



(51) International Patent Classification:

C08G 18/48 (2006.01) *C08G 18/20* (2006.01)
C08G 18/50 (2006.01) *C08G 18/32* (2006.01)
C08G 18/76 (2006.01) *C09J 175/00* (2006.01)
C08G 18/10 (2006.01) *C07D 487/20* (2006.01)

(21) International Application Number:

PCT/US2017/063577

(22) International Filing Date:

29 November 2017 (29.11.2017)

(25) Filing Language:

English

(26) Publication Language:

English

(30) Priority Data:

62/428,242 30 November 2016 (30.11.2016) US

(71) Applicant: DOW GLOBAL TECHNOLOGIES LLC
[US/US]; 2040 Dow Center, Midland, MI 48674 (US).

(72) Inventors: DE VRIES, Timothy; 1776 Building, Midland, MI 48674 (US). JIALANELLA, Gary, L.; 1250 Harmon Road, Auburn Hill, MI 48326 (US). LUTZ, Andreas; Bachtobelstrasse 3, CH-8810 Horgen (CH). SCH-

MATLOCH, Stefan; Bachtobelstrasse 3, CH-8810 Horgen (CH).

(74) Agent: PACYNSKI, Katherine, M. et al.; The Dobrusin Law Firm, P.C., 29 W. Lawrence Street, Suite 210, Pontiac, MI 48342 (US).

(81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DJ, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, JO, JP, KE, KG, KH, KN, KP, KR, KW, KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, ST, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK,

(54) Title: ISOCYANATE-BLOCKED AMIDINES AS LATENT POLYURETHANE CATALYSTS

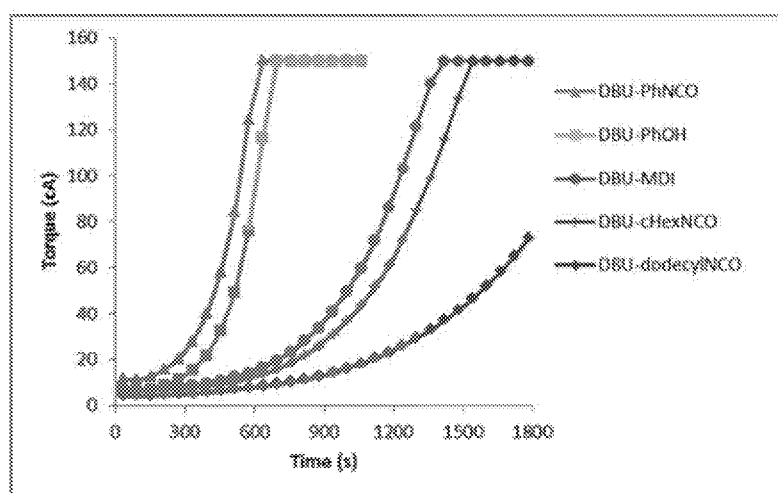


FIG. 1

(57) Abstract: Disclosed are compositions including an adduct that is an isocyanate-blocked amidine having a multi-cyclic structure having hydrocarbon based substituents. The composition is useful as a latent catalyst for a two-component polyurethane adhesive. Further disclosed are compositions useful as a two-component polyurethane adhesive, including a polyol component and an isocyanate component and one or more isocyanate-blocked amidines having multiple non-aromatic rings and having hydrocarbyl groups off the residue of the isocyanate nitrogen atoms contained in the cyclic ring that is formed. The one or more isocyanate-blocked amidines may be located in the polyol component or the isocyanate component. Further disclosed are methods of forming the adduct and methods of bonding structures together using the latent two-component polyurethane adhesives.



EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV,
MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM,
TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW,
KM, ML, MR, NE, SN, TD, TG).

Published:

— *with international search report (Art. 21(3))*

ISOCYANATE-BLOCKED AMIDINES AS LATENT POLYURETHANE CATALYSTS

FIELD

[001] Disclosed is an isocyanate-blocked amidine that is useful as a latent catalyst for forming two-part polyurethane adhesives. Further disclosed are methods of forming the isocyanate-blocked amidine and bonding structures together using the latent two-part polyurethane adhesives.

BACKGROUND

[002] Polyurethanes are a well-known type of adhesive. They contain precursor materials that cure in place to form an adhesive layer. Polyurethane adhesives come in one-part and two-part types. One-part types generally exhibit a moisture cure or a heat-activated cure. Two-part types consist of a resin component that includes one or more polyisocyanate compounds, and a curative component that includes one or more polyols. When the two components mixed, the polyisocyanates and polyols react to form a cured polyurethane adhesive. A polyurethane adhesive can be formulated to cure at room temperature or upon exposure to certain conditions, an example of which is an elevated temperature. As the adhesive cures, it can form a strong adhesive bond to many types of substrates.

[003] Two-part curable compositions are used in a variety of applications such as adhesives, coatings, foams and the like. Two-part compositions are used where rapid cure is required for the application, especially where the two parts are not shelf stable when in contact with one another. "Shelf stable" means that the composition does not cure in storage. It is desirable that the adhesive composition exhibits a suitable open time and cures rapidly. The "open time" of a two-part adhesive refers to the amount of time after the two components are mixed that the adhesive remains flowable and capable of bonding to a substrate. The "latency" of catalysts used in forming the two-part adhesive refers to the amount of time during which there is a lack of activity of a catalyst, which is therefore a property of a catalyst that provides the open time. Upon activation of the catalyst, the latency may be removed or the latency period may end.

[004] One way of obtaining both a long open time or latency and a fast cure is by formulating the adhesive to have a heat-activated cure. Such an adhesive cures slowly at ambient temperature, thereby allowing the adhesive to be applied and the substrates

positioned while the adhesive remains flowable. The resulting assembly is then heated to an elevated temperature at which rapid curing takes place.

[005] Previous work on improving latency in adhesive systems has focused on acid-base complexes with amine catalysts to block the catalytic site, with heat activation thought to release the amine catalyst. However, it is desired to improve the needed balance between inertness at room temperature and high activity after a short time at moderate elevated temperatures.

[006] Isocyanate complexes of amidines and guanidines have been described in literature for use as blocked isocyanates to mitigate exposure issues on handling these reagents (Chem. Rev. 2013, 113, p. 80-118) or as blocked catalysts for acrylate polymerization (Polym. Chem. 2014, 5, p. 6678-86). However, the stoichiometric use as described therein would generate a large amount of amine byproduct into the final product. In forming two-part polyurethane adhesives, a large amount of amine byproduct could cause an undesired or a premature reaction. Furthermore, the complexes formed in the literature are often solid or waxy, which is incompatible with the typical application and mixing equipment if used for the bulk of isocyanate formulation. Guanidine catalysts blocked by isocyanates have also been described in literature (Polym. Chem. 2013, 4, p. 904-7); however, the amidine-isocyanate complexes examined, by the author's own admission, were shown to be poor catalysts or behave as poor catalytic systems.

[007] Thus, what is needed is a composition that includes a latent catalyst, and a two-part adhesive formed when employing the latent catalyst, that provides improved latency of the system to increase open time for working with the adhesive, provides a snap-cure profile on thermal activation, where snap-cure refers to an engineered cure time with slow viscosity growth and then quick curing upon thermal activation and/or mixing of components. What is also needed is a composition that provides sufficient cure strength to allow for handling of bonded parts. What is also needed are methods for forming the catalyst that give improved latency and bonding methods using two-part adhesives that allow for reasonable time to contact and locate substrates to one another with the adhesive disposed between the substrates, while maintaining a snap-cure profile on thermal activation.

SUMMARY

[008] Disclosed is a composition comprising a polyol component, an isocyanate component, and an adduct comprising a residue of a cyclic amidine and an isocyanate to

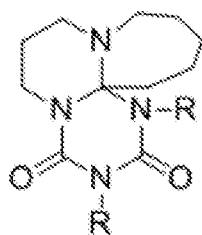
form one or more isocyanate-blocked amidines. The polyol component may include one or more polyols. The polyol component may include one or more aliphatic diol chain extenders. The polyol component may include one or more latent room temperature organometallic catalysts. The isocyanate component may include one or more polyisocyanate compounds. The composition may include one or more isocyanate-blocked amidines which may have multiple non-aromatic rings and may have hydrocarbyl groups off the residue of the isocyanate nitrogen atoms contained in a cyclic ring that is formed. The groups off the residue of the isocyanate nitrogen atoms may optionally include one or more isocyanate groups. The one or more isocyanate-blocked amidines may be located in the polyol component or the isocyanate component. The composition may be useful as a two-component polyurethane adhesive. The one or more isocyanate-blocked amidines may be present in an amount of about 0.01 weight percent or greater, about 0.1 weight percent or greater, or about 0.2 weight percent or greater based on the weight of the polyol component. The one or more isocyanate-blocked amidines may be present in an amount of about 5 weight percent or less, about 3 weight percent or less, or about 1 weight percent or less based on the weight of the polyol component. For example, the one or more isocyanate-blocked amidines may be present in an amount of about 0.2 weight percent to about 1 weight percent based on the weight of the polyol component. The composition as described herein may widen the open time of a two-part adhesive. The latency of the composition after contacting the polyol component and the isocyanate component may be about 5 minutes or greater, about 8 minutes or greater, or about 10 minutes or greater, measured by mixing the composition until the lap shear strength reaches 1 MPa. The latency of the composition after contacting the polyol component and the isocyanate component may be about 1 hour or less, about 30 minutes or less, or about 20 minutes or less, measured by mixing the composition until the lap shear strength reaches 1 MPa.

[0009] Also disclosed is an adduct that is an isocyanate-blocked amidine having a multi-cyclic structure having hydrocarbon based substituents. The adduct may comprise a residue of cyclic amidine and an isocyanate. The isocyanate may comprise an aryl isocyanate, polyisocyanate, or both. The composition may be useful as a latent catalyst for a two-component polyurethane adhesive.

[0010] Disclosed is a method of forming the adduct or the one or more isocyanate-blocked amidines, comprising adding a multi-cyclic amidine to a solvent; and adding an isocyanate to the multi-cyclic amidine and solvent, wherein the method forms an adduct

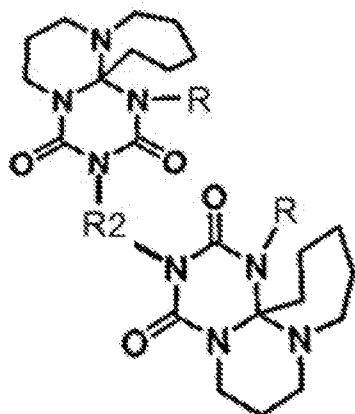
having multiple non-aromatic rings and having hydrocarbyl groups off a residue of isocyanate nitrogen atoms contained in a cyclic ring that is formed. The adduct may be useful as a latent catalyst for a two-component polyurethane adhesive. The adduct may be an isocyanate-blocked amidine comprising a residue of a cyclic amidine and an isocyanate. The isocyanate may be a cyclic isocyanate. The solvent may be a polar aprotic solvent.

[0011] The amidine of the one or more isocyanate-blocked amidines of the compositions and methods described herein may correspond to the formula $C_nH_{2(n-1)}N_2$, where n is an integer. The integer n may be about 7 or greater. The integer n may be about 9 or less. The hydrocarbyl groups off the residue of the isocyanate nitrogen atoms, separately in each occurrence, may be a C_2 to C_{12} alkyl, a C_2 to C_{12} cycloalkyl, a C_2 to C_{12} aryl, or a C_2 to C_{12} alkyl substituted aryl. The groups off the residue of the isocyanate nitrogen atoms, separately in each occurrence, may include one or more or two or more isocyanates. The groups off the residue of the isocyanate nitrogen atoms, separately in each occurrence, may be formed from bisisocyanates, such as methylene diphenyl diisocyanate (MDI) or hexamethylene diisocyanate (HMDI). The groups off the residue of the isocyanate nitrogen atom, separately in each occurrence may be formed from or include multi-functional materials, including difunctional materials. The one or more isocyanate-blocked amidines may be prepared in a mole ratio of about 1:1 to about 1:3 amidine to isocyanate. The amidine of the one or more isocyanate-blocked amidines may have a multi-cyclic structure including 1,8-diazabicycloundec-7-ene (DBU) or 1,5-diazabicyclo[4.3.0]non-5-ene (DBN). The one or more isocyanate-blocked amidines may correspond to the formula:

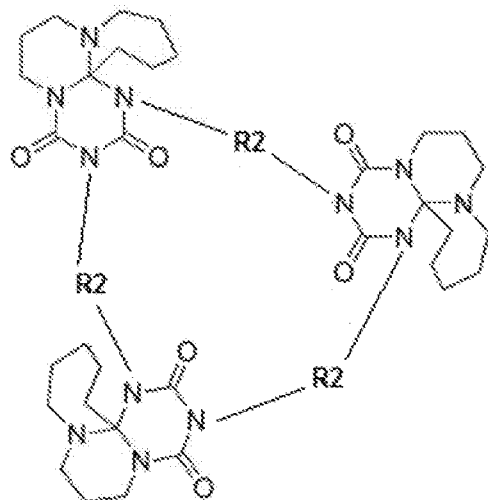


where R , separately in each occurrence, may be aromatic or aliphatic. The isocyanate of the one or more isocyanate-blocked amidines may comprise one or more of the residue of: methylene diphenyl diisocyanate (MDI); hexamethylene diisocyanate (HMDI); butylisocyanate; dodecylisocyanate; cyclohexylisocyanate; and isophorone diisocyanate.

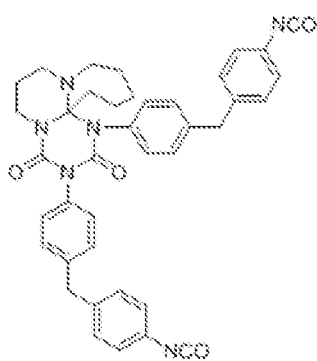
R, separately in each occurrence, may include a pendant isocyanate group. The pendant isocyanate group may form a network with one or more other isocyanate-blocked amidines and acts as a bridge or linking group R2 between two amidines. The linked amidines may correspond to the formula:



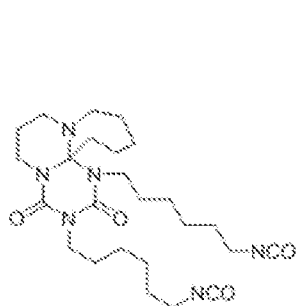
where R, R2, or both, separately in each occurrence, may be aromatic or aliphatic. The isocyanate-blocked amidines may be linked in a ring-like structure that may correspond to the formula:



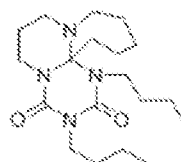
where R2, separately in each occurrence, may be aromatic or aliphatic. The one or more isocyanate-blocked amidines may be selected from:



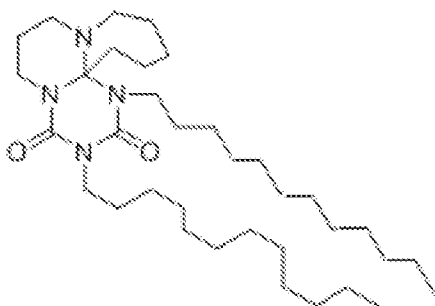
DBU-MDI



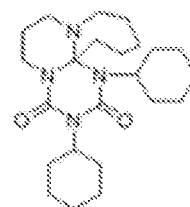
DBU-HMDI



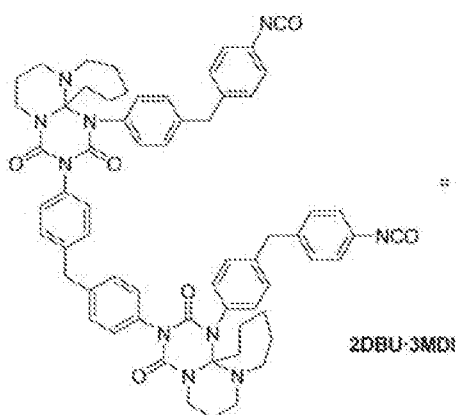
DBU-Butylisocyanate



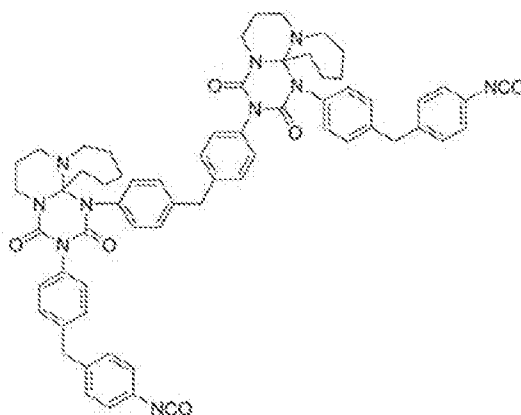
DBU-Dodecylisocyanate

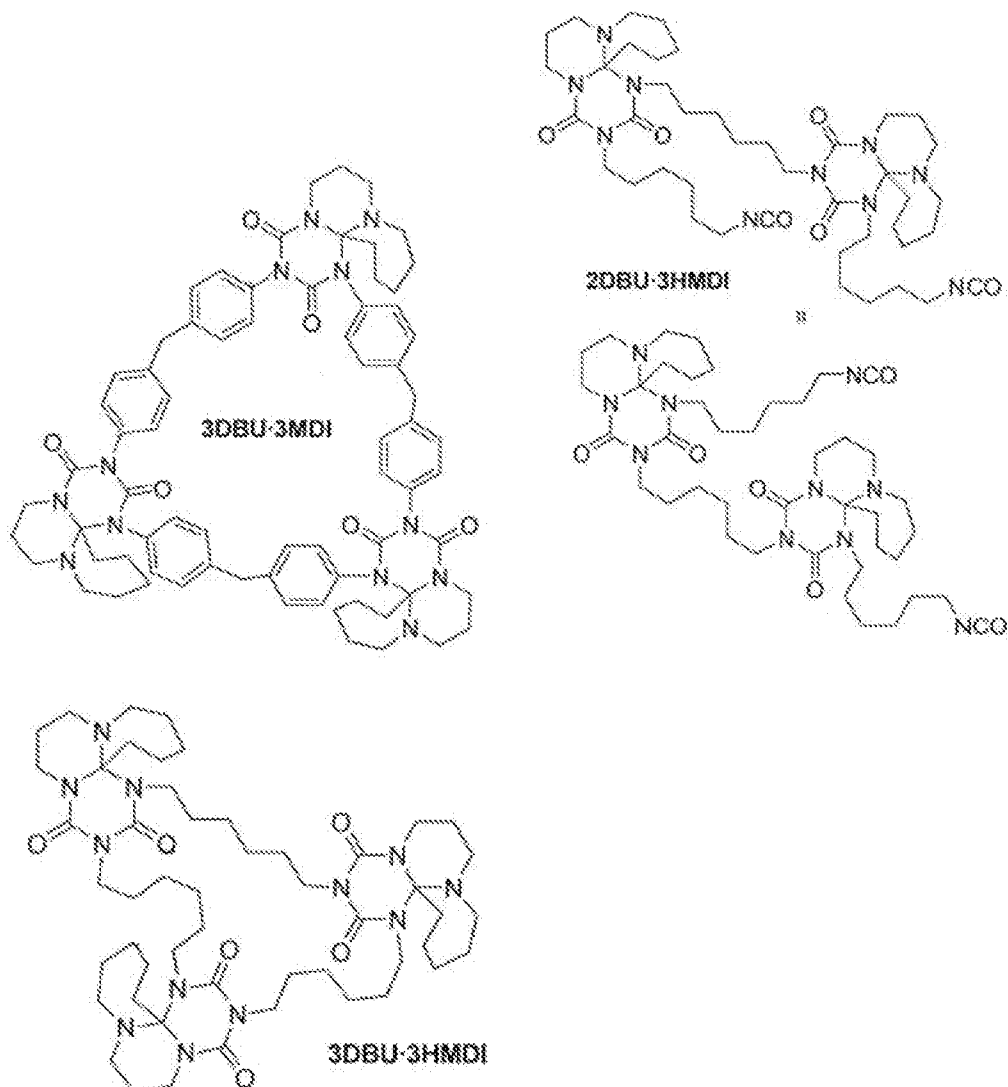


DBU-Cyclohexylisocyanate



2DBU-3MDI





[0012] Disclosed is a method of bonding two substrates, comprising forming a two-component polyurethane adhesive by contacting a polyol component and an isocyanate component and employing an adduct as disclosed herein (or in accordance with the method of forming as disclosed herein). The adduct may be located in the polyol component or the isocyanate component. The method may include contacting a polyol component and an isocyanate component, where the adduct is located in either the polyol component or the isocyanate component. The method may include applying the adhesive to a first substrate and contacting a second substrate with the first substrate, with the two-component polyurethane adhesive disposed between the first substrate and the second substrate. The latency of the two-component polyurethane adhesive after contacting the

polyol component and the isocyanate component may be about 5 minutes or greater, about 8 minutes or greater, or about 10 minutes or greater, measured by mixing the composition until the lap shear strength reaches 1 MPa. The latency of the composition after contacting the polyol component and the isocyanate component may be about 1 hour or less, about 30 minutes or less, or about 20 minutes or less, measured by mixing the composition until the lap shear strength reaches 1 MPa. The method may further comprise a step of heating the first substrate and the second substrate at a temperature for a time to fully cure the mixture to bond the two substrates together. One of the substrates may comprise fiber reinforced plastics. One of the substrates may comprise a different material such as metal, glass, plastics, or thermoset resins. The second substrate may not contain fibers as reinforcing structures.

[0013] The adhesive composition adheres strongly to many substrates. The adhesives bond well to fiber reinforced plastic substrates. The adhesive composition exhibits good latency. The adhesive composition exhibits relatively long open times. The adhesive composition exhibits rapid strength build up.

BRIEF DESCRIPTION OF THE DRAWINGS

[0014] FIG. 1 is a graph illustrating the effect of an isocyanate blocking group on latency of a catalyst in accordance with the present teachings.

DETAILED DESCRIPTION

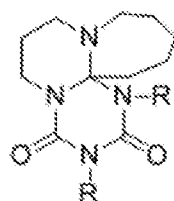
[0015] The explanations and illustrations presented herein are intended to acquaint others skilled in the art with the invention, its principles, and its practical application. Accordingly, the specific embodiments of the present invention as set forth are not intended as being exhaustive or limiting of the invention. The scope of the invention should, therefore, be determined not with reference to the above description, but should instead be determined with reference to the appended claims, along with the full scope of equivalents to which such claims are entitled. The disclosures of all articles and references, including patent applications and publications, are incorporated by reference for all purposes. Other combinations are also possible as will be gleaned from the following claims, which are also hereby incorporated by reference into this written description.

[0016] Disclosed is a composition comprising a) a polyol component and an isocyanate component, wherein: i) the polyol component includes; 1) one or more polyols; 2) one or more aliphatic diol chain extenders; and 3) one or more latent room temperature

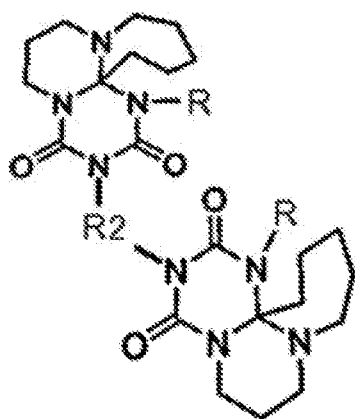
organometallic catalysts; ii) the isocyanate component includes one or more polyisocyanate compounds; and b) one or more isocyanate-blocked amidines having multiple non-aromatic rings and having hydrocarbyl groups off the residue of the isocyanate nitrogen atoms contained in the cyclic ring that is formed and optionally one or more isocyanate groups; wherein the one or more isocyanate-blocked amidines are located in the polyol component or the isocyanate component; and wherein the composition is useful as a two-component polyurethane adhesive. Also disclosed is a composition comprising an adduct that is an isocyanate-blocked amidine having a multi-cyclic structure having hydrocarbon-based substituents, wherein the adduct comprises a residue of a cyclic amidine and an isocyanate, wherein the isocyanate comprises an aryl isocyanate, a polyisocyanate, or both, and wherein the composition is useful as a latent catalyst for a two-component polyurethane adhesive. Also disclosed is a method comprising: a) adding a multi-cyclic amidine to a solvent; b) adding an isocyanate to the multi-cyclic amidine and solvent, wherein the method forms an adduct having multiple non-aromatic rings and having hydrocarbyl groups off a residue of isocyanate nitrogen atoms contained in a cyclic ring that is formed, and wherein the adduct is useful as a latent catalyst for a two-component polyurethane adhesive.

[0017] The compositions disclosed may further comprise any one or more of the features described in this specification in any combination, including the preferences and examples listed in this specification, and includes the following features: the adduct is prepared in a mole ratio of about 1:1 to about 1:3 amidine having a multi-cyclic structure to isocyanate; the amidine has a multi-cyclic structure that includes 1,8-diazabicycloundec-7-ene (DBU) or 1,5-diazabicyclo[4.3.0]non-5-ene (DBN); the isocyanate of the adduct is a cyclic isocyanate; the solvent is a polar aprotic solvent; the one or more isocyanate-blocked amidines are located in the isocyanate component; the one or more isocyanate-blocked amidines are present in an amount of about 0.01 to about 5 weight percent based on the weight of the polyol component; latency of the composition after contacting the polyol component and the isocyanate component is about 5 minutes or greater, about 8 minutes or greater, or about 10 minutes or greater; latency of the composition after contacting the polyol component is about 1 hour or less, about 30 minutes or less, or about 20 minutes or less; the amidine of the one or more isocyanate-blocked amidines corresponds to the formula $C_nH_{2(n-1)}N_2$, where n is an integer; n is an integer of about 7 or greater or about 9 or less; the hydrocarbyl groups off the residue of the isocyanate nitrogen atoms, separately in each occurrence, are a C_2 to C_{12} alkyl, a C_2

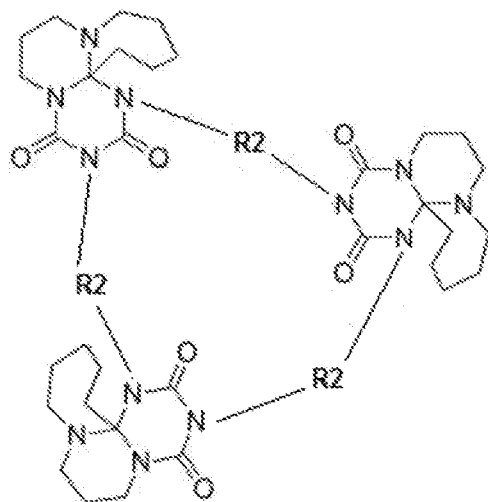
to C₁₂ cycloalkyl, a C₂ to C₁₂ aryl, or a C₂ to C₁₂ alkyl substituted aryl; the one or more isocyanate-blocked amidines correspond to the formula:



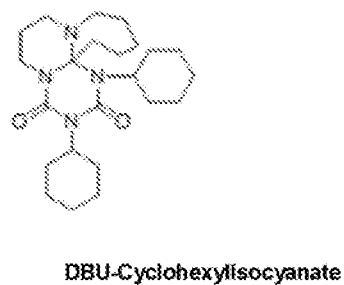
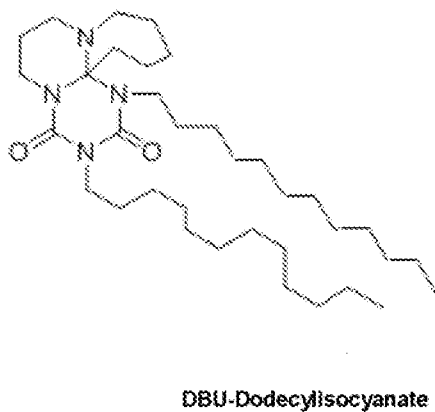
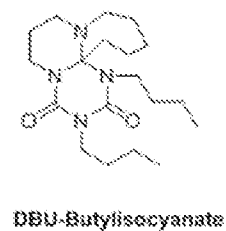
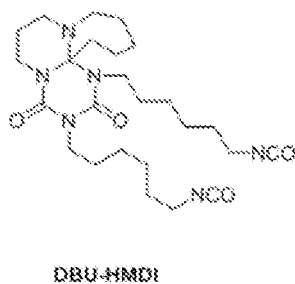
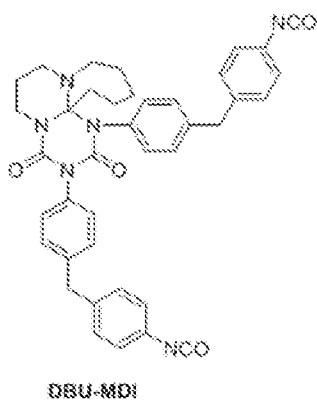
wherein R, separately in each occurrence, is aromatic or aliphatic; the isocyanate of the one or more isocyanate-blocked amidines comprises one or more of: methylene diphenyl diisocyanate (MDI), hexamethylene diisocyanate (HMDI), butylisocyanate, dodecylisocyanate, and cyclohexylisocyanate; R, separately in each occurrence, includes a pendant isocyanate group; the pendant isocyanate group forms a network with one or more other isocyanate-blocked amidines and acts as a bridge or linking group R₂ between two isocyanate-blocked amidines; the linked amidines correspond to the formula:

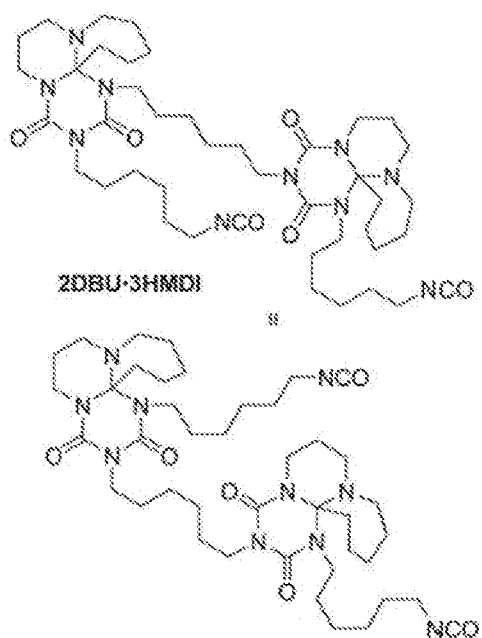
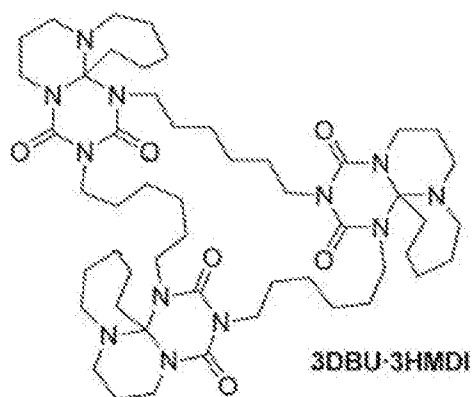
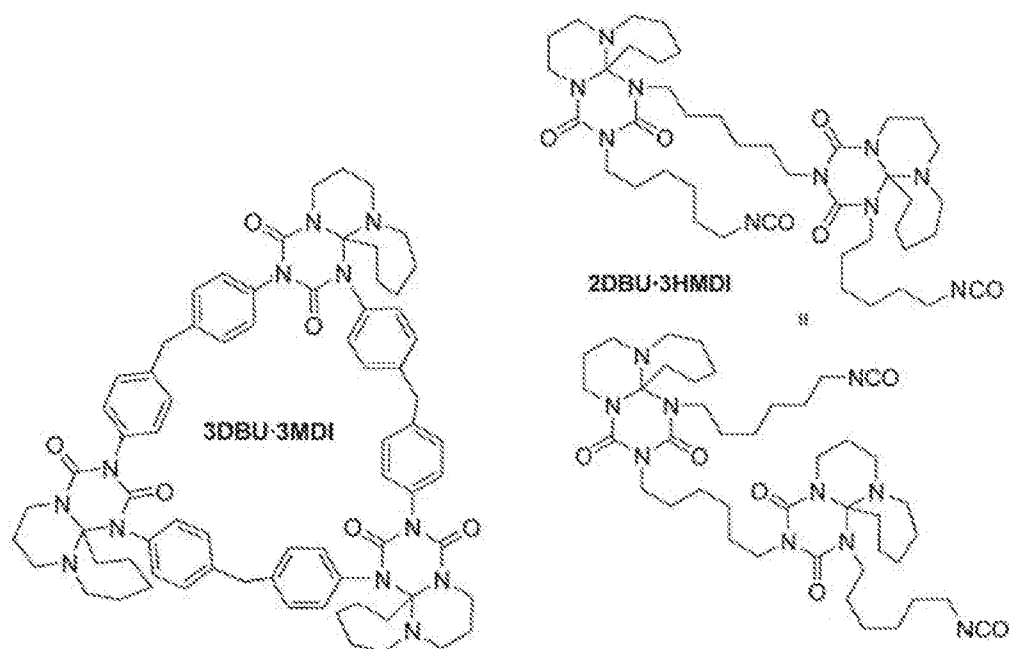
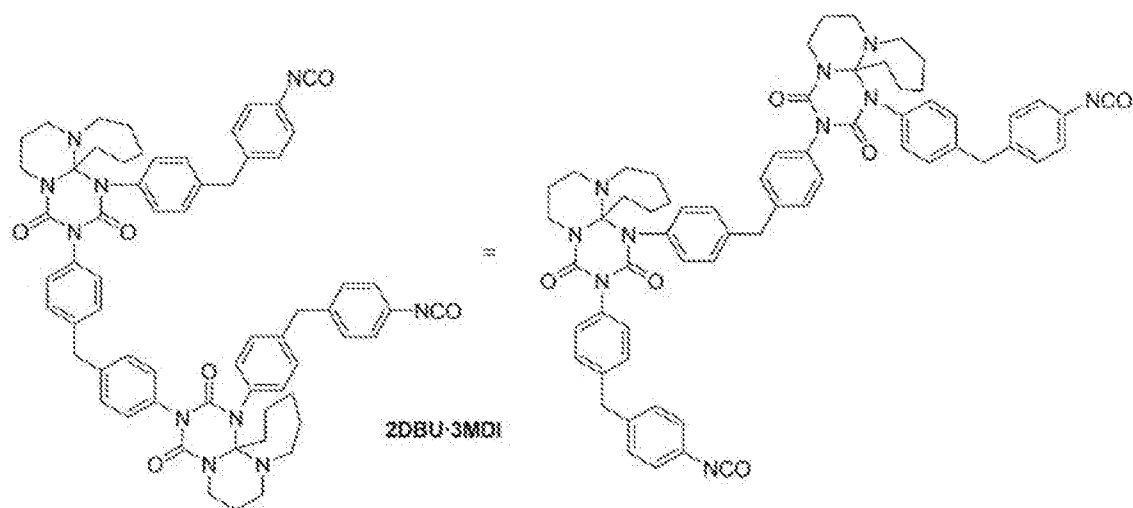


where R, R₂, or both, separately in each occurrence, is aromatic or aliphatic; the isocyanate-blocked amidines are linked in a ring-like structure that corresponds to the formula:



where R2, separately in each occurrence, is aromatic or aliphatic; or the one or more isocyanate-blocked amidines are selected from:





[0018] The methods disclosed may further comprise any one or more of the features described in this specification in any combination, including the preferences and examples listed in this specification, and includes the following features: the method further includes forming a two-component polyurethane adhesive by contacting a polyol component and an isocyanate component and employing the adduct as disclosed herein or as formed in accordance with the methods disclosed herein, where the adduct is located in the polyol component or the isocyanate component; applying the adhesive to a first substrate; contacting a second substrate with the first substrate, with the two component polyurethane adhesive disposed between the first substrate and the second substrate; the latency of the two-component polyurethane adhesive after contacting the polyol component and the isocyanate component being about 5 minutes or greater, about 8 minutes or greater, or about 10 minutes or greater, measured by mixing the composition until the lap shear strength reaches 1 MPa; the latency of the composition after contacting the polyol component and the isocyanate component being about 1 hour or less, about 30 minutes or less, or about 20 minutes or less, measured by mixing the composition until the lap shear strength reaches 1 MPa; locating the adduct in the isocyanate component; heating the first substrate and the second substrate at a temperature for a time to fully cure the mixture to bond the two substrates together; and at least one of the substrates is glass, a vehicle frame, a fiber-reinforced substrate, or a combination thereof.

[0019] 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 the theoretical functionality, generally this 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 this context 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 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) may exhibit excellent results during accelerated aging. This may mean that after a set of substrates bonded with the adhesive is exposed to heat aging, the failure mode in Quick Knife adhesion or Lap Shear testing is cohesive, meaning the adhesive breaks before the bond of the adhesive to the substrate breaks. The adhesive may exhibit elongation when fully cured. Elongation may be about 50% or greater, about 60% or greater; or about 100% or greater. Elongation may be about 200%

or less, about 180% or less, or about 160% or less. The adhesive may exhibit a high modulus of elasticity when tested at 1 mm thickness and 6 mm in length. The modulus of elasticity may be about 2 MPa or more, about 10 MPa or more, or about 20 MPa or more. The modulus may be about 300 MPa or less, about 150 MPa or less, or about 60 MPa or less. Isocyanate content means the weight percent of isocyanate groups in the designated component, such as prepolymer. The isocyanate content can be measured by analytical techniques known to one skilled in the art, for example by potentiometric titration with an active hydrogen containing compound, such as dibutyl amine. Typically, the residual content of a component can be calculated from the ingredients utilized to prepare the component or composition. Alternatively, it can be determined utilizing known analytical techniques. Residue with respect to an ingredient used to prepare the adduct as disclosed herein means that a portion of the ingredient, such as a cyclic amidine and/or an isocyanate (which may be a cyclic isocyanate), remains in the compound after inclusion as a result of the methods disclosed herein. Heteroatom means nitrogen, oxygen, sulfur and phosphorus, more preferred heteroatoms include nitrogen and oxygen. Hydrocarbyl as used herein refers to a group containing one or more carbon atom backbones and hydrogen atoms, which may optionally contain one or more heteroatoms. Where the hydrocarbyl group contains heteroatoms, the heteroatoms may form one or more functional groups well known to one skilled in the art. Hydrocarbyl groups may contain cycloaliphatic, aliphatic, aromatic or any combination of such segments. The aliphatic segments can be straight or branched. The aliphatic and cycloaliphatic segments may include one or more double and/or triple bonds. Included in hydrocarbyl groups are alkyl, alkenyl, alkynyl, aryl, cycloalkyl, cycloalkenyl, alkaryl and aralkyl groups. Cycloaliphatic groups may contain both cyclic portions and noncyclic portions. Hydrocarbylene means a hydrocarbyl group or any of the described subsets having more than one valence, such as alkylene, alkenylene, alkynylene, arylene, cycloalkylene, cycloalkenylene, alkarylene and aralkylene. As used herein percent by weight or parts by weight refer to, or are based on, the weight or the curable compositions unless otherwise specified. Based on the weight of or total weight the composition means the weight of both the polyol and the isocyanate component unless stated otherwise.

[0020] The term isocyanate-reactive compound as used herein includes any organic compound having nominally at least two isocyanate-reactive moieties. An isocyanate reactive moiety can be an active hydrogen containing moiety, which refers to a moiety 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). Illustrative of such isocyanate reactive moieties, such as active hydrogen moieties, are —COOH , —OH , —NH_2 , —NH— , —CONH_2 , —SH , and —CONH— . Active hydrogen containing compounds, isocyanate reactive moiety containing compounds, may include polyols, polyamines, polymercaptans and polyacids. The isocyanate reactive compound may be a polyol, or may be a polyether polyol.

[0021] The present teachings contemplate a composition comprising an adduct that is useful as a latent catalyst for a two-component polyurethane adhesive. The adduct may be an isocyanate-blocked amidine. Any isocyanate-blocked amidine which provides good open time, which provides acceptable lap shear strengths, which provides improved latency, which maintains an acceptable level of reactivity after partial curing and storage, or any combination thereof, may be utilized. The isocyanate-blocked amidine catalyst may be incorporated into either the polyol component or the isocyanate or polyisocyanate component of the two-component adhesive. The isocyanate-blocked amidine catalyst may be present in an amount sufficient to provide good open time, improved latency, acceptable initial lap shear strengths, and which maintains an acceptable level of reactivity after partial curing and storage. The isocyanate-blocked amidine catalyst may be added to the polyol component and may be present in an amount of about 0.01 percent by weight or greater, about 0.25 percent by weight or greater, or about 0.50 percent by weight or greater based on the weight of the polyol component. The isocyanate-blocked amidine catalyst may be present in an amount of about 2.0 percent by weight or less, about 1.5 percent by weight or less, or about 1.0 percent by weight or less based on the weight of the polyol component. The isocyanate-blocked amidine catalyst may be added to the isocyanate or polyisocyanate component and may be present in an amount of about 0.01 percent by weight or greater, about 0.25 percent by weight or greater, or about 0.50 percent by weight or greater based on the weight of the isocyanate component. The isocyanate-blocked amidine catalyst may be present in an amount of about 2.0 percent by weight or less, about 1.5 percent by weight or less, or about 1.0 percent by weight or less based on the weight of the isocyanate component.

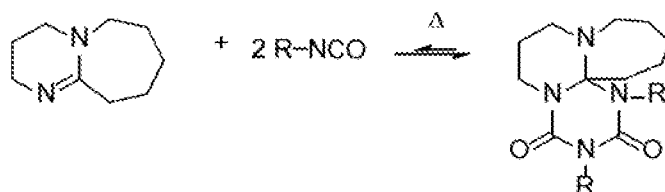
[0022] The adduct may include a residue of an amidine and an isocyanate. Exemplary amidines may have a multi-cyclic structure having hydrocarbon based substituents. The amidine may be any amidine suitable for use as a catalyst in polyurethane production, for promoting a reaction between active hydrogen groups. For example, the reaction may be

between polyol components and isocyanate components. The catalyst may comprise any compound containing a non-aromatic polycyclic structure containing an amidine group or a cycloaliphatic compound containing two or more rings having an amidine structure incorporated into the cyclic rings. The cyclic structure may contain two or more cycloaliphatic rings. The cyclic structure may include 2 or 3 cycloaliphatic rings. The cyclic structure may include two cyclic aliphatic rings. Exemplary amidines correspond to the generic formula $C_nH_{2(n-1)}N_2$, where n is an integer. For example, n may be equal to 7 or 9. Exemplary cyclic amidine catalysts include 1,8-diazabicycloundec-7-ene (DBU), 1,5-diazabicyclo[4.3.0]non-5-ene (DBN), and the like.

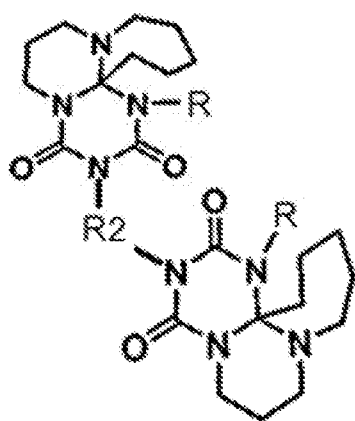
[0023] The amidine may be blocked by a blocking agent so that premature reaction or undesired reactions are reduced or prevented. The blocking agent may be a compound that is released in the presence of heat. The blocking agent may be a compound that does not introduce corrosive byproducts when deblocked. The blocking agent may be an isocyanate. The isocyanate may be a monofunctional isocyanate. The isocyanate may be a polyfunctional isocyanate. The release of the isocyanate into the system after deblocking may be advantageous over a more corrosive blocking agent, as an isocyanate is already present in the polyurethane adhesive. The isocyanate released into the system may react with the adhesive components.

[0024] The adduct may be formed by adding the multi-cyclic amidine to a solvent. The solvent may be an organic solvent. The solvent may be a polar solvent, an aprotic solvent, or both. The solvent used may depend upon the blocking agent used. The blocking agent, which may be an isocyanate, such as a monofunctional isocyanate or a polyfunctional isocyanate, may then be added to the multi-cyclic amidine and solvent. The reaction that occurs may form an adduct having multiple non-aromatic rings. The adduct may have hydrocarbyl groups off of a residue of the isocyanate nitrogen atoms contained in the cyclic ring that is formed. The reaction that occurs may form an adduct that may include the residue of two or more multi-cyclic amidines that are bridged by a hydrocarbylene group off of a residue of the isocyanate nitrogen atoms contained in the cyclic rings that are formed. The adduct may include the residue of the monofunctional or polyfunctional isocyanate. The reaction to form the adduct (e.g., of the cyclic amidine and the isocyanate) may proceed immediately at room temperature. The mole ratio of isocyanate to amidine may be any ratio that is capable of reacting to form the adduct but that would release only a catalytic amount of amine upon deblocking of the isocyanate-blocked amidine. The mole ratio of amidine to isocyanate may be in an amount that would not generate a large

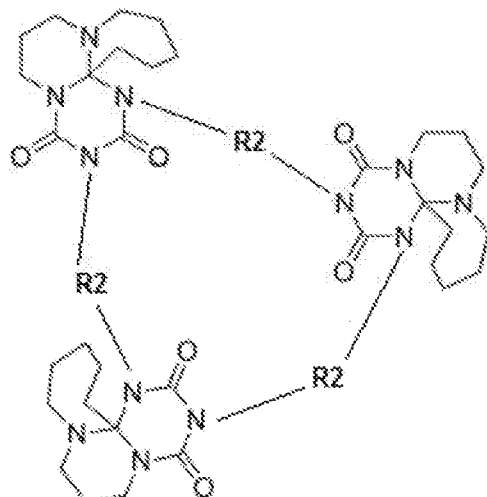
amount of amine byproduct upon deblocking of the isocyanate-blocked amidine. The adduct may be formed by introducing the amidine to isocyanate in a mole ratio of about 1:1000 or less, or about 1:500 or less. The adduct may be formed by introducing the amidine to isocyanate in a mole ratio of about 1:1, about 1:2, or about 1:3 or greater. For example, the adduct may be formed by introducing the amidine to isocyanate in a mole ratio up to about 1:1000. The reaction scheme may be illustrated as follows:



The adduct (e.g., an isocyanate-blocked amidine) may be formed at room temperature. Upon application of heat, the adduct may become deblocked, so the isocyanate is released from the amidine. For example, the adduct may be heated to a temperature of about 70°C or greater, about 80°C or greater, or about 90°C for initiating deblocking. The adduct may be heated to a temperature of about 130°C or less, about 120°C or less, or about 110°C to initiate deblocking. The heating may be performed using infrared heating. The amidine may then serve as a catalyst for forming a two-component polyurethane adhesive. The R group, separately in each occurrence, may include a pendant isocyanate group. The pendant isocyanate group may react with another amidine to form a network with one or more other amidines. The residue of the pendant isocyanate group and the additional amidine acts as a bridge or linking group between two amidines. The residue of the bridging isocyanate group and two amidines may be a hydrocarbylene, or a divalent radical formed by removing two hydrogen atoms from a hydrocarbon. The linked isocyanate-blocked amidines may correspond to the formula:

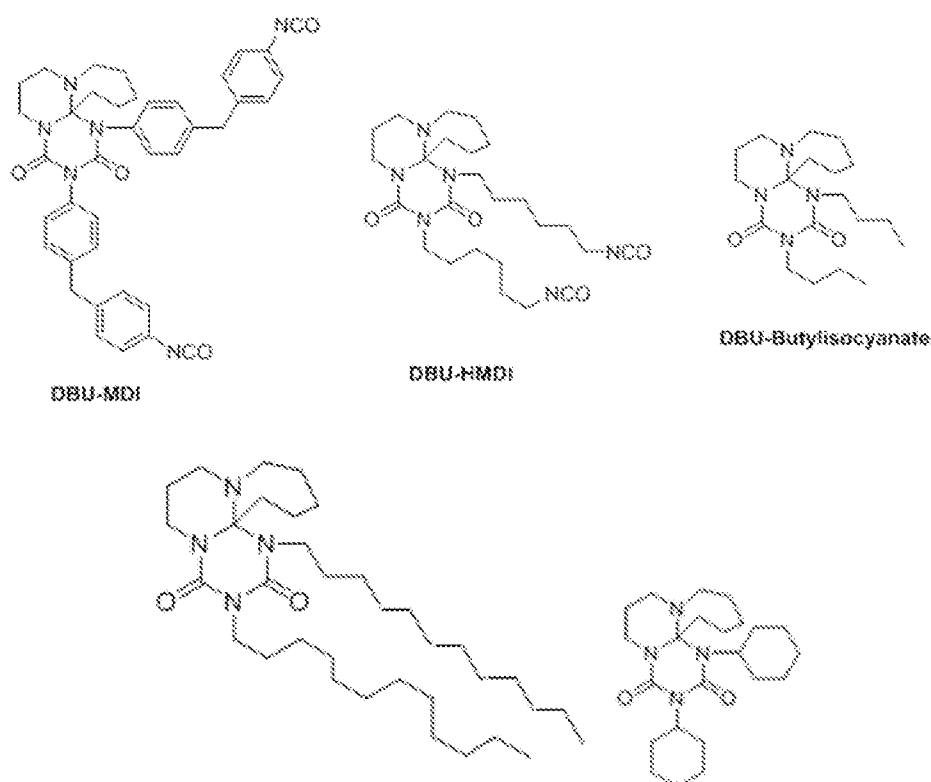


The isocyanate-blocked amidines may be linked in a ring-like structure that may correspond to the formula:



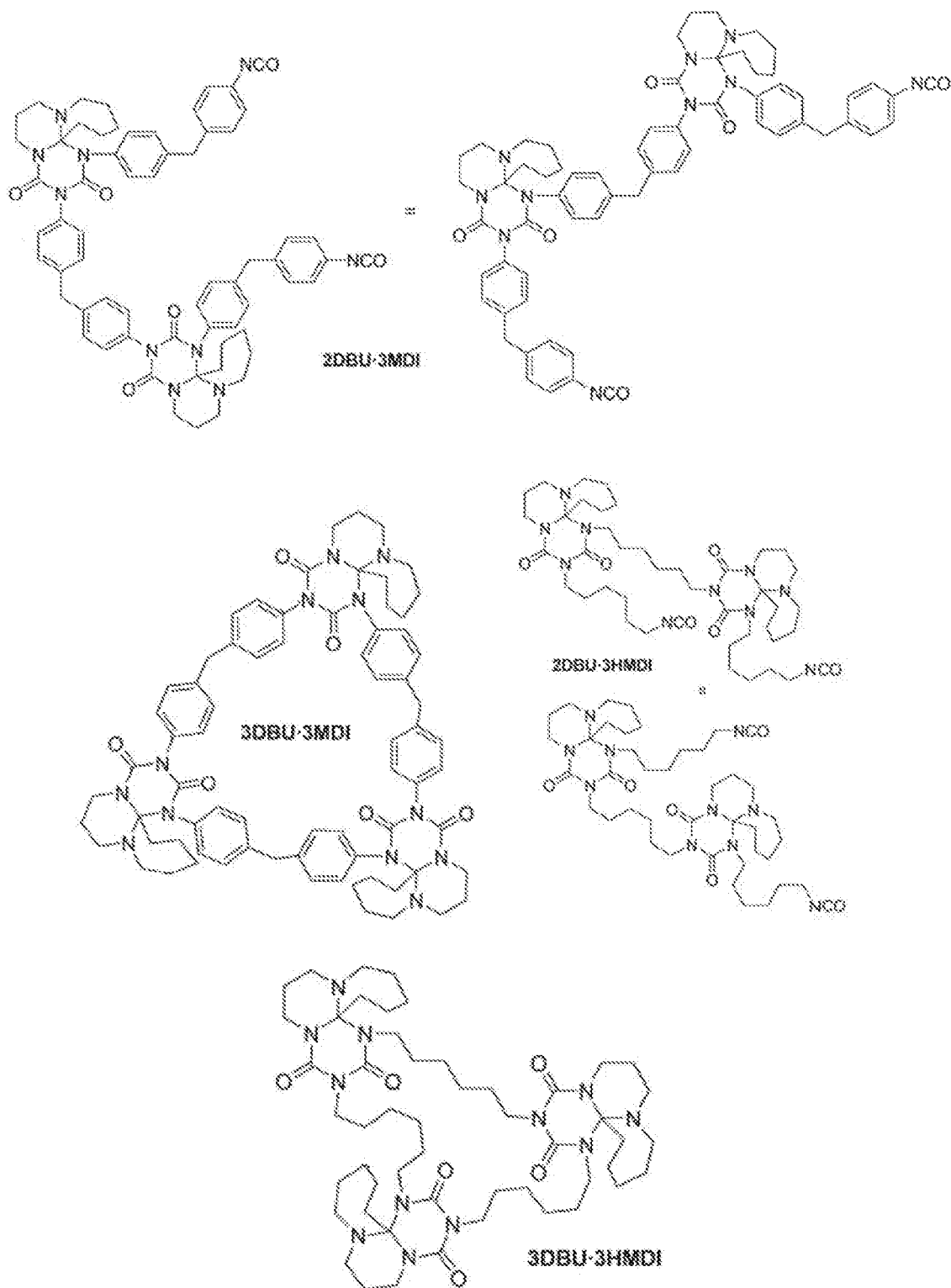
[0025] The R group of the isocyanate of any of the formulas may be, separately in each occurrence, aromatic or aliphatic. The R group may be cycloaliphatic. The R group off the residue of the isocyanate nitrogen atoms of the isocyanate may contain one or more isocyanate groups. The R group may be hydrocarbon-based. The hydrocarbon base may be a C₂ hydrocarbon or greater, a C₃ hydrocarbon or greater, or a C₄ hydrocarbon or greater. The hydrocarbon base may be a C₁₂ hydrocarbon or less, a C₁₀ hydrocarbon or less, or a C₈ hydrocarbon or less. The R group may be an aryl group or an isocyanato aryl group. The R group may be a polypropylene-bridged polyaryl group. The R group may be a C₂ to C₁₂ alkyl, a C₂ to C₁₂ cycloalkyl, a C₂ to C₁₂ aryl, or a C₂ to C₁₂ alkyl substituted aryl. Included in the aryl substituted alkyl are polyaryl structures having

alkylene groups disposed between the aryl groups. Exemplary alkyl substituted aryls include phenyl and alkylene phenyl structures. The isocyanate may be a cyclic isocyanate. Exemplary isocyanates include, but are not limited to, phenylisocyanate, butylisocyanate, cyclohexylisocyanate, benzylisocyanate, dodecylisocyanate, 4,4'-methylenebis(phenylisocyanate), hexamethylenediisocyanate, and isophorone diisocyanate. The R2 group off the residue of the isocyanate nitrogen atoms of the isocyanate bridging two amidines may be a hydrocarbylene. The hydrocarbon base of the hydrocarbylene may be a C₂ hydrocarbon or greater, a C₃ hydrocarbon or greater, or a C₄ hydrocarbon or greater. The hydrocarbon base of the hydrocarbylene may be a C₁₂ hydrocarbon or less, a C₁₀ hydrocarbon or less, or a C₈ hydrocarbon or less. The hydrocarbylene may include one or more ring structures, such as phenyl and alkylene phenyl structures. Therefore, exemplary adducts include the following:

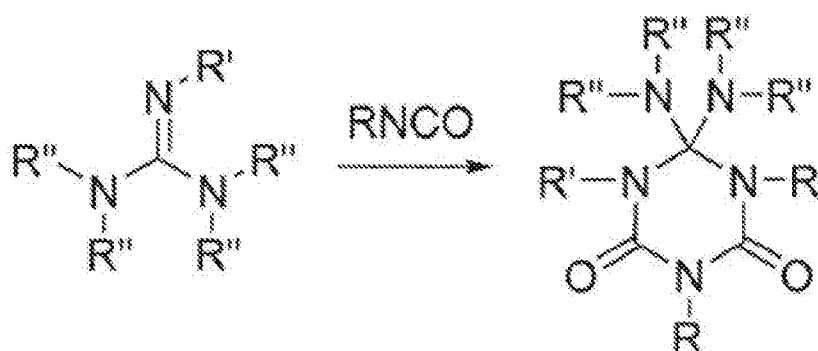


DBU-Dodecylisocyanate

DBU-Cyclohexylisocyanate

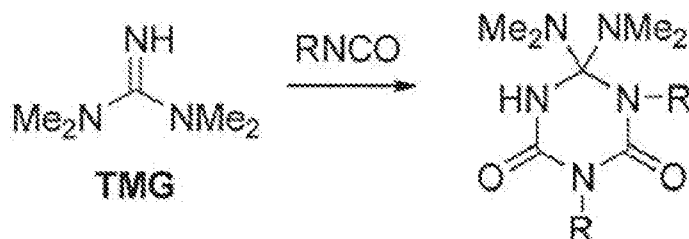


[0026] It is contemplated that the adduct may include a guanidine instead of or in addition to a cyclic amidine. It is contemplated that a mixture of guanidines and amidines may be provided in any ratio that provides the desired functions. The adduct may be formed by adding the guanidine to a solvent. The solvent may be an organic solvent. The solvent may be a polar solvent, an aprotic solvent, or both. The solvent used may depend upon the blocking agent used. The blocking agent, which may be an isocyanate, may then be added to the guanidine and solvent. The reaction that occurs may form an adduct having one or more non-aromatic rings. The adduct may have hydrocarbyl groups off of a residue of the isocyanate nitrogen atoms contained in the cyclic ring that is formed. The groups off of the residue of the isocyanate nitrogen atoms may be any of the groups discussed with respect to the adduct formed between a cyclic amidine and isocyanate. Therefore, any of the R groups as described therein are also applicable with respect to an adduct formed between a guanidine and one or more isocyanates. The reaction to form the adduct (e.g., of the guanidine and the isocyanate) may proceed immediately at room temperature. The mole ratio of guanidine to isocyanate may be any ratio that is capable of reacting to form the adduct but that would release only a catalytic amount of guanidine upon deblocking of the isocyanate-blocked guanidine. The mole ratio of guanidine to isocyanate may be in an amount that would not generate a large amount of guanidine byproduct upon deblocking of the isocyanate-blocked guanidine. The adduct may be formed by introducing the guanidine to isocyanate in a mole ratio of about 1:1000 or less, or about 1:500 or less. The adduct may be formed by introducing the guanidine to isocyanate in a mole ratio of about 1:1, about 1:2, or about 1:3. The reaction scheme may be illustrated as follows:



where R, R', and R'' may be, separately in each occurrence, aromatic or aliphatic. The R, R', and R'' groups may include hydrocarbonyl groups. R, for example, may be an ethyl group, methyl group, phenyl group, or a CH₂Ph group. R', for example, may be an ethyl group, methyl group, phenyl group, or a CH₂Ph group. R'' may be a methyl group.

[0027] In another example, a catalyst having an imine base such as 2-tert-butyl-1,1,3,3-tetramethylguanidine is contemplated. The reaction scheme may be illustrated as follows:



where R, separately in each occurrence, is aromatic or aliphatic. R may be any of the groups discussed with respect to the isocyanate-blocked amidine.

[0028] Two-component polyurethane adhesives may include a polyol component and an isocyanate component. The polyol component may include one or more polyols (e.g., polyether polyols). The polyol component may include one or more aliphatic diol chain extenders. The polyol component may include one or more latent room temperature organometallic catalysts.

[0029] Ingredient a) of the polyol component is one or more polyether polyols. Each such polyether polyol may have a hydroxyl equivalent weight of 400 to 2000. The hydroxyl equivalent weight of each polyol may be at least 500, at least 800 or at least 1000, and may be up to 1800, up to 1500, or up to 1200.

[0030] Each such polyether polyol may have a nominal hydroxyl functionality of 2 to 4. By "nominal functionality" of a polyether polyol, it is meant the average number of oxyalkylatable hydrogen atoms on the initiator compound that is alkoxyated to form the polyether polyol. The actual functionalities of the polyether polyol(s) may be somewhat lower than the nominal functionality, due to side-reactions that occur during the alkoxylation process. In the case of a mixture of polyether polyols, the number average nominal functionality may be 2 to 3.5 or may be 2.5 to 3.5.

[0031] The polyether polyol(s) may be propylene- or polypropylene-based polyethers. The polyether polyol(s) may be selected from homopolymers of propylene oxide and copolymers of 70 to 99% by weight propylene oxide and 1 to 30% by weight ethylene oxide. Such a copolymer of propylene oxide and ethylene oxide is generally preferred if a single polyether polyol is present. If two or more polyether polyols are present, it is preferred that at least one is such a copolymer of propylene oxide and ethylene oxide. In the case of a copolymer, the propylene oxide and ethylene oxide may be randomly copolymerized, block copolymerized, or both. In some embodiments, 50% or more of the hydroxyl groups of the polyether polyol or mixture of polyether polyols are primary hydroxyl, with the remainder being secondary hydroxyl groups. 70% or more of the hydroxyl groups in the polyether polyol or mixture thereof may be primary hydroxyl. The polyether polyols may be ethylene terminated. The polyether polyols may be polypropylene chains capped with ethylene oxide chains.

[0032] The polyether polyol(s) (ingredient a)) may constitute about 30 weight percent or greater of the polyol component. The polyether polyol(s) may constitute 40 weight percent or greater or about 50 weight percent or greater of the polyol component, may constitute about 85 weight percent or less, about 65 weight percent or less or about 55 weight percent or less. Exemplary polyether polyols are high reactivity capped polyether triols with an average molecular weight of about 4,900 g/mol molecular weight and an OH number of approximately 34 mg KOH/g, such as VORANOL™ 4701; nominal 5000 molecular weight, high reactivity capped polyether triols with an OH number of approximately 34 mg KOH/g, such as VORANOL™ 4703; high functional polyether polyols for high density polyurethane foams, such as VORANOL™ RH 360; and high functionality, ethylene oxide capped polyether products with an OH number of approximately 31 mg KOH/g, such as SPECFLEX™ NC 630.

[0033] Ingredient b) of the polyol component is one or more aliphatic diol chain extenders. The aliphatic diol chain extender(s) each have a hydroxyl equivalent weight of about 200 or less, about 100 or less, about 75 or less and about 60 or less, and about two aliphatic hydroxyl groups per molecule. Examples of these are monoethylene glycol, diethylene glycol, triethylene glycol, 1,2-propane diol, 1,3-propane diol, 2,3-dimethyl-1,3-propanediol, dipropylene glycol, tripropylene glycol, 1,4-butanediol, 1,6-hexanediol, 2-ethyl-1,3-hexanediol, and other linear or branched alkylene diols having up to about 20 carbon atoms. The aliphatic diol chain extender may be monoethylene glycol, 1,4-butanediol or a mixture thereof. The chain extender may be present in an amount of

about 0.1 percent by weight or greater of the polyol component, about 1.0 percent by weight or greater, about 2.0 percent by weight or greater, about 3 percent by weight or greater, or about 4 percent by weight or greater. The chain extender may be present in an amount of about 25 percent by weight or less of the polyol component, about 10 percent by weight or less, about 9 percent by weight or less, about 8 percent by weight or less, about 7 percent by weight or less, or about 6 percent by weight or less. The aliphatic diol chain extender or mixture thereof is present in an amount of 2.5 to 6 equivalents per equivalent of ingredient a) of the polyol component.

[0034] The polyol component contains ingredient c), one or more latent room temperature organometallic catalysts. A latent room temperature organometallic catalyst is a catalyst that functions to catalyze the reaction of the nucleophiles (polyols, polyamines) present in the polyol component with the isocyanates present in the isocyanate component. The latent organometallic catalyst may show delayed action. Any latent room temperature organometallic catalysts which provides good open time, acceptable initial lap shear strengths and which maintains an acceptable level of reactivity after partial curing and storage may be utilized. Exemplary classes of latent room temperature organometallic catalysts include organometallic catalysts containing tin, zinc or bismuth. Exemplary latent room temperature organometallic catalysts include zinc alkanoates, bismuth alkanoates, dialkyltin alkanoates, dialkyl tin mercaptides, dialkyl tin bis(alkylmercaptoacetates), dialkyltin thioglycolates or mixtures thereof. Exemplary latent room temperature organometallic catalysts include zinc neoalkanoates, bismuth neoalkanoates, dialkyltin neoalkanoates, dialkyl tin mercaptides, dialkyl tin bis(alkylmercaptoacetates), dialkyltin thioglycolates, dibutyltin dilaurates or mixtures thereof. The latent room temperature organometallic catalysts may be dialkyl tin mercaptides, dialkyl tin bis(alkylmercaptoacetates), dialkyltin thioglycolates or mixtures thereof. The latent room temperature organometallic catalysts may be dialkyltin thioglycolates, dibutyltin dilaurates, or mixtures thereof. The alkyl groups on the latent room temperature organometallic catalysts may be any alkyl groups of about 1 or more carbon atoms or 4 or greater carbon atoms. The alkyl groups on the latent room temperature organometallic catalysts may be any alkyl groups of about 20 or less carbon atoms or 12 or less carbon atoms. Exemplary alkyls groups include methyl, butyl, octyl and dodecyl groups. The latent room temperature organometallic catalysts may be present in an amount sufficient to provide good open time, acceptable initial lap shear strengths and which maintains an acceptable level of reactivity after partial curing and storage. The latent room temperature

organometallic catalysts may be present in an amount of about 0.005 percent by weight or greater based on the weight of polyol component, about 0.01 percent by weight or greater, about 0.020 percent by weight or greater, or about 0.030 percent by weight or greater. The latent room temperature organometallic catalysts may be present in an amount of about 1.0 percent by weight or less based on the weight of the polyol component, about 0.080 percent by weight or less, about 0.070 percent by weight or less or about 0.050 percent by weight or less. These amounts are based on active catalyst, and ignore the mass of solvents or other materials as may be present in a commercially available dialkyltin glycolate catalyst product or a dibutyltin dilaurate catalyst product.

[0035] The polyol component may contain compounds having primary and/or secondary amino groups. Exemplary compounds having primary and/or secondary amino groups include polyoxyalkylene polyamines having 2 or greater amines per polyamine, 2 to 4 amines per polyamine, or 2 to 3 amines per polyamine. The polyoxyalkylene polyamines may have a weight average molecular weight of about 200 or greater or about 400 or greater. The polyoxyalkylene polyamine may have a weight average molecular weight of about 5,000 or less or about 3,000 or less. Exemplary polyoxyalkylene polyamines are JEFFAMINE™ D-T-403 polypropylene oxide triamine, having a molecular weight of about 400, and JEFFAMINE™ D-400 polypropylene oxide diamine having a molecular weight of about 400. The compounds having primary and/or secondary amino groups are present in a sufficient amount to prevent the composition from sagging once mixed and applied. The compounds having primary and/or secondary amino groups may be present in the polyol component in an amount of about 0.2 percent by weight or greater, about 0.3 percent by weight or greater or about 0.5 percent by weight or greater. The compounds having primary and/or secondary amino groups may be present in the polyol component in an amount of about 6 percent by weight or less, about 4 percent by weight or less or about 2 percent by weight or less.

[0036] The polyol component may further include one or more optional components. The polyol component may contain at least one particulate filler; however, if a filler is present, it constitutes no more than about 60 weight percent of the total weight of the polyol component. The filler may constitute about 25 weight percent or greater of the polyol component, or about 30 weight percent or greater. The filler may constitute about 50 weight percent or less of the polyol component. The particulate filler is in the form of particles having a size of about 50 nm to about 100 μ m. The fillers may have a particle size (d50) of about 250 nm or greater, about 500 nm or greater or about 1 μ m or greater.

The fillers may have a particle size (d_{50}) of about 50 μm or less, about 25 μm or less or about 10 μm or less. Particle sizes are conveniently measured using dynamic light scattering methods, or laser diffraction methods for particles having a size below about 100 nm. The particulate filler is a solid material at room temperature, is not soluble in the other ingredients of the polyol component or in the polyisocyanate component or any ingredient thereof. The filler is a material that does not melt, volatilize or degrade under the conditions of the curing reaction between the polyol and polyisocyanate components. The filler may be, for example, an inorganic filler, such as glass, silica, boron oxide, boron nitride, titanium oxide, titanium nitride, fly ash, calcium carbonate, various alumina-silicates including clays such as wollastonite and kaolin, metal particles such as iron, titanium, aluminum, copper, brass, bronze and the like; thermoset polymer particles such as polyurethane, cured particles of an epoxy, phenol-formaldehyde, or cresol-formaldehyde resin, crosslinked polystyrene and the like; thermoplastics such as polystyrene, styrene-acrylonitrile copolymers, polyimide, polyamide-imide, polyether ketone, polyether-ether ketone, polyethyleneimine, poly(p-phenylene sulfide), polyoxymethylene, polycarbonate and the like; and various types of carbon such as activated carbon, graphite, carbon black and the like. In some embodiments, the particulate filler excludes carbon particles. The particles in some embodiments have an aspect ratio of about 5 or less, about 2 or less, or about 1.5 or less. Some or all of the filler particles can be grafted onto one or more of the polyether polyol(s) that constitute ingredient (a) of the polyol component.

[0037] Another optional ingredient is one or more dispersing aids, which wet the surface of the filler particles and help them disperse into the polyether polyol(s). These may also have the effect of reducing viscosity. Exemplary classes of dispersing aids include alkylammonium salt of a low-molecular-weight polycarboxylic acid polymer and salts of unsaturated polyamine amides and low-molecular acidic polyesters, and fluorinated surfactants. Among these are, for example, various dispersing agents sold by BYK Chemie under the BYK, DISPERBYK and ANTI-TERRA-U tradenames, such as alkylammonium salt of a low-molecular-weight polycarboxylic acid polymer and salts of unsaturated polyamine amides and low-molecular acidic polyesters, and fluorinated surfactants such as FC-4430, FC-4432 and FC-4434 from 3M Corporation. Such dispersing aids may constitute, for example, up to 2 weight percent or up to 1 weight percent of the polyol component.

[0038] Another useful optional ingredient of the polyol component is a desiccant such as fumed silica, hydrophobically modified fumed silica, silica gel, aerogel, various zeolites and molecular sieves, and the like. One or more desiccants may constitute about 1 percent by weight or greater based on the weight of the polyol component and about 5 weight percent or less, or about 4 weight percent or less of the polyol component, and may be absent from the polyol component.

[0039] The polyol component may further include one or more additional isocyanate-reactive compounds, different from ingredients a), b) and c) of the polyol component, and which do not contain amine hydrogen atoms. If any such additional isocyanate-reactive compound(s) are present, they may constitute no more than 10 percent, no more than 5 percent, or no more than 2 percent, of the weight of the polyol component. Examples of such additional isocyanate-reactive compounds include, for example, one or more polyester polyols; one or more polyether polyols containing at least 50 weight percent polymerized ethylene oxide; one or more polyether polyols having a hydroxyl equivalent weight of 100 to 499; and one or more hydroxy-functional crosslinkers having three or more isocyanate-reactive groups per molecule and a hydroxyl equivalent weight of up to 499.

[0040] The adhesive may be non-cellular, and for that reason, the polyol component may contain about 0.5% by weight or less, about 0.1%, by weight or less of organic compounds having a boiling temperature of 80°C or below, and about 0.1% by weight or less, or about 0.05% by weight or less, of water and/or other chemical blowing agents that produce a gas under the conditions of the curing reaction.

[0041] The polyol component may contain about 10 weight percent or less, about 5 weight percent or less, or about 1 weight percent or less, of a plasticizer such as a phthalate, terephthalate, mellitate, sebacate, maleate or other ester plasticizer, a sulfonamide plasticizer, a phosphate ester plasticizer, or a polyether di(carboxylate) plasticizer. Such a plasticizer may be absent from the polyol component.

[0042] The polyisocyanate component of the two-component adhesive contains one or more polyisocyanate compounds. The polyisocyanate component of the two-component adhesive may be different from the isocyanate used in forming the isocyanate-blocked amidine or isocyanate-blocked guanidine as disclosed herein. The polyisocyanate may be a mixture of one or more isocyanate-terminated prepolymers having at least 2 isocyanate groups per molecule and an isocyanate equivalent weight of 700 to 3500, and one or more low equivalent weight polyisocyanate compounds that have

an isocyanate equivalent weight of up to 350 and 2 to 4 isocyanate groups per molecule. When such a mixture is present, the prepolymer may constitute 20 to 65 percent of the weight of the polyisocyanate component. In some embodiments, the prepolymer constitutes 20 to 60 percent, 20 to 50 percent or 25 to 35 percent of the weight of the polyisocyanate component. The low equivalent weight polyisocyanate, when such a mixture is present, may constitute 20 to 50 weight percent of weight of the polyisocyanate component. The isocyanate content of the prepolymers may be about 1 percent by weight or greater, about 6 percent by weight or greater, about 8 percent by weight or greater or about 10 percent by weight or greater. The isocyanate content in the isocyanate functional prepolymers may be about 35 percent by weight or less, about 30 percent by weight or less, about 25 percent by weight or less or about 15 percent by weight or less.

[0043] The prepolymer may be a reaction product of one or more aromatic diisocyanates having a molecular weight of up to 350 with i) at least one 700 to 3000 molecular weight homopolymer of poly(propylene oxide) having a nominal hydroxyl functionality of 2 to 4, or ii) a mixture of i) with up to 3 parts by weight, per part by weight of i), of a 2000 to 8000 molecular weight polyether polyol which is a copolymer of 70 to 99 weight percent propylene oxide and 1 to 30 weight percent ethylene oxide and has a nominal hydroxyl functionality of 2 to 4. The poly(propylene oxide) used to make the prepolymer may have a molecular weight of 800 to 2000 or from 800 to 1500, and has and may have a nominal functionality of 2 to 3, especially 2. A copolymer of 70 to 99 weight percent propylene oxide and 1 to 30 weight percent ethylene oxide used to make the pre-polymer may have a molecular weight of 3000 to 5500 and a nominal functionality of 2 to 3.

[0044] The reaction of polyisocyanate and polyol(s) produces prepolymer molecules having a polyether segment that is capped with the polyisocyanate, so the molecules have terminal isocyanate groups. Each prepolymer molecule contains a polyether segment that corresponds to the structure, after removal of hydroxyl groups, of a polyol used in the prepolymer-forming reaction. If a mixture of polyols is used to make the prepolymer, a mixture of prepolymer molecules is formed.

[0045] The isocyanate-terminated prepolymer has an isocyanate equivalent weight of about 700 to about 3500, about 700 to about 3000 or about 1000 to about 3000. The equivalent weight for purposes of this invention is calculated by adding the weight of the polyol(s) used to prepare the prepolymer and the weight of polyisocyanate(s) consumed in reaction with the polyol(s), and dividing by the number of moles of isocyanate groups in

the resulting prepolymer. The polyisocyanate used to make the prepolymer can be any of the low equivalent weight polyisocyanate compounds mentioned below, or a mixture of two or more of these. The prepolymer has at least 2, 2 to 4, or 2 to 3, isocyanate groups per molecule. The isocyanate groups of the prepolymer may be aromatic, aliphatic (including alicyclic), or a mixture of aromatic and aliphatic isocyanate groups. The isocyanate groups on the prepolymer molecules may be aromatic. The low equivalent weight polyisocyanate compound(s) in some embodiments have an isocyanate equivalent weight of 80 to 250, 80 to 200, or 80 to 180. If a mixture of polyisocyanate compounds is present, the mixture may have, for example, an average of 2 to 4 or 2.3 to 3.5 isocyanate groups per molecule.

[0046] All or a portion of the low equivalent weight polyisocyanate compound may have aromatic isocyanate groups. Among the useful aromatic polyisocyanate compounds m-phenylene diisocyanate, toluene-2,4-diisocyanate, toluene-2,6-di-isocyanate, naphthylene-1,5-diisocyanate, methoxyphenyl-2,4-diisocyanate, diphenyl-methane-4,4'-diisocyanate, diphenylmethane-2,4'-diisocyanate, 4,4'-bi-phenylene diisocyanate, 3,3'-dimethoxy-4,4'-biphenyl diisocyanate, 3,3'-dimethyl-4,4'-biphenyl diisocyanate, 3,3'-dimethyldiphenyl methane-4,4'-diisocyanate, 4,4',4"-triphenyl methane triisocyanate, polymethylene polyphenylisocyanate (PMDI), toluene-2,4,6-triisocyanate and 4,4'-dimethyldiphenylmethane-2,2',5,5'-tetraisocyanate. Modified aromatic polyisocyanates that contain urethane, urea, biuret, carbodiimide, uretoneimine, allophonate or other groups formed by reaction of isocyanate groups are also useful. The aromatic polyisocyanate may be MDI or PMDI (or a mixture thereof that is commonly referred to as "polymeric MDI"), and so-called "liquid MDI" products that are mixtures of MDI and MDI derivatives that have biuret, carbodiimide, uretoneimine and/or allophonate linkages. All or a portion of the low equivalent weight polyisocyanate compounds may be one or more aliphatic polyisocyanates. Examples of these include cyclohexane diisocyanate, 1,3- and/or 1,4-bis(isocyanatomethyl)cyclohexane, 1-methyl-cyclohexane-2,4-diisocyanate, 1-methyl-cyclohexane-2,6-diisocyanate, methylene dicyclohexane diisocyanate, isophorone diisocyanate and hexamethylene diisocyanate.

[0047] At least some of the polyisocyanate groups present in the polyisocyanate component may be aromatic isocyanate groups. If a mixture of aromatic and aliphatic isocyanate groups are present, about 50% or more by number, or even about 75% or more by number, are aromatic isocyanate groups. 80 to 98% by number of the isocyanate groups may be aromatic, and 2 to 20% by number may be aliphatic. All of the isocyanate

groups of the prepolymer may be aromatic, and the isocyanate groups of the polyisocyanate compound(s) having an isocyanate equivalent weight of up to 350 may be a mixture of 80 to 95% aromatic isocyanate groups and 5 to 20% aliphatic isocyanate groups.

[0048] A prepolymer may be prepared by combining the polyol or polyol mixture with an amount of low equivalent weight polyisocyanate compound(s) significantly greater than needed to simply cap the polyol(s). After reaction, this produces a mixture of the prepolymer and unreacted low equivalent weight polyisocyanate compounds. If desired, an additional amount of polyisocyanate compound(s) can then be blended into this mixture. The polyol(s) may be combined and reacted with an excess of one or more aromatic polyisocyanates to produce a mixture of prepolymer and unreacted starting polyisocyanate compounds, and this mixture then is combined with one or more aliphatic polyisocyanates. The prepolymer may be made in a reaction of the polyol(s) with MDI, PMDI, a polymeric MDI, a derivative of any one or more of these that contains biuret, carbodiimide, uretoneimine and/or allophonate, or a mixture of any two or more of these, to produce a mixture of prepolymer and unreacted starting polyisocyanates, and the mixture is then combined with one or more aliphatic polyisocyanates, especially an aliphatic polyisocyanate based on hexamethylene diisocyanate.

[0049] The polyisocyanate component may contain up to 50% by weight of one or more particulate inorganic fillers as described before. The polyisocyanate component contains about 10% by weight or more, about 20% by weight or more of one or more such fillers, and may contain, for example, 20 to 50% or 30 to 40% by weight thereof. The filler amounts are based on the weight of the polyisocyanate component. The filler may exclude carbon particles.

[0050] The polyisocyanate component may also contain one or more other additional ingredients, such as those described above with respect to the polyisocyanate compound. As with the polyol component, the polyisocyanate component may contain about 0.5% by weight or less, about 0.1% by weight or less of organic compounds having a boiling temperature of 80°C or less, about 0.1% by weight or less, or about 0.05% by weight or less, of water and/or other chemical blowing agents that produce a gas under the conditions of the curing reaction. The polyisocyanate compound may contain at most, amounts of plasticizers as described before with respect to the polyol component. The isocyanate component may be devoid of a plasticizer.

[0051] The polyol component and polyisocyanate component are formulated such that when equal volumes of the components are provided, the isocyanate index may be 1.0 to 1.8, 1.1 to 1.8, or 1.15 to 1.65. "Isocyanate index" is the ratio of the number of isocyanate groups in the polyisocyanate component to the number of isocyanate-reactive groups in the polyol component. The isocyanate index, at a 1:1 volume ratio, may be 1.15 to 1.65.

[0052] Disclosed, therefore, is an adhesive composition that includes a polyol component, an isocyanate component, and an adduct as disclosed herein comprising a residue of a cyclic amidine and an isocyanate to form one or more isocyanate-blocked amidines. The adduct may serve as a catalyst for the adhesive composition (e.g., a two-component polyurethane adhesive). The isocyanate-blocked amidines may have multiple non-aromatic rings. The isocyanate-blocked amidines may include hydrocarbyl groups off the residue of the isocyanate nitrogen atoms contained in the cyclic ring that is formed. The one or more isocyanate isocyanate-blocked amidines may be located in the polyol component of the adhesive composition. The one or more isocyanate-blocked amidines may be located in the isocyanate component of the adhesive composition. The one or more isocyanate-blocked amidines may be present in an amount that is sufficient to provide a catalytic effect for polyurethane production. The one or more isocyanate-blocked amidines may be present in an amount that does not generate a large amount of amine byproduct into the final product. The isocyanate-blocked amidine catalyst may be present in an amount of about 0.01 percent by weight or greater, about 0.25 percent by weight or greater, or about 0.50 percent by weight or greater based on the weight of the polyol component. The isocyanate-blocked amidine catalyst may be present in an amount of about 2.0 percent by weight or less, about 1.5 percent by weight or less, or about 1.0 percent by weight or less based on the weight of the polyol component.

[0053] Disclosed is a process for bonding two substrates. The polyol component and the isocyanate component are mixed to form the mixed adhesive. The adduct of an isocyanate-blocked amidine may improve latency of the adhesive so that the adhesive remains flowable and capable of bonding to a substrate over a desired period of time. The adduct may be added to the polyol component or the isocyanate component prior to mixing the polyol component and isocyanate component. The component containing the adduct, the mixed adhesive, or both, may be heated, to initiate the de-blocking of the isocyanate-blocked amidine to allow the amidine to function as a catalyst for the polyurethane production.

[0054] The ratio of the polyol component and isocyanate component is generally sufficient to provide an isocyanate index of 1.0 to 1.8, 1.1 to 1.8, or 1.15 to 1.65. The mixed adhesive is formed into an adhesive layer between and in contact with the two substrates. An adhesion promoter may be applied to one or both of the substrates prior to contacting the substrate(s) with the adhesive. The adhesive layer is then cured between and in contact with the two substrates to form a layer of cured adhesive bonded to each of the two substrates.

[0055] The methods used to mix the isocyanate component with the polyol component, form the adhesive layer and cure the adhesive are, broadly speaking, not critical and a variety of apparatuses can be used to perform these steps. Thus, the isocyanate component and polyol component can be mixed and applied to the substrates manually, in various types of batch apparatus, and/or using various sorts of automated metering, mixing and dispensing equipment.

[0056] The polyol component and isocyanate component may react to provide a snap cure profile upon thermal activation, where snap cure is an engineered cure time with slow viscosity growth and then when mixed is quickly cured. The profile of curing therefore would have a generally horizontal slope and then the slope rapidly increases, as the adhesive begins curing rapidly, similar to the shape of a hockey stick. Heating can be applied to the adhesive to obtain a more rapid cure or to initiate curing. Heat may be applied via infrared (IR) heating. The polyol and isocyanate components can be heated separately and then mixed and cured, with or without further applied heat. Alternatively, the polyol and isocyanate components can be mixed at a lower temperature, such as 0 to 35°C and then heated to a higher cure temperature. The substrate can be heated before applying the adhesive if desired. If an elevated temperature is used in the curing step, such a temperature may be, for example, about 36°C or greater, about 50°C or greater, or about 70 °C or greater. Such a temperature may be, for example, about 150°C or less, about 130°C or less, or about 110°C or less. For example, the temperature range may be between about 90°C and about 110°C.

[0057] In specific embodiments, a layer of the two-component polyurethane adhesive is formed at a bondline between two substrates to form an assembly. The adhesive layer is then at least partially cured at the bondline by applying infrared radiation to the assembly. Infrared radiation may be applied, for example, until the temperature of the adhesive layer reaches about 80 °C or greater, or about 90 °C or greater, or about 150°C or less, or about 130°C or less. The assembly so heated may be maintained under

infrared radiation until the adhesive layer has been exposed to such temperatures for a period of 5 seconds or more to effect the partial or complete cure. For example, the infrared radiation may be continued until the temperature of adhesive layer is 80 to 150°C, or 90 to 130°C, for 5 to 60 seconds, 5 to 45 seconds, for 10 to 30 seconds or for 10 to 20 seconds, at which time the exposure to infrared radiation is discontinued.

[0058] If only a partial cure is performed by applying infrared radiation, the partial curing can be either or both of two types. In one type of partial curing, the entire adhesive layer is cured, but only partially. Such partial curing may be at least to the gel point, at which a three-dimensional polymeric network is formed in the adhesive layer by the curing of the components. In another type of partial curing, only one or more predetermined, localized portions of the adhesive layer at the bondline are cured. This produces an adhesive layer having at least partially cured portions and portions that have undergone little or no cure. The predetermined, localized portions of the adhesive layer may constitute, for example, 5 to 80%, 5 to 50% or 5 to 25% of the total area of the adhesive layer. Subsequent to the partial curing step, the uncured or only partially cured portions of the adhesive layer then are cured further to form a fully-cured adhesive. The subsequent step of completing the cure can be done approximately room temperature (such as from 15 to 35°C) or an elevated temperature such as greater than 35°C to 80°C.

[0059] A two-step curing process as just described is useful in a variety of manufacturing, building and construction, and in-field assembly and repair applications. By performing only a partial cure by applying infrared radiation, a rapid bonding of the adhesive to the substrate can be obtained in a very short time, often a matter of 10 seconds to 2 minutes. The bonded parts can be handled after 1 hour or less from partial cure, after about 10 minutes or less after partial cure, about 3 minutes or less after partial cure or about 1 minute or less after partial cure. This initial bond is often robust enough that the assembly can withstand further handling. Further handling may include, for example, transporting the assembly to a downstream work station, and further manufacturing steps which might include joining the assembly to one or more other components, various shaping and/or machining steps, the application of a coating, and the like. The completion of the cure can take place during and/or after such additional handling steps. Often, the adhesive will fully cure without exposing it to elevated temperature, infrared radiation or other energy source, due at least in part to the catalytic action of the dialkyltinthioglycolate catalyst. It is believed that the isocyanate-blocked cyclic amidine catalyst de-blocks during the heating stage, to produce an active catalyst

that also promotes the cure during the subsequent curing step, even if that subsequent step is performed without additional applied energy.

[0060] The substrates are not limited. They can be, for example, a metal, a metal alloy, an organic polymer, a lignocellulosic material such as wood, cardboard or paper, a ceramic material, various types of composites, or other materials. Carbon fiber reinforced plastic is a substrate of particular interest. The substrates in some embodiments are vehicular parts or vehicular sub-assemblies that are adhered together with a cured adhesive composition disclosed. The substrates in other embodiments are individual plies that are glued together using the adhesive to form a multilayer laminate. The substrates in other embodiments are building members. The substrates may be formed from or include a material such as glass. The substrates may be a fiber-reinforced substrate. The substrates may include reinforcing fibers, such as glass or carbon fibers. The substrates may be e-coated materials. The substrates may be metallic or may include metallic components, such as aluminum. The substrates may be coated or non-coated metals. The substrates may be formed from a combination of materials as disclosed herein.

[0061] Other components commonly used in curable compositions may be used in the compositions disclosed. Such materials are well known to those skilled in the art and may include ultraviolet stabilizers and antioxidants and the like. The compositions may also contain durability stabilizers known in the art. Among preferred durability stabilizers are alkyl substituted phenols, phosphites, sebacates and cinnamates. A preferred class of durability stabilizers includes organophosphites. The organophosphites may be present in a sufficient amount to enhance the durability of bond of the adhesive composition to the substrate surface. Such phosphites are disclosed in Hsieh et al. US 7,416,599, column 10, line 47 to column 11 line 25, incorporated herein by reference. Among preferred organophosphites are poly(dipropyleneglycol) phenyl phosphite (available from Dover Chemical Corporation under the trademark and designation DOVER-PHOS 12), tetrakis isodecyl 4,4'-isopropylidene diphosphite (available from Dover Chemical Corporation under the trademark and designation DOVERPHOS 675), and phenyl diisodecyl phosphite (available from Dover Chemical Corporation under the trademark and designation DOVERPHOS 7). The organophosphite may be present in the composition in an amount of about 0.1 percent by weight or greater or about 0.2 percent by weight or greater based on the weight of the composition. The organophosphite may be present in the composition in an amount of about 1.0 percent by weight or less or about 0.5 percent by weight or less based on the weight of the composition.

[0062] The composition 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 may be conducted in an inert atmosphere in the absence of oxygen and atmospheric moisture to prevent premature reaction.

[0063] The two-part adhesive compositions disclosed may be formulated to provide an improved open time and latency. "Open time" is understood to mean the time after application of the composition to a first substrate until it starts to become a high viscous paste and is not subject to deformation during assembly to conform to the shape of the second substrate and to adhere to it. Open time may be measured by rheology reactivity wherein the rheology reactivity is about 500 seconds or greater or about 600 seconds or greater. The "latency" of catalysts used in forming the two-part adhesive refers to the amount of time during which there is a lack of activity of a catalyst, which is therefore a property of a catalyst that provides the open time. Upon activation of the catalyst, the latency may be removed or the latency period may end. For example, as shown in the examples herein, latency can be measured by the ability to stir the adhesive over a certain period of time. Therefore, latency of the two-part adhesive composition may be about 5 minutes or greater, about 8 minutes or greater, or about 10 minutes or greater, measured by mixing the composition until the lap shear strength reaches 1 MPa. The latency of the composition after contacting the polyol component and the isocyanate component may be about 1 hour or less, about 30 minutes or less, or about 20 minutes or less, measured by mixing the composition until the lap shear strength reaches 1 MPa.

[0064] 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.

ILLUSTRATIVE EMBODIMENTS

[0065] The following examples are provided to illustrate the disclosed compositions, but are not intended to limit the scope thereof. All parts and percentages are by weight unless otherwise indicated.

[0066] Ingredients

Polyether Polyol A is a high reactivity capped polyether triol with an average molecular

weight of about 4,900 g/mol molecular weight and an OH number of approximately 34 mg KOH/g.

Polyether Polyol B is a nominal 5000 molecular weight, high reactivity capped polyether triol with an OH number of approximately 34 mg KOH/g.

Polyether Polyol C is a high functionality, ethylene oxide capped polyether product with an OH number of approximately 31 mg KOH/g.

1,4-butane diol.

Ethylene glycol.

2-ethyl-1,3-hexanediol.

The Aminated Polyether is a 400 g/mol, difunctional poly(propylene oxide) terminated in primary amine groups, sold as Jeffamine™ D-400 by Huntsman Corporation.

Molecular sieve paste.

The Liquid MDI is a commercially available modified MDI product having an isocyanate functionality of about 2.2 and an isocyanate equivalent weight of about 144.5.

The Polymeric MDI is a commercially available polymeric MDI product having an isocyanate functionality of about 2.7 and an isocyanate equivalent weight of about 134.

The polyethylene glycol is a commercially available product having an average molecular weight of about 2000 g/mol molecular weight.

The catalyst is an isocyanate-blocked 1,8-diazabicycloundec-7-ene (DBU) catalyst.

1% solution dibutyltin dilaurate cocatalyst.

[0067] Polyol Part Preparation Process

The following ingredients are combined, blended and stored in air moisture proof containers useful in two-part manual dispensing guns. Three polyols are formed: Polyol A, Polyol B, and Polyol C.

Table 1 – Polyol Component

Component	Polyol A (w/w%)	Polyol B (w/w%)	Polyol C (w/w%)
Polyether Polyol A	82.0	84.0	
Polyether Polyol B			31.0
Polyether Polyol C			47.7
1,4-butanediol	8.5		
Ethylene glycol		6.0	

2-ethyl-1,3-hexanediol			17.7
Aminated Polyether	1.3	1.4	0.5
Molecular sieve paste	8.2	8.4	3.1

[0068] Isocyanate Component

The following ingredients are combined, blended and stored in air moisture proof containers useful in two-part manual dispensing guns. The liquid MDI and polymeric MDI are combined and heated to 90°C under vacuum for 30 minutes. The polyethylene glycol is then added to the liquid MDI and polymeric MDI and heated under vacuum for 90°C for an additional 90 minutes.

Table 2 – Isocyanate components

Component	Weight Percent
Liquid methylene diphenyl diisocyanate	33.2
Polymeric methylene diphenyl diisocyanate	41.6
Polyethylene glycol	25.2

[0069] Testing

Various isocyanate blocking groups are tested to determine latency of DBU•2RNCO catalysts, indicated by viscosity over time at 30°C. The latency is measured by monitoring the amount of time for the two-component polyurethane adhesive employing the DBU•2RNCO catalyst to reach the viscosity limit of the reactor at 30°C and the amount of force required for stirring the adhesive over a period of 1800 seconds, where the viscosity limit is about 200,000 centipoise. Once the adhesive reaches the viscosity limit, the adhesive is no longer able to be stirred.

[0070] The results are summarized in Table 3. The testing is conducted for each of Polyol A, Polyol B, and Polyol C, which is pre-mixed with a blocked amidine catalyst and 40 mg of a 1% solution dibutyltin dilaurate cocatalyst. The isocyanate is added to form the two-component polyurethane adhesive. The tests are performed using the same molar amount of DBU•2RNCO catalyst with 40 mg of a 1% solution dibutyltin dilaurate cocatalyst premixed into: 12.6 g Polyol A before adding 7.4 g isocyanate and commencing monitoring; 12.5 g Polyol B before adding 7.5 g isocyanate and commencing monitoring; or 11.8 g Polyol C before adding 8.2 g isocyanate and commencing monitoring. The comparative example is a phenol-blocked 1,8-diazabicycloundec-7-ene catalyst. The

blocked amidine catalysts tested are: phenylisocyanate-blocked 1,8-diazabicycloundec-7-ene catalyst; butylisocyanate-blocked 1,8-diazabicycloundec-7-ene catalyst; cyclohexylisocyanate-blocked 1,8-diazabicycloundec-7-ene catalyst; benzylisocyanate-blocked 1,8-diazabicycloundec-7-ene catalyst; dodecylisocyanate-blocked 1,8-diazabicycloundec-7-ene catalyst; 4,4'-methylenebis(phenylisocyanate)-blocked 1,8-diazabicycloundec-7-ene catalyst; and hexamethylenediisocyanate-blocked 1,8-diazabicycloundec-7-ene catalyst.

[0071] Each two-component polyurethane adhesive formed with Polyol A reached the viscosity limit of the reactor at 30°C in less than 1000 seconds. The two-component polyurethane adhesive formed with Polyol B reach the viscosity limit of the reactor at 30°C in less than 1800 seconds with phenol, phenylisocyanate, cyclohexylisocyanate, benzylisocyanate, 4,4'-methylenebis(phenylisocyanate), and hexamethylenediisocyanate as the blocking agent for the DBU catalyst. The two-component polyurethane adhesive formed with Polyol B and the DBU catalysts having butylisocyanate and dodecylisocyanate do not reach the viscosity limit within 1800 seconds, and is, therefore, more latent than the other catalysts. The adhesives formed using butylisocyanate-blocked and dodecylisocyanate-blocked DBU catalysts are still able to be stirred after 1800 seconds, with less torque required for stirring the adhesive formed using the dodecylisocyanate catalyst. Of the tests performed for the two-component polyurethane adhesive formed with Polyol C, only the adhesive using the phenylisocyanate-blocked DBU catalyst reaches the viscosity limit of the reactor at 30°C within 1800 seconds.

Table 3 – Results

Blocking Agent for DBU Catalyst	Time (s) to viscosity limit of reactor at 30 °C			Torque (A) required for stirring after 1800 s at 30 °C		
	Polyol A	Polyol B	Polyol C	Polyol A	Polyol B	Polyol C
Phenol	455	696	—	—	—	0.99
Phenylisocyanate	242	634	1692	—	—	—
Butylisocyanate	755	—	—	—	1.30	0.35
Cyclohexylisocyanate	695	1541	—	—	—	0.70
Benzylisocyanate	936	967	—	—	—	0.75
Dodecylisocyanate	634	—	—	—	0.73	0.56
4,4'-Methylenebis(phenylisocyanate)	725	1420	—	—	—	0.08
Hexamethylenediisocyanate	574	1299	—	—	—	0.15

[0072] Fig. 1 is a graph illustrating the data in Table 3 for Polyol B, comparing the effects of the isocyanate blocking group on latency of the DBU•2RNCO catalyst, indicated by viscosity over time at 30°C. The adduct of DBU and phenol salt (DBU-PhOH) is formed in an amount of 12 mg. The adduct of DBU and phenylisocyanate (DBU-PhNCO) is formed in an amount of 45 mg. The adduct of DBU and butylisocyanate is formed in an amount of 40 mg. The adduct of DBU and cyclohexylisocyanate (DBU-cHexNCO) is formed in an amount of 45 mg. The adduct of DBU and benzylisocyanate is formed in an amount of 45 mg. The adduct of DBU and dodecylisocyanate (DBU-dodecylNCO) is formed in an amount of 65 mg. The adduct of DBU and 4,4'-methylenebis(phenylisocyanate) (DBU-MDI) is formed in an amount of 75 mg. The adduct of DBU and hexamethylenediisocyanate (DBU-HMDI) is formed in an amount of 55 mg. The reactions are performed using the same molar amount of DBU•2RNCO catalyst with 40 mg of a 1% solution dibutyltin dilaurate cocatalyst premixed into 12.5 g Polyol B before adding 7.5 g isocyanate and commencing monitoring. The two component polyurethane adhesive employing the phenol salt of DBU (DBU-PhOH), which is a typical commercially relevant latent catalyst, serves as a comparative example. As shown, the two-component polyurethane adhesive employing DBU blocked by phenylisocyanate (DBU-PhNCO) reaches the viscosity limit of the reactor the fastest. The two-component polyurethane adhesive employing DBU blocked by dodecylisocyanate (DBU-dodecylNCO) is still able to be stirred at 1800 seconds and has not yet reached the viscosity limit of the reactor at 30°C.

[0073] In summary, the above examples show that open time can be extended as compared to using DBU-PhOH as the blocked catalyst by use of the isocyanate complexes described.

[0074] Parts by weight as used herein refers to 100 parts by weight of the composition specifically referred to. Any numerical values recited in the above application include all values from the lower value to the upper value in increments of one unit provided that there is a separation of at least 2 units between any lower value and any higher value. These are only examples of what is specifically intended and all possible combinations of numerical values between the lowest value, and the highest value enumerated are to be considered to be expressly stated in this application in a similar manner. Unless otherwise stated, all ranges include both endpoints and all numbers between the endpoints. The use of "about" or "approximately" in connection with a range applies to both ends of the range.

Thus, "about 20 to 30" is intended to cover "about 20 to about 30", inclusive of at least the specified endpoints. The term "consisting essentially of" to describe a combination shall include the elements, ingredients, components or steps identified, and such other elements ingredients, components or steps that do not materially affect the basic and novel characteristics of the combination. The use of the terms "comprising" or "including" to describe combinations of elements, ingredients, components or steps herein also contemplates embodiments that consist essentially of the elements, ingredients, components or steps. Plural elements, ingredients, components or steps can be provided by a single integrated element, ingredient, component or step. Alternatively, a single integrated element, ingredient, component or step might be divided into separate plural elements, ingredients, components or steps. The disclosure of "a" or "one" to describe an element, ingredient, component or step is not intended to foreclose additional elements, ingredients, components or steps.

CLAIMS

What is claimed is:

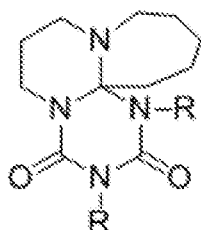
- Claim 1. A composition comprising:
- a. a polyol component and an isocyanate component, wherein:
 - i. the polyol component includes:
 1. one or more polyols;
 2. one or more aliphatic diol chain extenders; and
 3. one or more latent room temperature organometallic catalysts;
 - ii. the isocyanate component includes one or more polyisocyanate compounds;
 - b. one or more isocyanate-blocked amidines having multiple non-aromatic rings and having hydrocarbyl groups off the residue of the isocyanate nitrogen atoms contained in the cyclic ring that is formed and optionally one or more isocyanate groups;
wherein the one or more isocyanate-blocked amidines are located in the polyol component or the isocyanate component; and
wherein the composition is useful as a two-component polyurethane adhesive.
- Claim 2. The composition of claim 1, wherein the one or more isocyanate-blocked amidines are located in the isocyanate component.
- Claim 3. The composition of claim 1 or 2, wherein the one or more isocyanate-blocked amidines are present in an amount of about 0.01 weight percent to about 5 weight percent based on the weight of the polyol component.
- Claim 4. The composition of any of the preceding claims, wherein latency of the composition after contacting the polyol component and the isocyanate component is about 5 minutes or greater.
- Claim 5. The composition of any of the preceding claims, wherein the one or more isocyanate-blocked amidines is prepared in a mole ratio of about 1:1 to about 1:3 amidine to isocyanate.

Claim 6. The composition of any of the preceding claims, wherein the amidine of the one or more isocyanate-blocked amidines corresponds to the formula $C_nH_{2(n-1)}N_2$, where n is an integer.

Claim 7. The composition of claim 6, wherein n is an integer of about 7 or greater and about 9 or less.

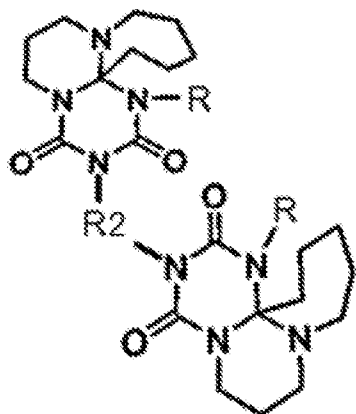
Claim 8. The composition of any of the preceding claims, wherein the amidine of the one or more isocyanate-blocked amidines has a multi-cyclic structure that includes 1,8-diazabicycloundec-7-ene (DBU) or 1,5-diazabicyclo[4.3.0]non-5-ene (DBN).

Claim 9. The composition of any of the preceding claims, wherein the one or more isocyanate-blocked amidines correspond to the formula:

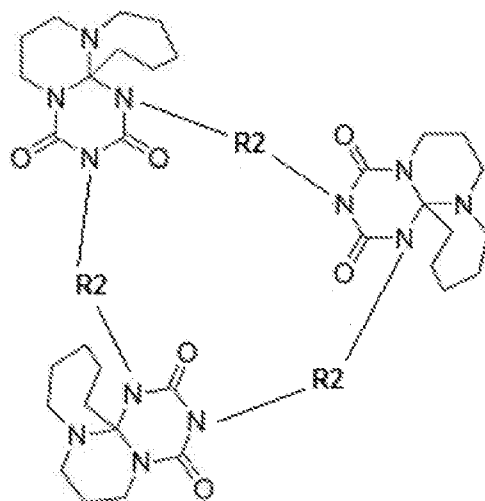


wherein R, separately in each occurrence, is aromatic or aliphatic.

Claim 10. The composition of claim 9, wherein R2, separately in each occurrence, acts as a linking group between two or more isocyanate-blocked amidines and corresponds to the formula:



Claim 11. The composition of claim 9 or 10, wherein R2 separately in each occurrence, acts as a linking group between two or more isocyanate-blocked amidines forming a ring-like structure and corresponds to the formula:

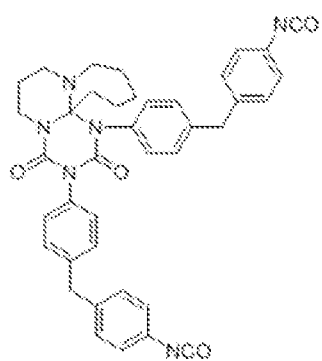


Claim 12. The composition of any of the preceding claims, wherein hydrocarbyl groups off the residue of the isocyanate nitrogen atoms, separately in each occurrence, are a C₂ to C₁₂ alkyl, a C₂ to C₁₂ cycloalkyl, a C₂ to C₁₂ aryl, or a C₂ to C₁₂ alkyl substituted aryl.

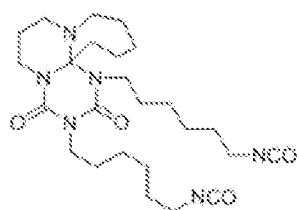
Claim 13. The composition of any of the preceding claims, wherein the isocyanate of the one or more isocyanate-blocked amidines comprises one or more of:

- a. methylene diphenyl diisocyanate (MDI);
- b. hexamethylene diisocyanate (HMDI);
- c. butylisocyanate;
- d. dodecylisocyanate; and
- e. cyclohexylisocyanate.

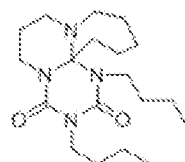
Claim 14. The composition of any of the preceding claims, wherein the one or more isocyanate-blocked amidines are selected from:



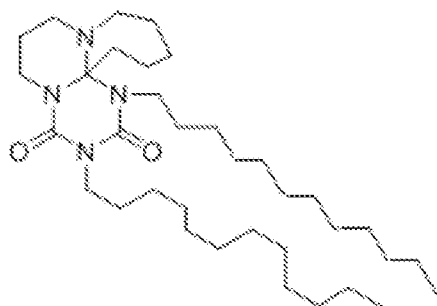
DBU-MDI



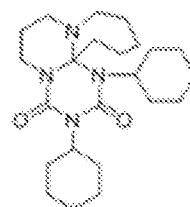
DBU-HMDI



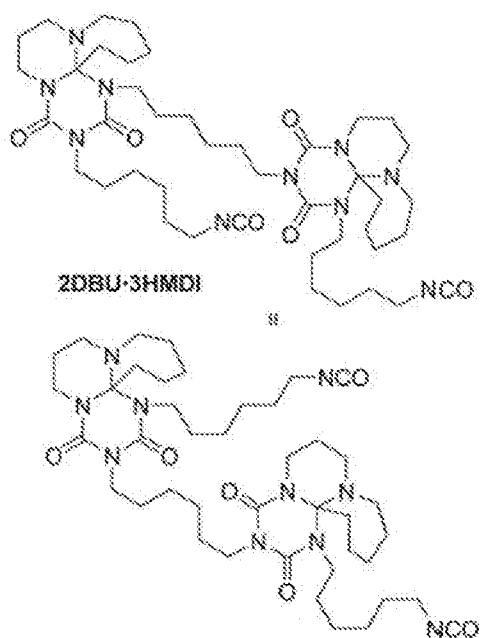
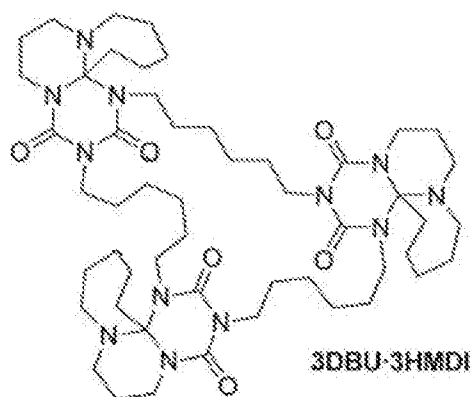
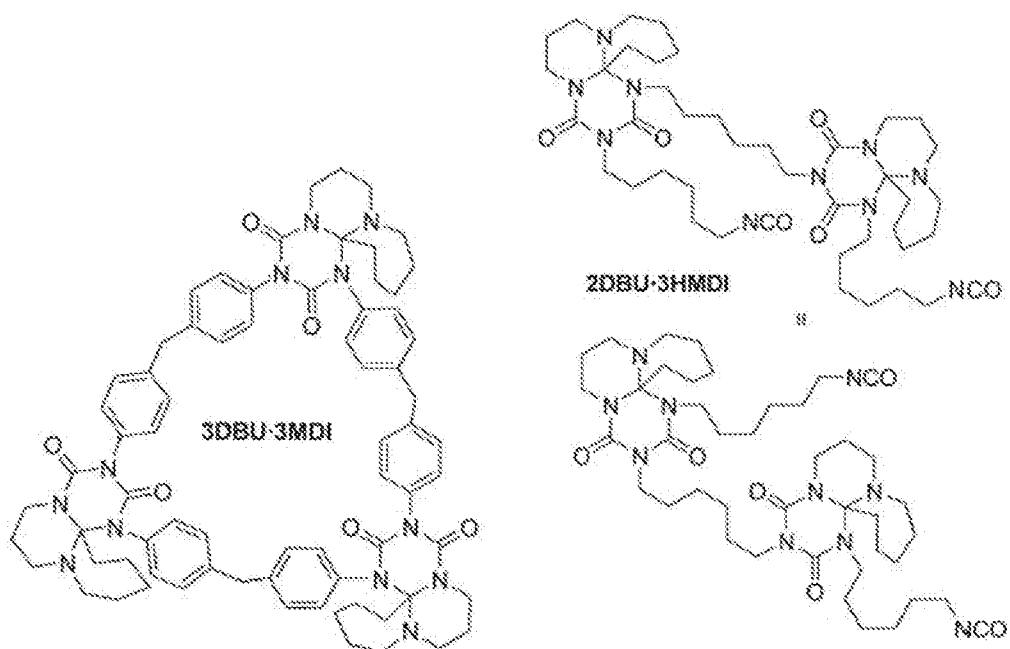
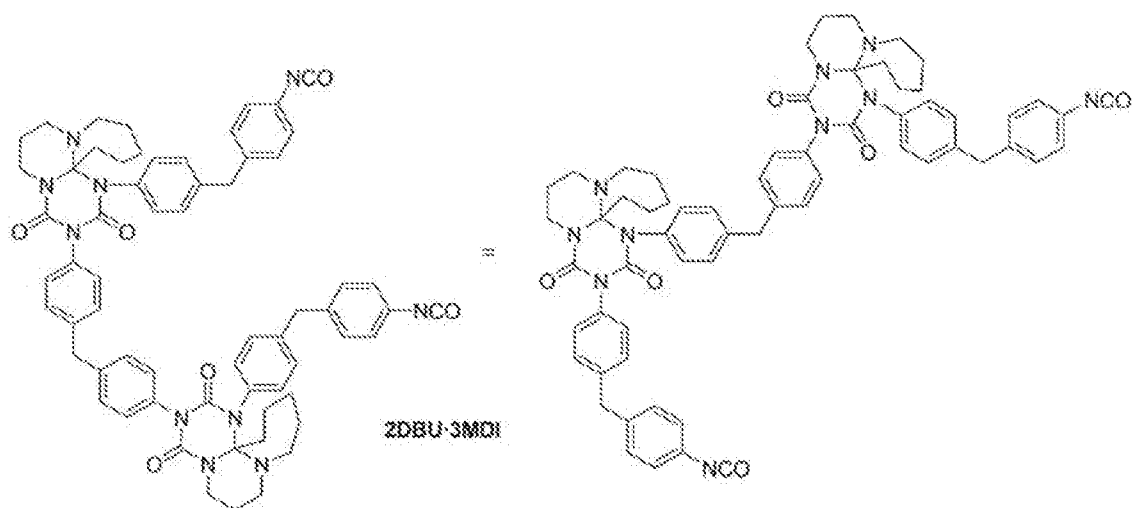
DBU-Butylisocyanate



DBU-Dodecylisocyanate



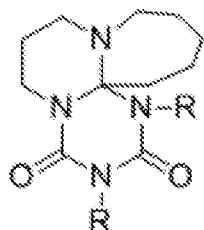
DBU-Cyclohexylisocyanate



- Claim 15. A composition comprising:
- an adduct that is an isocyanate-blocked amidine having a multi-cyclic structure having hydrocarbon based substituents,
 - wherein the adduct comprises a residue of a cyclic amidine and an isocyanate,
 - wherein the isocyanate comprises a polyisocyanate, and
 - wherein the composition is useful as a latent catalyst for a two-component polyurethane adhesive.
- Claim 16. The composition of claim 15, wherein the composition is prepared in a mole ratio of about 1:1 to about 1:3 amidine having a multi-cyclic structure to isocyanate.
- Claim 17. The composition of claim 15 or 16, wherein the amidine having a multi-cyclic structure includes 1,8-diazabicycloundec-7-ene (DBU) or 1,5-diazabicyclo[4.3.0]non-5-ene (DBN).
- Claim 18. A method comprising:
- a. adding a multi-cyclic amidine to a solvent;
 - b. adding an isocyanate to the multi-cyclic amidine and solvent;
- wherein the method forms an adduct having multiple non-aromatic rings and having hydrocarbyl groups off a residue of isocyanate nitrogen atoms contained in a cyclic ring that is formed, and
 - wherein the adduct is useful as a latent catalyst for a two-component polyurethane adhesive.
- Claim 19. The method of claim 18, wherein the adduct is an isocyanate-blocked amidine comprising a residue of a cyclic amidine and an isocyanate.
- Claim 20. The method of claim 18 or 19, wherein the isocyanate is a cyclic isocyanate.
- Claim 21. The method of any of claims 18 to 20, wherein the adduct is prepared in a mole ratio of about 1:1 to about 1:3 multi-cyclic amidine to isocyanate.

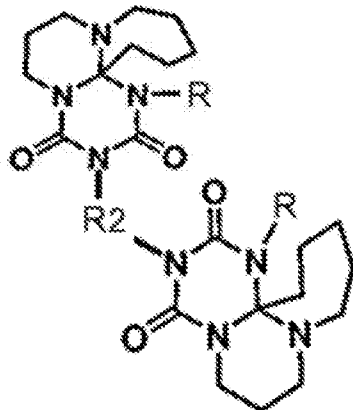
Claim 22. The method of any of claims 18 to 21, wherein the multi-cyclic amidine includes 1,8-diazabicycloundec-7-ene (DBU) or 1,5-diazabicyclo[4.3.0]non-5-ene (DBN).

Claim 23. The method of any of claims 18 to 22, wherein the adduct corresponds to the formula:

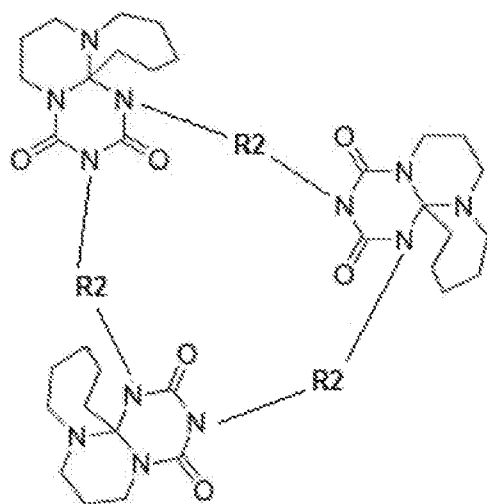


wherein R, separately in each occurrence, is aromatic or aliphatic.

Claim 24. The method of claim 23, wherein R2, separately in each occurrence, acts as a linking group between two or more isocyanate-blocked amidines and corresponds to the formula:



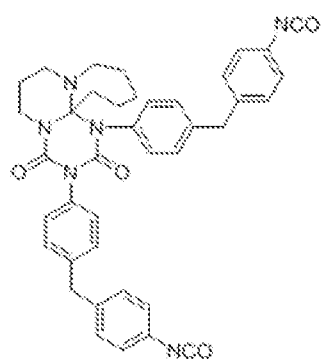
Claim 25. The method of claim 23 or 24, wherein R2, separately in each occurrence, acts as a linking group between three or more isocyanate-blocked amidines forming a ring-like structure and corresponds to the formula:



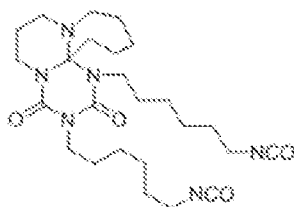
Claim 26. The method of any of claims 18 to 25, wherein the isocyanate comprises one or more of:

- a. methylene diphenyl diisocyanate (MDI);
- b. hexamethylene diisocyanate (HMDI);
- c. butylisocyanate;
- d. dodecylisocyanate; and
- e. cyclohexylisocyanate.

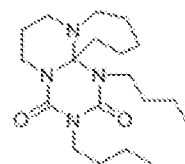
Claim 27. The method of any of claims 18 to 26, wherein the adduct is selected from:



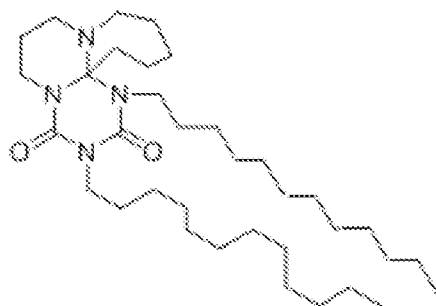
DBU-MDI



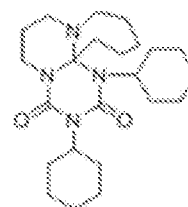
DBU-HMDI



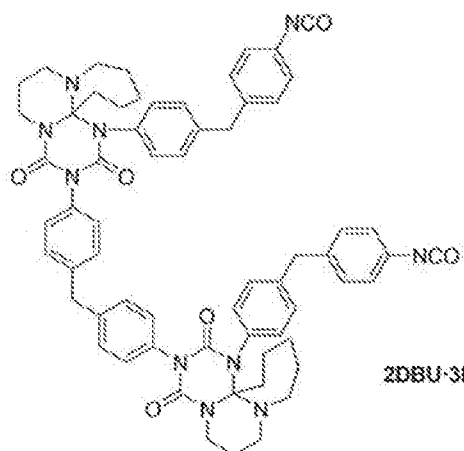
DBU-Butylisocyanate



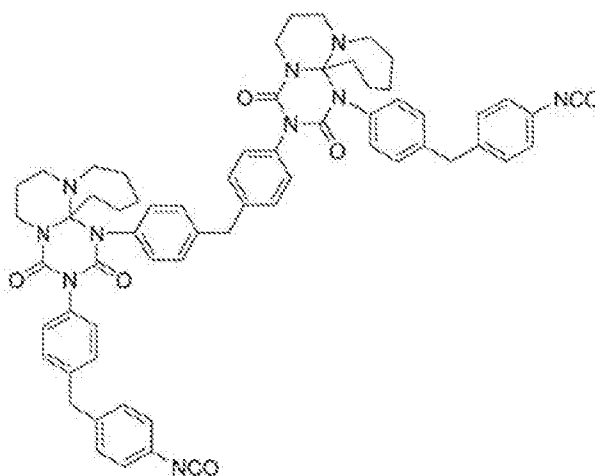
DBU-Dodecylisocyanate

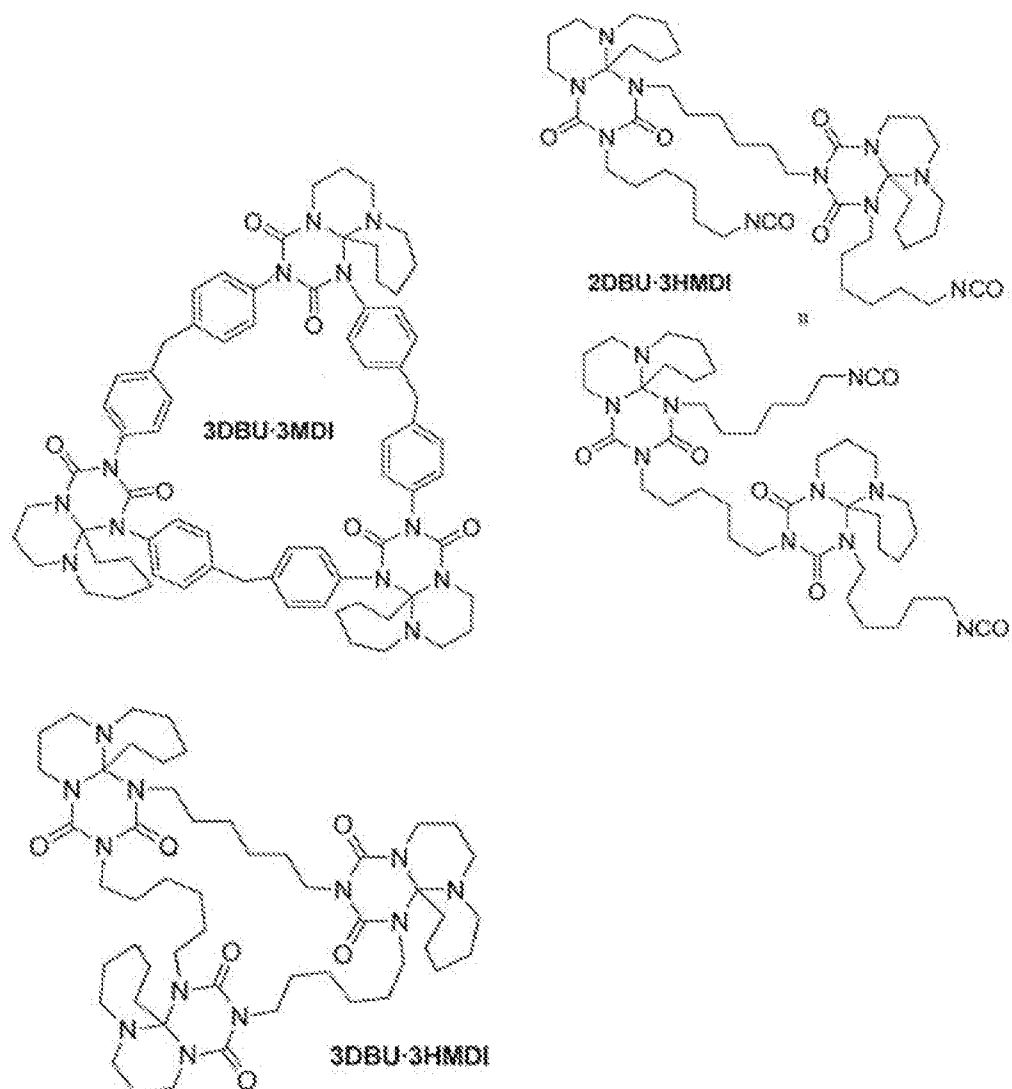


DBU-Cyclohexylisocyanate



2DBU-3MDI





Claim 28. The method of any of claims 18 to 27, wherein the solvent is a polar aprotic solvent.

Claim 29. A method comprising:

- a. forming a two-component polyurethane adhesive by contacting a polyol component and an isocyanate component and employing the adduct formed in accordance with the method of any of claims 18 to 28, wherein the adduct is located in the polyol component or the isocyanate component;

- b. applying the adhesive to a first substrate;
- c. contacting a second substrate with the first substrate, with the two-component polyurethane adhesive disposed between the first substrate and the second substrate,
 - wherein latency of the two-component polyurethane adhesive after contacting the polyol component and the isocyanate component is about 8 minutes or greater.

Claim 30. The method of claim 29, wherein the adduct is located in the isocyanate component.

Claim 31. The method of claims 29 or 30, further comprising a step of heating the first substrate and the second substrate at a temperature for a time to fully cure the mixture to bond the two substrates together.

Claim 32. The method of any of claims 29 to 31, wherein at least one of the substrates is glass, a vehicle frame, a fiber-reinforced structure, or a combination thereof.

1/1

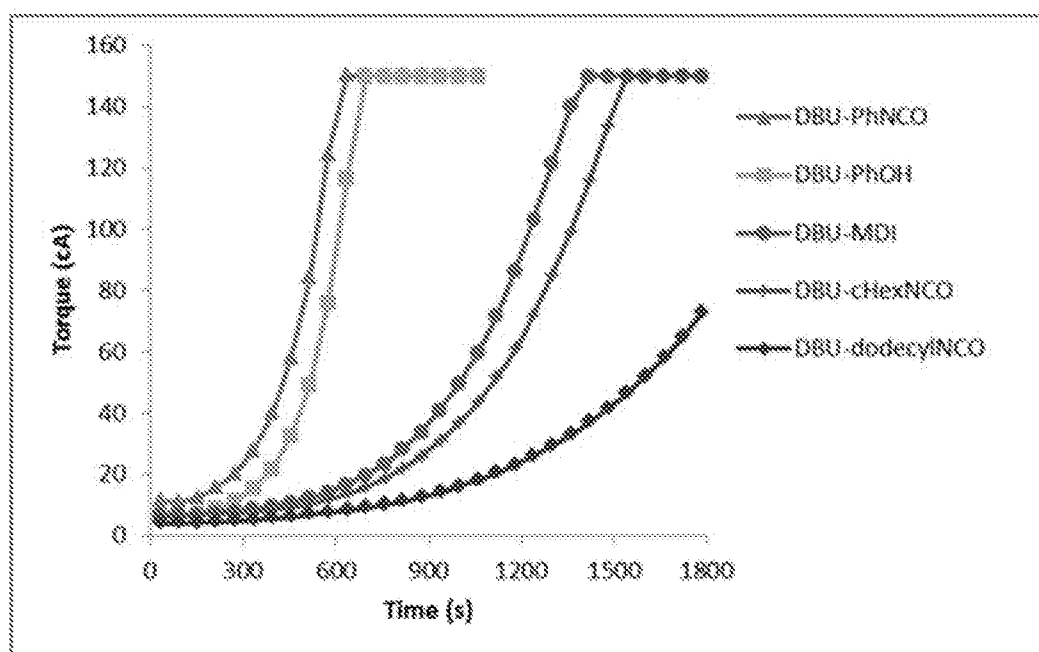


FIG. 1

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2017/063577

A. CLASSIFICATION OF SUBJECT MATTER		
INV.	C08G18/48	C08G18/50
	C08G18/32	C09J175/00
		C08G18/76
		C07D487/20
		C08G18/10
		C08G18/20
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 C07D		
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	I. POLENZ ET AL: "Thermally cleavable imine base/isocyanate adducts and oligomers suitable as initiators for radical homo- and copolymerization", POLYMER CHEMISTRY, vol. 5, no. 23, 2 September 2014 (2014-09-02), pages 6678-6686, XP055442161, GB ISSN: 1759-9954, DOI: 10.1039/C4PY01002G cited in the application Schemes 3 and 4; compounds 6a-d, 7a-d, 13a, b, 14a, b -----	15-28
X	JP S63 162718 A (HITACHI LTD) 6 July 1988 (1988-07-06) table 1 ----- -/--	15-28
☒ Further documents are listed in the continuation of Box C. ☒ See patent family annex.		
* Special categories of cited documents : "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier application or patent but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art "&" document member of the same patent family		
Date of the actual completion of the international search		Date of mailing of the international search report
25 January 2018		05/02/2018
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016		Authorized officer Lanz, Sandra

INTERNATIONAL SEARCH REPORT

International application No

PCT/US2017/063577

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	DE 197 11 225 A1 (HUELS CHEMISCHE WERKE AG [DE]) 24 September 1998 (1998-09-24) claim 1; table 1 -----	15-28
X	US 4 258 186 A (SCHOTT ANSGAR ET AL) 24 March 1981 (1981-03-24) examples 2,4,6,7,9,11 -----	15-17
X	US 4 546 165 A (GROEGLER GERHARD [DE] ET AL) 8 October 1985 (1985-10-08) examples 4,5 -----	15-17
X	US 4 200 725 A (GRAS RAINER [DE] ET AL) 29 April 1980 (1980-04-29) example 1 -----	15-17
X	DE 29 46 085 A1 (HUELS CHEMISCHE WERKE AG [DE]) 21 May 1981 (1981-05-21) example 1 -----	15-17
X	JÉROME ALSARRAF ET AL: "Cyclic Guanidines as Efficient Organocatalysts for the Synthesis of Polyurethanes", MACROMOLECULES, vol. 45, no. 5, 21 February 2012 (2012-02-21), pages 2249-2256, XP055440014, US ISSN: 0024-9297, DOI: 10.1021/ma2026258 Scheme 5; page 2255, left-hand column, paragraph 4 -----	18-28
X	JÉROME ALSARRAF ET AL: "Latent catalysts based on guanidine templates for polyurethane synthesis", POLYMER CHEMISTRY, vol. 4, no. 4, 21 December 2012 (2012-12-21), page 904, XP055442163, GB ISSN: 1759-9954, DOI: 10.1039/c2py21006a cited in the application page 905, left-hand column, paragraph 1; compounds 4a,4b ----- -/--	18-28

INTERNATIONAL SEARCH REPORT

International application No

PCT/US2017/063577

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	ARYA AND S P SHENOY V P: "Synthesis of New Heterocycles: Part XIV-Synthesis of New Heterocycles by Addition of Isocyanates to Cyclic Amidines", INDIAN JOURNAL OF CHEMISTRY, SECTION B, COUNCIL OF SCIENTIFIC AND INDUSTRIAL RESEARCH (C S I R), DE, vol. 14, October 1976 (1976-10), page 763, XP009502930, ISSN: 0376-4699 compounds IIa-g, Va-g -----	18-28
X	REINHARD RICHTER: "Die Addition aromatischer Isocyanate an N-substituierte Amidine", CHEMISCHE BERICHTE, vol. 101, no. 9, September 1968 (1968-09), pages 3002-3009, XP055058335, ISSN: 0009-2940, DOI: 10.1002/cber.19681010907 compounds 18,19 -----	18-28
X	DE 26 40 964 A1 (BAYER AG) 16 March 1978 (1978-03-16) examples 1-3,5; table 1 -----	18-28
X	WO 2013/117379 A1 (EVONIK DEGUSSA GMBH [DE]; SCHMIDT FRIEDRICH GEORG [DE]; SPANGE STEFAN) 15 August 2013 (2013-08-15) examples 3,4 -----	18-28
A	EP 0 279 566 A2 (LORD CORP [US]) 24 August 1988 (1988-08-24) claims 1,7 -----	1-32
A	WO 2016/077511 A1 (3M INNOVATIVE PROPERTIES CO [US]) 19 May 2016 (2016-05-19) claims 1,4 -----	1-32
T	Anonymous: "Hydrocarbyl group", 18 January 2018 (2018-01-18), XP055441988, Retrieved from the Internet: URL: http://www.rsc.org/publishing/journals/prospect/ontology.asp?id=CHEBI:33248&MSID=b813992j [retrieved on 2018-01-18] the whole document ----- -/--	

INTERNATIONAL SEARCH REPORT

International application No

PCT/US2017/063577

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
T	Anonymous: "Hydrocarbon - Wikipedia", 20 September 2017 (2017-09-20), XP055417470, Retrieved from the Internet: URL:https://en.wikipedia.org/wiki/Hydrocarbon [retrieved on 2017-10-19] page 1, paragraph 1 -----	

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/US2017/063577

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
JP S63162718	A	06-07-1988	NONE
DE 19711225	A1	24-09-1998	NONE
US 4258186	A	24-03-1981	DE 2751805 A1 23-05-1979 DK 512878 A 20-05-1979 EP 0002096 A1 30-05-1979 JP S5484584 A 05-07-1979 US 4258186 A 24-03-1981
US 4546165	A	08-10-1985	BR 8500463 A 17-09-1985 CA 1239403 A 19-07-1988 DE 3403500 A1 08-08-1985 EP 0150790 A2 07-08-1985 ES 8602055 A1 16-11-1985 HU 202564 B 28-03-1991 JP H0410898 B2 26-02-1992 JP S60252619 A 13-12-1985 US 4546165 A 08-10-1985
US 4200725	A	29-04-1980	DE 2729704 A1 11-01-1979 DK 297978 A 02-01-1979 EP 0000232 A1 10-01-1979 IT 1096841 B 26-08-1985 JP S5444670 A 09-04-1979 US 4200725 A 29-04-1980
DE 2946085	A1	21-05-1981	NONE
DE 2640964	A1	16-03-1978	NONE
WO 2013117379	A1	15-08-2013	DE 102012201895 A1 14-08-2013 WO 2013117379 A1 15-08-2013
EP 0279566	A2	24-08-1988	AU 593201 B2 01-02-1990 CA 1307866 C 22-09-1992 DE 3886564 D1 10-02-1994 DE 3886564 T2 11-05-1994 EP 0279566 A2 24-08-1988 JP S63225678 A 20-09-1988 US 4742113 A 03-05-1988
WO 2016077511	A1	19-05-2016	CN 107001571 A 01-08-2017 EP 3020744 A1 18-05-2016 US 2017335046 A1 23-11-2017 WO 2016077511 A1 19-05-2016