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(54) Title: ONE-PART MOISTURE CURABLE POLYURETHANE ADHESIVE

(57) **Abstract:** The present invention is a polyurethane prepolymer comprising the reaction product of: A) a polyisocyanate; B) one or more compounds or polymers having isocyanate-reactive moieties. C) a dispersion triol containing from 10 to 60 percent by weight based on the dispersion of particles of an organic polymer which is nonreactive with the polyols and polyisocyanates having a particle size of from 5 to 50 microns; wherein the prepolymer has a free isocyanate content of from 0.8 to 2.2 percent, the weight ratio of diol to triol and dispersion triol is from 0.8 to 1.2. In another embodiment the invention is a one-part adhesive composition comprising the polyurethane prepolymer of the invention and a catalyst capable of catalyzing the reaction of isocyanate moieties with water. In another embodiment the invention is a process for bonding two substrates together which comprises contacting the adhesive composition of the invention with at least one of the substrates and contacting the substrates together along the portion of the substrate(s) to which the adhesive has been applied before the adhesive applied cures and allowing the adhesive to cure and bond the substrates together.



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ONE-PART MOISTURE CURABLE POLYURETHANE ADHESIVE

This application is a Rule 53(b) application of copending provisional application Serial No. 60/223,135, filed August 7, 2000.

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This application relates to a one-part polyurethane based adhesive useful in bonding porous and nonporous materials. The adhesive is especially useful in bonding glass into window frames, for example windshields and other window glass into automobiles.

Polyurethane adhesive compositions typically comprise at least one urethane prepolymer. Adhesives useful for bonding to nonporous substrates, such as glass, to metal, are well-known. When glass is installed in automobiles on a production line, a one-part moisture curable polyurethane adhesive is preferably used, as the equipment needed for the application of such an adhesive in an automobile assembly plant is less expensive than the equipment needed to apply a two-part adhesive. One part polyurethane adhesives are disclosed in U.S. Patents 4,374,237 and 4,687,533.

US Patent 5,922,809 discloses a one-part polyurethane adhesive comprising a prepolymer comprising the reaction product of A) one or more polyisocyanates; B) one or more compounds containing an average of more than one isocyanate reactive moieties; preferably a mixture of a polyether diol and a polyether triol; and C) a dispersion triol containing from 10 to 60 percent by weight based on the dispersion of particles of an organic polymer having a particle size of from 5 to 50 microns, preferably comprising a polymer derived from styrene, halo or alkyl styrene; or a rubber modified polymer derived from styrene, or halo or alkyl substituted styrene; wherein the prepolymer has an isocyanate content of from 0.8 to 2.2 percent by weight; and D) a catalyst for the reaction of a polyisocyanate with water.

In the automotive after-market replacement industry, glass is often bound into automobiles through the use of two-part moisture curable polyurethane adhesives. Two-part polyurethane adhesives are used because they offer rapid initial cure allowing for rapid drive-away times. Two-part adhesives require special applicators which mix the two parts in specific proportions immediately prior to application. These applicators are more

difficult to and costly to use than applicators used for one-part adhesives. Further, the improper application or mixing of two-part adhesives can result in poor adhesion. Two-part polyurethane adhesives are well known, see U.S. Patent 4,835,012, and U.S. Patent 5,603,798 and DE 4,210,277.

5 The market demands simpler application systems and faster curing adhesives which allow even faster drive-away times. If the adhesive cures too rapidly, then the window installer loses the necessary time to install and properly place the glass into the frame before the adhesive becomes too intractable to work with. Working time is defined as the period from application of adhesive until the adhesive becomes too intractable to work
10 with.

 Regulations in the U.S. require dual airbags for the front seat of vehicles. During crashes the airbags inflate and exert additional pressure on the windshield. Federal Transportation Agency regulations require that windshield remain in place at crashes of up to 30 mph (48 KPH). This requires adhesives which have enhanced strength at the drive-
15 away time. To meet such a standard, the lap shear strengths of the adhesive should be preferably 150 psi (1033 kPa) or greater as determined according to ASTM D-3163 and demonstrate impact energy strength of 9 ft-lbs (12.2 Joules) or greater at 23°C/50 percent RH..

 There is a need for a one-part adhesive which can survive such a crash two
20 hours after application of the adhesive at 15°F (-9.4°C). Survive a crash means that the windshield remains bonded in the automobile during and after the crash.

 The present invention is a polyurethane prepolymer comprising the reaction product of

- A) one or more polyisocyanates;
- 25 B) one or more diols and one or more triols;
- C) one or more dispersion triols containing from 10 to 60 percent by weight based on the dispersion of particles of an organic polymer having a particle size of from 5 to 50 microns;

wherein the prepolymer has a free isocyanate content of from 0.8 to 2.2 percent and the weight ratio of diol to triol and dispersion triol is from 0.8 to 1.2. The free isocyanate content referred to here is measured 24 hours after prepolymer production.

5 In another embodiment the invention is a one-part adhesive composition comprising the polyurethane prepolymer of the invention and a catalyst capable of catalyzing the reaction of isocyanate moieties with water.

In another embodiment the invention is a process for bonding two substrates together which comprises contacting the two substrates together with the adhesive composition of the invention disposed between the two substrates and allowing the adhesive
10 to cure and bond the substrates together.

The adhesive of this invention is capable of bonding primed glass into an automobile such that glass will not delaminate from the window frame in a crash at 35 mph at 35°F (1.7°C) and 45 percent relative humidity 2.5 hours after adhesive application and at 30 mph at 15°F (-9.4°C) two hours after adhesive application. The adhesive of the invention
15 also provides reasonable working times, preferably 6 to 15 minutes, and more preferably 8 to 10 minutes. Additionally, many of the problems associated with two-part adhesives described before are eliminated.

The urethane prepolymers have an average isocyanate functionality sufficient to allow the preparation of a crosslinked polyurethane upon cure and not so high that the
20 polymers are unstable. Stability in this context means that the prepolymer or adhesive prepared from the prepolymer has 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 the prepolymer or adhesive prepared therefrom does not undergo an increase in viscosity of more than 50 percent during the stated period.

25 Preferably, the average isocyanate functionality is at least 2.2 and preferably at least 2.4. Below 2.2 the ability of the prepolymer to crosslink sufficiently to achieve the desired strength of the cured adhesive is compromised. Preferably the average isocyanate functionality of the prepolymer is 3.0 or less and more preferably 2.8 or less. Above 3.0 average isocyanate functionality the prepolymer and adhesives prepared from the

prepolymer may exhibit unacceptable stability. The prepolymer preferably has a free isocyanate content which facilitates acceptable strength in adhesives prepared from the prepolymers after 60 minutes and stability of the prepolymer. Preferably, the free isocyanate content is 0.8 percent by weight or greater based on the weight of the prepolymer and more preferably 0.9 percent by weight or greater, and preferably 2.2 percent by weight or less, more preferably 2.0 or less, even more preferably 1.4 percent by weight or less and even more preferably 1.1 percent by weight or less and most preferably 1.0 percent by weight or less. Above 2.2 percent by weight the adhesives prepared from the prepolymer may demonstrate lap shear strengths after 60 minutes which are too low for the intended use and foaming during cure of the adhesive prepared from the prepolymer may occur. Below 0.8 percent by weight the prepolymer viscosity is too high to handle and the working time is too short..

The free isocyanate content changes with time as the free isocyanate groups react with moisture. Primary free isocyanate content means the isocyanate content measured within a short period of time, less than 1 hour, after production of the prepolymer. Secondary free isocyanate content means the weight percent of isocyanate groups present in the prepolymer 24 hours after production of the prepolymer. The preferred isocyanate contents referred to above are secondary isocyanate contents.

The prepolymer preferably exhibits a viscosity which facilitates formulation of a pumpable adhesive which has good green strength. Preferably the viscosity of the prepolymer is 100,000 centipoise ($1000.49 \text{ c m}^2/\text{s}$) or less and more preferably 70,000 centipoise ($700.31 \text{ (m}^2/\text{s)})$ or less, preferably 30,000 centipoise ($300.14 \text{ c m}^2/\text{s}$) or greater, and more preferably 45,000 centipoise ($450.20 \text{ c m}^2/\text{s}$) or greater. The viscosity used herein is Brookfield viscosity determined using a number 5 spindle. The viscosity of the adhesive can be adjusted with fillers, although the fillers cannot improve the green strength of the final adhesive. Below 30,000 centipoise ($300.14 \text{ c m}^2/\text{s}$) the adhesive prepared from the prepolymer may exhibit poor green strength. Above 100,000 ($100.49 \text{ c m}^2/\text{s}$) the prepolymer may be unstable and hard to dispense. The prepolymer may be prepared by any suitable method, such as by reacting the diol, triol and dispersion triol with an excess over stoichiometry of one or more polyisocyanates under reaction conditions sufficient to form a

prepolymer having isocyanate functionality and free isocyanate content which meets the criteria discussed above.

Preferable polyisocyanates for use in preparing the prepolymer include those disclosed in US Patent 5,922,809 at column 3, line 32 to column 4, line 24. Preferably the polyisocyanate is an aromatic or cycloaliphatic polyisocyanate such as diphenylmethane-4,4'-diisocyanate, isophorone diisocyanate, tetramethylxylene diisocyanate, and is most preferably diphenylmethane-4,4'-diisocyanate.

The polyisocyanates are used in a sufficient amount to form an advanced polyurethane prepolymer having free reactive isocyanate moieties. Free reactive isocyanate moieties mean there are isocyanate groups bound to the prepolymer backbone which are free to react with reactive hydrogen atoms. Preferably the amount of polyisocyanate is 5 percent by weight or greater based on the starting materials and more preferably 9 percent by weight or greater and preferably 20 percent by weight or less, more preferably 15 percent by weight or less and even more preferably 11 percent by weight or less.

To prepare the prepolymer the polyisocyanates are reacted with one or more diols, one or more triols and a dispersion triol. The diol and triol are generically referred to as polyols. Polyols useful in this invention are diols and triols corresponding to the polyols described in US Patent 5,922,809 at column 4, line 60 to column 5, line 50.

Preferably, the polyol(s) have an average functionality of at least 1.5, more preferably at least 1.8 and most preferably at least 2.0; and is preferably no greater than 4.0, more preferably no greater than 3.5 and most preferably no greater than 3.0. Preferably, the equivalent weight of the polyol(s) is at least 200, more preferably at least 500 and more preferably at least 1,000; and is preferably no greater than 3,500, more preferably no greater than 3,000 and most preferably no greater than 2,500.

Preferably the polyols (diols and triols) are polyether polyols and more preferably polyoxyalkylene oxide polyols. Most preferred, triols are ethylene oxide-capped polyols prepared by reacting glycerin with propylene oxide, followed by reacting the product with ethylene oxide.

The prepolymer also comprises a dispersion triol having dispersed therein particles of an organic based polymer. Preferably the triol used to disperse the organic particles is a polyether triol and more preferably a polyoxyalkylene based triol. Preferably, such polyoxyalkylene oxide triol comprises a polyoxypropylene chain with a

5 polyoxyethylene end cap. Such materials are well known in the art and initiators and alkylene oxides which may be used in the preparation of the triol are described hereinbefore. A particularly preferred polyether triol is a 1,2,3-propane triol initiated polyoxypropylene with a polyoxyethylene end cap. Preferably the triols used have a molecular weight of 4,000 or greater, more preferably 5,000 or greater and most preferably 6,000 or greater.

10 Preferably such triol has molecular weight of 8,000 or less and more preferably 7,000 or less. Below 4,000 molecular weight the elongation and impact properties of the finally cured adhesive are too low for the intended use. Above 8,000 molecular weight the adhesive prepared from the prepolymer is too elastomeric for the intended use. The triol preferably has a hydroxyl number which is high enough such that the adhesive prepared

15 from the prepolymer cures rapidly enough and provides the desired open times. If the hydroxyl number is too low the adhesive cures too slowly and the desired open times and drive-away times cannot be achieved. The hydroxyl number should not be so high as to reduce the elongation of the cured adhesive prepared from the prepolymer. Preferably, the hydroxyl number of the triol is 30 or greater and more preferably 40 or greater. Preferably,

20 the hydroxyl number of the triol is 75 or less and more preferably 60 or less.

Preferably the particles comprise a thermoplastic polymer, rubber-modified thermoplastic polymer or a polyurea dispersed in a triol. The polyurea preferably comprises the reaction product of a polyamine and a polyisocyanate. Preferable thermoplastic polymers are those based on monovinylidene aromatic monomers and copolymers of

25 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 dispersed in the triol comprise copolymers of unsaturated nitriles, conjugated dienes and a monovinylidene aromatic monomer, a copolymer of an unsaturated nitrile and a monovinylidene aromatic monomer or a polyurea.

30 Even more preferably the particles comprise a polyurea or polystyrene-acrylonitrile copolymer with the polystyrene-acrylonitrile copolymers being most preferred.

The organic polymer particles useful in this invention described hereinbefore are commonly available and well-known to those skilled in the art.

Representative monovinylidene aromatic compounds which can be employed herein include styrene, alkyl-substituted styrenes (for example, alpha-methylstyrene and
5 alpha-ethylstyrene) and ring-substituted styrenes (for example, vinyl toluene, particularly para-vinyltoluene, ortho-ethylstyrene and 2,4-dimethylstyrene); ring-substituted halogenated styrenes such as chlorostyrene and 2,4-dichlorostyrene; styrenes substituted with both a halo and an alkyl group such as 2-chloro-4-methylstyrene and vinylanthracene. In general, the preferred monovinylidene aromatic compound(s) employed in preparing the
10 styrenic polymer resin is styrene or a combination of styrene and alpha-methylstyrene (advantageously such combinations contain alpha-methylstyrene in amounts from 10 to 50, more advantageously from 15 to 40, weight percent of the total weight of the styrene and alpha-methylstyrene); with styrene being the most preferred monovinylidene aromatic compound.

15 Conjugated dienes useful in the block copolymer include straight- and branched-chain aliphatic hydrocarbons containing two double bonds attached to adjacent carbon atoms. Preferred dienes contain 4 to 6 carbon atoms and include butadiene, isoprene, 1,3-pentadiene, 1,3-hexadiene, 2,3-dimethylbutadiene and mixtures thereof. More preferably, such conjugated dienes contain from 4 to 5 carbon atoms and include, for
20 example, butadiene, isoprene, cis-1,3-pentadiene, trans-1,3-pentadiene and mixtures thereof. The most preferred dienes are butadiene and isoprene.

Preferred unsaturated nitriles useful herein include acrylonitrile, ethacrylonitrile, methacrylonitrile and mixtures thereof, more preferred is acrylonitrile. In preparing copolymers useful in this invention, the amount of the unsaturated nitrile(s) most
25 advantageously employed will vary depending on the physical and chemical properties desired in the copolymer particles. The copolymer will advantageously be derived from 5 to 35, preferably from 15 to 25, weight percent of the unsaturated nitrile(s) wherein said weight percent is based on the total weight of the polymer.

To prepare the copolymers based on styrene and optionally other unsaturated compounds, mass or a combination of mass/suspension polymerization techniques are most commonly employed. Illustrative mass polymerization techniques are described in U.S. Patents 2,727,884 and 4,782,127. Processes for the preparation of block copolymers of monovinylidene aromatic monomers and conjugated dienes are described in U.S. Patents 5,242,984 and 5,134.

The organic polymer particles dispersed in the triol 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 ultimate strength of the adhesive after cure. Preferably the particle size is 10 microns or greater and more preferably the particle size is 20 microns or greater. Preferably the particle size is 50 microns or less and more preferably the particle size is 40 microns or less. The triol dispersion 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 that the cured adhesive has too much elasticity as defined by elongation. Preferably the dispersion contains 20 percent by weight or greater of organic polymer particles copolymer based on the dispersion, preferably 30 percent by weight or greater and more preferably 35 percent by weight or greater. Preferably the dispersion contains 60 percent by weight or less of organic polymer particles based on the dispersion, preferably 50 percent by weight or less and more preferably 45 percent by weight or less.

The polyols (diols and triols and dispersion triols) are present in an amount sufficient to react with most of the isocyanate groups of the isocyanates leaving enough isocyanate groups to correspond with the desired free isocyanate content of the prepolymer. Preferably the polyols are present in an amount of 30 percent by weight or greater based on the prepolymer, more preferably 40 percent by weight or greater and most preferably 55 percent by weight or greater. Preferably the polyols are present in an amount of 75 percent by weight or less based on the prepolymer, more preferably 65 percent by weight or less and most preferably 60 percent by weight or less. The weight ratio of diols to triols and dispersion triols is important to achieving the desired cure rate and strength of the adhesive.

If the weight ratio is too low the formulation is too viscous to handle and the resulting adhesive has insufficient elasticity to retain glass in an automobile window frame under crash conditions. If the ratio is too high the adhesive does not have adequate green strength. The weight ratio of diol to triol and dispersion triol is preferably 0.8 or greater and
5 more preferably 0.85 or greater and most preferably 0.9 or greater. The weight ratio of diol to triol and dispersion triol is 1.2 or less; more preferably 1.0 or less and most preferably 0.95 or less. In the embodiment where the polyols comprise a mixture of diols and triols the amount of diols present is preferably 15 percent by weight or greater based on the prepolymer, more preferably 25 percent by weight or greater and most preferably 28 percent
10 by weight or greater; and 40 percent by weight or less based on the prepolymer, more preferably 35 percent by weight or less and most preferably 30 percent by weight or less. In the embodiment where the polyols comprise a mixture of diols and triols the amount of triols (non dispersion triol and dispersion triol) present is preferably 15 percent by weight or greater based on the prepolymer, more preferably 25 percent by weight or greater and most
15 preferably 28 percent by weight or greater; and preferably 45 percent by weight or less based on the prepolymer, more preferably 35 percent by weight or less and most preferably 32 percent by weight or less.

The dispersion of organic polymer particles in a triol is present in the prepolymer in an amount of 10 percent by weight or greater of the prepolymer and more
20 preferably 12 percent by weight or greater, and 18 percent by weight or less of the prepolymer and more preferably 15 percent by weight or less.

In one embodiment the thermoplastic polymer particles may be rubber-modified. Generally this involves blending an elastomeric or rubbery polymer with the thermoplastic polymer. A preferred rubbery material is acrylonitrile-butadiene-styrene
25 interpolymer. Preferably, the rubber-modified thermoplastic polymer particles contain 15 to 25 percent by weight of rubber polymer particles.

In one embodiment the organic polymer particles comprise a polyurea, comprising the reaction product of a polyamine and a polyisocyanate.. Preferably, the polyurea is prepared by the reaction of a polyamine, preferably a diamine, with a
30 polyisocyanate, preferably a diisocyanate. The polyurea and polyamine are mixed and

undergo immediate reaction at room temperature. Thereafter the polyurea is contacted with triols, preferably under high shear conditions to disperse the polyurea into the triol.

Preferably the isocyanate used to prepare the polyurea is a cycloaliphatic or aliphatic polyisocyanate, as the use of cycloaliphatic and aliphatic isocyanates facilitate handling and stability of the polyurea. Preferably the polyurea has a urea functionality of 8 percent or greater, more preferably 10 percent or greater and most preferably 15 percent or greater. Preferably the polyurea has a functionality of 40 percent or less and more preferably 20 percent or less. Functionality as used herein relative to polyureas refers to weight percent of urea groups present in the polyurea.

The polyurethane prepolymers of the invention may further comprise a plasticizer. The plasticizers useful in the prepolymer are common plasticizers useful in polyurethane adhesive applications and well known to those skilled in the art. The plasticizer is present in an amount sufficient to disperse the prepolymer in the final adhesive composition. The plasticizer can be added to the adhesive either during preparation of the prepolymer or during compounding of the adhesive composition. Preferably the plasticizer is present in 1 percent by weight or greater of the prepolymer formulation (prepolymer plus plasticizer), more preferably 20 percent by weight or greater and most preferably 30 percent by weight or greater. Preferably the plasticizer is present in 45 percent by weight or less of the prepolymer formulation and more preferably 35 percent by weight or less.

The polyurethane prepolymer may be prepared by any suitable method, such as bulk polymerization and solution polymerization. Preferable processes for the preparation of the prepolymers are disclosed in US patent 5,922,809 at column 9, line 4 to 5. The polyurethane prepolymers are present in the adhesive composition in an amount sufficient such that when the resulting adhesive cures substrates are bound together.

Preferably the lap shear strengths of bonds so formed is 150 psi (206 kPa) or greater after 2 hours. Preferably the polyurethane prepolymers are present in an amount of 55 parts by weight of the adhesive composition or greater, more preferably 60 parts by weight or greater and most preferably 66 parts by weight or greater. Preferably the polyurethane prepolymers are present in an amount of 80 parts by weight of the adhesive composition or less, more preferably 75 parts by weight or less and even more preferably 68 parts by weight or less.

The adhesive of the invention 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 can be modified. However, to prevent premature hydrolysis of the moisture sensitive groups of the polyurethane prepolymer, fillers should be thoroughly dried before admixture therewith.

Optional components of the adhesive of the invention include 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, fume silica and talc. Preferred reinforcing fillers comprise carbon black. In one embodiment, more than one reinforcing filler may be used, of which one is carbon black and a sufficient amount of carbon black is used to provide the desired black color to the adhesive. The reinforcing fillers are used in sufficient amount to increase the strength of the adhesive and to provide thixotropic properties to the adhesive. Preferably the reinforcing filler is present in an amount of 1 part by weight of the adhesive composition or greater, more preferably 20 parts by weight or greater and most preferably 24 parts by weight or greater. Preferably the reinforcing filler is present in an amount of 40 parts by weight of the adhesive composition or less, more preferably 32 parts by weight or less and most preferably 28 parts by weight or less.

Among optional materials in the adhesive composition are 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 0 parts by weight of the adhesive composition or greater, more preferably 1 part by weight or greater and even more preferably 6 parts by weight or greater. Preferably the clays are used in an amount of 20 parts by weight or less of the adhesive composition and more preferably 10 parts by weight or less.

The adhesive composition of the invention may further comprise a catalyst known for promoting the cure of polyurethanes in the presence of moisture. Preferable catalysts include metal salts such as tin carboxylates, organo silicon titanates, alkyl titanates,

metal carboxylates, and dimorpholinodiethyl ether or alkyl-substituted dimorpholinodiethyl ethers. Preferably the catalyst comprises a mixture of metal carboxylates and one of a dimorpholino-diethyl ether or an alkyl substituted dimorpholino diethyl ether. Preferred metal carboxylates include bismuth carboxylates. Among preferred catalysts are bismuth octoate, dimorpholinodiethyl ether and (di-(2-(3,5-dimethylmorpholino)ethyl)) ether. Such catalysts, when employed are preferably employed in an amount based on the weight of the adhesive composition of 0 parts by weight or greater, more preferably 0.1 parts by weight or greater, even more preferably 0.2 parts by weight or greater and most preferably 0.4 parts by weight or greater. Such catalysts are preferably employed in an amount, based on the weight of the adhesive composition of 5 parts by weight or less, more preferably 1.75 parts by weight or less, even more preferably 1 part by weight or less and most preferably 0.6 parts by weight or less.

The adhesive composition of this invention may further comprise plasticizers so as to modify the rheological properties to a desired consistency. Such materials should be free of water, inert to isocyanate groups and compatible with a polymer. Suitable plasticizers are well known in the art and preferable plasticizers include alkyl phthalates such as dioctylphthalate or dibutylphthalate, partially hydrogenated terpene commercially available as "HB-40", trioctyl phosphate, epoxy plasticizers, toluene-sulfamide, chloroparaffins, adipic acid esters, castor oil, toluene and alkyl naphthalenes. The amount of plasticizer in the adhesive composition is that amount which gives the desired rheological properties and which is sufficient to disperse the catalyst in the system. The amounts disclosed herein include those amounts added during preparation of the prepolymer and during compounding of the adhesive. Preferably plasticizers are used in the adhesive composition in an amount of 0 parts by weight or greater based on the weight of the adhesive composition, more preferably 5 parts by weight or greater and most preferably 10 parts by weight or greater. The plasticizer is preferably used in an amount of 45 parts by weight or less based on the total amount of the adhesive composition and more preferably 40 parts by weight or less.

The adhesive of this invention 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.

Included among such stabilizers are diethylmalonate and alkylphenol alkylates. Such stabilizers are preferably used in an amount of 0.1 parts by weight or greater based on the total weight of the adhesive composition, preferably 0.5 parts by weight or greater and more preferably 0.8 parts by weight or greater. Such stabilizers are used in an amount of 5.0 parts by weight or less based on the weight of the adhesive composition, more preferably 2.0 parts by weight or less and most preferably 1.4 parts by weight or less.

The adhesive composition may further comprise a hydrophilic material which functions to draw atmospheric moisture into the composition. This material enhances the cure speed of the formulation by drawing atmospheric moisture to the composition.

10 Preferably the hydrophilic material is a liquid. Among preferred hygroscopic materials are pyrrolidinones such as 1-methyl-2-pyrrolidinone, available from under the trademark m-pyrrol. The hydrophilic material is preferably present in an amount of 0.1 percent by weight or greater and more preferably 0.3 percent by weight or greater and preferably 1.0 percent by weight or less and most preferably 0.6 percent by weight or less. Optionally the adhesive

15 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) and cyclodextrin. 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 0 parts by weight or greater

20 based on the weight of the adhesive composition, preferably 1 part by weight or greater. Preferably the optional thixotrope is present in an amount of 10 parts by weight or less based on the weight of the adhesive composition and more preferably 2 parts by weight or less.

Other components commonly used in adhesive compositions may be used in

25 the adhesive composition of this invention. Such materials are well known to those skilled in the art and may include ultraviolet stabilizers and antioxidants.

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.

The adhesive composition of this invention 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 the absence of oxygen and atmospheric moisture to prevent premature reaction. It may
5 be advantageous to add any plasticizers to the reaction mixture for preparing the isocyanate containing prepolymer so that such mixture may be easily mixed and handled. Alternatively, the plasticizers 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
10 oxygen could result in premature crosslinking of the polyurethane prepolymer-containing isocyanate groups.

The adhesive composition of the invention is 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
15 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. 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 the adhesive. Curing can be accelerated by the addition of additional water or by applying
20 heat to the curing adhesive by means of convection heat and microwave heating. Preferably the adhesive of the invention is formulated to provide a working time of 6 minutes or greater more preferably 10 minutes or greater. Preferably the working time is 15 minutes or less and more preferably 12 minutes or less.

The adhesive composition is preferably used to bond glass to other substrates
25 such as metal or plastics. In a preferred embodiment the first substrate is a glass window and the second substrate is a window frame. In another preferred embodiment the first substrate is a glass 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.

Preferably the adhesive compositions of the invention demonstrate a lap shear strength after 2 hours from application to substrates of 150 psi (1033 kPa). Lap shears are determined according to ASTM D-3163. Preferably the cured adhesive compositions of the invention demonstrate an elongation of 300 percent or greater as determined according to ASTM D-638-91 and preferably greater than 600 percent. Preferably the elongation is 700 percent or less.

Viscosities as described herein are determined according to the following procedure: measured using the Brookfield Viscometer, Model RVT at standard conditions of 72°F (22°C) and 50 percent RH. The viscometer is calibrated using silicone oils of known viscosities, which vary between 5,000 cps to 50,000 cps. A set of RV spindles that attach to the viscometer are used for the calibration. All measurements are done using the No. 5 spindle at a speed of 5 revolution per second for 5 minutes until the viscometer equilibrates. The viscosity corresponding to the equilibrium reading is then calculated using the calibration.

Molecular weights as described herein are determined according to the following procedure: determined using the Waters Model 590 Gel Permeation Chromatograph. This unit is connected to a multiwavelength detector and a differential refractometer to measure the elution volume. A column of styrogel is used for the size exclusion and it can determine molecular weights from 250 to 50,000. The molecular weight of the prepolymer is then determined by measuring the elution volume through this column using tetrahydrofuran as the eluting solvent. The molecular weight is then calculated from a calibration curve of molecular weight vs. elution volume obtained from a polystyrene polyethylene glycol column. The quoted molecular weights are weight average molecular weights unless otherwise specified.

In reference to polyurethane prepolymers, average isocyanate functionality is determined according to the following formula,

$$\text{moles diol-NCO adduct} \times \text{diol-NCO functionality} + \text{moles triol-NCO adduct} \times \text{triol-NCO functionality} + \text{moles excess polyisocyanate monomer} \times \text{its functionality}$$

moles diol-NCO adduct + moles triol-NCO adduct + moles excess
polyisocyanate monomer

wherein moles excess polyisocyanate monomer are calculated according to
the following formula,

5 moles of isocyanate - (2x moles of diol + 3x moles of triol)

and the moles of isocyanate, diol and triol are based on the amount of each in
the starting formulation.

The theoretical average molecular weight of the prepolymer is calculated as
equal to the average isocyanate functionality times the isocyanate equivalent weight of the
10 prepolymer.

Functionality of the raw material is generally disclosed by the raw material
supplier. It can be determined empirically by means of titrating the polyol or isocyanate to
determine the average number functional group per molecule. One skilled in the art knows
how to determine the functionality based on data developed by titration.

15 Illustrative Embodiments of the Invention

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.

Example 1 - Preparation of Prepolymer

20 A polyether polyurethane prepolymer was prepared by mixing 980 g of a
polyoxypropylene diol having an average molecular weight of 2,000 with 595 g of a
polyoxypropylene triol having an average molecular weight of 4,500 and 455 g of a styrene
acrylonitrile dispersed polyoxypropylene triol with an average molecular weight of 5,400.
Mixing was carried out in a reactor by heating the mixture to 48°C. 320 g of
25 diphenylmethane-4,4'-diisocyanate and 0.17 g of stannous octoate was added to the
mixture. The whole mixture was then reacted for one hour. Finally, 1120 g of a plasticizing

agent dialkyl phthalate was added to the mixture and the mixing was continued for one hour. The diol to triol and dispersion triol ratio was 0.93.

Example 2 - Preparation of Adhesive Composition

An adhesive composition was prepared under anhydrous conditions using 1070 g of prepolymer of this Example 1 in a planetary mixer, and degassed for 20 minutes, to the prepolymer, 408 g of carbon black and 106 g of clay were added. The composition was mixed for 20 minutes under vacuum. Finally 7.2 g of dimorpholinodiethyl ether (DMDEE) 4 g of bismuth octoate (BiO) and 4.8 grams of m pyrol, 1-methyl-2-pyrrolidinone were added to the mixture. The mixture was mixed for another 20 minutes and packaged in tubes.

Example 3

A prepolymer was prepared using the procedure and ingredients of Example 1 except the following amounts were used; 1050 g of diol; 717.5 g of triol, 525 g of dispersion triol and 381.5 g of methylene diphenyl isocyanate, 0.17 g of catalyst and 791 g of plasticizer. The diol to triol and dispersion triol ratio was 0.85. an adhesive was prepared according to the process of Example 2 using 1070 g of prepolymer, 408 g of carbon black and 106 g of clay, 8 g of DMDEE, 4 g of bismuth octoate and 4.8 g of m-pyrol.

Example 4 – Comparative Example

A prepolymer was prepared using the components described in Example 1 in the following percentages by weight, diol, 21 percent, triol, 30.21 percent, dispersion triol 13.7 percent; MDI 12 percent, plasticizer 22.088 percent, and catalyst 0.002 percent. The composition also included 1 percent of diethyl malonate. The adhesive composition was compounded as Example 2.

Examples 5 to 9

In Examples 5 to 9 to ingredients described in Examples 1 and 2 were used to prepare prepolymers and adhesives. The amounts of the ingredients used in the prepolymers are listed in Table 1 along with properties of the prepolymers.

Table 1

Prepolymer Ingredient/Examples	5	6	7	8	9
Isocyanate	9	8.2	13	9	9
Diol	28	28	28	27	31
Triol	17	17	17	22	13
Dispersion triol	13	13	13	13	13
Plasticizer	32	32.8	28	28	33
Catalyst	5 drops	5 drops	5 drops	5 drops	5 drops
Stabilizer ¹	1	1	1	1	1
Total	100	100	100	100	100
Diol/triol ratio (wt)	0.93	0.93	0.93	0.77	1.19
Primary NCO Percent ²	0.983	0.65	2.206	0.764	0.935
Secondary NCO Percent ³	0.933	n/a	2.142	0.72	0.823
Viscosity (cps) ⁴	36240	220000	6080	127000	35280
(cm ² /s)	(362.6)	(2201)	(60.83)	(1271)	353.0
Spindle	s5	semi-gel/s ⁷	s5	s6	S5
Heat Aged NCO Percent ⁵	0.941		2.001	n/a	0.77
Heat Aged Viscosity ⁶	46400		6080	220000	45200
(cps)/(cm ² /s)	(464.2)		(60.83)		(452.2)
Spindle	5		5	Semi-gel/s ⁷	5
Percent Viscosity Growth	28		0		28

1. Diethyl Malonate

2. Viscosity shortly after preparation of the prepolymer at 25°C.

3. Viscosity 24 hours after prepolymer preparation.

5 4. Viscosity 24 hours after prepolymer preparation.

5. Heat aged NCO percentage is measured after 3 days of heating at 54°C.

6. Heat aged viscosity is measured after heating for 3 days at 54°C, viscosity is measured at 25°C.

7. The prepolymer had gelled to a point that viscosity could not be measured.

Cure Rate Testing

Each of the adhesives prepared were tested for cure rate according to the following test. A bead of adhesive 6.35 mm (width) x 6.35 mm (height) x 25.4 mm (length) size bead was placed on 25.4 mm x 101.6 mm piece of primed glass and a metal coupon and allowed to cure for 2 hours at 23°C, 50 percent humidity. Cure rate was determined by pulling the lap-shear samples by Instron using 2 inches per minute speed. Load and extension were recorded in pounds and inches respectively. The results are recorded in Table 2.

Table 2

Example	Lap Shear		Lap Shear		Diol/Triol
	Strength after 2		Extension after		
	hours psi	(KPa)	2 hours (in)	(cm)	
2	167	(1150)	.85	2.2	.93
3	157	(1082)	.83	2.1	.85
4	97	(668)	.36	.91	.48
9	125	(862)	.82	2.1	1.1*

*The tackfree time was too short 3 minutes.

The adhesives of Examples 5 and 7 to 9 were tested in the press flow test, and working time test described below and for cure rate and extension as described above. All tests were performed in triplicate and results are the average of the three actual tests. The press flow is the time it takes for 20g of adhesive to pass through a .203 in. (5.16 mm) orifice at 80 psi (552 kPa) pressure.

The tack free time test was performed according to ASTM D2377-84. The results are compiled in Table III.

Table 3

Examples		5	7	8	9
Press flow (sec.) ⁸		39	14	116	41
Tack Free		6	13	1	3
Time (min.) ⁹					
Cure Rate ¹⁰		Psi (kPa)	Psi (kPa)	Psi (kPa)	Psi (kPa)
1 hour	Run 1	72 (496)	16.8 (116)	98.8 (681)	72.4 (499)
	Run 2	71.6 (494)	18.8 (130)	117.2 (808.0)	69.6 (480)
	Run 3	60 (414)	17.6 (121)	104 (717)	63.2 (436)
	Avg	67.8 (467)	17.7 (122)	107 (738)	68.4 (472)
2 hours	Run 1	235.5 (1624)	64.1 (442)	182 (1255)	134.4 (927)
	Run 2	169.5 (1169)	66.2 (456)	225.7 (1556)	121.1 (835)
	Run 3	233.8 (1612)	74.5 (514)	187.2 (1291)	120.3 (829)
	Avg	212.9 (1468)	68.2 (470)	198.3 (1367)	125.3 (864)
Extension		in/cm	in/cm	in/cm	in/cm
1 hour	Run 1	0.703 (1.79)	0.280 (.711)	0.845 (2.15)	0.830 2.11
	Run 2	0.721 (1.83)	0.515 (1.31)	0.715 (1.82)	0.823 2.09
	Run 3	0.765 (1.94)	0.362 (.919)	0.863 (2.19)	0.811 2.06
	Avg	.730 (1.85)	.386 (.980)	.808 (2.05)	.821 (2.09)
2 hours	Run 1	0.908 (2.31)	0.55 (1.40)	0.765 (1.94)	0.866 (2.20)
	Run 2	0.851 (2.16)	0.359 (.911)	0.846(2.15)	0.794 (2.02)
	Run 3	0.784 (1.99)	0.694 (1.76)	0.753 (1.91)	0.814 (2.07)
	Avg	.847 (2.15)	.535 (1.36)	.788 (2.00)	.825 (2.10)

8. at 24°C.

9. At 25.7°C and 58 Percent Relative Humidity.

5 10. At 23°C and 50 Percent Relative Humidity.

WHAT IS CLAIMED IS:

1. A polyurethane prepolymer comprising the reaction product of:

A) one or more polyisocyanates;

5 B) a mixture of one or more diols and one or more triols;

C) a dispersion triol containing from 10 to 60 percent by weight based on the dispersion of organic polymer particles having a particle size of from 10 to 50 microns ;

10 wherein the prepolymer has a free isocyanate content of from 0.8 to 2.2 percent , the weight ratio of diol to triol and dispersion triol is from 0.8 to 1.2.

2. A prepolymer according to Claim 1 wherein the triol in the dispersion triol has a molecular weight of 4,000 to 8,000 and a hydroxyl number of from 30 to 70.

3. A prepolymer according to Claims 1 or 2 wherein the isocyanate content is from 0.9 to 1.1 percent by weight.

15 4 A polyurethane prepolymer according to any one of Claims 1 to 3 which comprises:

A) i. the reaction product of from 5 to 20 percent by weight of a polyisocyanate;

B) ii) from 20 to 40 percent by weight of a diol,

20 iii) from 15 to 35 percent by weight of a triol;

iv) from 10 to 30 percent by weight of a dispersion triol; and

B) from 1 to 40 percent by weight of a plasticizer.

5. A one-part adhesive composition comprising a polyurethane prepolymer according to any one of Claims 1 to 4 and a catalyst capable of catalyzing the reaction of isocyanate moieties with water.

6. A one-part adhesive according to Claim 5 comprising:

- 5 1) from 55 to 80 parts by weight of prepolymer;
 2) from 15 to 40 parts by weight of a reinforcing filler;
 3) from 1 to 20 parts by weight of clay;
 4) from 0.1 to 5.0 parts by weight of a catalyst
 5) from 5 to 45 parts by weight of plasticizer;

10 wherein the adhesive contains 100 parts.

7. An adhesive according to Claims 5 or 6 wherein the catalyst comprises a mixture of a dimorpholino diethyl ether or an alkyl substituted dimorpholino diethyl ether and a bismuth carboxylate.

8. A method of bonding two substrates together comprising contacting
15 the two substrates with an adhesive according to any one of Claims 5 to 7 disposed between the substrates and curing the adhesive composition.

9. The method of Claim 8 wherein one substrate is glass and the other is a coated surface.

10. The method of Claim 8 wherein the glass is window glass for an
20 automobile and the coated surface is the part of the automobile adapted to hold the window glass in place.