to 80 percent by weight or 50 to 80 percent by weight.

[00029] In another embodiment, the amine may include aliphatic amine. It is believed that the presence of aliphatic amine may provide enhanced durability. In this embodiment, the amine typically is provided as a liquid having a relatively low viscosity, for example, less than about 100 mPa*s at 25°C.

[00030] In an embodiment, the coating composition of the present invention may include a blend of polyurea and polyurethane. It will be appreciated by those skilled in the art that polyurethane can be formed as a by-product in the production of the polyurea. In alternate embodiments, the polyurethane can be formed in-situ and/or it can be added to the reaction mixture during formation of the polyurea. A non-limiting example of polyurethane formed in-situ may include the reaction product of polyisocyanate and hydroxyl-functional material. Non-limiting examples of suitable polyisocyanates may include those described herein. Non-limiting examples of suitable hydroxyl-functional material may include polyol such as those described herein. Another example of polyurethane formed in-situ may include the reaction product of prepolymer and isocyanate-functional material. Suitable examples of these reactants may include those described herein.

[00031] The adduct for use in the coating composition of the present invention may be prepared by combining an aminosilane and an acrylate, or
an aminosilane and a methacrylate, or an aminosilane and a lactone, or by combining an aminosilane with any combination of acrylate, methacrylate and/or lactone. The amount of aminosilane, and acrylate, methacrylate and lactone may vary. In an embodiment, wherein aminosilane is combined with acrylate and/or methacrylate, the amount of these reactants used is such that substantially all of the acrylate functionality is consumed in the reaction. In a further embodiment, the equivalent ratio of amino functional groups to acrylate functional groups may be from 1.0:1.0 to 1.1:1.0, or from 1.01:1.0 to 1.05:1.0. In another embodiment, wherein aminosilane is combined with lactone, the equivalent ratio of amino functional groups to lactone functional groups may be from 1.0:1.0 to 1.0 to 20.0, or from 1.0:1.0 to 1.0:2.0.

[00032] Any suitable aminosilanes may be used. Non-limiting examples of suitable aminosilanes may include aminotrialkoxysilanes such as 3-aminopropyltriethoxysilane, 3-aminopropyltrimethoxysilane, 2-aminoethyl-3-aminopropyltrimethoxysilane, and 2-aminoethyl-3-aminopropyltriethoxysilane; aminodialkoxyalkylsilanes such as 3-aminopropylmethyldimethoxysilane and 3-aminopropylmethyldiethoxysilane, and mixtures thereof.

[00033] Any suitable acrylate and/or methacrylate may be used. Suitable acrylates and methacrylates may include mono-, di-, tri-functional and higher-functional acrylates and methacrylates, and mixtures thereof. As used herein, the term "(meth)acrylate" is understood to include both the analogous acrylate and methacrylate. Non-limiting examples of mono (meth)acrylates may include but are not limited to methyl (meth)acrylate, ethyl (meth)acrylate, butyl (meth)acrylate, isobutyl (meth)acrylate, cyclohexyl (meth)acrylate, 2-ethylhexyl (meth)acrylate, isoctyl (meth)acrylate, isodecyl (meth)acrylate, lauryl (meth) acrylate, stearyl (meth)acrylate, isobornyl (meth)acrylate, hydroxyethyl (meth)acrylate, hydroxypropyl (meth)acrylate, 4-hydroxybutyl (meth)acrylate, and adducts of hydroxy (meth)acrylates with lactones such as the adducts of hydroxyethyl (meth)acrylate with ε-caprolactone, and mixtures thereof.

[00034] Non-limiting examples of di(meth)acrylates may include but are not limited to ethylene glycol di(meth)acrylate, 1,3-butylene glycol
di(meth)acrylate, 1,4-butanediol di(meth)acrylate, 2,3-dimethylpropane 1,3-di(meth)acrylate, 1,6-hexanediol di(meth)acrylate, propylene glycol di(meth)acrylate, dipropylene glycol di(meth)acrylate, tripropylene glycol di(meth)acrylate, tetrapropylene glycol di(meth)acrylate, ethoxylated hexanediol di(meth)acrylate, propoxylated hexanediol di(meth)acrylate, neopentyl glycol di(meth)acrylate, alkoxylated neopentyl glycol di(meth)acrylate, hexylene glycol di(meth)acrylate, diethylene glycol di(meth)acrylate, polyethylene glycol di(meth)acrylate, polybutadiene di(meth)acrylate, thiodiethylene glycol di(meth)acrylate, trimethylene glycol di(meth)acrylate, triethylene glycol di(meth)acrylate, alkoxylated hexanediol di(meth)acrylate, alkoxylated hexanediol di(meth)acrylate, pentaerythritol tetra(meth)acrylate, ethoxylated pentaerythritol tetra(meth)acrylate, propoxylated pentaerythritol tetra(meth)acrylate, and dipentaerythritol penta(meth)acrylate, and mixtures thereof.

Non-limiting examples of tri and higher (meth)acrylates may include but are not limited to trimethylolpropane tri(meth)acrylate, ethoxylated trimethylolpropane tri(meth)acrylate, propoxylated trimethylolpropane tri(meth)acrylate, ditrimethylolpropane tetra(meth)acrylate, pentaerythritol tetra(meth)acrylate, ethoxylated pentaerythritol tetra(meth)acrylate, propoxylated pentaerythritol tetra(meth)acrylate, and dipentaerythritol penta(meth)acrylate, and mixtures thereof.

Further, (meth)acrylate monomers and mixtures thereof may also be used.

In a non-limiting embodiment, the (meth)acrylate may be selected from ethyl acrylate, butyl acrylate, 1,6-hexanediol diacrylate, and trimethylolpropane triacrylate, and mixtures thereof.

Any suitable lactone may be used. Non-limiting examples of suitable lactones may include those known in the art such as but not limited to β-propiolactone, β-butyrolactone, γ-butyrolactone, γ-valerolactone, δ-valerolactone, γ-caprolactone, δ-caprolactone, and ε-caprolactone. In a non-limiting embodiment, the lactone may be ε-caprolactone.

In an embodiment, the adduct of aminosilane and acrylate and/or methacrylate, and/or lactone may include additives such as but not
limited to free radical polymerization inhibitors and catalysts. Such suitable inhibitors and catalysts may include those known in the art. Non-limiting examples of inhibitors may include hydroquinone, 4-methoxyphenol, 2,6-di-tert-butyl p-cresol, phenothiazine, and mixtures thereof. Non-limiting examples of catalysts may include tin compounds such as dibutyltin dilaurate and dibutyltin diacetate; zinc compounds, titanium compounds, tertiary amines and mixtures thereof.

[00040] The reaction of an aminosilane with an acrylate, and/or a methacrylate, and/or a lactone, may produce a material that is hydroxyl terminal and/or secondary amino functional. Not intending to be bound by any mechanism or theory, it is believed that the reaction of a primary aminosilane with an acrylate and/or a methacrylate may produce an adduct that is secondary amino functional. An adduct that is both secondary amino functional and hydroxyl functional may be produced wherein the acrylate and/or methacrylate is additionally hydroxyl functional. Further, not intending to be bound by any mechanism or theory, it is believed that the reaction of an aminosilane with a lactone may initially produce an adduct that is hydroxyl terminal comprising an amide linkage, for example, when 1.0 mole of aminosilane is combined with 1.0 mole of lactone. The further reaction of the initial adduct with additional lactone may produce a material that is hydroxyl terminal having both ester and amide linkages.

[00041] The addition of aminosilane with an acrylate, and/or a methacrylate, and/or a lactone can be carried out at a wide range of temperatures. In an embodiment, the reaction can be carried out at a temperature within a range of from ambient temperature to 160°F. The aminosilane and the acrylate and/or methacrylate and/or lactone may be combined in the presence or the absence of solvent. In an embodiment, wherein a solvent is present, the solvent may be selected any suitable organic solvents known in the art. Non-limiting examples may include but are not limited to aromatic petroleum distillates such as toluene, xylene, and aromatic blends; aliphatic solvents such as cyclohexane and naphthas; ketones such as acetone, methyl ethyl ketone, methyl isobutyl ketone, and methyl amyl
ketone; alcohols such as ethyl alcohol, propyl alcohol, and diacetone alcohol; mono- and dialkyl ethers of ethylene and diethylene glycol like ethylene glycol monoethyl ether, ethylene glycol monobutyl ether, ethylene glycol monoethyl ether acetate, diethylene glycol monobutyl ether, and diethylene glycol diethyl ether, acetates such as n-butyl acetate and 1-methoxy-2-propanol acetate; methyl benzene; 2-butanone; and mixtures thereof.

[00042] In the coating composition of the present invention, the adduct may be combined with the isocyanate and/or the amine which are then reacted to form the polyurea or polurea and polyurethane. The adduct can be present in the coating composition of the present invention in varying amounts. In an embodiment, the adduct may be present in the coating composition in an effective amount. As used herein, the term "effective amount" means that amount which results in any degree of improved adhesion. In another embodiment, the adduct is added to the amine, and the adduct is present in an amount of from 0.01 to 2.0% by weight, or from 0.1 to 1.0% by weight of the amine.

[00043] In an embodiment, the coating composition of the present invention may include catalyst and/or an imidazole silane. A wide variety of catalysts can be used and can include those known in the art for use with polyureas and polyurethanes. Non-limiting examples can include but are not limited to tertiary amine catalysts, tin compounds or mixtures thereof. In alternate non-limiting embodiments, the catalyst can be dimethyl cyclohexylamine, dibutyl tin dilaurate or mixtures thereof. The catalyst and/or imidazole silane may be combined with the isocyanate and/or the amine components. In an embodiment, the catalyst and/or imidazole silane may be combined with the amine and adduct of the present invention.

[00044] In other embodiments, the coating composition of the present invention may optionally include inert materials such as but not limited to fillers, flame retardants, fiberglass, stabilizers, thickeners, other adhesion promoters, catalysts, colorants, other performance or property modifiers which are well known in the art of surface coatings, and mixtures thereof. In alternate embodiments, such additives may be combined with the isocyanate,
the amine, or both. In a further embodiment, at least one of these materials is
added to the amine prior to reaction with isocyanate.

[00045] In another embodiment, the composition may further comprise a
filler such as but not limited to clay, silica or mixtures thereof. In a further
embodiment, the filler may be added to the amine. Such a coating
composition has been found to have better adhesion to a metal substrate than
a similar coating composition without clay or silica (as determined in
accordance with the test method in ASTM D 1876, without use of a fixturing
device).

[00046] The clay may be selected from any of a variety of clays known in
the art including montmorillonite clays such as bentonite, kaolin clays,
attapulgite clays, sepiolite clay, and mixtures thereof. Additionally, the clay
may be surface treated as is known in the art. Any suitable surface treatment
may be used. In a non-limiting embodiment, the clay may be treated with one
or more of the following amines:

\[
\begin{align*}
R^1-N & \quad R^2 \quad R^3 \\
R^1-N^+ & \quad R^2 \quad R^3 \quad R^7 \\
R^4-C(O)-NR & \quad 5. \quad R^6\cdot N \quad R^2 \quad R^3 \\
R^4-C(O)-NR & \quad 5. \quad R^6\cdot N^+ \quad R^2 \quad R^3 \quad R^7
\end{align*}
\]

[00048] wherein \( R^1 \) and \( R^4 \) are independently \( C_4-C_{24} \) linear, branched, or
cyclic alkyl, aryl, alkenyl, aralkyl or aralkyl, \( R^2, R^3, R^5 \) and \( R^7 \) are
independently \( H \) or \( \text{CrC}_2 \) linear, branched, or cyclic alkyl, aryl, alkenyl,
aralkyl or aralkyl, and \( R^6 \) is \( C_1-C_{24} \) linear, branched, or cyclic alkylene,
arylene, alkenylene, aralkylene or aralkylene.

[00049] In a non-limiting embodiment, surface treated bentonite may be
used.

[00050] In an embodiment, the clay may be present in the coating
composition of the present invention in an amount of at least 0.5 percent by
weight, or at least 1 percent by weight, or at least 1.5 percent by weight. In
other embodiments, the clay can be present in an amount of up to 6 percent
by weight, or up to 5 percent by weight, or up to 4 percent by weight of the composition. The amount of clay in the coating composition can be any value or range between any values recited above, with the proviso that the adhesion properties and application viscosity of the coating composition are not adversely affected.

[00051] In another embodiment, the coating composition of the present invention may include silica. Any suitable silica can be used, provided that application and coating performance properties are not adversely impacted. The silica may be selected from surface-treated/surface-modified silica, untreated/unmodified silica and mixtures thereof. Non-limiting examples of suitable silica may include but are not limited to precipitated, fumed, colloidal and mixtures thereof. In alternate non-limiting embodiments, the silica may be present in an amount such that it constitutes at least 0.5 percent by weight, or at least 1 percent by weight, or at least 1.5 percent by weight of the coating composition. In other embodiments, the silica can be present such that it constitutes up to 6 percent by weight, or up to 5 percent by weight, or up to 4 percent by weight of the composition. The amount of silica in the two-component coating composition can be any value or range between any values recited above, provided that the adhesion properties and application viscosity of the coating composition are not adversely affected.

[00052] In a non-limiting embodiment, the coating composition of the present invention may include flame and/or heat resistant material such as flame retardant. The flame retardant may be selected from a wide variety of flame retardants that are known in the art. Non-limiting examples of suitable flame retardants may include the flame retardant polymers disclosed in United States Patent Nos. 6,015,510 (column 4, line 31 thru column 5, line 41) and 5,998,503 (column 4, line 31 thru column 5, line 41). Further suitable flame retardants may include halogenated phosphates or halogen free phosphates, powdered or fumed silica, layered silicates, aluminum hydroxide, brominated fire retardants, tris(2-chloropropyl) phosphate, tris(2,3-dibromopropyl)phosphate, tris(1,3-dichloropropyl)phosphate, diammonium
phosphate, various halogenated aromatic compounds, antimony oxide, alumina trihydrate, polyvinyl chloride and the like, and mixtures thereof.

[00053] The coatings of the present invention can also include a colorant. As used herein, the term "colorant" means any substance that imparts color and/or other opacity and/or other visual effect to the composition. The colorant can be added to the coating in any suitable form, such as discrete particles, dispersions, solutions and/or flakes. A single colorant or a mixture of two or more colorants can be used in the coatings of the present invention.

[00054] Example colorants include pigments, dyes and tints, such as those used in the paint industry and/or listed in the Dry Color Manufacturers Association (DCMA), as well as special effect compositions. A colorant may include, for example, a finely divided solid powder that is insoluble but wettable under the conditions of use. A colorant can be organic or inorganic and can be agglomerated or non-agglomerated. Colorants can be incorporated into the coatings by use of a grind vehicle, such as an acrylic grind vehicle, the use of which will be familiar to one skilled in the art.

[00055] Example pigments and/or pigment compositions include, but are not limited to, carbazole dioxazine crude pigment, azo, monoazo, disazo, naphthol AS, salt type (lakes), benzimidazolone, condensation, metal complex, isoindolinone, isoindoline and polycyclic phthalocyanine, quinacridone, perylene, perinone, diketopyrrolo pyrrole, thioindigo, anthraquinone, indanthrone, anthrapyrimidine, flavanthrone, pyranthrone, anthanthrone, dioxazine, triarylcyanonium, quinophthalone pigments, diketo pyrrolo pyrrole red ("DPPBO red"), titanium dioxide, carbon black and mixtures thereof. The terms "pigment" and "colored filler" can be used interchangeably.

[00056] Example dyes include, but are not limited to, those that are solvent and/or aqueous based such as pthalo green or blue, iron oxide, bismuth vanadate, anthraquinone, perylene, aluminum and quinacridone.

[00057] Example tints include, but are not limited to, pigments dispersed in water-based or water miscible carriers such as AQUA-CHEM 896.
commercially available from Degussa, Inc., CHARISMA COLORANTS and MAXITONER INDUSTRIAL COLORANTS commercially available from Accurate Dispersions division of Eastman Chemical, Inc.

As noted above, the colorant can be in the form of a dispersion including, but not limited to, a nanoparticle dispersion. Nanoparticle dispersions can include one or more highly dispersed nanoparticle colorants and/or colorant particles that produce a desired visible color and/or opacity and/or visual effect. Nanoparticle dispersions can include colorants such as pigments or dyes having a particle size of less than 150 nm, such as less than 70 nm, or less than 30 nm. Nanoparticles can be produced by milling stock organic or inorganic pigments with grinding media having a particle size of less than 0.5 mm. Example nanoparticle dispersions and methods for making them are identified in U.S. Patent No. 6,875,800 B2, which is incorporated herein by reference. Nanoparticle dispersions can also be produced by crystallization, precipitation, gas phase condensation, and chemical attrition (i.e., partial dissolution). In order to minimize re-agglomeration of nanoparticles within the coating, a dispersion of resin-coated nanoparticles can be used. As used herein, "dispersion of resin-coated nanoparticles" refers to a continuous phase in which is dispersed discreet "composite microparticles" that comprise a nanoparticle and a resin coating on the nanoparticle. Example dispersions of resin-coated nanoparticles and methods for making them are identified in United States Patent Application Publication 2005-0287348 A1, filed June 24, 2004, U.S. Provisional Application No. 60/482,167 filed June 24, 2003, and United States Patent Application Serial No. 11/337,062, filed January 20, 2006, which is also incorporated herein by reference.

Example special effect compositions that may be used in the coating of the present invention include pigments and/or compositions that produce one or more appearance effects such as reflectance, pearsence, metallic sheen, phosphorescence, fluorescence, photochromism, photosensitivity, thermochromism, goniocromism and/or color-change. Additional special effect compositions can provide other perceptible
properties, such as opacity or texture. In a non-limiting embodiment, special
effect compositions can produce a color shift, such that the color of the
coating changes when the coating is viewed at different angles. Example
color effect compositions are identified in U.S. Patent No. 6,894,086,
incorporated herein by reference. Additional color effect compositions can
include transparent coated mica and/or synthetic mica, coated silica, coated
alumina, a transparent liquid crystal pigment, a liquid crystal coating, and/or
any composition wherein interference results from a refractive index
differential within the material and not because of the refractive index
differential between the surface of the material and the air.

[00060] In certain non-limiting embodiments, a photosensitive
composition and/or photochromic composition, which reversibly alters its color
when exposed to one or more light sources, can be used in the coating of the
present invention. Photochromic and/or photosensitive compositions can be
activated by exposure to radiation of a specified wavelength. When the
composition becomes excited, the molecular structure is changed and the
altered structure exhibits a new color that is different from the original color of
the composition. When the exposure to radiation is removed, the
photochromic and/or photosensitive composition can return to a state of rest,
in which the original color of the composition returns. In one non-limiting
embodiment, the photochromic and/or photosensitive composition can be
colorless in a non-excited state and exhibit a color in an excited state. Full
color-change can appear within milliseconds to several minutes, such as from
20 seconds to 60 seconds. Example photochromic and/or photosensitive
compositions include photochromic dyes.

[00061] In a non-limiting embodiment, the photosensitive composition
and/or photochromic composition can be associated with and/or at least
partially bound to, such as by covalent bonding, a polymer and/or polymeric
materials of a polymerizable component. In contrast to some coatings in
which the photosensitive composition may migrate out of the coating and
crystallize into the substrate, the photosensitive composition and/or
photochromic composition associated with and/or at least partially bound to a
polymer and/or polymerizable component in accordance with a non-limiting embodiment of the present invention, have minimal migration out of the coating. Example photosensitive compositions and/or photochromic compositions and methods for making them are identified in U.S. Application Serial No. 10/892,919 filed July 16, 2004 and incorporated herein by reference.

[00062] In general, the colorant can be present in the coating composition in any amount sufficient to impart the desired visual and/or color effect. The colorant may comprise from 1 to 65 weight percent of the present compositions, such as from 3 to 40 weight percent or 5 to 35 weight percent, with weight percent based on the total weight of the compositions.

[00063] In another embodiment, the coating composition of the present invention when applied to a substrate possesses color that matches the color of an associated substrate. As used herein and in the claims, the term "matches" or like terms when referring to color matching means that the color of the coating composition of the present invention substantially corresponds to a desired color or the color of an associated substrate. This can be visually observed, or confirmed using spectroscopy equipment. For example, the substrate may be an article of manufacture or structure. The article or structure may be a multi-layer coating composite comprising a pretreated substrate with various coating layers such as electocoat, primer, base coat and clear coat. At least one of the base coat and clear coat may contain colorant and/or the clear coat may contain an adhesion promoter. It is believed that the addition of adhesion promoter to the clear coat may improve the adhesion between the clear coat and the coating composition applied thereover, although the inventors do not wish to be bound by any mechanism. In this embodiment, the coating composition of the present invention may be the reaction product of isocyanate and amine with a colorant additive. The coating composition of the present invention containing colorant may be applied to at least a portion of the article or structure. The color of the coated article or structure may match the color of an associated substrate. An "associated substrate" may refer to a substrate which comprises the article or
structure but is not coated with the coating composition of the present invention; or a substrate which is attached, connected or in close proximity to the article or structure, but is not coated with the coating composition of the present invention.

In another embodiment, the coating composition of the present invention may include additional adhesion promoters. Non-limiting examples of suitable adhesion promoters for use in the present invention may include amine-functional materials such as 1,3,4,6,7,8-hexahydro-2H-pyrimido-(1,2-A)-pyrimidine, hydroxyethyl piperazine, N-aminoethyl piperizine, dimethylamine ethylether, tetramethyliminopropylamine (commercially available as POLYCAT 15 from Air Products and Chemicals, Inc.), blocked amines such as an adduct of IPDI and dimethylamine, tertiary amines, such as 1,5-diazabicyclo[4.3.0]non-5-ene, 1,8-diazabicyclo[5.4.0]undec-7-ene, 1,4-diazabicyclo[2.2.2]octane, 1,5,7-triazabicyclo[4.4.0]dec-5-ene, and 7-methyl-1,5,7-triazabicyclo[4.4.0]dec-5-ene, amino silanes such as γ-aminopropyltriethoxysilane (commercially available as Silquest A1100 from GE Silicones, General Electric Company), melamine or amino melamine resin (e.g. Cymel 220 or Cymel 303, available from Cytec Industries Inc.), metal complexes including metal chelate complexes such as an aluminum chelate complex (e.g. K-KAT 5218 available from King Industries) or tin-containing compositions such as stannous octoate and organotin compounds such as dibutyltin dilaurate and dibutyltin diacetate, urethane acrylate compositions, salts such as chlorine phosphate, butadiene resins such as an epoxidized, hydroxyl terminated polybutadiene resin (e.g. POLY BD 605E available from Atofina Chemicals, Inc.), polyester polyols (e.g. CAPA 3091, a polyester triol available from Solvay America, Inc., and urethane acrylate compositions such as an aromatic urethane acrylate oligomer (e.g. CN999 available from Sartomer Company, Inc.); and mixtures thereof. In an embodiment, the adhesion promoter may comprise at least one component selected from melamine, urethane acrylate, metal chelate complex, salt, tin-containing compound and polyhydric polymer.
The polyurea coating composition of the present invention may be prepared and applied using various techniques known in the art. Non-limiting examples of suitable application techniques may include, but are not limited to, brushing, wiping, spraying, dipping or flowcoating. In an embodiment, the coating composition can be applied using conventional spraying techniques. In this embodiment, the isocyanate and amine may be combined such that the ratio of equivalents of isocyanate groups to equivalents of amine groups is greater than 1 and the isocyanate and amine can be applied to a substrate at a volume mixing ratio of 1:1; and the reaction mixture may be applied to an uncoated or coated substrate to form a first coating on the uncoated substrate or a subsequent coating on the coated substrate. In alternate embodiments, the adduct of the present invention may be combined with the isocyanate, or the amine, or both. In an embodiment, the adduct may be combined with the amine component.

In an embodiment, the sprayable coating composition may be prepared using a two-component mixing device. In this embodiment, isocyanate and amine are added to a high pressure impingement mixing device. The isocyanate is added to the "A-side" and amine is added to the "B-side". The adduct of the present invention may be added to the A-side and/or the B-side. In an embodiment, the adduct may be added to the B-side. The A- and B-side streams are impinged upon each other and immediately sprayed onto at least a portion of an uncoated or coated substrate. The isocyanate and the amine react to produce a coating composition which is cured upon application to the uncoated or coated substrate.

The volume mixing ratio of the isocyanate and amine may be such that the resulting isocyanate and amine reaction mixture can be applied to a substrate at a volume mixing ratio of 1:1.

It is believed that the ratio of equivalents of isocyanate groups to amine groups may be selected to control the rate of cure of the coating composition of the present invention. It has been found that cure and adhesion advantages may result when applying the coating in a 1:1 volume ratio wherein the ratio of the equivalents of isocyanate groups to amine
groups (also known as the reaction index) is greater than one, such as from
1.01 to 1.10:1, or from 1.03 to 1.10:1, or from 1.05 to 1.08:1, or from 1.01 to
1.20:1, or from 1.01 to 1.30:1, or from 1.01 to 1.40:1, or from 1.01 to 1.50:1.
The term “1:1 volume ratio” means that the volume ratio varies by up to 20%
for each component, or up to 10% or up to 5%.

[00069] In a non-limiting embodiment, a mixing device available
commercially under the designation GUSMER VR-H-3000 proportioner fitted
with a GUSMER Model GX-7 spray gun may be used. In this device,
pressurized streams of the A- and B-side components are delivered from two
separate chambers, are impacted or impinged upon each other at high
velocity, to mix the two components and form a coating composition, which
may be applied to an uncoated or coated substrate using the spray gun. The
mixing forces experienced by the component streams may be depend upon
the volume of each stream entering the mixing chamber per unit time and the
pressure at which the component streams are delivered. A 1:1 volume ratio
of the isocyanate and amine per unit time may equalize these forces.

[00070] Another suitable application device known in the industry
includes a "static mix tube" applicator. In this device, the isocyanate and
optionally adduct may be stored in one chamber, and the amine and
optionally adduct stored in a separate chamber. As pressure is applied, each
of the isocyanate and amine components is brought into a mixing tube in a 1:1
ratio by volume. Mixing of the components is effected by way of a torturous or
cork screw pathway within the tube. The exit end of the tube may have
atomization capability useful in spray application of the reaction mixture.
Alternatively, the fluid reaction mixture may be applied to a substrate as a
bead. A static mix tube applicator is commercially available from Cammda
Corporation.

[00071] The polyurea coating composition of the present invention may
be applied to a wide variety of substrates. Non-limiting examples of suitable
substrates can include but are not limited to metal, natural and/or synthetic
stone, ceramic, glass, brick, cement, concrete, cinderblock, wood and
composites and laminates thereof; wallboard, drywall, sheetrock, cement
board, plastic, paper, PVC, Styrofoam, plastic composites, acrylic composites, asphalt, fiberglass, soil, gravel and the like. Further, the coating composition of the present invention can be applied to said substrates to impart one or more of a wide variety of properties such as but not limited to corrosion resistance, abrasion resistance, impact damage, flame and/or heat resistance, chemical resistance, UV light resistance, structural integrity, ballistic mitigation, blast mitigation, sound dampening, decoration and the like. As used herein, "ballistic mitigation" refers to reducing or alleviating the effects of a bullet or other type of firearm ammunition. As used herein, "blast mitigation" refers to reducing or alleviating the secondary effects of a blast. In non-limiting examples, the coating composition of the present invention can be applied to at least a portion of the following substrates: an article of manufacture such as but not limited to civilian, commercial, and military land-, water-, and air-vehicles, for example, trucks, boats, ships, submarines, airplanes, helicopters, humvees and tanks; and at least a portion of a structure including commercial and military structures, for example, roofs, floors, support beams, walls and the like. As used herein, the term "substrate" may refer to a surface on at least a portion of an article or the article itself which comprises the substrate. In an embodiment, the substrate is a truck bed.

[00072] In an embodiment, the polyurea/polyurethane coating composition of the present invention may be applied to a carrier film. The carrier film can be selected from a wide variety of such materials known in the art. Non-limiting examples of suitable carrier films may include, but are not limited to thermoplastic materials, thermosetting materials, metal foils, cellulosic paper, synthetic papers, and mixtures thereof. As used herein, the term "thermoplastic material" refers to any material that is capable of softening or fusing when heated and of solidifying (hardening) again when cooled. Non-limiting examples of suitable thermoplastic materials may include polyolefins, polyurethanes, polyesters, polyamides, polyureas, acrylics, and mixtures thereof. As used herein, the term "thermosetting material" refers to any material that becomes permanently rigid after being heated and/or cured.
Non-limiting examples may include polyurethane polymers, polyester polymers, polyamide polymers, polyurea polymers, polycarbonate polymers, acrylic polymers, resins, aminoplasts, isocyanates, epoxies and copolymers thereof, and mixtures thereof. As used herein, the term "foil" refers to a thin and flexible sheet of metal. Non-limiting examples may include aluminum, iron, copper, manganese, nickel, combinations thereof, and alloys thereof. This embodiment is shown in FIG. 1, where metal foil carrier film 4 is coated by coating layer 2. As used herein, the term "synthetic paper" refers to synthetic plain or calendered sheets that can be coated or uncoated and are made from films containing polypropylene, polyethylene polystyrene, cellulose esters, polyethylene terephthalate, polyethylene naphthalate, poly 1,4-cyclohexanediyl terephthalate, polyvinyl acetate, polyimide, polycarbonate, and combinations and mixtures thereof. A non-limiting example of suitable synthetic paper is available under the tradename TESLIN from PPG Industries, Inc., Pittsburgh, PA.

[00073] In an embodiment, a carrier film having a first and second major surface may serve as a substrate and the coating composition of the present invention may be applied to the first surface of the film to form a coating layer. A further embodiment is shown in FIG. 2, where carrier film 8 is a thermoplastic material, a thermosetting material, or a synthetic paper, which is coated by coating layer 6.

[00074] In alternate embodiments, the carrier film may have a film thickness of at least 0.5 μm, or at least 1 μm, or at least 2 μm, or at least 3 μm or at least 5 μm. In other embodiments, the carrier film may have a thickness of up to 100 μm, or up to 90 μm, or up to 75 μm, or up to 50 μm, or up to 40 μm thick. The carrier film can vary and range between any thickness recited above provided that the carrier film can adequately support the coating layer and is sufficiently flexible for a desired end use application.

[00075] In another embodiment, the carrier film may include an adhesive layer superimposed on the second surface of the film. Any suitable adhesive composition known in the art can be used to form the adhesive layer. Suitable adhesive compositions include those that contain at least one
acrylic latex polymer prepared from a monomer composition that includes C1-C5 linear, branches, or cyclic alkyl (meth)acrylate monomers.

[00076] In a further embodiment, a temporary protective cover may be superimposed over the adhesive layer. Any suitable material can be used as the protective cover. Suitable materials include, but are not limited to, paper and polymeric materials. This embodiment may include the composite shown in FIG. 3, where carrier film 12 is a thermoplastic material, a thermosetting material, or a synthetic paper, which is coated on a first side by coating layer 10. Adhesive layer 14 is coated on a second side of carrier film 12, which is in turn covered by protective layer 16. In these embodiments, the temporary protective cover can be removed and the second side of the carrier film may be applied or adhered to a desired substrate.

[00077] In alternate embodiments, the polyurea composition of the present invention may be applied to a bare (e.g., untreated, uncoated) substrate, a pretreated substrate and/or coated substrate having a first coating or subsequent coatings to enhance adhesion between a coating and a substrate and/or between two coatings. In a non-limiting embodiment, the coating composition of the present invention may be applied to a multi-layer coating composite. The first coating applied to a substrate may be selected from a variety of coating compositions known in the art for surface coating substrates. Non-limiting examples may include but are not limited to electrodepositable film-forming compositions, primer compositions, pigmented or non-pigmented monocoat compositions, pigmented or non-pigmented base coat compositions, transparent topcoat compositions, industrial coating compositions, and the like. In an embodiment, the polyurea coating composition of the present invention then may be at least partially applied over the first coating to improve adhesion between the first coating and the coating formed by the polyurea coating composition of the present invention. In another non-limiting embodiment, the polyurea coating composition of the present invention may be applied to a multi-layer coating composite comprising a pretreated substrate and coating layers such as but not limited to electrocoat, primer, base coat, clear coat, and combinations thereof. In a
further embodiment, the polyurea coating composition of the present invention may be applied to a clear coat to improve adhesion between the clear coat layer and the layer formed by the coating composition of the present invention. In this embodiment, the clear coat may comprise silane functional groups. In an embodiment, silane functional groups may be present in the clear coat composition prior to crosslinking and curing of the clear coat. In another embodiment, silane functional groups may be present in the clear coat composition following crosslinking and curing of the clear coat.

[00078] Not intending to be bound by any mechanism or theory, it is believed that the adduct of aminosilane with an acrylate and/or methacrylate, and/or lactone when present in the polyurea or polyurethane coating composition, may migrate to the interface of the two coating layers formed between the coated substrate and the polyurea/polyurethane coating composition, wherein the silane end chemically bonds to the coating layer on the substrate and the amino or hydroxyl functional end chemically bonds to the coating layer formed by the polyurea/polyurethane composition to enhance adhesion. In an embodiment, the pull strength of the bond between the coated substrate and the polyurea/polyurethane coating composition of the present invention can be at least 30 lbs / in2. The pull strength can be measured using various means such as that described in the Examples herein.

[00079] In another embodiment, the polyurea coating composition of the present invention can be used in a two-coat application resulting in a textured surface.

[00080] A first coat may be applied to an uncoated or coated substrate to produce a smooth, substantially tack-free layer. The Tack-Free Method may be used to determine if the layer is substantially tack-free. The Tack-Free Method includes spraying the coating composition in one coat onto a non-adhering plastic sheet to a thickness of from 10 to 15 mil (254-381 microns). When spraying is complete, an operator, using a loose fitting, disposable vinyl glove, such as one commercially available under the trade name Ambidex Disposable Vinyl Glove by Marigold Industrial, Norcross GA,
gently touches the surface of the coating. The coating may be touched more than one time by using a different fingertip. When the glove tip no longer sticks to, or must be pulled from, the surface of the layer, the layer is said to be substantially tack-free. The time beginning from the completion of spraying until when the coating is substantially tack-free is said to be the tack-free time. In a non-limiting embodiment, the tack-free time and the cure time may be controlled by balancing levels of various composition components such as the ratio of primary amine to secondary amine.

[00081] A second coat may then be applied to the first coating layer as a texturizing layer or "dust coating". The second coating layer can be applied by increasing the distance between the application/mixing device and the coated substrate to form discrete droplets of the coating composition prior to contacting the coated substrate thereby forming controlled non-uniformity in the surface of the second layer. The substantially tack-free first layer of the coating is at least partially resistant to the second layer; i.e., at least partially resistant to coalescence of the droplets of coating composition sprayed thereon as the second layer or dust coating such that the droplets adhere to but do not coalesce with the previous layer(s) to create surface texture. The final coating layer typically exhibits more surface texture than the first or previous coating layers. An overall thickness of the coating layers may range from 20 to 1000 mils, or from 40 to 150 mils, or from 60 to 100 mils (1524-2540 microns), or from 500 to 750 mils. In a non-limiting embodiment, the first layer may be the majority of the total thickness and the dust coating may be from 15-50 mils (381-1270 microns).

[00082] In various embodiments of the present invention, the "first" coating layer may comprise one, two, three or more layers; and the "second" coating layer may be one or more subsequent layers applied thereover. For example, four polyurea layers may be applied, with the fourth layer being the dust coating and each layer having a thickness of from 15 to 25 mil (381-635 microns).

[00083] In alternate embodiments, the coating layers may comprise the same or different polyurea coating compositions. For example, the first layer
may be a polyurea composition comprising aliphatic and/or aromatic amine and/or, aliphatic and/or aromatic polyisocyanate; and the second layer may comprise the same or different combination of aliphatic and/or aromatic amine and/or, aliphatic and/or aromatic polyisocyanate.

In a further embodiment, the outermost coating layer may comprise a coating composition that provides a desired durability. The desired durability may vary widely and may be dependent on the intended use of the coating composition of the present invention and/or the substrate to which the coating is applied. For example, varying levels of chalking, fading, color change and gloss change may be acceptable for different applications or uses. The durability of a coating may be measured using various equipment and methods known in the art. In general, the outermost coating layer may be placed in an apparatus wherein it may be subjected to artificial and accelerated weathering tests which simulate natural weathering. The specimen may be subjected to controlled cycles of ultraviolet radiation, light, salt, water and heat which are used to simulate the natural conditions of sun, rain and temperature changes. In an embodiment, durability may be tested using a Weatherometer (manufactured by and commercially available from Atlas Material Testing Solutions) in accordance with method SAE J1960. In further embodiments, the durability value as measured by the Weatherometer may be from 1000 kJ to 6000 kJ, or from 800 hours to 4000 hours.

In an embodiment, a combination of aliphatic and/or aromatic amine and/or polyisocyanate may be selected such that the composition of the outermost layer has substantial durability. In this embodiment, the first layer may be a polyurea composition comprising polyisocyanate, amine and adduct, wherein at least one of the amine and/or polyisocyanate may be aromatic, and the second layer may be a polyurea composition comprising aliphatic amine, aliphatic polyisocyanate and adduct. In a further embodiment, the coating composition of the second layer may include aromatic amine and/or aromatic polyisocyanate in an amount consistent with attaining a desired durability.
In another embodiment, the present invention is directed to an adhesion promoting composition comprising an adduct of aminosilane with an acrylate and/or a methacrylate and/or a lactone as previously described herein. In this embodiment, the adduct may be present in the adhesion promoting composition in varying amounts. In an embodiment, the adduct is present in the adhesion promoting composition in an amount of 100% by weight of the composition. In other embodiments, the adhesion promoting composition may further comprise solvent. In alternate embodiments, the adduct may be present in the adhesion promoting composition of the invention in amounts of from greater than 0 percent by weight to 100% by weight of the composition. Any suitable solvent may be used and may include those previously disclosed herein. In a further embodiment, the adhesion promoting composition may comprise adduct and acetone wherein the adduct is present in an amount such that its concentration is from greater than 0 to 5 percent by weight. In an embodiment, water may be present in the adhesion promoting composition in an amount effective to enhance the adhesion properties. It will, however, be recognized by those skilled in the art that the presence of water in excessive amounts can result in self-condensation reaction of the adduct with itself thereby reducing its effectiveness.

The adhesion promoting composition may be applied directly onto a substrate using various techniques known in the art. Non-limiting examples of application techniques may include but are not limited to wiping, dipping, brushing, spraying, rolling, roll coating, curtain coating, or wetting by applying a pool of material and tilting the substrate, and combinations thereof.

The adhesion promoting composition may be applied to any suitable substrate. Suitable substrates may include those previously disclosed herein. Further, the substrate may be uncoated, untreated, treated or coated with at least one coating composition as previously described herein. In an embodiment, the substrate may be bare metal. In another embodiment, the substrate may be coated with a multilayer coating composition. In a further embodiment, the top layer of the multilayer coating composition may be a pigmented monocoat or clearcoat. The clearcoat may
comprise silane functional groups. In this embodiment, the silane functional
groups may be present in the clear coat composition prior to crosslinking and
curing of the clear coat, or the silane functional groups may be present in the
clear coat composition following crosslinking and curing of the clearcoat. In
another embodiment, the substrate may be a truck bed coated with a
multilayer coating composition. Moreover, the adhesion promoting
composition may be applied to a carrier film as previously described herein.
In this embodiment, the carrier film having a first and second major surface
may serve as a substrate and the adhesion promoting composition may be
applied to the first surface of the film and a polyurea or polyurea and
polyurethane coating layer may be formed over at least a portion of the
adhesion promoting composition.

[00089] The adhesion promoting composition can be used in any
amount effective to yield improved adhesion between the substrate and
coating layer(s) applied.

[00090] Following application of the adhesion promoting composition to
a substrate, a period of time may be allowed to pass prior to applying the
polyurea or polyurea and polyurethane coating composition over at least a
portion of the substrate with adhesion promoting composition. The amount of
time may vary. Further, the temperature during the time between application
of the adhesion promoting composition and application of the polyurea coating
composition may also vary. In a non-limiting embodiment, the time may be
such that it is effective to activate the adduct and the temperature may be
ambient temperature. In a further non-limiting embodiment, the time is thirty
(30) minutes.

[00091] Not intending to be bound by any mechanism or theory, it is
believed that the hydroxyl groups or amino groups of the adhesion promoting
composition of the present invention may react with the isocyanate of the
polyurea or polyurea and polyurethane coating composition, and the silane
groups react with the substrate, each forming a chemical bond. The pull
strength between the substrate and the polyurea or polyurea and
polyurethane coating composition wherein the adhesion promoting
composition is present at the interface, may be superior when compared with the pull strength between the substrate and the polyurea or polyurea and polyurethane coating composition wherein either the parent aminosilane and/or secondary amine functional aminosilane that are not the reaction product of an aminosilane and a (meth)acrylate are present at the interface of the two layers.

[00092] Further, without intending to be bound by any mechanism or theory, it is believed that the adduct of the present invention may be capable of orienting itself on the surface of the substrate to enhance or even maximize the degree of chemical bonding occurring between the substrate and the polyurea coating composition.

[00093] In an embodiment, the adhesion promoting composition of the present invention may include adhesion promoting materials in addition to the adduct of an aminosilane and an acrylate, and/or a methacrylate, and/or a lactone. Non-limiting examples of such optional adhesion promoting materials may include those previously disclosed herein.

[00094] The polyurea coating compositions and adhesion promoting compositions of the present invention may be at least partially applied to a wide variety of substrates or portions thereof, or used to form a component of a substrate. Non-limiting examples of uses for the coating composition of the present invention or the adhesion promoting composition in combination with a polyurea or polyurea and polyurethane coating composition, may include but are not limited to roofing systems, sprayed or molded insulating material, tanks and pressure vessels, electrical equipment and components, garments and woven fiber, paper and packaging, sports equipment, paving material or pavement coating, HVAC and related equipment, agricultural and garden equipment, household appliances and the like. In further embodiments, the coating composition of the present invention may be applied as an under body protective coating in the wheel wells and surrounding or related areas of a vehicle; or to encapsulate a battery in a vehicle, particularly a military vehicle, to essentially preclude acid leakage and resulting damage to the vehicle underneath the battery; or to encapsulate printed wire boards; or as a chip
resistant coating applied to the landing gear of an airplane to prevent chips from stones and rocks on the runway; or to provide chip resistance in general to a vehicle or portions thereof.

[00095] Other than in any operating examples, or where otherwise indicated, all numbers expressing quantities of ingredients, reaction conditions and so forth used in the specification and claims are to be understood as being modified in all instances by the term "about." Accordingly, unless indicated to the contrary, the numerical parameters set forth in the following specification and attached claims are approximations that may vary depending upon the desired properties to be obtained by the present invention. At the very least, and not as an attempt to limit the application of the doctrine of equivalents to the scope of the claims, each numerical parameter should at least be construed in light of the number of reported significant digits and by applying ordinary rounding techniques.

[00096] Notwithstanding that the numerical ranges and parameters setting forth the broad scope of the invention are approximations, the numerical values set forth in the specific examples are reported as precisely as possible. Any numerical value, however, inherently contain certain errors necessarily resulting from the standard deviation found in their respective testing measurements.

[00097] Also, it should be understood that any numerical range recited herein is intended to include all sub-ranges subsumed therein. For example, a range of "1 to 10" is intended to include all sub-ranges between (and including) the recited minimum value of 1 and the recited maximum value of 10, that is, having a minimum value equal to or greater than 1 and a maximum value of equal to or less than 10.

[00098] Also, it should be understood that plural encompasses singular and vice versa; for example, "a" or "an" can include more than one. For example, although all references are made herein to "an" isocyanate, "an" amine, "a" (meth)acrylate, "a" lactone, "an" aminosilane and the like, one or more of any of these compounds or things can be used. As used herein, the
term "polymer" refers to oligomers and both homopolymers and copolymers, and the prefix "poly" refers to two or more.

[00099] The following examples are intended to illustrate the invention, and should not be construed as limiting the invention in any way.

EXAMPLES

EXAMPLE A

[000100] An adduct of 3-aminopropyl triethoxysilane and ethyl acrylate was prepared as follows:

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>Wt (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3-aminopropyl triethoxysilane</td>
<td>116.3</td>
</tr>
<tr>
<td>2,6-di-tert-butyl p-cresol</td>
<td>0.2</td>
</tr>
<tr>
<td>Ethyl acrylate</td>
<td>50.0</td>
</tr>
</tbody>
</table>

[000101] The first two ingredients were charged to a flask equipped with an overhead stirrer, thermocouple, and N2 inlet. A N2 blanket was applied to the flask and contents. Ethyl acrylate was added to the flask over a period of 71 minutes without any heating. The temperature of the contents of the flask was 20°C at the start of the addition and 26°C at the end of the addition. The temperature of the reaction mixture was increased to 50°C and held for 195 minutes. An infrared spectrum of the reaction mixture at that time indicated that ethyl acrylate was still present (peaks at ~ 1635, 1621 cm⁻¹); the temperature of the reaction mixture was raised to 70°C. The reaction mixture was held at this temperature for 150 minutes, then cooled. The following day the reaction mixture was heated to a maximum of 52°C for 85 minutes. Infrared analysis at this time indicated that the reaction was complete. The resulting thin, clear liquid was found to have a total amine content of 3.265 meq/g, a 1° amine content of 0.032 meq/g, a 2° amine content of 3.233 meq/g, a 3° amine content of 0.000 meq/g, and a viscosity of A on the Gardner-Holt scale.
EXAMPLES B - H

[000102] The following adducts of acrylates with amino functional silanes were prepared as follows:

<table>
<thead>
<tr>
<th>Ingredient (wt in g)</th>
<th>Ex B</th>
<th>Ex C</th>
<th>Ex D</th>
<th>Ex E</th>
<th>Ex F</th>
<th>Ex G</th>
<th>Ex H</th>
</tr>
</thead>
<tbody>
<tr>
<td>3-aminopropyl trimethoxysilane</td>
<td>22.6</td>
<td>22.6</td>
<td>18.8</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3-aminopropyl triethoxysilane</td>
<td></td>
<td></td>
<td></td>
<td>27.9</td>
<td>23.2</td>
<td>27.9</td>
<td>28.8</td>
</tr>
<tr>
<td>2,6-di-tert-butyl p-cresol</td>
<td>0.04</td>
<td>0.04</td>
<td>0.03</td>
<td>0.04</td>
<td>0.03</td>
<td>0.04</td>
<td>0.04</td>
</tr>
<tr>
<td>Methyl acrylate</td>
<td>10.3</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ethyl acrylate</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>12.0</td>
</tr>
<tr>
<td>Butyl acrylate</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>12.8</td>
<td>12.8</td>
</tr>
<tr>
<td>1,6-hexanediol diacrylate</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>13.6</td>
</tr>
<tr>
<td>Trimethylolpropane triacrylate</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>12.2</td>
</tr>
</tbody>
</table>

[000103] The aminosilane and 2,6-di-tert-butyl p-cresol were charged in glass jars, mixed, capped with N2, and sealed with a lid in which a small hole had been punched. The corresponding acrylates were added through the hole with a pipet and the contents were swirled to mix. A moderate exotherm was noted when the acrylates were added. Examples F, G, and I were placed in a 120o F hot room for 2.5 hours, then in a 160o F hot room for 1 hr. Examples H and J were placed in a 120o F hot room for 2.5 hours, and then placed in a 160o F hot room for 3 hours. Examples K and L were placed in a 120o F hot room for 19 hours, and then placed in a 160o F hot room for 5.5 hours. All the reactions between the aminosilanes and acrylates were determined to be complete based on infrared spectroscopy (disappearance of peaks at ~ 1635, 1621 cm-1 attributable to the acrylate double bond).

EXAMPLES I - L

[000104] The following adducts of e-caprolactone with amino functional silanes were prepared as follows:
The ingredients were charged to 8 oz glass jars, mixed, capped with N2, sealed, and placed in a 160°F hot room. Example I was removed from the hot room after 26.6 hours, Example J after 50.75 hours, Example K after 29.75 hours, and Example L after 50.75 hours. The reaction between the aminosilane and e-caprolactone was determined to be complete by inspection of the infrared spectrum, in particular disappearance of a band attributable to the e-caprolactone ring at 571 cm⁻¹. They were characterized as follows:

<table>
<thead>
<tr>
<th>Ingredient (wt in g)</th>
<th>Ex I</th>
<th>Ex J</th>
<th>Ex K</th>
<th>Ex L</th>
</tr>
</thead>
<tbody>
<tr>
<td>3-aminopropyl triethoxysilane</td>
<td>66.4</td>
<td>50.9</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3-aminopropyl trimethoxysilane</td>
<td></td>
<td></td>
<td>62.7</td>
<td>44.8</td>
</tr>
<tr>
<td>e-caprolactone</td>
<td>34.2</td>
<td>52.4</td>
<td>39.9</td>
<td>57.0</td>
</tr>
<tr>
<td>2,6-di-tert-butyl p-cresol</td>
<td>0.1</td>
<td>0.1</td>
<td>0.1</td>
<td>0.1</td>
</tr>
</tbody>
</table>

Examples 1-2

Solutions of the adhesion promoters were prepared as follows:

<table>
<thead>
<tr>
<th>Ingredient (wt in g)</th>
<th>Example 1</th>
<th>Example 2 (comparative)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aminosilane of Example A</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>3-aminopropyltriethoxysilane</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>Acetone</td>
<td>49</td>
<td>49</td>
</tr>
</tbody>
</table>
The solutions of Examples 1 and 2 were applied by pipet to 1 inch x 4 inch steel panels coated with an acrylosilane clearcoat (DuPont Gen IV), by tilting the panels so the solution completely wet the panels, and allowing the panels to dry under ambient conditions for approximately 30 minutes. The top 2 cm of the panels was covered with masking tape to provide a "pull tab" for subsequent testing.

A polyurea composition was applied to the treated panels by mixing a 1:1 volume ratio of CAT 128 isocyanate package (the A-side component) and BDL 1724S amine package (the B-side component), both available from PPG Industries, Inc., at a temperature of 140o F using a static mixing cartridge gun manufactured by Cammda Corporation. The composition was applied at a thickness of approximately 60 - 80 mil. Excess material on the edges of the panels was trimmed with a razor blade.

After a period of 3 days adhesion of the polyurea coating to the substrate was tested by pulling the aforementioned tab at an angle of 90o relative to the panel at a rate of 2 inches / minute on an Model 5567 Universal Materials Testing Machine manufactured by Instron Corporation to measure the force required to peel the coating from the substrate. The results are summarized in the table below:

<table>
<thead>
<tr>
<th>Example</th>
<th>90° Peel Adhesion Strength (lb / in²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>50, 58</td>
</tr>
<tr>
<td>2 (comparative)</td>
<td>21</td>
</tr>
</tbody>
</table>

In this experiment the example with the adduct of 3-aminopropyl triethoxysilane with ethyl acrylate showed enhanced adhesion of the polyurea composition to the substrate compared to 3-aminopropyl triethoxysilane itself.

In this experiment the example with the adduct of 3-aminopropyl triethoxysilane with ethyl acrylate showed enhanced adhesion of the polyurea composition to the substrate compared to 3-aminopropyl triethoxysilane itself.

Examples 3 - 8

Solutions of the adhesion promoters were prepared as follows:
The solutions of Examples 3-7 were applied to 1 inch x 4 inch steel panels coated with an acrylosilane clearcoat (DuPont Gen IV) as previously described in Examples 1-2. A polyurea composition was applied to the treated panels by mixing a 1:1 volume ratio of CAT 128 (the A-side component) and BDL 1724D amine package (the B-side component), both available from PPG Industries, Inc., in the manner described in Examples 1 and 2. In a like manner, the polyurea composition was applied to an untreated panel (i.e., coated only with the acrylosilane clearcoat) as a comparative (Example 8).

After a period of 1 day adhesion of the polyurea coating to the substrates was tested as described in Examples 1-2. The results are summarized in the table below:

<table>
<thead>
<tr>
<th>Ingredient (wt in g)</th>
<th>Example 3</th>
<th>Example 4</th>
<th>Example 5</th>
<th>Example 6</th>
<th>Example 7 (comparative)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aminosilane of Example A</td>
<td>0.1</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Aminosilane of Example F</td>
<td></td>
<td>0.1</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Aminosilane of Example G</td>
<td></td>
<td></td>
<td>0.1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Aminosilane of Example H</td>
<td></td>
<td></td>
<td></td>
<td>0.1</td>
<td></td>
</tr>
<tr>
<td>N-butylaminopropyl trimethoxysilane</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.1</td>
</tr>
<tr>
<td>Acetone</td>
<td>10</td>
<td>10</td>
<td>10</td>
<td>10</td>
<td>10</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Example</th>
<th>90° Peel Adhesion Strength (lb / in²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>50, 51</td>
</tr>
<tr>
<td>4</td>
<td>&gt; 50 (polyurea coating ripped), 82</td>
</tr>
<tr>
<td>5</td>
<td>78, 20</td>
</tr>
<tr>
<td>6</td>
<td>60, 60</td>
</tr>
<tr>
<td>7 (comparative)</td>
<td>22, 25</td>
</tr>
<tr>
<td>8 (comparative)</td>
<td>2, 1</td>
</tr>
</tbody>
</table>
Overall, in this experiment the examples with the Michael adducts of 3-aminopropyl triethoxysilane with the various acrylates showed enhanced adhesion of the polyurea composition to the substrate compared to the simple N-alkyl substituted aminosilane (Example 7) and far superior adhesion compared to the control in which no adhesion promoter was applied (Example 8).

**EXAMPLES 9 - 15**

Solutions of the adhesion promoters were prepared as follows:

<table>
<thead>
<tr>
<th>Ingredient (wt in g)</th>
<th>Example 9</th>
<th>Example 10</th>
<th>Example 11</th>
<th>Example 12</th>
<th>Example 13</th>
<th>Example 14</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aminosilane of Example A</td>
<td>0.2</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Aminosilane of Example B</td>
<td></td>
<td>0.2</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Aminosilane of Example C</td>
<td></td>
<td></td>
<td>0.2</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Aminosilane of Example D</td>
<td></td>
<td></td>
<td></td>
<td>0.2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Aminosilane of Example E</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.2</td>
<td></td>
</tr>
<tr>
<td>Aminosilane of Example F</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.2</td>
</tr>
<tr>
<td>Acetone</td>
<td>10</td>
<td>10</td>
<td>10</td>
<td>10</td>
<td>10</td>
<td>10</td>
</tr>
</tbody>
</table>

The solutions of Examples 9 - 15 were applied to 1 inch x 4 inch steel panels coated with a acrylosilane clearcoat (Du Pont Gen IV) as previously described in Examples 1 and 2. A polyurea composition was applied to the treated panels by mixing a 1:1 volume ratio of CAT 128 (the A-side component) and BDL 1724D amine package (the B-side component), both available from PPG Industries, Inc., in the manner described in Examples 1 and 2. In a like manner, the polyurea composition was applied to an untreated panel coated with the acrylosilane clearcoat as a comparative (Example 15).

After a period of 3 days adhesion of the polyurea coating to the substrates was tested as described in Examples 1 and 2. The results are summarized in the table below:
In this experiment the examples with the Michael adducts of 3-aminopropyl triethoxysilane with the various acrylates again showed far superior adhesion compared to the control in which no adhesion promoter was applied (Example 15).

**EXAMPLES 16 - 20**

Solutions of the adhesion promoters were prepared as follows:

<table>
<thead>
<tr>
<th>Ingredient (wt in g)</th>
<th>Example 16</th>
<th>Example 17</th>
<th>Example 18</th>
<th>Example 19</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aminosilane of Example D</td>
<td>0.2</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Aminosilane of Example F</td>
<td></td>
<td>0.2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>N-butylaminopropyl trimethoxysilane</td>
<td></td>
<td></td>
<td>0.2</td>
<td></td>
</tr>
<tr>
<td>N-cyclohexylaminomethyl triethoxysilane</td>
<td></td>
<td></td>
<td></td>
<td>0.2</td>
</tr>
<tr>
<td>Acetone</td>
<td>10</td>
<td>10</td>
<td>10</td>
<td>10</td>
</tr>
</tbody>
</table>

The solutions of Examples 16 - 19 were applied to 1 inch x 4 inch panels coated with a acrylosilane clearcoat (DuPont Gen IV) as previously described in Examples 1 and 2. They were also applied to panels coated with an epoxy / acid clearcoat (available as NDCT 5002 from PPG Industries, Inc.). A polyurea composition was applied to the treated panels by mixing a 1:1 volume ratio of CAT 128 (the A-side component) and BDL 1724D amine package (the B-side component), both available from PPG Industries, Inc., in the manner as described in Examples 1 and 2. In a like manner, the polyurea composition was applied to an untreated panel coated with the acrylosilane clearcoat as a comparative (Example 20).
After a period of 3 days adhesion of the polyurea coating to the substrate was tested by manually pulling the aforementioned tab at an angle of 90° relative to the panel. The adhesion strength was rated on a scale of 0 to 5, with 0 indicating total failure, 1 indicating poor adhesion, and 5 indicating excellent adhesion.

<table>
<thead>
<tr>
<th>Example</th>
<th>Acid / epoxy clearcoat</th>
<th>Silane clearcoat</th>
</tr>
</thead>
<tbody>
<tr>
<td>16</td>
<td>3</td>
<td>5</td>
</tr>
<tr>
<td>17</td>
<td>1</td>
<td>4</td>
</tr>
<tr>
<td>18 (comparative)</td>
<td>1</td>
<td>0</td>
</tr>
<tr>
<td>19 (comparative)</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>20 (comparative)</td>
<td>3</td>
<td>0</td>
</tr>
</tbody>
</table>

In this experiment over the silane containing clearcoat the examples with the Michael adducts of 3-aminopropyl triethoxysilane and 3-aminopropyltrimethoxysilane with butyl acrylate showed superior adhesion compared to the two simple N-alkyl substituted amines (Examples 18 and 19) and the untreated control (Example 20).

**EXAMPLES 21 - 26**

Solutions of the adhesion promoters were prepared as follows:

<table>
<thead>
<tr>
<th>Ingredient (wt in g)</th>
<th>Example 21</th>
<th>Example 22</th>
<th>Example 23</th>
<th>Example 24</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aminosilane / ( \square )-caprolactone adduct of Example I</td>
<td>1</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Aminosilane / ( \square )-caprolactone adduct of Example J</td>
<td></td>
<td>1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Aminosilane / ( \square )-caprolactone adduct of Example K</td>
<td></td>
<td></td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>Aminosilane / ( \square )-caprolactone adduct of Example L</td>
<td></td>
<td></td>
<td></td>
<td>1</td>
</tr>
<tr>
<td>Acetone</td>
<td>49</td>
<td>49</td>
<td>49</td>
<td>49</td>
</tr>
</tbody>
</table>

The solutions of Examples 21-24 were applied to 1 inch x 4 inch panels coated with a acrylosilane clearcoat (DuPont Gen IV) as
previously described in Examples 1-2. Another panel (Example 25) was treated in this manner with acetone alone. A polyurea composition was applied to the treated panels by mixing a 1:1 volume ratio of CAT 128 (the A-side component) and BDL 1724S amine package (the B-side component), both available from PPG Industries, Inc., in the manner as described in Examples 1 and 2. In a like manner, the polyurea composition was applied to an untreated panel coated with the acrylosilane clearcoat as a comparative (Example 26).

After a period of 3 days, adhesion of the polyurea coating to the substrates was tested as described in Examples 1 and 2. The results are summarized in the table below:

<table>
<thead>
<tr>
<th>Example</th>
<th>90° Peel Adhesion Strength (lb/ in²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>21</td>
<td>30</td>
</tr>
<tr>
<td>22</td>
<td>20</td>
</tr>
<tr>
<td>23</td>
<td>35</td>
</tr>
<tr>
<td>24</td>
<td>30</td>
</tr>
<tr>
<td>25 (comparative)</td>
<td>4</td>
</tr>
<tr>
<td>26 (comparative)</td>
<td>2</td>
</tr>
</tbody>
</table>

The examples with the e-caprolactone adducts of 3-aminopropyltrimethoxysilane and 3-aminopropytriethoxysilane demonstrate adhesion, while the comparative samples demonstrate little to no adhesion. This example also illustrates that merely treating the panels with acetone does not in itself promote adhesion of the polyurea composition to the substrate.
THEREFORE, WHAT IS CLAIMED IS:

1. A coating composition comprising: (a) polyurea formed from a reaction mixture comprising isocyanate and amine wherein the ratio of equivalents of isocyanate groups to equivalents of amine groups is greater than 1 and the isocyanate and the amine can be applied to a substrate at a volume mixing ratio of 1:1; and (b) an adduct of aminosilane and a material chosen from (meth)acrylate, lactone and mixtures thereof.

2. The coating composition of claim 1 wherein said aminosilane comprises 3-aminopropyltriethoxysilane, 3-aminopropyltrimethoxysilane, 2-aminoethyl-3-aminopropyltrimethoxysilane, 2-aminoethyl-3-aminopropyltriethoxysilane, 3-aminopropylmethyldimethoxysilane, or 3-aminopropylmethyldiethoxysilane.

3. The coating composition of claim 1 wherein said lactone comprises β-propiolactone, β-butyrolactone, γ-butyrolactone, γ-valerolactone, δ-valerolactone, γ-caprolactone, δ-caprolactone, or ε-caprolactone.

4. The coating composition of claim 1 wherein said (meth)acrylate comprises ethyl (methyl)acrylate, butyl (meth)acrylate, 1,6-hexanediol di(meth)acrylate, or trimethylolpropane tri(meth)acrylate.

5. The coating composition of claim 1 wherein the adduct is present in the amine.

6. The coating composition of claim 5 wherein the adduct is present in an amount of from 0.01% to 2.0% by weight of the amine.

7. The coating composition of claim 5 wherein the adduct is present in an amount of from 0.1% to 1.0% by weight of the amine.

8. The coating composition of claim 1 further comprising polyurethane.
9. The coating composition of claim 1, wherein the ratio of equivalents of isocyanate groups to equivalents of amine groups is 1.01 to 1.50:1.

10. The coating composition of claim 1, wherein the isocyanate comprises isophorone diisocyanate.

11. The coating composition of claim 1, wherein the amine comprises primary amine, secondary amine or mixtures thereof.

12. The coating composition of claim 1 further comprising a flame retardant component.

13. An adhesion promoting composition comprising an adduct of aminosilane and a material chosen from (meth)acrylate, lactone and mixtures thereof.

14. The adhesion promoting composition of claim 13 further comprising solvent.

15. The adhesion promoting composition of claim 14 wherein the solvent is acetone.

16. The adhesion promoting composition of claim 14 wherein the adduct is present in a concentration of from greater than 0 to 5 percent by weight.

17. A composition for improving adhesion between a substrate and a polyurea coating comprising an adduct of aminosilane and a material chosen from (meth)acrylate, lactone and mixtures thereof.

18. A method for improving adhesion between a coating composition comprising polyurea and a substrate comprising:
applying to at least a portion of the substrate the composition of claim 1.

19. A method for improving adhesion between a coating composition and a substrate comprising:
applying to at least a portion of the substrate the composition of claim 13.

20. The method of claim 19 wherein the substrate comprises an at least partially coated substrate.

21. The method of claim 19 wherein the composition of claim 13 is added to a coating composition prior to application to the substrate.

22. The method of claim 21 wherein the coating composition comprises a polyurea formed from a reaction mixture comprising isocyanate and amine.

23. The method of claim 22 wherein the ratio of equivalents of isocyanate groups to equivalents of amine groups is greater than 1 and the isocyanate and amine can be applied to a substrate at a volume mixing ratio of 1:1.

24. The method of claim 19 wherein the coating composition comprises a) a polyurea formed from a reaction mixture comprising isocyanate and amine and b) a polyurethane.

25. The method of claim 20 wherein the at least partially coated substrate comprises a clear coat.

26. The method of claim 25 wherein the clear coat comprises silane functional groups.
27. The method of claim 19 wherein the substrate comprises at least a portion of a vehicle.

28. The method of claim 27 wherein the substrate is a truck bed.

29. A method of improving adhesion between two coating layers comprising:

   providing a substrate having a clear coat composition deposited thereon;
   applying the adhesion promoting composition of claim 13 over at least a portion of the coated substrate; and
   applying over the adhesion promoting composition a coating composition comprising polyurea.

30. A coated article, comprising:

   a substrate; and
   a coating layer formed by the coating composition of claim 1 deposited on at least a portion of the substrate.

31. A coated article, comprising:

   a substrate; and
   a coating layer formed by the coating composition of claim 17 deposited on at least a portion of the substrate.

32. A coated article comprising:

   a substrate; and
   a coating layer formed by the adhesion promoting composition of claim 13.

33. The coated article of claim 30, wherein the substrate is at least a portion of a vehicle or structure.