MDI-BASED POLYURETHANE PREPOLYMER WITH LOW MONOMERIC MDI CONTENT

Inventors: Andrea Karen Smith, Macungie, PA (US); Richard Joseph Goddard, Souderton, PA (US); Evelyn Jennifer Lin Paulsen, Macungie, PA (US)

Correspondence Address:
AIR PRODUCTS AND CHEMICALS, INC.
PATENT DEPARTMENT
7201 HAMILTON BOULEVARD
ALLENTOWN, PA 181951501

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ABSTRACT
An MDI/polypropylene polyether prepolymer composition consisting essentially of at least 80 wt % perfect precursors and less than 2 wt % free MDI monomer suitable for use in polyurethane adhesive compositions optionally also comprising a curative for isocyanate groups.
MDI-BASED POLYURETHANE PREPOLYMER WITH LOW MONOMIC MDI CONTENT

CROSS-REFERENCE TO RELATED APPLICATIONS

[0001] This application is a divisional of application Ser. No. 09/883,278 filed 12 Apr. 2001, which is incorporated herein by reference in its entirety.

FIELD OF THE INVENTION

[0002] This invention relates to 4,4'-diphenylmethane diisocyanate (MDI) based polyurethane prepolymers having a controlled structure.

BACKGROUND OF THE INVENTION

[0003] Isocyanate terminated prepolymers are commonly used to produce polyurethane and/or polyurea products like elastomers, foams, coatings, adhesives, sealants, caulks, and binders. However, the prepolymer manufacturing process can often result in high residual concentrations of the polyisocyanates used in the prepolymer synthesis. The residual polyisocyanate can lead to potential health and safety issues, and may also be detrimental to the performance and attributes of the end use product. For example, residual polyisocyanate can lead to undesired losses in open time, product instability, increased moisture sensitivity and decreased adhesion due to migration of these molecules to the interface. Polyurethane prepolymers that contain controlled levels of residual polyisocyanate, preferably below 1 wt %, can reduce health and safety risks and improve end product performance.

[0004] Since residual polyisocyanate can pose significant health and safety risks as well as reductions in product performance, a number of products and processes have been introduced that offer reduced residual polyisocyanate levels. A variety of methods are taught in the patented art for reducing the residual isocyanate content of polyisocyanate adducts: wiped film evaporation, solvent aided distillation/co-distillation, molecular sieves, and solvent extraction.

[0005] JP 08176432 discloses preparing MDI with straight chain molecule with MW 250-4000 and two active hydrogens at an equivalent ratio (NCO/OH) of 2.5-10:1. Free MDI is vacuum distilled to 1 wt % or less. The examples show polytetramethylene glycol (PTMG) and ethylene glycol adipate.

[0006] U.S. Pat. No. 5,220,001 discloses preparing urethane prepolymers having low levels of residual organic diisocyanate. The examples show only prepolymers made from toluene diisocyanate TDI, isophorone diisocyanate IPDI and methylene-bis(4-cyclohexyl)-diisocyanate] CHDI.

[0007] U.S. Pat. No. 5,703,193 discloses a process for reducing the amount of residual organic diisocyanate monomer in a polyurethane prepolymer reaction product by distilling in the presence of an inert solvent blend, one with boiling point above the monomer and one with boiling point below. Comparative examples show the removal of MDI monomer from a PTMEG 1000/MDI prepolymer reaction product.

[0008] U.S. Pat. No. 5,441,080 discloses a reactive hot melt composition comprising a polyester polyether thermoplastic elastomer and a polyisocyanate prepolymer. A MDI/PTMEG prepolymer is shown blended with a thermoplastic copolymer.

[0009] U.S. Pat. No. 6,133,415 discloses a reactive hot melt composition method for making a polyurethane prepolymer. The examples show MDI/PTMEG prepolymers processed to give free MDI.

[0010] U.S. Pat. No. 4,888,442 discloses a process for reducing the free monomer content of a polyisocyanate adduct by treating the adduct with 2-30 wt % inert solvent in an agitated thin-layer evaporator under conditions sufficient to reduce the free monomer content of the polyisocyanate adduct mixture below that level which is obtainable in the absence of a solvent. There are no examples showing the use of MDI as a suitable diisocyanate to prepare the polyisocyanate adduct.

[0011] U.S. Pat. No. 5,825,146 discloses an isocyanate-terminated polyurethane prepolymer comprising the reaction product of a polyisocyanate and a particular polyol composition. While the examples show the use of polypropylene oxide glycols, only TDI was used as the polyisocyanate.

[0012] EP 0 827 995 discloses hot melt adhesives comprising a polyisocyanate prepolymer prepared by reacting a polyisocyanate with a functionality of at least 2 with a polyol having a functionality of at least 2, the reaction product comprising at least 90 wt % “perfect” prepolymer and less than 2 wt % unreacted isocyanate monomer and the prepolymer having a free NCO functionality ranging from 2 to 8 wt %.

[0013] Airthane® prepolymers marketed by Air Products and Chemicals, Inc. are controlled structure prepolymer compositions. These prepolymer compositions which are based on TDI and IPDI contain >90 wt % perfect 2:1 prepolymer adducts, i.e., <10 wt % oligomer, and <0.1 wt % residual monomeric isocyanate.

[0014] We have found that 4,4'-diphenylmethane diisocyanate/polypropylene glycol (MDI/PPG) prepolymers low in free MDI monomer content can be synthesized which show performance advantages over conventional MDI/PPG prepolymers.

SUMMARY OF THE INVENTION

[0015] The present invention is directed to a controlled structure isocyanate terminated prepolymer composition based on the reaction of 4,4'-diphenylmethane diisocyanate (MDI) with a polyol composition comprising a propylene oxide based polyether polyl. The prepolymer reaction product has low levels of residual MDI monomer and low oligomer content. The residual, or free, MDI monomer content is less than 2 wt % of the prepolymer composition.

[0016] The MDI prepolymer composition is the product resulting from the reaction of a polypropylene polymer polyl containing “n” (at least 2) OH groups and an MDI-type polyisocyanate. The MDI/polyol prepolymer reaction product comprises oligomers and “perfect” prepolymers. The requisite low oligomer content of the prepolymer composition is 20 wt % or, reciprocally, it can be expressed in terms of its “perfect” prepolymer content which should be 80 wt %.
The prepolymer of the present invention in terms of stoichiometry is a prepolymer of n MDI molecules and one polypropylene polyester polyol molecule. The stoichiometric proportions for the MDI and polyol in the reaction products are 2:1 in the case of diols and 3:1 for triols. The perfect prepolymer is essentially an adduct containing only one molecule of the polyol in each prepolymer molecule. The invention requires that this polyisocyanate prepolymer reaction product (1) consists essentially of at least 80 wt % of a stoichiometric “perfect” prepolymer and (2) contains less than 2 wt % unreacted MDI monomer.

Also provided is a method for adhesively joining or sealing two substrates using such MDI/polypropylene polyester polyol prepolymer compositions as adhesives. The method generally comprises

1. Applying onto a substrate a urethane adhesive composition comprising the controlled structure MDI/polypropylene polyester prepolymer reaction product having the defined low levels of oligomers and free MDI monomer, and

2. Contacting the adhesive composition disposed on the substrate to a second substrate such that a bond is formed.

Advantages associated with the use of such controlled structure isocyanate prepolymer include

- An ability to formulate adhesives that show improved bond strength compared to those formulated using conventionally prepared isocyanate terminated prepolymer,
- An ability to formulate adhesives showing improved ambient, or room, temperature development of bond
- The ability to tailor oligomer content and monomer content for controlling properties like viscosity, processability, and the health and safety benefits associated with lower levels of volatile diisocyanate monomer content.
- An ability to formulate laminating adhesives showing longer pot lives while maintaining faster development of adhesive strength.

Detailed description of the invention

This invention relates to certain polyurethane prepolymer compositions based on the reaction of an MDI-type polyisocyanate and a polyol composition comprising a polypropylene polyester polyol, the prepolymer compositions having a low level of residual MDI monomer and a low oligomer content. These prepolymer are controlled structure polyurethane prepolymer comprising the reaction product of an MDI-type polyisocyanate (A) having a functionality (f) of at least two, and a polypropylene polyester polyol (B) of functionality (f) ≥ 2. The prepolymer reaction product should contain free prepolymer NCO functionality ranging from 0.2 to 15 wt %. The molecular weight distribution, i.e., distribution of perfect prepolymer to high order oligomers, is controlled in these prepolymer compositions as well as the amount of free MDI monomer content. Thus the prepolymer compositions contain free prepolymer NCO ranging from 0.2 to 15 wt % preferably 0.5 to 8 wt %, and less than 2 wt % unreacted MDI monomer, preferably less than 1 wt %, and most desirably less than 0.5 wt %. At least 80 wt %, preferably 90 wt %, of the prepolymer reaction product obtained by the reaction of the MDI-type polyisocyanate with the polyol should comprise “perfect” prepolymer, or reciprocally no more than 20 wt % oligomers, preferably no more than 10 wt % oligomers.

A “perfect” prepolymer, or adduct, is the perfect end capping product of a polypropylene polyester polyol (B) with n MDI molecules (A), where n=the functionality (f) of B. For a difunctional B, the perfect prepolymer is represented as A:B:A. Oligomers, for a difunctional B (n=2), are any species with a composition greater than the perfect 2:1 molecular ratio (A:B:A), for example 3:2 (A:B:A:B:A) or 4:3 (A:B:A:B:A:B:A). For a trifunctional B (n=3), the perfect prepolymer is represented as B:3A. Oligomers in this instance are any species with a composition greater than the perfect 3:1 molecular ratio.

The urethane adhesive composition used in the present method comprises the above-described MDI/polypropylene polyester prepolymer reaction product which can be prepared by reacting an MDI-type polyisocyanate having an NCO functionality of at least 2 with a polypropylene polyester polyol, preferably the reaction in an NCO:OH equivalent ratio of ≥ 4:1, preferably 6:10:1. The unreacted MDI monomer in the prepolymer reaction product is removed by distillation or other treatment to a concentration of < 2 wt %, preferably < 1 wt %, most preferably < 0.5 wt %. The prepolymer reaction product should contain prepolymer isocyanate, i.e., free prepolymer NCO functionality, ranging from 0.2 to 15 wt %, preferably 0.5 to 8 wt %.

Such MDI/polypropylene polyester polyol prepolymer may be prepared according to the teachings of U.S. Pat. Nos. 4,786,703 and 5,202,001, which disclosures are incorporated by reference.

The prepolymer reaction products are prepared using MDI as exemplified by the polyisocyanates of the diphenylmethane series - including, but not limited to various isomeric mixtures of MDI and/or polymeric MDI (MDI); isomeric mixtures of MDI containing 30 - 98 wt % of 4,4’ isomer, 2-70 wt % of the 2,4’ isomer, and 0-5 wt % of the 2,2’ isomer (with the wt % totaling 100%); polymethylene poly(phenylisocyanate) having an average isocyanate functionality of 2.1 to 3.5, isocyanate group content of 18.0 to about 33.6, and containing about 30 to 95 wt % monomeric 4,4’ MDI, about 2-70 wt % monomeric 2,4’ MDI, and less than 5 wt % monomeric 2,2’ MDI, and from 2 to 60 wt % higher ring homologues of the MDI series (with the wt % totaling 100%).

Suitable polypropylene oxide based polypolyols, also known as polypropylene glycols (PPG), include, but are not limited to, polypropylene polyester polyls with functionality of two or greater, average equivalent weight between 100 and 8000. Also included are ethylene oxide capped PPGs and low monol containing PPGs, marketed as Acclaim® polyls from Bayer. Additionally polyls which may be used at 0 to 60 wt % of the polyol composition include other di- or multi-functional alkylene ether polyols like PTMEG and polyethylene oxide, polyester polyls, polyester polyls from polyacrylates and hydroxyl terminated polybutadienes.
The above polyether and polyester polyols are commonly used for producing polyurethane prepolymers and can be blended such that the polyol composition (single or blend) used in making the prepolymer typically has an average Mn ranging from about 400 to 16,000, and typically from 700 to about 8000.

In the preferred prepolymer synthesis, it is important to maintain a high equivalent ratio of MDI to the polyol, e.g., a range from 4 to 20:1. As the level of MDI to polyol approaches 4:1 and then stoichiometric, greater quantities of higher molecular weight oligomers are formed which detract from the handling and/or performance characteristics of the urethane prepolymer composition. Preferably, the equivalent ratio of MDI to polyol in the reaction is from 6 to 10:1 equivalents of MDI to polyol to produce oligomers at less than 20 wt %, preferably less than 10 wt %.

In addition to the MDI/polypropylene polyether prepolymer, the urethane adhesive composition optionally contains a curative composition as is well known in the art. Suitable curative compositions include diamines, polyols, or blends thereof, as well as optional catalyst, thickening agent, or drying agent. Examples of diamines include both aromatic and aliphatic diamines, primary and secondary amine terminated polyether polyols, and difunctional, trifunctional, and polymeric amines. Examples of polyols include polyether or polyester polyols, which can be diols, triols and tetrals, having primary, secondary and/or tertiary alcohol groups. These polyols may be mixed with the diamines. Optional catalysts include tertiary amine catalysts and suitable organometallic catalysts, such as those derived from tin, zirconium, and bismuth. Other optional additives include thickening, coloring and drying agents.

Substrates that may be bonded with the adhesive include cold rolled steel, aluminum, fiberglass reinforced polyester (FRP), sheet molding compound (SMC), plastics, wood, and glass.

The following materials were used in the Examples:

- Arco® PPG 725, from Bayer Corp.
- Arco® PPG 2025, from Bayer Corp.
- Tri(propylene)glycol (TPG), from Morton Thiokol.
- Quadrol® polyol from BASF Corp.
- Microstuff 325F talc from Barretts Minerals Inc.
- Cab-o-sil TS 720 fumed silica from Cabot Corp.
- Aluminum Powder, 325 Mesh, Grade 101, from Tosal America Inc.
- Microbeads (10 mil), from Cataphote.
- Zinc coated cold rolled steel (Zn CRS) from ACT Laboratories, Inc.
- Mondur M (MDI) from Bayer Corp.
- Oriented polypropylene (OPP) film Bicor® SPW or AQS from Mobil Chemical Corp.
- Polyethylene Adipate (PEA) 550 of Mn.
- 1,4-Butanediol (BDO) from BASF Corp.

EXAMPLE 1

4186 g of Methylene diisocyanate (MDI) were added to a reactor and heated to 80°C. 1264 g of PPG 725 was then added. The reaction temperature was held at 80°C overnight. Excess residual MDI was removed by distillation under reduced pressure from the reaction product to a level of 0.63 wt % residual MDI, and total % NCO content of 6.74%.

EXAMPLE 2

606 g of MDI were added to a reactor and heated to 80°C. 897 g of PPG 725 was then added. The reaction temperature was held at 80°C overnight. The reaction product had a % NCO content of 6.49%.

EXAMPLE 3

4192 g of MDI were added to a reactor and heated to 80°C. 1143 g of PPG 2025 and 246 g of tri(propylene)glycol (TPG) was then added. The reaction temperature was held at 80°C overnight. Excess residual MDI was removed by distillation under reduced pressure from the reaction product to a level of 0.40 wt % residual MDI, and total % NCO content of 6.57%.

EXAMPLE 4

604 g of MDI were added to a reactor and heated to 80°C. 812 g of PPG 2025 and 174 g of tri(propylene)glycol (TPG) was then added. The reaction temperature was held at 80°C overnight. The reaction product had a % NCO content of 6.60%.

Table 1 presents the % NCO, residual free MDI and oligomer content for the MDI/PPG prepolymers of Examples 1-4.

<table>
<thead>
<tr>
<th>Example</th>
<th>Polyol</th>
<th>% NCO</th>
<th>residual MDI (wt %)</th>
<th>% oligomer</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>PPG725</td>
<td>6.74</td>
<td>0.63</td>
<td>4</td>
</tr>
<tr>
<td>2</td>
<td>PPG725</td>
<td>6.49</td>
<td>&gt;5</td>
<td>&gt;50</td>
</tr>
<tr>
<td>3</td>
<td>PPG2025/TPG</td>
<td>6.57</td>
<td>0.40</td>
<td>8</td>
</tr>
<tr>
<td>4</td>
<td>PPG2025/TPG</td>
<td>6.60</td>
<td>&gt;5</td>
<td>&gt;50</td>
</tr>
</tbody>
</table>

EXAMPLE 5

The prepolymer compositions of Examples 1-4 were evaluated in the following structural adhesive composition by room temperature curing on a Zn CRS substrate:

<table>
<thead>
<tr>
<th>Part A</th>
<th>wt %</th>
<th>Part B</th>
<th>wt %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Prepolymer (1-4)</td>
<td>60</td>
<td>Arco® PPG2025</td>
<td>16.7</td>
</tr>
<tr>
<td>Aluminum Powder</td>
<td>38</td>
<td>Quadrol®</td>
<td>33.3</td>
</tr>
<tr>
<td>Cab-o-sil TS720</td>
<td>2</td>
<td>Microstuff 325 F</td>
<td>27</td>
</tr>
<tr>
<td>Cab-o-sil TS720</td>
<td>1</td>
<td>Aluminum Powder</td>
<td>22</td>
</tr>
</tbody>
</table>

The adhesive was prepared by mixing Part A and Part B in an NCO:OH ratio of 1.0:0.9 while adding 1 wt % of microbeads. The adhesive mixture was then applied to one
side of a 1”x4” (2.54x10.16 cm) substrate coupon to cover at least 0.5 in² (3.23 cm²) of area then mated with a second substrate coupon to give a total lap shear overlap of 0.5 in² (3.23 cm²). Samples were cured at room temperature and 50% humidity. Samples were prepared and tested according to ASTM D1002 after 1 day and 7 days. All testing done at room temperature.

**TABLE 2**

<table>
<thead>
<tr>
<th>Prepolymer</th>
<th>Cure</th>
<th>Shear strength (psi) after 1 day</th>
<th>Shear strength (psi) after 7 days</th>
<th>% Cure (1 d/7 d)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ex 1</td>
<td>RT</td>
<td>1240</td>
<td>1452</td>
<td>85</td>
</tr>
<tr>
<td>Ex 2</td>
<td>RT</td>
<td>981</td>
<td>1367</td>
<td>72</td>
</tr>
<tr>
<td>Ex 3</td>
<td>RT</td>
<td>1324</td>
<td>1617</td>
<td>82</td>
</tr>
<tr>
<td>Ex 4</td>
<td>RT</td>
<td>874</td>
<td>1684</td>
<td>52</td>
</tr>
</tbody>
</table>

The data in Table 2 shows that structural adhesives exhibiting fast room temperature cure on zinc cold rolled steel (Zn CRS), i.e. high % cure (1d/7d), can be prepared with the low monomeric, low oligomer MDI/polypropylene polyether prepolymer in Examples 1 and 3 according to the invention.

**EXAMPLE 6**

The prepolymer compositions of Examples 1-4 were evaluated in a two component laminating adhesive composition prepared by mixing the prepolymer with polyethylene adipate (MW 550) at the NCO-OH ratio show in Table 3. The substrate was an oriented polypropylene (OPP) film (Mobil Bicor® SPW or AQ5). Laminates were prepared by applying the adhesive to a corona treated film, drawing down the adhesive with a 0 size teflon treated rod, mating with a second sheet of corona treated film, and cutting the laminate into 1 inch (2.54 cm) strips. The laminate was heat sealed at 186°F (85°C) for 2 minutes and placed in a 350°C oven for one hour before testing. The 180° peel strength of the films was obtained by pulling the two ends of a thin strip of film from a 180° configuration at a crosshead speed of 12 in/minute (30.4 cm/minute) for a total distance of 1 inch on an Instron testing machine. Report average peel strength (psi) as determined by an Instron method perimeter. This perimeter is usually displacement, where the average peel results are calculated between two set points; an initial starting point (after initial load) and ending after 1 inch of sample peel. The pot life or working life of the laminating adhesive compositions was also determined. Pot life was defined as the time when the adhesive composition can no longer be drawn down effectively. The data are shown in Table 3.

**TABLE 3**

<table>
<thead>
<tr>
<th>Prepolymer</th>
<th>Pot Life (hours)</th>
<th>T-peel Strength (psi) after x hours</th>
</tr>
</thead>
<tbody>
<tr>
<td>Example</td>
<td>NCO-OH</td>
<td>Film</td>
</tr>
<tr>
<td>1</td>
<td>1.03%:1</td>
<td>AQ5</td>
</tr>
<tr>
<td>2</td>
<td>1.05%:1</td>
<td>SPW</td>
</tr>
<tr>
<td>3</td>
<td>1.11%:1</td>
<td>SPW</td>
</tr>
<tr>
<td>4</td>
<td>1.11%:1</td>
<td>SPW</td>
</tr>
</tbody>
</table>

The low monomeric, low oligomer prepolymer of Example 3 showed superior modulus, tensile strength and % elongation in comparison to Example 4.

**STATEMENT OF INDUSTRIAL APPLICATION**

The invention is a controlled structure MDI/PPG polyurethane prepolymer composition for making products like elastomers, foams, coatings, adhesives, sealants, caulks, and binders.

We claim:

1. A prepolymer composition comprising the reaction product of 4,4’-diphenylmethane diisocyanate with a polyl composition comprising a propylene oxide based polyether polyl and consisting essentially of at least 80 wt% % perfect prepolymer and less than 2 wt% free MDI monomer.
2. The prepolymer composition of claim 1 in which the 4,4’-diphenylmethane diisocyanate comprises isocyanate mixtures of MDI and/or polymeric MDI.
3. The prepolymer composition of claim 1 in which the 4,4’-diphenylmethane diisocyanate comprises an isocyanate mixture of MDI containing 30-58 wt% of 4,4’ isomer, 2-70 wt% of the 2,4 isomer, and 0-5 wt% of the 2,2’ isomer (with the wt% totaling 100%); and/or polyol poly(phenylisocyanate) containing a greater isocyanate functionality of 2.1 to 3.5; isocyanate group content of 14.0 to about 33.6, and containing about 30 to 96 wt% % monomeric 4,4’ MDI, about 2-70 wt% % monomeric 2,4’ MDI, and less than 5 wt% monomer 2,2’ MDI, and from 2-60 wt% % higher ring homologues of the MDI series (with the wt% totaling 100%)
4. The prepolymer composition of claim 1 in which the propylene oxide based polyether polyl is a polypropylene polyether polyl with functionality of two or greater and an average equivalent weight between 100 and 3000.
5. The prepolymer composition of claim 1 in which the propylene oxide based polyether polyl is an ethylene oxide capped polypropylene polyether polyl.
6. The prepolymer composition of claim 1 in which 0 to 60 wt% % of the polyol composition comprises a di- or
multi-functional alkylene ether polyol, a polyester polyol, a polyester polyol from polycaprolactones or a hydroxyl terminated polybutadienes.

7. The prepolymer composition of claim 1 consisting essentially of at least 90 wt % perfect prepolymer.

8. The prepolymer composition of claim 1 consisting essentially of less than 1 wt % free MDI monomer.

9. The prepolymer composition of claim 1 containing a free prepolymer NCO functionality ranging from 0.2 to 15 wt %.

10. The prepolymer composition of claim 1 in which each polyol composition has an average Mn ranging from about 400 to 16,000.

11. A prepolymer composition comprising the reaction product of 4,4'-diphenylmethane diisocyanate with a polyol composition comprising a polypropylene polyether polyol with functionality of two or greater and an average equivalent weight between 100 and 8000 and consisting essentially of at least 90 wt % perfect prepolymer, less than 2 wt % free MDI monomer and a free prepolymer NCO functionality ranging from 0.2 to 15 wt %.

12. The prepolymer composition of claim 11 in which the 4,4'-diphenylmethane diisocyanate comprises an isomeric mixture of MDI containing 50-98 wt % of 4,4' isomer, 2-70 wt % of the 2,4' isomer, and 0-5 wt % of the 2,2' isomer (with the wt % totaling 100%); and/or polymethylene poly(phenylisocyanate) having an average isocyanate functionality of 1.0 to 3.5, isocyanate group content of 18.0 to about 33.6, and containing about 30 to 95 wt % monomeric 4,4' MDI, about 2-70 wt % monomeric 2,4' MDI, and less than 5 wt % monomeric 2,2' MDI, and from 2-60 wt % higher homologues of the MDI series (with the wt % totaling 100%).

13. The prepolymer composition of claim 11 in which the propylene oxide based polyether polyol is an ethylene oxide capped polypropylene polyether polyol.

14. The prepolymer composition of claim 11 in which 0 to 60 wt % of the polyol composition comprises a di- or multi-functional alkylene ether polyol, a polyester polyol, a polyester polyol from polycarbonate or a hydroxyl terminated polybutadiene.

15. The prepolymer composition of claim 14 consisting essentially of less than 0.5 wt % free MDI monomer containing a free prepolymer NCO functionality ranging from 0.5 to 8 wt %.

16. The prepolymer composition of claim 15 in which the polyol composition has an average Mn ranging from about 400 to 16,000.

17. In a polyurethane adhesive composition comprising a polyurethane prepolymer composition and, optionally, an isocyanate-reactive curative, the improvement which comprises the prepolymer composition of claim 1.

18. In a polyurethane adhesive composition comprising a polyurethane prepolymer composition and, optionally, an isocyanate-reactive curative, the improvement which comprises the prepolymer composition of claim 11.

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