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(54) Title: ADHESIVE USEFUL FOR INSTALLING VEHICLE WINDOWS

(57) Abstract: Disclosed are compositions comprising: a) one or more isocyanate functional components; b) one or more one or more bis (glycol ether) alkylates; and c) one or more catalysts for the reaction of isocyanate moieties with hydroxyl groups. Disclosed is a method of bonding two or more substrates together comprising contacting two or more substrates together with a composition disclosed herein disposed along at least a portion of the area wherein the substrates are in contact. At least one of the substrates may be window glass. One of the other substrates may be a building or a vehicle.



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ADHESIVE USEFUL FOR INSTALLING VEHICLE WINDOWS

Field of Invention

[001] The invention relates to a composition useful as an adhesive and a method of bonding two or more substrates together using the composition, wherein such substrates may include glass, plastics, composites, coated metals for use in buildings and vehicles. The composition can be utilized for replacing a window in a vehicle.

Background of Invention

[002] Adhesive compositions are used to bond glass (windows) into buildings and vehicles, see Rizk, U.S. 4,780,520; Bhat, U.S. 5,976,305; Hsieh et al, U.S. 6,015,475 and Zhou, U.S. Patent 6,709,539, all incorporated herein by reference. In automobile factories windows are installed using robots and computer controlled processing which facilitates the use of a variety of high performance adhesives, for instance nonconductive adhesives and high modulus adhesives. The speed of cure is not a significant issue because new vehicles are not driven a significant distance for several days after window installation. When a vehicle needs a window replaced, it is often performed in a remote location by an installer working at the vehicle to be repaired. In this environment, speed of cure is important as the vehicle owner desires to drive the vehicle as soon as possible after installation of the window. Adhesives useful in replacing windows for vehicles which facilitate fast drive away times are known see Bhat, U.S. 5,976,305 and Zhou, U.S. 6,709,539. The introduction of various high performance adhesive compositions used for installing windows in automobile factories presents a problem for replacement window installers. First, adhesives that meet all the varied performance requirements are not available in the market place. Second, it is difficult to formulate many high performance adhesive compositions to allow rapid drive away times that do not sag or string. Sag is the loss of the shape of the adhesive bead, often as the result of gravitational forces. If severe enough, this deformation can interfere in the proper installation and sealing of the window on the vehicle. Stringing of an adhesive is the formation of a long string of adhesive at the end of the bead after dispensing which can complicate application and cause imperfections in the installed adhesive bead. Replacement window installers often carry a variety of adhesives to match the adhesive to the properties of the original adhesive used.

[003] Isocyanate functional adhesives are utilized for bonding glass into structures and contain plasticizers to adjust the rheology and dispensability of these adhesives. Typically,

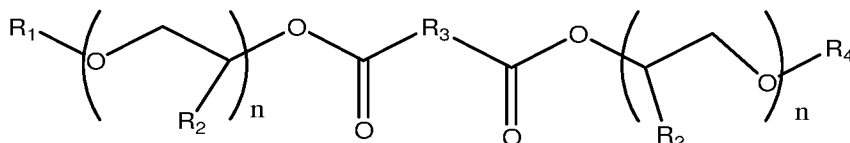
plasticizers used in isocyanate functional adhesives were adopted initially from plasticizers developed for use in polyvinyl chloride plastisol compositions because of their cost and availability. One common class of plasticizers used in isocyanate functional adhesives are alkyl phathates. Such compounds, to date, have been available and cost effective. Recently, however, EH&S concerns have been raised about these materials negatively impacting the cost and availability. There is a need to find new plasticizers for isocyanate functional adhesives.

[004] Automotive paint technology has evolved over the past few decades. The newer paints have top coats that are made up of low surface energy, hydrophobic materials (e.g., siloxanes, acrylic polyol based polyurethanes) to improve their acid-etch resistance and scratch resistance. Such paints are very hard and have little to no polar groups on the surface which makes adhesion extremely difficult. Therefore, traditional urethane elastomeric adhesives are not sufficiently capable of bonding to these low surface energy paints. Another aspect about automotive adhesives is that the adhesive should maintain bond strength under hydrolytic conditions (e.g., high temperature and humidity). Adhesive bonds formed between the clear coat and the urethane adhesive tend to fail rapidly when exposed to high temperatures and humidity conditions. Adhesives which are durable enough to withstand these conditions are needed. It is desirable that such adhesives be capable to cure and bond to the low energy paint surface under low temperature conditions. In traditional adhesives, this is achieved by including additional catalyst to speed up cure. However such an approach can result in poor storage stability as well as poor hydrolytic stability of the cured adhesive.

[005] What is needed is a composition which is useful as an adhesive for bonding glass into a structure which may be formulated to exhibit a variety of high performance properties (such as high modulus and nonconductive nature), exhibits fast safe drive away times when applied under a variety of conditions, fast strength development, can be applied without the need for heating the adhesive, can be applied under a wide range of environmental conditions, does not require expensive ingredients, can be applied to glass without the need for a primer and does not sag or string when applied. Compositions which are capable of bonding in a primerless manner to low surface energy, hydrophobic materials (e.g., siloxanes, acrylic polyol based polyurethanes) coatings are needed. Compositions that are capable of bonding to such surfaces under low temperature conditions, below about 23 °C are desired.

Summary of Invention

[006] Disclosed are compositions comprising: a) one or more isocyanate functional components; b) one or more bis (glycol ether) alkylates; and c) one or more catalysts for the reaction of isocyanate moieties with hydroxyl groups. The one or more bis (glycol ether) alkylates may correspond to the formula



wherein: R₁ and R₄ independently are C₁ – C₈ alkyl groups, phenyl or benzyl; R₂ independently is either hydrogen, methyl or ethyl; R₃ is a carbon chain containing 0 to 5 carbon atoms and may contain a double bond; and n is independently 1 to 4. R₁ and R₄ may be independently C₁ – C₈ alkyl groups. The one or more bis (glycol ether) alkylates may comprise one or more of one or more of bis-dipropylene glycol n-butyl ether adipate, bis-dipropylene glycol n-propyl ether adipate, bis-diethylene glycol n-butyl ether malonate, bis-diethylene glycol n-butyl ether succinate, and bis-dipropylene glycol n-butyl ether maleate. The one or more bis (glycol ether) alkylates may comprise bis-dipropylene glycol n-butyl ether adipate. The composition may further comprise one or more carbon blacks. The one or more carbon blacks may comprise one or more conductive carbon blacks and/or one or more non-conductive carbon blacks. It may be desirable that if conductive carbon blacks are present they are present in an amount of about 18 percent by weight or less such that the formed composition is non-conductive.

[007] The composition may comprise a) the one or more isocyanate functional components present in an amount of about 20 to about 60 percent by weight; b) one or more alkoxyalkyl benzoates present in an amount of about 5 to about 40 percent by weight; c) one or more catalysts for the reaction of isocyanate moieties with hydroxyl groups present in an amount of about 0.005 to about 2 percent by weight and d) one or more carbon blacks present in an amount of about 10 to about 35 parts by weight; wherein percentages are based on the weight of the composition. The composition may further comprise one or more isocyanate functional polyester based prepolymers which are solid at 23°C. The composition may further comprise one or more polyisocyanates having a nominal functionality of about 3 or greater.

[008] Disclosed is a method of bonding two or more substrates together comprising contacting two or more substrates together with a composition disclosed herein disposed

along at least a portion of the area wherein the substrates are in contact. At least one of the substrates may be window glass. One of the other substrates may be a building or a vehicle.

[009] Disclosed is a method of replacing a window of a vehicle comprising: i) removing the window from the vehicle; ii) applying a composition disclosed to a replacement window or to the flange of the vehicle adapted to hold the window into the vehicle; iii) contacting the flange of the vehicle and the replacement window with the composition disclosed between the replacement window and the flange of the vehicle; and iv) allowing the adhesive to cure.

[010] The composition is useful as an adhesive to bond substrates together. A variety of substrates, similar or dissimilar, may be bonded together using the composition, for instance, plastics, glass, wood, ceramics, metal, coated substrates, such as plastics with an abrasion resistant coating disposed thereon, and the like. The compositions are especially useful for bonding glass or a plastic with an abrasion resistant coating disposed thereon to other substrates such as vehicles and buildings. The compositions are also useful in bonding parts of modular components together, such as vehicle modular components. The glass or plastic with an abrasion resistant coating disposed thereon can be bonded to coated and uncoated portions of vehicles.

[011] The compositions typically demonstrate, after being cured for two weeks, a modulus of about 2.0 MPa or greater, preferably about 2.5 MPa or greater and typically about 5.0 MPa or less according to ASTM D4065 measured at 25°C. The compositions of the invention typically exhibit a storage modulus, G' , of about 1×10^6 MPa or greater, preferably about 1.3×10^6 MPa or greater and most preferably about 1.8×10^6 MPa or greater after being fully cured, for instance for 7 days at 25 °C/ 50 percent relative humidity.

[012] The composition's pumpability may be indicated by measuring the press flow viscosity according to the test described herein and preferably exhibit a press flow viscosity of about 25 to about 100 seconds, most preferably about 25 to about 50 seconds. The compositions allow preparation of adhesives with a reduced filler level and an acceptable modulus in the uncured state (G-Modulus), that is the compositions maintain the modulus at reduced filler levels. The compositions bond well to low surface energy, hydrophobic coatings (e.g., siloxanes, acrylic polyol based polyurethanes). The compositions bond well to low surface energy, hydrophobic coatings (e.g., siloxanes, acrylic polyol based polyurethanes) under low temperature conditions.

[013] The compositions disclosed exhibit improved room temperature adhesion to low surface energy paints compared to the adhesive that contains traditional plasticizers (e.g., Diisononyl phthalate, Soy Methyl Ester, Trimethyl Pentanyl Diisobutyrate). The compositions disclosed exhibit improved low temperature adhesion to low surface energy paints compared

to an adhesive that contains traditional plasticizers (e.g., Diisononyl phthalate, Soy Methyl Ester, Trimethyl Pentanyl Diisobutyrate). The compositions disclosed exhibit improved hydrolytic stability and maintains adhesion to low surface energy paints at high temperature and humidity conditions compared to an adhesive that contains traditional plasticizers (e.g.,
5 Diisononyl phthalate, Soy Methyl Ester, Trimethyl Pentanyl Diisobutyrate. The compositions exhibit excellent shelf stability, that is stability in packaging protected from moisture.

Detailed Description of Invention

[0014] One or more as used herein means that at least one, or more than one, of the recited components may be used as disclosed. Nominal as used with respect to functionality means
10 the theoretical functionality, which can be calculated from the stoichiometry of the ingredients used. Generally, the actual functionality is different due to imperfections in raw materials, incomplete conversion of the reactants and formation of by-products. "Durability" in herein means that the composition once cured remains sufficiently strong to perform its designed function, in the embodiment wherein the cured composition is an adhesive the adhesive
15 holds substrates together, for the life or most of the life of the structure containing the cured composition. As an indicator of this durability the curable composition (e.g. adhesive) preferably exhibits excellent results during accelerated aging testing as described herein. Preferably this means that after a set of substrates bonded with the adhesive of the invention is exposed to heat aging, the failure mode in Quick Knife adhesion or Lap Shear testing is
20 cohesive, meaning the adhesive breaks before the bond of the adhesive to the substrate breaks. "Isocyanate content" means the weight percentage of isocyanate moieties based on the total weight of the prepolymer. The term "isocyanate-reactive compound" as used herein includes any organic compound having nominally at least two isocyanate-reactive moieties. For the purposes of this invention, isocyanate-reactive moieties include active hydrogen
25 containing moieties and preferably refer to moieties containing a hydrogen atom which, because of its position in the molecule, displays significant activity according to the Zerewitinoff test described by Wohler in the Journal of the American Chemical Society, Vol. 49, p. 3181 (1927). Isocyanate reactive moieties include -COOH, -OH, -NH₂, -NH-, -CONH₂, -SH, and -CONH-. Preferable isocyanate reactive moiety containing compounds include
30 polyols, poly-amines, polymercaptans and polyacids, more preferably polyols, and most preferably a polyether polyols.

[0015] The compositions invention can be any reactive system containing isocyanate functional components which are curable. "Reactive" means herein that the curable composition (e.g. adhesive) contains components which react to form a polymeric matrix that

is set irreversibly once cured. The curable systems can be either one or two-part systems. Preferably the curable systems are useful as adhesives.

[0016] Isocyanate based (polyurethane or polyurea forming) curable systems comprise an isocyanate functional component. An isocyanate functional component contains one or more
5 compounds having on average more than one isocyanate group per molecule. The isocyanate functional compound can be any compound which contains on average more than one isocyanate moiety. The isocyanate functional compound can be in the form of an isocyanate functional prepolymer or in the form of a monomer or oligomer having on average
10 greater than 1 isocyanate group, and preferably 2 or more isocyanate groups. The isocyanate prepolymer can be any prepolymer prepared by reaction of an isocyanate functional compound with one or more compounds having on average more than one isocyanate reactive functional groups, such as hydroxyl, amine, thiol, carboxyl and the like, under conditions such that the prepolymer prepared have on average more than one
15 isocyanate moiety (group) per molecule. Preferably the compounds having isocyanate reactive groups have on average about 2 to about 4 isocyanate reactive groups. The isocyanate functional component is present in the curable composition in a sufficient amount to form a cured component when exposed to curing conditions. In two-part adhesive compositions, the isocyanate functional components when combined with isocyanate reactive compounds are capable of bonding substrates together in a manner that the
20 substrates remain bound together when exposed to temperatures of about -30°C to about 100°C for long periods of time, such as 10 years; and up to temperatures of about 180°C for short periods of up to 30 minutes.

[0017] In a one-part system, the isocyanate functional component further comprises a catalyst and other components as described hereinafter. The one component adhesive
25 systems typically cure by moisture curing. Once formulated the one-part adhesive systems are generally packaged in air and moisture proof containers to prevent curing before application.

[0018] The curable system may be a two-part polyisocyanate containing curable system. The two parts are reactive with one another and when contacted undergo a curing reaction.
30 One part of the composition comprises, or contains, an isocyanate functional component, typically referred to as the resin-side or A side. The other component of the composition is an isocyanate reactive component which comprises, or contains, one or more compounds, oligomers or prepolymers having on average more than one group reactive with isocyanate moieties as described herein, commonly known as the curative or B side. Compounds having
35 on average one or more isocyanate reactive groups can be prepolymers or can be small

chain compounds such as difunctional chain extenders or polyfunctional crosslinking agents known in the art. A catalyst as described herein may be utilized in the curative side. The reaction product is a cured product which is capable of performing the desired function, such as bonding certain substrates together.

5 [0019] The isocyanate functional components, such as isocyanate functional prepolymers, are present in sufficient quantity to provide adhesive character to the composition. Such isocyanate functional components have an average isocyanate functionality sufficient to allow the preparation of a crosslinked polyurethane upon cure and not so high that the curable compositions are unstable. Stability in this context means that the isocyanate
10 functional components or adhesive prepared from the isocyanate functional components have a shelf life of at least 6 months at ambient temperatures, in that it does not demonstrate an increase in viscosity during such period which prevents its application or use. Preferably, it does not undergo an increase in viscosity of more than about 50 percent during the stated period. The isocyanate functional components preferably have a free isocyanate content
15 which facilitates acceptable strength in adhesives prepared therefrom after 60 minutes and stability of the curable composition. The isocyanate functional components preferably have a free isocyanate content which facilitates acceptable strength in the compositions prepared therefrom, preferably after 30 minutes, more preferably after 15 minutes. In one component adhesives, the free isocyanate content is about 0.8 percent by weight or greater based on
20 the weight of the prepolymer and more preferably about 0.9 percent by weight or greater, and preferably about 2.2 percent by weight or less, more preferably about 2.0 or less, even more preferably about 1.4 percent by weight or less and even more preferably about 1.1 percent by weight or less and most preferably about 1.0 percent by weight or less. In two part compositions the isocyanate content in the isocyanate functional components is
25 preferably about 1 percent by weight or greater based on the weight of the isocyanate functional components, more preferably about 2 percent by weight or greater, even more preferably about 6 percent or greater, even more preferably about 8 percent by weight or greater and most preferably about 10 percent by weight or greater. The isocyanate content in the isocyanate functional components of two part compositions is preferably about 35
30 percent by weight or less based on the weight of the isocyanate functional components, more preferably about 25 percent by weight or less, even more preferably about 20 percent by weight and most preferably about 15 percent by weight or less.

[0020] Polyisocyanates for use in preparing the isocyanate functional components include those disclosed in U.S. Patent 5,922,809 at column 3, line 32 to column 4, line 24
35 incorporated herein by reference. The polyisocyanate may be an aromatic or cycloaliphatic

polyisocyanate such as diphenylmethane-4,4'-diisocyanate, isophorone diisocyanate, tetramethyl-xylene diisocyanate, and is most preferably diphenylmethane-4,4'-diisocyanate.

The polyols reacted with the polyisocyanates preferably comprise one or more polyols having from about 2 to about 4 hydroxyl groups, and are preferably a mixture of diols and triols.

5 Polyols useful in this invention are diols and triols corresponding to the polyols described in U.S. Patent 5,922,809 at column 4, line 60 to column 5, line 50, incorporated herein by reference. Preferably, the polyols (diols and triols) are polyether polyols and more preferably polyoxyalkylene oxide polyols. The most preferred triols are ethylene oxide-capped polyols prepared by reacting glycerin with propylene oxide, followed by reacting the product with
10 ethylene oxide.

[0021] The isocyanate functional prepolymers may contain one or more organic based polymer particles dispersed therein or grafted to the backbone thereof. The organic based polymer particle may be included in the prepolymer by inclusion of a triol having dispersed therein or grafted to the backbone particles of an organic based polymer. The preferable
15 triols are disclosed in Zhou, U.S. Patent 6,709,539 at column 4, line 13 to column 6, line 18, incorporated herein by reference. Preferably, the triol is a polyether triol and more preferably a polyoxyalkylene based triol. Preferably, such polyoxyalkylene oxide triol comprises a polyoxy-propylene chain with a polyoxyethylene end cap. Preferably, the organic based polymer particles comprise a thermoplastic polymer, rubber-modified thermoplastic polymer
20 or a polyurea dispersed in a triol. Preferable thermoplastic polymers are those based on monovinylidene aromatic monomers and copolymers of monovinylidene aromatic monomers with conjugated dienes, acrylates, methacrylates, unsaturated nitriles or mixtures thereof. The copolymers can be block or random copolymers. More preferably the particles comprise copolymers of unsaturated nitriles, conjugated dienes and a monovinylidene aromatic
25 monomer, a copolymer of an unsaturated nitrile and a monovinylidene aromatic monomer or a polyurea, even more preferably a polyurea or polystyrene-acrylonitrile copolymer with the polystyrene-acrylonitrile copolymers being most preferred. The organic polymer particles preferably have a particle size which is large enough to improve the impact properties and elastomeric properties of the finally cured adhesive, but not so large so as to reduce the
30 ultimate strength of the adhesive after cure. Preferably, the particle size is about 10 microns or greater and more preferably the particle size is about 20 microns or greater. Preferably, the particle size is about 50 microns or less and more preferably the particle size is about 40 microns or less. The triol contains a sufficient amount of organic polymer particles such that the adhesive upon cure has sufficient hardness for the desired use and not so much such
35 that the cured adhesive has too much elasticity as defined by elongation. Preferably, the

polyols contain about 20 percent by weight or greater of organic polymer particles copolymer based on the polyols and particles, preferably about 30 percent by weight or greater and more preferably about 35 percent by weight or greater. Preferably, the polyols contain about 60 percent by weight or less of organic polymer particles based on the polyols and particles,
5 preferably about 50 percent by weight or less and more preferably about 45 percent by weight or less. The polyols containing organic polymer particles in a triol may be present in the prepolymer in an amount of about 10 percent by weight or greater of the prepolymer and more preferably about 12 percent by weight or greater, and about 18 percent by weight or less of the prepolymer.

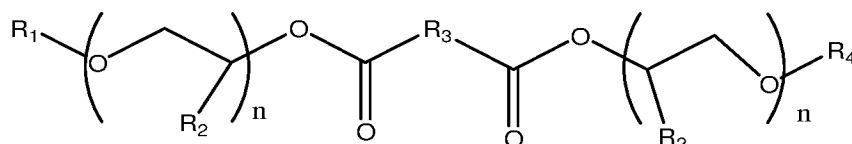
10 **[0022]** The polyols are present in an amount sufficient to react with most of the isocyanate groups leaving enough isocyanate groups to correspond with the desired free isocyanate content of the isocyanate functional component. Preferably, the polyols are present in an amount of about 30 percent by weight or greater based on the prepolymer, more preferably about 40 percent by weight or greater and most preferably about 55 percent by weight or
15 greater. Preferably, the polyols are present in an amount of about 75 percent by weight or less based on the prepolymer, more preferably about 65 percent by weight or less and most preferably about 60 percent by weight or less.

[0023] The isocyanate functional components prepolymers may be prepared by any suitable method, such as by reacting polyols with an excess over stoichiometry of one or more
20 polyisocyanates under reaction conditions sufficient to form a prepolymer having isocyanate functionality and free isocyanate content which meets the criteria discussed above. Preferable processes for the preparation of the isocyanate functional components are disclosed in U.S. Patent 5,922,809 at column 9, lines 4 to 51 incorporated herein by reference. The isocyanate functional components are present in the adhesive composition
25 in an amount sufficient such that when the resulting adhesive cures substrates are bound together. Preferably, the isocyanate functional components are present in an amount of about 20 parts by weight of the adhesive composition or greater, more preferably about 30 parts by weight or greater and most preferably about 35 parts by weight or greater. Preferably, the isocyanate functional components are present in an amount of about 60 parts
30 by weight of the adhesive composition or less, more preferably about 50 parts by weight or less and even more preferably about 45 parts by weight or less.

[0024] The isocyanate functional component may further comprise, one or more bis (glycol ether) alkylates; one or more common plasticizers or mixtures thereof. The plasticizers useful in the isocyanate functional component are common plasticizers useful in polyurethane
35 adhesive applications and well known to those skilled in the art. The plasticizers are present

in an amount sufficient to disperse the isocyanate functional component in the final adhesive composition. The one or more bis (glycol ether) alkylates and optionally other common plasticizers can be added to the adhesive either during preparation of an isocyanate functional component or during compounding of the adhesive composition. The one or more bis (glycol ether) alkylates and optionally common plasticizers may be present in about 1 percent by weight or greater of the isocyanate functional component formulation (for example prepolymer plus plasticizer or an adhesive composition), about 20 percent by weight or greater or about 30 percent by weight or greater. The one or more bis (glycol ether) alkylates and optionally other common plasticizers may be present in about 45 percent by weight or less of the isocyanate functional component formulation, about 40 percent by weight or about 35 percent by weight or less.

[0025] The composition comprises one or more bis (glycol ether) alkylates. The one or more bis (glycol ether) alkylates may correspond to the formula:



15 wherein:

R₁ and R₄ independently are C₁ – C₈ alkyl groups, phenyl or benzyl;

R₂ independently is either hydrogen, methyl or ethyl;

R₃ is a carbon chain containing 0 to 5 carbon atoms and may contain a double bond; and

n is independently 1 to 4, wherein R¹ is straight or branched chain alkyl and R² is straight or branched chain alkylene. R₁ and R₄ may be straight or branched chain alkyl groups. The R₁ and R₄ alkyl groups may be straight chained. The one or more bis (glycol ether) alkylates may comprise one or more of bis-dipropylene glycol n-butyl ether adipate, bis-dipropylene glycol n-propyl ether adipate, bis-diethylene glycol n-butyl ether malonate, bis-diethylene glycol n-butyl ether succinate, and bis-dipropylene glycol n-butyl ether maleate. The one or more bis (glycol ether) alkylates comprise one or more of bis-dipropylene glycol n-butyl ether adipates. The one or more bis (glycol ether) alkylates may be prepared by the process disclosed in WO2015/200088, incorporated herein by reference for all purposes in its entirety. The one or more bis (glycol ether) alkylates may contains less than 1% of volatile organic compounds as defined by EPA Method 24; may exhibit color of less than 25 APHA, as measured ASTM D1209; and/or exhibits a boiling point above 250°C at 760 mmHg, measured as defined in the 2004/42/EC Solvents Directive for Decorative Paints.

Preferably the composition exhibits a sufficient low viscosity such that they can be pumped and applied, preferably at temperatures from 15 to 35°C, particularly with standard application equipment used in original equipment manufacture and in glass replacement processes. In some embodiments, the viscosity of the composition may be about 100,000 Pascal Second or less at 25 °C to about 60,000 Pascal Second or less at 25 °C. In some other embodiments, the viscosity of the composition may be about 1,000 Pascal Second or greater at 25 °C to about 10,000 Pascal Second at 25 °C or greater. The viscosity is measured on a Model DHR-1 Rheometer from TA Instruments, with a 1000 micron gap and a 25 mm parallel plate at a shear rate of 0.2 s⁻¹ at a temperature of 25° C.

10 [0026] Exemplary common plasticizers include one or more of alkyl esters of sulfonic acid, alkyl alkylethers diesters, polyester resins, formals, polyglycol diesters, polymeric polyesters, tricarboxylic esters, dialkylether diesters, dialkylether aromatic esters, aromatic phosphate esters, and aromatic sulfonamides, aromatic diesters, aromatic triesters, aliphatic diesters, epoxidized esters, epoxidized oils, chlorinated hydrocarbons, aromatic oils, alkylether
15 monoesters, naphthenic oils, alkyl monoesters, glyceride oils, paraffinic oils and silicone oils. Common plasticizers may be used in the adhesive composition in an amount of about 5 parts by weight or greater based on the weight of the adhesive composition, more preferably about 10 parts by weight or greater, and most preferably about 18 parts by weight or greater. The common plasticizers may be used in an amount of about 40 parts by weight or less based
20 on the total amount of the adhesive composition, more preferably about 30 parts by weight or less and most preferably about 25 parts by weight or less.

[0027] The composition may comprise one or more isocyanate functional prepolymers containing one or more polyester based polyols which are solid at ambient temperature, about 23°C. The polyester based polyols have melting points such that the prepolymer
25 provides sufficient green strength to prevent the substrates from moving in relation to one another due to gravitational forces at ambient temperatures. In terms of installing a window in a vehicle or building, the polyester based prepolymer prevents the window from sliding after installation. Preferably, the polyester polyols have melting points of about 40°C or greater, even more preferably about 45°C or greater and most preferably about 50°C or
30 greater. Preferably, the polyester polyols exhibit melting points of about 85°C or less, even more preferably about 70°C or less and most preferably about 60°C or less. The polyester based isocyanate prepolymer can be prepared using one or more polyester polyols. The amount of polyester polyol in the prepolymer is a sufficient amount to provide the needed green strength to the composition of the invention and to render it solid at ambient

temperatures. Preferably, the polyester polyol is present in the polyester polyol based isocyanate prepolymer in an amount of about 70 percent by weight or greater based on the weight of the prepolymer and more preferably about 80 percent by weight or greater. Preferably, the polyester polyol is present in the polyester polyol based isocyanate prepolymer in an amount of about 95 percent by weight or less based on the weight of the prepolymer and more preferably about 90 percent by weight or less. Preferably, the polyester polyol based isocyanate prepolymer is present in the adhesive composition in sufficient amount to give the needed green strength and the desired rheology of the composition. Preferably, the polyester polyol based isocyanate prepolymer is present in the adhesive composition in an amount of about 0 parts by weight or greater based on the weight of the adhesive composition, more preferably about 1 parts by weight or greater and most preferably about 2 parts by weight or greater. Preferably, the polyester polyol based isocyanate prepolymer is present in the adhesive composition in an amount of about 10 parts by weight or less, even more preferably about 5 parts by weight or less and most preferably about 2.5 parts by weight or less. The polyester polyol can be any polyester composition that meets the property requirements defined, which is crystalline at ambient temperatures and melts in the desired temperature range. Preferred polyester polyols are available from Creanova under the trade name Dynacol and the designations 7360 and 7330, with 7360 more preferred.

20 **[0028]** The composition may further comprise a polyfunctional isocyanate for the purpose of improving the modulus of the composition in the cured form. Polyfunctional as used in the context of the isocyanates refers to isocyanates having a functionality of 3 or greater and more preferably about 3.2 or greater. Preferably, the polyfunctional isocyanate has a nominal functionality of about 5 or less, even more preferably about 4.5 or less and most preferably about 4.2 or less. The polyfunctional isocyanate can be any isocyanate which is reactive with the isocyanate polyisocyanate prepolymers used in the composition and which improves the modulus of the cured composition. The polyisocyanates can be monomeric; trimeric isocyanurates or biurets of monomeric isocyanates; oligomeric or polymeric, the reaction product of several units of one or more monomeric isocyanates. Examples of preferred polyfunctional isocyanates include trimers of hexamethylene diisocyanate, such as those available from Bayer under the trademark and designation Desmodur[®] N3300, and polymeric isocyanates such as polymeric MDI (methylene diphenyl diisocyanates) such as those marketed by The Dow Chemical Company under the trademark of PAPI[™], including PAPI[™] 20 polymeric isocyanate. The polyfunctional isocyanates are present in sufficient amount to impact the modulus of the cured compositions of the invention. The polyfunctional

isocyanate is preferably present in an amount of about 0.5 parts by weight or greater based on the weight of the adhesive composition, more preferably about 1.0 parts by weight or greater and most preferably about 1.4 parts by weight or greater. The polyfunctional isocyanate is preferably present in an amount of about 8 parts by weight or less, based on
5 the weight of the adhesive composition, more preferably about 5 parts by weight or less and most preferably about 2 parts by weight or less.

[0029] The composition may comprise one or more reinforcing fillers. Such fillers are well known to those skilled in the art and include carbon black, titanium dioxide, calcium carbonate, surface treated silicas, titanium oxide, fumed silica, talc, and the like. Preferred
10 reinforcing fillers comprise carbon black. More than one reinforcing filler may be used, preferably one is carbon black. The reinforcing fillers are used in sufficient amount to increase the strength of the adhesive, to provide thixotropic properties to the adhesive, and to give the composition the desired viscosity and sag resistance. Carbon black is commonly used to provide the desired black color. The carbon black used in this invention may be a
15 standard carbon black which is not specially treated (surface treated or oxidized) to render it nonconductive. Alternatively one or more nonconductive carbon blacks may be used exclusively or in conjunction with the standard carbon black. The amount of carbon black in the composition is that amount which provides the desired color, viscosity, sag resistance and where nonconductivity is important in an amount such that the composition is
20 nonconductive to the level defined herein. The reinforcing fillers are preferably used in the amount of about 10 parts by weight or greater based on the weight of the composition, more preferably about 12 parts by weight or greater and most preferably about 14 parts by weight or greater. Where non-conductive properties are desired, standard carbon black is preferably present in an amount of about 20 parts by weight or less based on the weight of the
25 composition, more preferably about 18 parts by weight or less and most preferably about 16 parts by weight or less. The total reinforcing filler present, including conductive or standard and non-conductive carbon black, is preferably about 35 parts by weight or less based on the weight of the composition, more preferably about 30 parts by weight or less and most preferably about 20 parts by weight or less. Standard carbon blacks are well known in the
30 art and include RAVEN™ 790, RAVEN™ 450, RAVEN™ 500, RAVEN™ 430, RAVEN™ 420 and RAVEN™ 410 carbon blacks available from Colombian and CSX™ carbon blacks available from Cabot, and PRINTEX™30 carbon black available from Degussa, ELFTEX S7100, MONARCH 470, MONARCH 570 and MONARCH 580 carbon blacks. Nonconductive carbon blacks are well known in the art and include RAVEN™ 1040 and
35 RAVEN™ 1060 carbon black from Colombian.

[0030] The composition contains catalyst which catalyzes the reaction of isocyanate moieties with water or an active hydrogen containing compound, which are well known in the art. Exemplary catalysts are organotin compounds, metal alkanoates, and tertiary amines, and mixtures thereof. A mixture of a tertiary amine, such as dimorpholino diethyl ether, and a metal alkanoate, such as bismuth octoate is preferred. Organotin compounds include alkyl tin oxides, stannous alkanoates, dialkyl tin carboxylates and tin mercaptides. Stannous alkanoates include stannous octoate. Alkyl tin oxides include dialkyl tin oxides, such as dibutyl tin oxide and its derivatives. The organotin compounds preferably include a dialkyltin dicarboxylate or a dialkyltin dimercaptide. The preferred dialkyl dicarboxylates include 1,1-dimethyltin dilaurate, 1,1-dibutyltin diacetate and 1,1-dimethyl dimaleate. Preferred metal alkanoates include bismuth alkanoates, such as bismuth octoate or bismuth neodecanoate and zirconium alkanoates. The organo tin compound or metal alkanoate catalyst is present in an amount of about 60 parts per million or greater based on the weight of the adhesive, more preferably 120 parts by million or greater. The organo tin compound or metal alkanoate catalyst is present in an amount of about 1.0 percent or less based on the weight of the adhesive, more preferably 0.5 percent by weight or less and most preferably 0.1 percent by weight or less. Exemplary tertiary amine catalysts include dimorpholinodialkyl ether, a di((dialkylmorpholino)alkyl) ether, bis-(2-dimethylamino ethyl)ether, triethylene diamine, pentamethyldiethylene triamine, N,N-dimethyl cyclo hexyl amine, N,N-dimethyl piperazine 4-methoxyethyl morpholine, N-methyl morpholine, N-ethyl morpholine and mixtures thereof. A preferred dimorpholino dialkyl ether is dimorpholinodiethyl ether. A preferred di((dialkylmorpholino)alkyl) ether is (di-(2-(3,5-dimethylmorpholino) ethyl) ether). Tertiary amines are preferably employed in an amount, based on the weight of the adhesive of about 0.01 percent by weight or greater, more preferably about 0.05 percent by weight or greater, even more preferably about 0.1 percent by weight or greater and most preferably about 0.2 percent by weight or greater and about 2.0 percent by weight or less, more preferably about 1.75 percent by weight or less, even more preferably about 1.0 percent by weight or less and most preferably about 0.4 percent by weight or less.

[0031] The adhesive may be formulated with fillers and additives known in the prior art for use in adhesive compositions. By the addition of such materials physical properties such as viscosity flow rates and the like can be modified. However, to prevent premature hydrolysis of the moisture sensitive groups of the isocyanate functional compounds, fillers should be thoroughly dried before admixture therewith. Exemplary fillers include clays. Preferred clays useful in the invention include kaolin, surface treated kaolin, calcined kaolin, aluminum silicates and surface treated anhydrous aluminum silicates. The clays can be used in any

form, which facilitates formulation of a pumpable adhesive. Preferably, the clay is in the form of pulverized powder, spray-dried beads or finely ground particles. Clays may be used in an amount of about 10 percent by weight of the adhesive composition or greater, more preferably about 12 part by weight or greater and even more preferably about 18 percent by weight or greater. Preferably, the clays are used in an amount of about 30 percent by weight or less of the adhesive composition, more preferably about 28 percent by weight or less and most preferably about 24 percent by weight or less. Other components commonly used in adhesive compositions may be used in the composition of this invention. Such materials are well known to those skilled in the art and may include ultraviolet stabilizers and antioxidants and the like. As used herein all parts by weight relative to the components of the adhesive composition are based on 100 total parts by weight of the adhesive composition.

[0032] The composition may further comprise stabilizers, which function to protect the adhesive composition from moisture, thereby inhibiting advancement and preventing premature crosslinking of the isocyanates in the adhesive formulation. Stabilizers known to the skilled artisan for moisture curing adhesives may be used preferably herein. Included among such stabilizers are diethylmalonate, alkylphenol alkylates, paratoluene sulfonic isocyanates, benzoyl chloride and orthoalkyl formates. Such stabilizers are preferably used in an amount of about 0.1 parts by weight or greater based on the total weight of the adhesive composition, preferably about 0.5 parts by weight or greater and more preferably about 0.8 parts by weight or greater. Such stabilizers are used in an amount of about 5.0 parts by weight or less based on the weight of the adhesive composition, more preferably about 2.0 parts by weight or less and most preferably about 1.4 parts by weight or less.

[0033] The composition may further comprise an adhesion promoter or adhesion promoting component, such as those disclosed in Mahdi, U.S. Patent Publication 2002/0100550 paragraphs 0055 to 0065 and Hsieh, U.S. 6,015,475 column 5, line 27 to column 6, line 41 incorporated herein by reference. Preferably the adhesion promoter contains a silane present in some form. Preferable methods of including silane functionality in the compositions are disclosed in Wu et al., U.S. Patent 6,512,033 at column 5, line 38 to column 7, line 27; U.S. Patents 5,623,044; 4,374,237; 4,345,053 and 4,625,012, relevant portions incorporated herein by reference. The silane may be blended with the prepolymer. In some embodiments the silane has one or more active hydrogen atom which are reactive with an isocyanate. Preferably such silane is a mercapto-silane or an amino-silane and more preferably is a mercapto-trialkoxo-silane or an amino-trialkoxo silane. In some embodiments, the silanes having, active hydrogen atoms reactive with isocyanate moieties, can be reacted with the terminal isocyanate moieties of the prepolymer. Such reaction products are

disclosed in U.S. Pat. No. 4,374,237 and 4,345,053 relevant parts incorporated herein by reference. In other embodiments, silanes having reactive hydrogen moieties reactive with isocyanate moieties can be reacted into the backbone of the prepolymer by reacting such silane with the starting materials during the preparation of the prepolymer. The process for the preparation of prepolymers containing silane in the backbone is disclosed in U.S. Pat. No. 4,625,012, relevant portions incorporated herein by reference. Such silane, having active hydrogen moieties, can be reacted with a polyisocyanate to form an adduct which is blended with the prepolymer reacted with a polyurethane prepolymer or reacted with a polyisocyanate and a compound having on average more than one moiety reactive with an isocyanate moiety. Preferably the adduct is a reaction product of a secondary amino- or mercapto-alkoxy silane and a polyisocyanate, the adduct having an average of at least one silane group and at least one isocyanate group per molecule (hereinafter "adduct"). Exemplary organofunctional silanes useful as adhesion promoters or to prepare adducts include amino- or mercapto-alkoxy silanes, isocyanato alkoxy silanes, methacryloxy silanes, epoxy alkoxy silanes, alkenyl alkoxy silanes and the like. Examples of such compounds include: N,N-bis[(3-triethoxysilyl) propyl]amine; N,N-bis [(3-tripropoxy-silyl) propyl]amine; N-(3-trimethoxysilyl) propyl-3-[N-(3-trimethoxysilyl)-propyl amino]propionamide; N-(3-triethoxysilyl) propyl-3-[N-(3-triethoxysilyl)-propyl-amino]propionamide; N-(3-trimethoxysilyl)propyl-3-[N-(3-triethoxysilyl)-propylamino]propionamide; 3-trimethoxysilylpropyl 3-[N-(3-trimethoxysilyl)-propylamino]-2-methyl propionate; 3-triethoxysilyl propyl 3-[N-(3-triethoxysilyl) -propylamino]-2-methyl propionate; 3-trimethoxysilylpropyl 3-[N-(3-triethoxysilyl)propyl amino]-2-methyl propionate; and the like. Preferably the organofunctional silane is gamma-mercaptopropyl-trimethoxysilane (available as A189 from Union Carbide) or N,N'-bis((3-trimethoxysilyl)propyl)amine. The amount of adhesion promoter present is that amount which enhances the adhesion of the adhesive to the substrate surface. The amount of adhesion promoter present is preferably about 0.1 percent by weight or greater based on the weight of the adhesive and most preferably about 0.5 percent by weight or greater. The amount of adhesion promoter used is preferably about 10 percent by weight or less and most preferably about 2.0 percent by weight or less. The adhesion promoter can be located in either or both parts of a two part adhesive or in a one part adhesive.

[0034] The composition may further comprise a hydrophilic material that functions to draw atmospheric moisture into the composition. This material enhances the cure speed of the formulation by drawing atmospheric moisture to the composition. Preferably, the hydrophilic material is a liquid. Among preferred hydroscopic materials are pyrrolidinones such as 1-methyl-2-pyrrolidinone, available from under the trademark M-Pyrol. The hydrophilic material

is preferably present in an amount of about 0.1 parts by weight or greater and more preferably about 0.3 parts by weight or greater and preferably about 1.0 parts by weight or less and most preferably about 0.6 parts by weight or less. Optionally the adhesive composition may further comprise a thixotrope. Such thixotropes are well known to those skilled in the art and include alumina, limestone, talc, zinc oxides, sulfur oxides, calcium carbonate, perlite, slate flour, salt (NaCl), cyclodextrin and the like. The thixotrope may be added to the adhesive of composition in a sufficient amount to give the desired rheological properties. Preferably, the thixotrope is present in an amount of about 0 parts by weight or greater based on the weight of the adhesive composition, preferably about 1 part by weight or greater. Preferably, the optional thixotrope is present in an amount of about 10 parts by weight or less based on the weight of the adhesive composition and more preferably about 2 parts by weight or less.

[0035] The two part compositions may contain a curing agent located in the B side. Such curing agent comprises one or more compounds that contain greater than one isocyanate reactive group. The curing agents preferably contain hydroxyl groups. The curing agents can be one or more low molecular weight compounds or polyols. Polyols as described hereinbefore can be utilized as curing agents. One class of polyols can be prepolymers as described hereinbefore prepared utilizing excess equivalents of isocyanate reactive groups such that the resulting prepolymers contain isocyanate reactive groups, preferably hydroxyl. The one or more low molecular weight compounds have two or more isocyanate reactive groups and a hydrocarbon backbone wherein the backbone may further comprise one or more heteroatoms. Such low molecular weight compounds may be compounds known in the art as chain extenders, such compounds are difunctional, or crosslinkers, which have, on average, greater than two active hydrogen groups per compound. The heteroatoms in the backbone can be oxygen, sulfur, nitrogen or a mixture thereof, wherein oxygen, nitrogen or a mixture thereof is more preferred and oxygen most preferred. Preferably, the molecular weight of the low molecular weight compound is about 120 or less and more preferably about 100 or less. Preferably, the low molecular weight compound comprises one or more multifunctional alcohols, or one or more adducts of multifunctional alcohol and an alkylene oxide or a mixture thereof. Among preferred multifunctional alcohols are ethane diol, propane diol, butane diol, hexane diol, heptane diol, octane diol, glycerine, trimethylol propane, pentaerythritol, neopentyl glycol, and the like. Blends of various low molecular weight compounds may be used. The low molecular weight compound is used in a sufficient amount to obtain the desired G-Modulus (E-Modulus). In two-part compositions, the low molecular compound may be located in the resin side, the curative side or both. Preferably, the low

molecular weight compound is located in the curative side. Preferably, the low molecular weight compound is present in the composition in an amount of about 2 percent by weight or greater, more preferably about 2.5 percent by weight or greater and most preferably about 3.0 percent by weight or greater. Preferably, the low molecular weight compound is present
5 in the composition in an amount of about 10 percent by weight or less, more preferably about 8 percent by weight or less and most preferably about 6 percent by weight or less.

[0036] The composition or a part of the formulation may be formulated by blending the components together using means well known in the art. Generally, the components are blended in a suitable mixer. Such blending is preferably conducted in an inert atmosphere in
10 the absence of oxygen and atmospheric moisture to prevent premature reaction. In embodiments where a polyester based isocyanate functional prepolymer is used, the adhesive compositions are blended at a temperature above the melting point of the polyester based isocyanate functional prepolymer and below a temperature at which significant side reactions occur. In this embodiment, the temperatures utilized are from about 40°C to less
15 than about 90°C, more preferably about 50°C to about 70°C. It may be advantageous to add any plasticizers and/ or a blend of one or more alkyl esters of alkenoates and one or more alkyl esters of alkanoates to the reaction mixture for preparing the isocyanate containing prepolymer so that such mixture may be easily mixed and handled. Alternatively, the plasticizers and/or a blend of one or more alkyl esters of alkenoates and one or more alkyl
20 esters of alkanoates can be added during blending of all the components. Once the adhesive composition is formulated, it is packaged in a suitable container such that it is protected from atmospheric moisture and oxygen. Contact with atmospheric moisture and oxygen could result in premature crosslinking of the isocyanate functional prepolymer.

[0037] The composition is used to bond a variety of substrates together as described
25 hereinbefore. The composition can be used to bond porous and nonporous substrates together. The adhesive composition is applied to a substrate and the adhesive on the first substrate is thereafter contacted with a second substrate. In preferred embodiments, the surfaces to which the adhesive is applied are cleaned and primed prior to application, see for example, U.S. Patents 4,525,511; 3,707,521 and 3,779,794; relevant parts of all are
30 incorporated herein by reference. Generally the adhesives of the invention are applied at ambient temperature in the presence of atmospheric moisture. Exposure to atmospheric moisture is sufficient to result in curing of one part adhesives. Curing can be accelerated by the addition of additional water or by applying heat to the curing adhesive by means of convection heat, microwave, infrared or ultrasonic heating and the like. Preferably, the
35 adhesive of the invention is formulated to provide a working time of about 6 minutes or

greater more preferably about 10 minutes or greater. Preferably, the working time is about 15 minutes or less and more preferably about 12 minutes or less.

[0038] The composition may be used to bond glass or plastic coated with an abrasion resistant coating, to other substrates such as metal or plastics. In a preferred embodiment, the first substrate is a glass, or plastic coated with an abrasion resistant coating, window and the second substrate is a window frame. In another preferred embodiment the first substrate is a glass, or plastic coated with an abrasion resistant coating, window and the second substrate is a window frame of an automobile. Preferably, the glass window is cleaned and has a glass primer applied to the area to which the adhesive is to be bonded. The plastic coated with an abrasion resistant coating can be any plastic which is clear, such as polycarbonate, acrylics, hydrogenated polystyrene or hydrogenated styrene conjugated diene block copolymers having greater than 50 percent styrene content. The coating can comprise any coating which is abrasion resistant such as a polysiloxane coating. Preferably, the coating has an ultraviolet pigmented light blocking additive. Preferably, the glass or plastic window has an opaque coating disposed in the region to be contacted with the adhesive to block UV light from reaching the adhesive.

[0039] The composition may be used to replace windows in structures or vehicles and most preferably in vehicles. The first step is removal of the previous window. This can be achieved by cutting the bead of the adhesive holding the old window in place and then removing the old window. Thereafter the new window is cleaned and primed. The old adhesive that is located on the window flange can be removed, although it is not necessary and in most cases it is left in place. The window flange is preferably primed with a paint primer. The adhesive is applied in a bead to the periphery of the window located such that it will contact the window flange when placed in the vehicle. The window with the adhesive located thereon is then placed into the flange with the adhesive located between the window and the flange. The adhesive bead is a continuous bead that functions to seal the junction between the window and the window flange. A continuous bead of adhesive is a bead that is located such that the bead connects at each end to form a continuous seal between the window and the flange when contacted. Thereafter the adhesive is allowed to cure. In use, the components of two-part compositions are blended as would normally be done when working with such materials. For a two-part compositions to be most easily used in commercial and industrial environments, the volume ratio at which the two parts are combined should be a convenient whole number. This facilitates application of the curable composition with conventional, commercially available dispensers including static and dynamic mixing. Such dispensers with static mixing are shown in U.S. Patent Numbers 4,538,920 and 5,082,147 (incorporated

herein by reference) and are available from Conprotec, Inc. (Salem, New Jersey) under the trade name MIXPAC or SULZER™ QUADRO of Sulzer Ltd., Switzerland. Typically, these dispensers use a pair of tubular receptacles arranged side-by-side with each tube being intended to receive one of the two parts of the polymerizable composition. Two plungers, one for each tube, are simultaneously advanced (e.g., manually or by a hand-actuated ratcheting mechanism) to evacuate the contents of the tubes into a common, hollow, elongated mixing chamber that may also contain a static mixer to facilitate blending of the two parts. The blended polymerizable composition is extruded from the mixing chamber onto a substrate. When using electrically-driven equipment, dynamic mixing may be used. Once the tubes have been emptied, they can be replaced with fresh tubes and the application process continued. The volumetric ratio at which the two parts of the polymerizable composition are combined is controlled by the diameter of the tubes. (Each plunger is sized to be received within a tube of fixed diameter, and the plungers are advanced into the tubes at the same speed.) A single dispenser is often intended for use with a variety of different two-part polymerizable compositions and the plungers are sized to deliver the two parts of the polymerizable composition at a convenient mix ratio. Alternatively the two part composition may be disposed in a single tube with the curative part located in a bag within the resin. In this embodiment a single tube is used and when the two parts are extruded from the tube they are passed through a nozzle containing mixing elements so as to mix the components sufficiently such that the composition can undergo cure once mixed. Some common mix ratios are 1:1, 2:1, 4:1 and 10:1 and can also be odd ratios. Preferably, the two parts are blended at a mix ratio of about 1:1.

[0040] Preferably, the mixed two-part compositions of the invention have a suitable viscosity to allow application without dripping. Preferably, the viscosities of the two individual components should be of the same order of magnitude. For lower viscosities, the components may require gelling agent known in the art to prevent sag of the uncured adhesive system. Two-part adhesive compositions start to cure upon mixing the two parts. Curing can be accelerated by applying heat to the curing adhesive by means of infrared heat, induction heat, convection heat, microwave heating, application of ultrasonic vibration and the like.

[0041] In another embodiment the compositions of the invention can be used to bond modular components to a car body or to each other. Examples of modular components include vehicle modules, such as door, window or body. Molecular weights as described herein are number average molecular weights which may be determined by Gel Permeation Chromatography (also referred to as GPC). For polyurethane prepolymers, it is also possible

to calculate approximate number average molecular weight from the equivalent ratio of the isocyanate compounds and of the polyol compounds with which they are reacted as known to the persons skilled in the art. Viscosities as described herein are determined according to the procedure disclosed in Bhat, U.S. Patent 5,922, 809 at column 12, lines 38 to 49, incorporated herein by reference. In reference to polyurethane prepolymers, average isocyanate functionality is determined according to the procedure disclosed in Bhat, U.S. Patent 5,922,809 at column 12 lines 65 to column 13, line 26, incorporated herein by reference.

Illustrative Embodiments of the Invention

10 [0042] The following examples are provided to illustrate the invention, but are not intended to limit the scope thereof. All parts and percentages are by weight unless otherwise indicated.

[0043] The following components are needed for prepolymer synthesis.

Component	Type	Supplier
Isonate 125M	Pure MDI	Dow Chemical Company
Voranol 232 036N	Polyether Triol	Dow Chemical Company
Voranol 220 056N	Polyether Diol	Dow Chemical Company
Bis-Dipropylene Glycol n-Butyl Ether Adipate	Plasticizer	Dow Chemical Company
Dabco T-9	stannous octoate	Air Products
Diethyl malonate	Isocyanate stabilizer	Sigma Aldrich

[0044] The following components are needed for adhesive compounding

Component	Type	Supplier
Bis-Dipropylene Glycol n-Butyl Ether Adipate	Plasticizer	Dow Chemical Company
Elftex S7100	Carbon Black	Cabot Corporation
Burgess ICEBERG	General purpose kaolin clay	Burgess Pigment Company
Bismuth octoate	Catalyst	Shephard Chemical Company
Jeffcat DMDEE	dimorpholinodiethyl ether	Huntsman Corporation

[0045] VORANOL™ 220-056 polyol has an average molecular weight of 2000. VORANOL™ 232-236 polyol has an average molecular weight of 4500. VORANOL™ is a trademark of The Dow Chemical Company)

5 **[0046] EXAMPLE 1 (Inventive): Non-silanated elastomeric adhesive containing Bis-Dipropylene Glycol n-Butyl Ether Adipate**

[0047] Prepolymer Synthesis:

[0048] Table 1 shows the composition of the urethane prepolymer used for making the adhesive. Prepolymer was prepared using a combination of two polyol: one with hydroxyl functionality of 2 and the other with hydroxyl functionality of 3 and reacting both with excess
10 MDI to yield a prepolymer with NCO content of 2.33%. The molar ratio of the two polyols ($f = 2 / f = 3$) was maintained at 1.075.

[0049] To prepare the prepolymer, 18.12 g of Isonate 125M was added to a 1L round bottom flask in a glove box to prevent any moisture reaction. 40.51g of Voranol 220-56N (Polyether diol with Mn = 2000 and Hydroxyl number = 56 mg KOH/g available from Dow Chemical
15 Company) and 59.43g of the Voranol 232-036N (Polyether triol with Mn = 4500 and Hydroxyl number = 36 mg KOH/g available from Dow Chemical Company) was then added to the flask. Glassware assembly consisting of condenser, overhead stir shaft, N₂ in, N₂ out, and rubber septums were attached. The round bottom flask was then placed over a heating mantle and the heater was turned on and set at 70 °C. The components were mixed at 200
20 rpm by means of the overhead stir shaft. 3g of the bis-dipropylene glycol n-butyl ether adipate was then added to the round bottom flask using a syringe through the rubber septum. Dabco T-9 catalyst solution was then prepared by adding 0.075g of the catalyst in 5g of Voranol 220-56N. 0.5 g of this catalyst solution as then injected into the flask. The exotherm after catalyst addition was monitored as the temperature increased. As the temperature dropped to 70 °C, 1.44 g of diethyl malonate was then injected in the round bottom flask. Finally, 27g
25 of bis-dipropylene glycol n-butyl ether adipate was added into the flask and the reaction was continued for two hours. The contents of the flask were then transferred to pre-dried glass jars and stored under low humidity condition.

[0050] Adhesive Compounding

[0051] Adhesives were compounded using a Flacktek SpeedMixer (dual axis rotary mixer).
30 21.97g of the above prepolymer was added to a Max 60 polypropylene cup. 8.7g of Elftex S7100 (carbon black) was then added followed by 5.9g of Iceberg clay. The components were mixed inside a Flacktek SpeedMixer for 1 minute at 2500 rpm. 5.54g of bis-dipropylene glycol n-butyl ether adipate, 0.07g of Jeffcat DMDEE and 0.07g of bismuth octoate were then
35 added to the cup. The components were further mixed by another 2 minute at 2500 rpm. The

adhesive was then transferred to a cartridge. 0.5 inch adhesive beads were dispensed from the cartridge using a caulk gun on metal panel coated with PPG NCT X automotive paint system with a 2K non-isocyanate clear coat.

5 **[0052] EXAMPLE 3 (Comparative): Non-silanated elastomeric adhesive containing Diisononyl phthalate.**

[0053] Prepolymer and the corresponding adhesive was prepared using the method described for Example 1, except that the plasticizer was switched from bis-dipropylene glycol n-butyl ether adipate to Diisononyl phthalate. The compositions of prepolymer and the adhesive are given in Table 1 and 2, respectively.

10 **[0054] Example 4 (Comparative): Non-silanated elastomeric adhesive containing Soy Methyl Ester**

[0055] Prepolymer and the corresponding adhesive was prepared using the method described for Example 1, except that the plasticizer was switched from bis-dipropylene glycol n-butyl ether adipate to soy methyl ester (Soygold 1500 sold by Chempoint). The compositions of prepolymer and the adhesive are given in Table 1 and 2, respectively.

15 **[0056] Example 6 (Comparative): Non-silanated elastomeric adhesive containing Trimethyl Pentanyl Diisobutyrate**

20 [0057] Prepolymer and the corresponding adhesive was prepared using the method described for Example 1, except that the plasticizer was switched from bis-dipropylene glycol n-butyl ether adipate to trimethyl pentanyl diisobutyrate (Eastman TXIB sold by Eastman Chemical Company). The compositions of prepolymer and the adhesive are given in Table 1 and 2, respectively.

Table 1: Composition of prepolymers Components	Example 1	Example 2	Example 3	Example 4
Voranol 220-56N	41.01	34.09	42.76	41.01
Voranol 232-036N	59.43	49.41	61.97	59.43
Isonate 125M	18.12	15.06	18.89	18.12
Bis-Dipropylene Glycol n-Butyl Ether Adipate	30			
Diisononyl phthalate		50		
Soygold 1500			35.12	
Eastman TXIB				30
Dabco T-9	0.0075	0.0075	0.0075	0.0075
Diethyl Malonate	1.44	1.44	1.44	1.44

[0058] Table 2: Composition of adhesive

Components	Example 1	Example 2	Example 3	Example 4
Prepolymer from Table 1	21.97	21.97	21.97	21.97
Bis-Dipropylene Glycol n-Butyl Ether Adipate	5.54			
Diisononyl phthalate		2.22		
Soygold 1500			0	
Eastman TXIB				3.32
Elftek S7100	8.66	8.66	8.66	
Iceberg clay	5.86	5.86	5.86	5.86
Jeffcat DMDEE	0.07	0.07	0.07	0.07
bismuth octoate	0.07	0.07	0.07	0.07

[0059] Adhesive Testing**[0060] Viscosity measurement**

5 [0061] Brookfield Cap 2000 + viscometer with a cone and plate attachment and spindle #6 was used for viscosity of the prepolymer. Viscosity of the initial prepolymer was first measured. Plasticizer was then added to the prepolymer until the viscosity of 9000-9500 cP was attained. The additional plasticizer needed to reach this viscosity was noted. The prepolymer with the additional plasticizer was then used for the final adhesive compounding.

10 **[0062] Room temperature link up test**

[0063] Adhesion performance was measured according to the Quick Knife Test (SAE J1720). PPG NCT X, Silver were used as the painted substrates to test these adhesives. 6.3 mm (width) x 6.3 mm (height) x 100 mm (length) bead of adhesive was laid on the painted substrate. The adhesive was cured under the conditions of 23°C and 50 percent relative
15 humidity for 24 hours. The cured bead was then cut with a razor blade through to the substrate at a 45° angle while pulling back the end of the bead at 180° angle. Notches were cut every 3 mm on the substrate. The adhesion failure was noted as cohesive Failure (CF), i.e., failure occurring within the adhesive or adhesive failure (AF), i.e., failure occurring at adhesive/paint interface or a combination of the two expressed as %AF or CF.

20 [0064] Another set of adhesive beads were tested after 7 day cure at 23°C and 50 percent relative humidity.

[0065] Low temperature link up test

[0066] Adhesive beads were applied on PPG NCT X, Silver substrates and cured at -6 °C for 14 days. Quick Knife Test (SAE J1720) was then performed on these adhesive beads.

[0067] Hydrolytic Stability test

- 5 [0068] Adhesive beads were applied on PPG NCT X, Silver substrates and cured at 23°C and 50 percent relative humidity for 7 days. The panels were then placed in 90 °C water bath for 7 days. The panels were then removed and dried using paper towels. Quick Knife Test (SAE J1720) was performed on adhesive beads.

10 [0069] **Adhesive Performance**

[0070] The viscosity of the prepolymer including the additional plasticizer added during the compounding stage is listed in Table 3. The amount of plasticizer was adjusted to maintain a viscosity of 9000-9500 cP. For Examples 2 and 3, the plasticizer amount in the prepolymer resulted in a lower viscosity, as shown in Table 3. As a result, no additional plasticizer was
15 used in the compounding stage in these cases.

[0071] **Table 3: Viscosity of prepolymer**

	Example 1	Example 2	Example 3	Example 4
Plasticizer	Bis-Dipropylene Glycol n-Butyl Ether Adipate	Diisononyl phthalate	Soygold 1500	Eastman TXIB
Amount of Plasticizer*	23.6	24.6	13.1	19.3
Viscosity of prepolymer + additional plasticizer at 25 °C (cP)	9380	9190	9520	9000

* Amount of plasticizer expressed as percentage based on total weight of the adhesive. This includes plasticizer added during synthesis and during compounding of the final adhesive.

- 20 [0072] Adhesive performance as measured by the quick knife test is listed in Table 4. Clearly, the inventive adhesive has much better overall adhesion performance compared to the comparative adhesives. This is especially true for adhesive beads cured at room temperature and at low temperatures. The hydrolytic stability of the inventive adhesive is better than that of Example 2 and 4 but is similar to that of Example 3. The data illustrates
25 that the bis-dipropylene glycol n-butyl ether adipate plasticizer promotes bonding to low surface energy clear coats under ambient and low temperature cure conditions. In addition,

the bond strength is retained under hydrolytic condition resulting in a more durable adhesive relative to the adhesives made with industry standard plasticizers.

[0073]

[0074] **Table 4: Performance of adhesives**

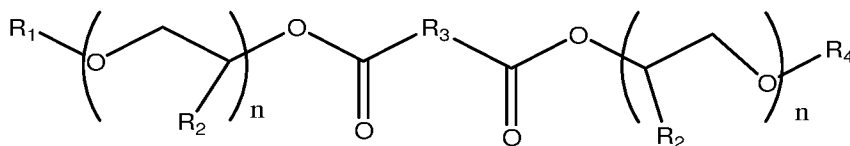
	Quick Knife after 1 day at 23 °C and 50% RH	Quick Knife after 7 days at 23 °C and 50% RH	Quick Knife after 7 days at 23 °C and 50% RH and 7 day 90 °C water soak	Quick Knife after 14 days at -6 °C
Example 1 (Inventive)	100C/0A	100C/0A	80C/20A	100C/0A
Example 2 (Comparative)	50C/50A	0C/100A	0C/100A	0C/100A
Example 3 (Comparative)	80C/20A	80C/20A	80C/20A	0C/100A
Example 4 (Comparative)	70C/30A	20C/80A	0C/100A	0C/100A

5

WHAT IS CLAIMED IS:

1. A composition comprising: a) one or more isocyanate functional components; b) one or more bis (glycol ether) alkylates; and c) one or more catalysts for the reaction of isocyanate moieties with hydroxyl groups.

5 2. A composition according to Claim 1 wherein the one or more bis (glycol ether) alkylates correspond to the formula:



wherein:

R_1 and R_4 independently are $C_1 - C_8$ alkyl groups, phenyl or benzyl;

10 R_2 independently is either hydrogen, methyl or ethyl;

R_3 is a carbon chain containing 0 to 5 carbon atoms and may contain a double bond; and n is independently 1 to 4.

3. A composition according to Claim 2 wherein: R_1 and R_4 independently are $C_1 - C_8$ alkyl groups.

15 4. A composition according to Claim 1 wherein the one or more bis (glycol ether) alkylates comprise one or more of bis-dipropylene glycol n-butyl ether adipate, bis-dipropylene glycol n-propyl ether adipate, bis-diethylene glycol n-butyl ether malonate, bis-diethylene glycol n-butyl ether succinate, and bis-dipropylene glycol n-butyl ether maleate.

20 5. A composition according to Claim 4 wherein the one or more bis (glycol ether) alkylates comprise one or more of bis-dipropylene glycol n-butyl ether adipate.

6. A composition according to Claim 1 further comprising one or more carbon blacks.

7. A composition according to Claim 1 wherein
 a) the one or more isocyanate functional components are present in an amount of about 20 to about 60 percent by weight; b) the one or more bis (glycol ether) alkylates are present in
 25 an amount of about 5 to about 40 percent by weight; c) one or more catalysts for the reaction of isocyanate moieties with hydroxyl groups are present in an amount of about 0.005 to about 2 percent by weight and d) one or more carbon blacks are present in an amount of about 10 to about 35 parts by weight; wherein percentages are based on the weight of the composition.

30 8. A composition according to Claim 1 wherein the composition further comprises one or more isocyanate functional polyester based prepolymers which are solid at 23°C.

9. A composition according to Claim 1 wherein the composition further comprises one or more polyisocyanates having a nominal functionality of about 3 or greater.
10. A method of bonding two or more substrates together which comprises contacting the two or more substrates together with a composition of Claim 1 disposed along at least a
5 portion of the area wherein the substrates are in contact.
11. The method of Claim 10 wherein the at least one of the substrates is window glass.
12. A method according to Claim 10 wherein at least one of the other substrates is a building or a vehicle.
13. The method according to Claim 10 wherein the substrate is a vehicle.
- 10 14. A method of replacing a window of a vehicle comprising: i) removing the window from the vehicle; ii) applying a composition according to Claim 1 to a replacement window or to the flange of the vehicle adapted to hold the window into the vehicle; iii) contacting the flange of the vehicle and the replacement window with the composition disposed between the replacement window and the flange of the vehicle; and iv) allowing the adhesive to cure.
- 15 15. The method of Claim 14 wherein the vehicle can be safely driven after 60 minutes from installation of the window into the vehicle.

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2018/064853

A. CLASSIFICATION OF SUBJECT MATTER
 INV. C08G18/76 C08G18/10 C08G18/48 C09J175/08
 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)
 C08G C09J

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	JP 2017 149899 A (TOYO INK SC HOLDINGS CO LTD) 31 August 2017 (2017-08-31) paragraphs [0190], [0220], [0252] -----	1-4, 10-15
X	US 2016/002511 A1 (ARAKI KIMINORI [JP]) 7 January 2016 (2016-01-07) paragraph [0035]; example 1 -----	1-15
X	US 2016/137815 A1 (ARAKI KIMINORI [JP] ET AL) 19 May 2016 (2016-05-19) paragraph [0064]; tables 1-1 -----	1-15

Further documents are listed in the continuation of Box C.

See patent family annex.

* Special categories of cited documents :

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No PCT/US2018/064853

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