

IMPACT RESISTANT POLYURETHANE AND METHOD OF MANUFACTURE THEREOF

This application is a continuation-in-part of U.S. Serial No. 08/595,262, which is a continuation-in-part of U.S. Serial No. 08/382,562, both of which are incorporated herein by reference.

BACKGROUND

Field of the Invention

The present invention relates to a rigid, optically transparent heat and impact resistant polyurethane.

Background of the Invention

Currently, the standard material to which all optically transparent plastic materials are compared to for impact resistance is polycarbonate. These materials can be characterized by impact resistance and the temperature and pressure at which the material undergoes distortion. The heat distortion temperature of polycarbonate is about 280°F at 264 psi fiber stress.

Polycarbonate extruded sheet at a thickness of 0.25 inches has a 0.22 caliber FSP (fragment simulating projectile) V-50 impact rating of 925 ft./sec. The V-50 is the measure of the velocity at which 50% of 22-caliber projectiles fired through a 0.25 inch polycarbonate sheet penetrate a 20 millimeter-thick 2024 T6 aluminum sheet (the "witness sheet") placed 6 inches behind the back surface of the polycarbonate sheet.

U.S. Patent No. 3,866,242, which is incorporated herein by reference, discloses a polyurethane polymer protective shield. The polyurethane is produced by:

(a) reacting either a polyether glycol or a polyester glycol having a molecular weight of from about 700 to 1,000 with methylenebis(cyclohexyl isocyanate) in an equivalent ratio of about three NCO to each hydroxyl to form a prepolymer, and

(b) reacting the prepolymer with an aromatic amine curing agent having a methylene bridge between two aromatic rings, such as 4,4'-methylenebis(2-chloroaniline), in an equivalent ratio of 0.90 to 1.04 $\text{NH}_2/1.0 \text{ NCO}$.

U.S. Patent No. 4,808,690, which is incorporated by reference herein, discloses a transparent polyurethane polymer made from a polyol cured prepolymer. The prepolymer is made from a polyisocyanate and at least one multifunctional hydroxy-containing intermediate.

U.S. Patent No. 4,208,507 discloses a flexible polyurethane-urea elastomer prepared by reacting: (A) a prepolymer obtained by reacting an essentially difunctional polyhydroxy compound having a molecular weight of from 600 to 10,000, and an organic diisocyanate having at least one NCO group bonded to a cycloaliphatic structure, in amounts which provide a total OH:NCO ratio of from 1:1.2 to 1:10, with (B) 3,3', 5,5'-tetramethyl-4,4'-diamino-diphenylmethane, A and B being reacted in a molar ratio of from about 1:0.8 to 1:1.2.

SUMMARY OF THE INVENTION

The optically clear polyurethane of this invention can be prepared by first producing a prepolymer by reacting one or more polyester glycols, polycaprolactone glycols, polyether glycols, or polycarbonate glycols having a weight average molecular weight of from about 400 to about 2000 with a cycloaliphatic diisocyanate in an equivalent ratio of about 2.5 to 4.0 NCO for each OH. The prepolymer is then reacted with an aromatic diamine curing agent such as diethyltoluene diamine in an equivalent ratio of about 0.85 to 1.02 $\text{NH}_2/1.0 \text{ NCO}$, preferably about 0.90 to 1.0 $\text{NH}_2/1.0 \text{ NCO}$, and more preferably about 0.92 to 0.96 $\text{NH}_2/1.0 \text{ NCO}$.

The polyurethane of the present invention is particularly useful for transparency applications that require excellent impact resistance coupled with high heat distortion temperatures, such as architectural glazings, vehicle glazings, riot shields, aircraft canopies, face masks, visors, ophthalmic and sun lenses, protective eyewear, and transparent armor.

One object of this invention is to provide transparent polyurethanes having excellent optical clarity, excellent ballistic properties, high chemical resistance, and high heat distortion temperatures compared to prior art materials.

Another object of this invention is to provide reduced cost transparent impact resistant polyurethanes for commercial applications.

Yet another object of this invention is to enhance production processing of transparent impact resistant polyurethanes by decreasing reaction time, processing temperature, and mold residence time.

These and other objects of the present invention are described in greater detail in the detailed description of the invention, the examples and the attached claims.

DETAILED DESCRIPTION OF THE INVENTION

The polyurethane of the present invention is prepared from cycloaliphatic diisocyanates, OH-containing intermediates, and aromatic diamine curing agents. The following is a detailed description of each of these constituents:

OH-Containing Intermediates

The OH-containing intermediates which can be used to prepare the polyurethanes of this invention include polyester glycols, polycaprolactone glycols, polyether glycols, and polycarbonate glycols having a weight average molecular weight of from about 400 to about 2000, preferably about 400 to about 1000.

Polyester glycols that can be used include the esterification products of one or more dicarboxylic acids having four to ten carbon atoms, such as adipic, succinic and sebacic acids, with one or more low molecular weight glycols having two to ten carbon atoms, such as ethylene glycol, propylene glycol, diethylene glycol, 1,4-butanediol, neopentyl glycol, 1,6-hexanediol

and 1,10-decanediol. Preferred polyester glycols are the esterification products of adipic acid with glycols of two to ten carbon atoms.

Polycaprolactone glycols that can be used include the reaction products of ϵ -caprolactone with one or more of the low molecular weight glycols listed above. In addition, useful OH-containing intermediates may include teresters produced from one or more low molecular weight dicarboxylic acids, such as adipic acid, and caprolactones with one or more of the low molecular weight glycols listed above.

The preferred polyester glycols and polycaprolactone glycols can be derived by well known esterification or transesterification procedures, as described, for example, in the article D.M. Young, F. Hostettler et al., "Polyesters from Lactone," Union Carbide F-40, p. 147.

Polyether glycols that can be used include polytetramethylene ether glycol.

Polycarbonate glycols that can be used include aliphatic polycarbonate glycols. Preferred aliphatic polycarbonate glycols are those manufactured and sold by Enichem under the tradename Ravecarb 102 (molecular weight = 1,000) and Ravecarb 106 (molecular weight = 2,000).

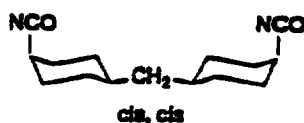
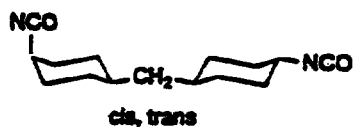
The most preferred OH-containing intermediates are: (a) esterification products of adipic acid with one or more diols selected from 1,4-butanediol, 1,6-hexanediol, neopentyl glycol, and 1,10-decanediol; (b) reaction products of ϵ -caprolactone with one or more diols selected from 1,4-butane diol, 1,6-hexane diol, neopentyl glycol, and 1,10-decanediol; (c)

polytetramethylene glycol; (d) aliphatic polycarbonate glycols, and (e) mixtures of such OH-containing intermediates.

Diisocyanates

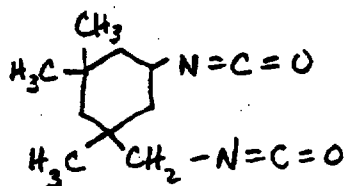
The cycloaliphatic diisocyanates which can be used to prepare the polyurethanes of this invention include dicyclohexylmethane diisocyanate and preferably isomeric mixtures thereof containing from about 20-100 percent of the trans,trans isomer of 4,4'-methylenebis(cyclohexyl isocyanate), hereinafter referred to as "PICM" (paraisocyanato cyclohexylmethane). Other components usually present in the mixtures of position and/or stereoisomers of the dicyclohexylmethane diisocyanate used in this invention are the cis,trans and cis,cis isomers of PICM and stereoisomers of 2,4'-methylenebis(cyclohexyl isocyanate). These, as well as the trans,trans PICM isomer, are present in amounts which can be controlled by the procedures used to prepare the dicyclohexylmethane diisocyanate. Preferred diisocyanates are isomeric PICM mixtures. An especially preferred mixture contains not less than about 20 percent of the trans,trans

isomer and no more than about 20 percent of the cis,cis isomer of 4,4'-methylenebis(cyclohexyl isocyanate). Three isomers of 4,4'-methylenebis(cyclohexyl isocyanate) are shown below:

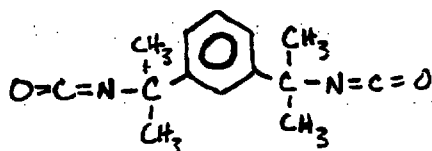


The PICM used in this invention is prepared by phosgenating the corresponding 4,4'-methylenebis(cyclohexyl amine) (PACM) by procedures well known in the art, as disclosed in, *e.g.*, U.S. Patent Nos. 2,644,007, 2,680,127, and 2,908,703, which are incorporated herein by reference. The PACM isomer mixtures, upon phosgenation, yield PICM in a liquid phase, a partially liquid phase, or a solid phase at room temperature. The PACM isomer mixtures can be obtained by the hydrogenation of methylenedianiline and/or by fractional crystallization of PACM isomer mixtures in the presence of water and alcohols such as methanol and ethanol.

Additional cycloaliphatic diisocyanates that may be used include 3-isocyanato-methyl-3,5,5-trimethyl cyclohexyl-isocyanate ("IPDI") from Arco Chemical, which has the following structural formula:



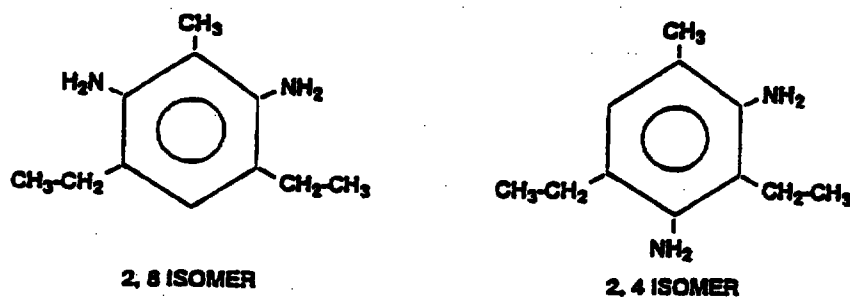
and meta-tetramethyl xylene diisocyanate ("TMXDI") from Cytex, Inc., which has the following structural formula:



Diamine Curing Agents

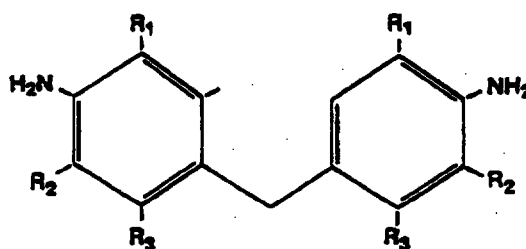
The preferred aromatic diamine curing agents for use in preparing the polyurethanes of the invention are 2,4-diamino-3,5-diethyl-toluene, 2,6-diamino-3, 5-diethyl-toluene and mixtures thereof (collectively "diethyltoluenediamine" or "DETDA"), which is sold by Albemarle

Corporation under the trade name Ethacure 100. DETDA is a liquid at room temperature with a viscosity of 156 cs at 25°C. DETDA is isomeric, with the 2,4-isomer range being 75-81 percent while the 2,6-isomer range is 18-24 percent. DETDA has the following structure:



The color stabilized version of Ethacure 100, which is available under the name Ethacure 100S, is particularly preferred.

Additional diamine curing agents for use in the present invention include compounds having the following chemical formula:



wherein R_1 and R_2 are each independently selected from methyl, ethyl, propyl, and isopropyl groups, and R_3 is selected from hydrogen and chlorine. Examples of the such additional diamine curing agents are the following compounds, manufactured by Lonza Ltd. (Basel, Switzerland):

LONZACURE® M-DIPA $R_1 = C_3H_7$; $R_2 = C_3H_7$; $R_3 = H$

LONZACURE® M-DMA: $R_1 = CH_3$; $R_2 = CH_3$; $R_3 = H$

LONZACURE® M-MEA: $R_1 = CH_3$; $R_2 = C_2H_5$; $R_3 = H$

LONZACURE® M-DEA: $R_1 = C_2H_5$; $R_2 = C_2H_5$; $R_3 = H$

LONZACURE® M-MIPA: $R_1 = CH_3$; $R_2 = C_3H_7$; $R_3 = H$

LONZACURE® M-CDEA: $R_1 = C_2H_5$; $R_2 = C_2H_5$; $R_3 = Cl$

wherein R_1 , R_2 and R_3 refer to the above chemical formula. Among these, the preferred diamine curing agent is 4,4'-methylenebis(3-chloro-2,6-diethylaniline), (Lonzacure® M-CDEA), which is also available from Air Products and Chemical, Inc. (Allentown, Pennsylvania). The foregoing diamine curing agents may be used in addition to or in place of DETDA, as a polyurethane curing agent.

Preparation of the Invention

The polyurethanes of this invention can be prepared by quasi-prepolymer or full prepolymer methods, both of which are well known in the art. The preferred method of preparing the polyurethanes according to the invention is as follows: The diisocyanate is first mixed with the OH-containing intermediate in an equivalent ratio of about 2.5 to 4.0 NCO/1.0 OH, preferably about 3.0 NCO/1.0 OH, and then reacted at 212° to 230°F for a period of 3 to 5 hours, or 260° to 265°F for 5 to 10 minutes, or 275° to

290°F for 3 to 5 minutes. The heat source is then removed, the prepolymer is cooled to about 160°F and allowed to stabilize at that temperature for about 24 hours prior to determining the percent NCO in the prepolymer. Additional diisocyanate can then be added to achieve an exact equivalent weight. The prepolymer is then reacted at about 160°F to 180°F with the aromatic diamine curing agent in an equivalent ratio of about 0.85 to 1.02 $\text{NH}_2/1.0 \text{ NCO}$, preferably about 0.90 to 1.0 $\text{NH}_2/1.0 \text{ NCO}$, and more preferably about 0.92 to 0.96 $\text{NH}_2/1.0 \text{ NCO}$. The polymer is then cured at 230-275°F for 4 to 24 hours. The curing time is longer at lower temperatures and shorter at higher temperatures.

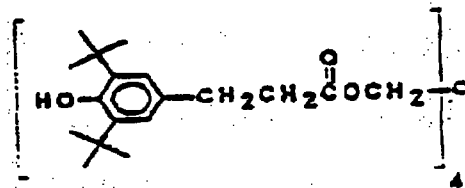
The polyurethane polymers of this invention can be cast or compression molded. Casting is the preferred method because it produces a polyurethane polymer with optimal optical characteristics.

The prepolymer and curing agent mixture is cast into a mold prior to curing. The polyurethane material according to the invention may also be partially cured, by selecting an appropriate curing time and temperature, and then removed from the casting molds and formed into the desired shape. Using this process, the polyurethane material can be formed into a simple or complex shape and then subsequently fully cured.

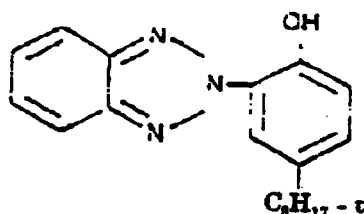
A triol may be added to the prepolymer in an amount sufficient to produce about one percent cross-linking based upon equivalents of reactants, for example 4 to 8% by weight based on total reactants. Triols that are useful in the present invention include trimethylol ethane and

trimethylol propane. The addition of a triol to the prepolymer increases the heat distortion temperature and in some cases improves the ballastic properties of the cured polyurethane.

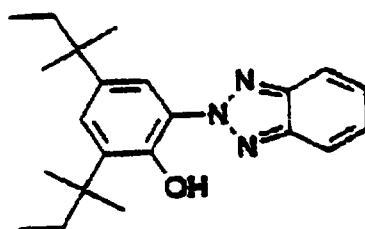
Various anti-oxidants, ultraviolet stabilizers, color blockers, optical brighteners, and mold release agents may be used in the preparation of the polyurethanes of this invention. For example, one or more anti-oxidants may be added to the prepolymer in an amount of up to 5% by weight based on total reactants. Anti-oxidants that are useful in the present invention include those of the multifunctional hindered phenol type. One example of a multifunctional hindered phenol type anti-oxidant is Irganox 1010, available from Ciba Geigy, which has the following chemical formula:



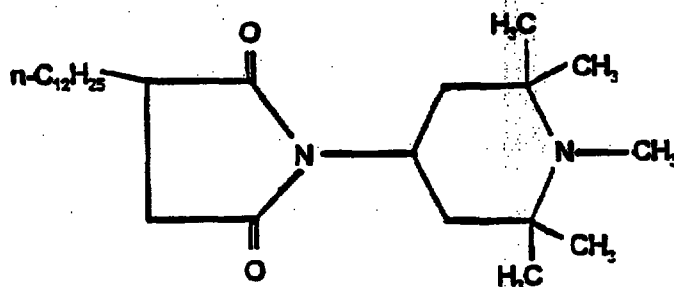
A UV-stabilizer may also be added to the prepolymer, either prior to or during the curing step, in an amount up to about 5.0%, preferably about 0.5 to 4.0% by weight based on total reactants. UV-stabilizers that are useful in the present invention include benzotriazoles. Examples of benzotriazole UV-stabilizers include Cyasorb 5411 and Tinuvin 328. Cyasorb 5411, available from American Cyanamid, has the following chemical formula:



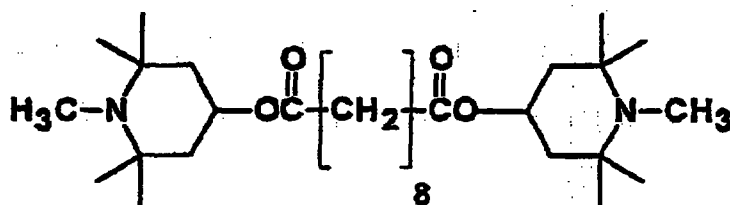
Tinuvin 328, available from Ciba Geigy, has the following chemical formula:



Another UV-stabilizer that may be used is Cyasorb 3604, available from American Cyanamid, which has the following chemical formula:



In addition to the benzotriazoles, a hindered amine light stabilizer may be added to further enhance UV protection. An example of a hindered amine light stabilizer is Tinuvin 765, available from Ciba-Geigy, which has the following chemical formula:



EXAMPLES I - VII

A cycloaliphatic diisocyanate is mixed with one or more polyester glycols, polycaprolactone glycols, polyether glycols, or polycarbonate glycols. The reactants are then heated to 275°F to 290°F under dry nitrogen, held at that temperature for 3 to 5 minutes, and allowed to react to form a prepolymer. The prepolymer is cooled to 220° to 250°F, and the UV stabilizer, anti-oxidant, color blocker, and/or optical brightener are added. The prepolymer is further cooled to 170° to 200°F and then evacuated and stored for 24 hours at 160°F. The percent NCO is then determined.

The prepolymer is then reacted at about 160°F to 180°F with an aromatic diamine curing agent in an equivalent ratio of 0.85 to 1.02 NH₂ to 1.0 NCO. The polymer is then cured at 230° to 275°F for 4 to 24 hours.

The reactants used in the Examples are described in Table I below:

TABLE I

Ingredient	Description	Available From
Ruco S-105-110	Polyester glycol prepared from adipic acid and 1,6 hexanediol; equivalent weight of about 500	Ruco Polymer Corp.
Ruco-S-105-210	Polyester glycol prepared from adipic acid and 1,6 hexanediol; equivalent weight of about 268	Ruco Polymer Corp.
Solvay Interrox 396-005	Polyester glycol prepared from E-caprolactone and 1,6-hexane diol; equivalent weight of about 387	Solvay Interrox
Solvay Interrox 524-021	Polyester glycol prepared from E-caprolactone and 1,6-hexane diol; equivalent weight of about 200	Solvay Interrox
Solvay Interrox 439-045	Polyester glycol prepared from E-caprolactone and 1,6-hexane diol; equivalent weight of about 954	Solvay Interrox
Ravecarb 102	Aliphatic polycarbonate glycol; equivalent weight of about 255	Enichem
Desmodur W	4,4'-methylenebis(cyclohexyl isocyanate) containing 20% of the trans, trans isomer and 80% of the cis, cis and cis, trans isomers	Bayer Corp.
Ethacure 100	2,4-diamino-3,5-diethyl-toluene and 2,6-diamino-3,5-diethyl-toluene	Albemarle Corporation
Ethacure 100S	2,4-diamino-3,5-diethyl-toluene and 2,6-diamino-3,5-diethyl-toluene with color stabilizer	Albemarle Corporation
Lonzacure® M-CDEA	4,4'-methylenebis(3-chloro-2,6-diethylaniline)	Lonza Ltd. (Basel, Switzerland); Air Products and Chemical, Inc. (Allentown, Pennsylvania).
Tinuvin 328	UV-stabilizer; see supra for chemical formula	Ciba Geigy
Tinuvin 765	UV-stabilizer; see supra for chemical formula	Ciba Geigy
Irganox 1010	Anti-oxidant; see supra for chemical formula	Ciba Geigy
Exalite Blue 78-13	Dye used as a color blocker	Exciton
Unitex OB	Optical brightener	Ciba Geigy

The amounts of each reactant used in each example are set forth in

Table II below:

TABLE II

Reactant	Example I	Example II	Example III	Example IV	Example V	Example VI	Example VII	Example VIII
Ruco S-105-110	1.0 equiv.	0.7 equiv.	0.4 equiv.					
Ruco S-105-210		0.3 equiv.	0.6 equiv.					
Solvay Interlox 396-005				0.5 equiv.				
Solvay Interlox 524-021				0.4 equiv.				
Solvay Interlox 439-045				0.1 equiv.				
Ravecarb 102					1.0 equiv.	1.0 equiv.	0.8 equiv.	0.8 equiv.
1,6 hexane diol							0.2 equiv.	0.2 equiv.
Desmodur W	3.0 equiv.	3.0 equiv.	3.0 equiv.	3.0 equiv.	3.0 equiv.	3.5 equiv.	3.0 equiv.	3.25 equiv.
Ethacure 100S ¹	0.93 equiv.	0.93 equiv.	0.93 equiv.	0.93 equiv.	0.93 equiv.	0.93 equiv.	0.93 equiv.	0.93 equiv.
Tinuvin 328	1.0 wt. %	1.0 wt. %	0.75 wt. %	0.75 wt. %	0.75 wt. %	0.75 wt. %	0.75 wt. %	0.75 wt. %
Tinuvin 765			0.75 wt. %	0.75 wt. %	0.75 wt. %	0.75 wt. %	0.75 wt. %	0.75 wt. %
Irganox 1010	0.40 wt. %	0.40 wt. %	0.40 wt. %	0.40 wt. %	0.40 wt. %	0.40 wt. %	0.40 wt. %	0.40 wt. %
Exalite Blue 78-13			1.25 ppm	1.25 ppm	1.25 ppm	1.25 ppm	1.25 ppm	1.25 ppm
Uvitex OB			0.60 ppm	0.60 ppm	0.60 ppm	0.60 ppm	0.60 ppm	0.60 ppm

¹ Amounts of Ethacure 100S (DETDA) are given in the number of equivalents NH_2 per 1.0 equivalent NCO as determined in the prepolymer.

The resulting materials are evaluated for their optical, hardness, solvent resistance, heat distortion, and ballistic properties.

The polyurethane materials of Examples I-IV all have excellent optical properties with haze as low as 0.3 percent, and luminous transmittance as high as 95% at a thickness of 0.080 to 0.250 inches. The Shore D hardness of Examples I-IV ranges from 79 to 82. For examples V-VIII, the Shore D hardness is 77 to 82.

The polyurethane materials of Examples I, II, and III have a stress craze resistance of >7000 pounds per square inch when measured using isopropanol.

The V-50 rating of Examples I-IV was evaluated using a 0.25 inch thick sheet and a 0.22 caliber fragment simulating projectile. After multiple tests, the average V-50 rating is about 1,210 feet per second.

For Examples I-III, the heat distortion temperature of a 0.25 inch thick sample at 264 psi fiber stress ranges from 290°F to 305°F, and a similar sample of the Example IV material has a heat distortion temperature of 270°F to 280°F at 264 psi fiber stress.

The heat distortion temperatures and ballistic properties for 0.25 inch thick samples of the Example V-VIII formulations are given in the following table:

TABLE III

Property	Example V	Example VI	Example VII	Example VIII
Heat distortion temperature, 264 psi fiber stress	126°C (259°F)	155°C (311°F)	145°C (293°F)	157°C (315°F)
V-50 0.22 caliber FSP rating	1,183 ft./sec.	1,233 ft./sec.	1,207 ft./sec.	1,169 ft./sec.

The foregoing disclosure of examples and other embodiments of the present invention has been presented for purposes of illustration and description. It is not intended to be exhaustive or to limit the invention to the precise examples and embodiments disclosed. Many variations and modifications of the examples and embodiments described herein will be obvious to one of ordinary skill in the art in light of the above disclosure. The scope of the invention is to be defined only by the claims appended hereto, and by their equivalents.

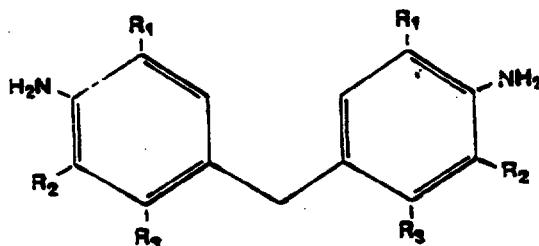
**WHAT IS CLAIMED IS:**

1. A transparent, high hardness, impact resistant polyurethane material comprising the reaction product of:

(a) a polyurethane prepolymer prepared by reaction of a cycloaliphatic diisocyanate with at least one OH-containing intermediate having a weight average molecular weight of from about 400 to about 2000 selected from the group consisting of polyester glycols, polycaprolactone glycols, polyether glycols, and polycarbonate glycols, and mixtures thereof in an equivalent ratio of about 2.5 to 4.0 NCO/1.0 OH; and

(b) at least one first aromatic diamine curing agent selected from the group consisting of 2,4-diamino-3,5-diethyl-toluene, 2,6-diamino-3,5-diethyl-toluene, and mixtures thereof in an equivalent ratio of about 0.85 to 1.02 NH₂/1.0 NCO.

2. The polyurethane of claim 1, wherein the polyurethane material is the reaction product of said polyurethane prepolymer, said at least one first aromatic diamine curing agent, and at least one second diamine curing agent selected from the group consisting of compounds of the formula:





wherein R_1 and R_2 are each independently selected from the group consisting of methyl, ethyl, propyl and isopropyl groups, and R_3 is selected from the group consisting of hydrogen and chlorine.

3. The polyurethane material of claim 1, wherein the cycloaliphatic diisocyanate is selected from the group consisting of 4,4'-methylenebis(cyclohexyl isocyanate), 3-isocyanato-methyl-3,5,5-trimethylcyclohexyl-isocyanate, meta-tetramethylxylene diisocyanate, and mixtures thereof.

4. The polyurethane material of claim 1, wherein the polyurethane material has a heat distortion temperature in the range of 210°F to 325°F at 264 psi.

5. The polyurethane material of claim 1, wherein the polyurethane material has a heat distortion temperature of at least 250°F at 264 psi.

6. The polyurethane material of claim 1, wherein the polyurethane material has a heat distortion temperature of at least 300°F at 264 psi.

7. The polyurethane material of claim 1, wherein the polyurethane material is optically clear having a luminous transmittance of at least about 80%.

8. The polyurethane material of claim 1, wherein a 0.25-inch thick sheet of the polyurethane material has a V-50 0.22 caliber FSP rating of at least 1100 feet per second.





9. The polyurethane material of claim 1, wherein the diamine curing agent is reacted with the prepolymer in an equivalent ratio of about 0.90 to 1.0 $\text{NH}_2/1.0 \text{NCO}$.

10. The polyurethane material of claim 1, wherein the weight average molecular weight of the OH-containing intermediate is from about 400 to about 1000.

11. The polyurethane material of claim 1, wherein the OH-containing intermediate is selected from the group consisting of: (a) esterification products of adipic acid with one or more diols selected from the group consisting of 1,4-butanediol, 1,6-hexanediol, neopentyl glycol, and 1,10-decanediol; (b) reaction products of E-caprolactone with one or more diols selected from the group consisting of 1,4-butane diol, 1,6-hexane diol, neopentyl glycol, and 1,10-decanediol; (c) polytetramethylene glycol; (d) aliphatic polycarbonate glycols; and (e) mixtures of such OH-containing intermediates.

12. The polyurethane material of claim 1, wherein the cycloaliphatic diisocyanate is an isomeric mixture of 4,4'-methylenebis(cyclohexyl isocyanate) which comprises at least 20 percent of the trans,trans isomer of 4,4'-methylenebis(cyclohexyl isocyanate).

13. The polyurethane material of claim 1, wherein the prepolymer further comprises a UV-stabilizer.





14. The polyurethane material of claim 13, wherein the UV-stabilizer is selected from the group consisting of benzotriazoles, hindered amine light stabilizers and mixtures thereof.

15. The polyurethane material of claim 1, wherein the prepolymer further comprises an anti-oxidant.

16. The polyurethane material of claim 16, wherein the anti-oxidant is a multifunctional hindered phenol.

17. The polyurethane material of claim 1, wherein the polyurethane material has a stress craze resistance of >7000 pounds per square inch when measured using isopropanol.

18. The polyurethane material of claim 1, wherein the prepolymer further comprises a triol in an amount sufficient to produce 1% cross-linking based upon equivalents of reactants.

19. The polyurethane material of claim 18, wherein the triol is selected from the group consisting of trimethylol ethane, trimethylol propane, and mixtures thereof.

20. A transparent, high hardness, impact resistant polyurethane material comprising the reaction product of:

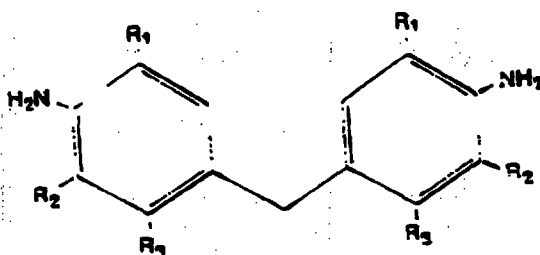
(a) a polyurethane prepolymer prepared by reaction of a cycloaliphatic diisocyanate with at least one OH-containing intermediate having a weight average molecular weight of from about 400 to about 2000 selected from the group consisting of polyester glycols, polycaprolactone





glycols, polyether glycols, and polycarbonate glycols, and mixtures thereof in an equivalent ratio of about 2.5 to 4.0 NCO/1.0 OH; and

(b) at least one aromatic diamine curing agent selected from the group consisting of 2,4-diamino-3,5-diethyl-toluene, 2,6-diamino-3,5-diethyl-toluene, compounds of the formula:



wherein R_1 and R_2 are each independently selected from the group consisting of methyl, ethyl, propyl and isopropyl groups, and R_3 is selected from the group consisting of hydrogen and chlorine and mixtures of such diamine curing agents in an equivalent ratio of about 0.85 to 1.02 $\text{NH}_2/1.0$ NCO, wherein the polyurethane material has a heat distortion temperature in the range of 210°F to 325°F at 264 psi.

21. The polyurethane material of claim 20, wherein the cycloaliphatic diisocyanate is selected from the group consisting of 4,4'-methylenabis(cyclohexyl isocyanate), 3-isocyanato-methyl-3,5,5-trimethylcyclohexyl-isocyanate, meta-tetramethylxylene diisocyanate, and mixtures thereof.





22. The polyurethane material of claim 20, wherein the polyurethane material has a heat distortion temperature of at least 250°F at 264 psi.

23. The polyurethane material of claim 20, wherein the polyurethane material has a heat distortion temperature of at least 300°F at 264 psi.

24. The polyurethane material of claim 20, wherein the polyurethane material is optically clear having a luminous transmittance of at least about 80%.

25. The polyurethane material of claim 20, wherein a 0.25-inch thick sheet of the polyurethane material has a V-50 0.22 caliber FSP rating of at least 1100 feet per second.

26. The polyurethane material of claim 20, wherein the diamine curing agent is reacted with the prepolymer in an equivalent ratio of about 0.90 to 1.0 NH₂/1.0 NCO.

27. The polyurethane material of claim 20, wherein the weight average molecular weight of the OH-containing intermediate is from about 400 to about 1000.

28. The polyurethane material of claim 20, wherein the OH-containing intermediate is selected from the group consisting of: (a) esterification products of adipic acid with one or more diols selected from the group consisting of 1,4-butanediol, 1,6-hexanediol, neopentyl glycol, and 1,10-decanediol; (b) reaction products of E-caprolactone with one or more





diols selected from the group consisting of 1,4-butane diol, 1,6-hexane diol, neopentyl glycol, and 1,10-decanediol; (c) polytetramethylene glycol; (d) aliphatic polycarbonate glycols; and (e) mixtures of such OH-containing intermediates.

29. The polyurethane material of claim 20, wherein the cycloaliphatic diisocyanate is an isomeric mixture of 4,4'-methylenebis(cyclohexyl isocyanate) which comprises at least 20 percent of the trans,trans isomer of 4,4'-methylenebis(cyclohexyl isocyanate).

30. The polyurethane material of claim 20, wherein the prepolymer further comprises a UV-stabilizer.

31. The polyurethane material of claim 30, wherein the UV-stabilizer is selected from the group consisting of benzotriazoles, hindered amine light stabilizers and mixtures thereof.

32. The polyurethane material of claim 20, wherein the prepolymer further comprises an anti-oxidant.

33. The polyurethane material of claim 32, wherein the anti-oxidant is a multifunctional hindered phenol.

34. The polyurethane material of claim 20, wherein the polyurethane material has a stress craze resistance of >7000 pounds per square inch when measured using isopropanol.

35. The polyurethane material of claim 20, wherein the prepolymer further comprises a triol in an amount sufficient to produce 1% cross-linking based upon equivalents of reactants.





36. The polyurethane material of claim 35, wherein the triol is selected from the group consisting of trimethylol ethane, trimethylol propane, and mixtures thereof.

37. A transparent, high hardness, impact resistant polyurethane material comprising the reaction product of:

(a) a polyurethane prepolymer prepared by reaction a cycloaliphatic diisocyanate selected from the group consisting of 4,4'-methylenebis(cyclohexyl isocyanate), 3-isocyanato-methyl-3,5,5-trimethylcyclohexyl-isocyanate, meta-tetramethylxylene diisocyanate, and mixtures thereof with at least one OH-containing intermediate having a weight average molecular weight of from about 400 to about 2000 selected from the group consisting of: (a) esterification products of adipic acid with one or more diols selected from the group consisting of 1,4-butanediol, 1,6-hexanediol, neopentyl glycol, and 1,10-decanediol; (b) reaction products of E-caprolactone with one or more diols selected from the group consisting of 1,4-butane diol, 1,6-hexane diol, neopentyl glycol, and 1,10-decanediol; (c) polytetramethylene glycol; (d) aliphatic polycarbonate glycols; and (e) mixtures of such OH-containing intermediates in an equivalent ratio of about 2.5 to 4.0 NCO/1.0 OH; and

(b) at least one diamine curing agent selected from the group consisting of 2,4-diamino-3,5-diethyl-toluene, 2,6-diamino-3,5-diethyl-toluene, and mixtures thereof, in an equivalent ratio of about 0.95



to 1.02 NH₂/1.0 NCO, wherein the polyurethane material has a heat distortion temperature of at least 300°F at 264 psi.



This Sheet Has Been Replaced

