



## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

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<b>(54) Title:</b> POLYISOCYANATE PREPOLYMERS PREPARED FROM RIGID POLYAROMATIC PRECURSOR MATERIALS, AND POLYURETHANES PREPARED THEREFROM		
<b>(57) Abstract</b>  This invention relates to a liquid prepolymer composition which contains free isocyanate groups and which is the reaction product of a stoichiometric excess of a polyisocyanate and an active hydrogen-containing compound which contains an internal rigid polyaromatic grouping. This invention also relates to polyurethane and/or polyurea polymers made from these prepolymer compositions.		

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POLYISOCYANATE PREPOLYMERS PREPARED FROM RIGID  
POLYAROMATIC PRECURSOR MATERIALS, AND POLYURETHANES  
PREPARED THEREFROM

5 This invention relates to polyisocyanate  
prepolymers or quasi-prepolymers, and to polyurethane  
and/or polyurea polymers made therefrom.

Polyurethanes, polyureas and similar polymers  
are commercially prepared by reacting an active  
10 hydrogen-containing composition with a polyisocyanate.  
By varying the characteristics of the polyisocyanate  
and the active hydrogen-containing composition,  
polymers having widely varying properties can be  
prepared. For example, by using relatively low  
15 equivalent weight, high functionality precursor  
materials, rigid polyurethanes are prepared.  
Conversely, flexible polyurethanes are prepared by  
using relatively high equivalent weight, low  
20 functionality precursor materials. By using or  
omitting blowing agents, cellular or noncellular  
polyurethanes are prepared. Accordingly, polyurethanes  
can be prepared which are useful in a wide variety of  
25 applications.

It is common practice to reinforce the polyurethane to give it better properties. For example, in preparing flexible polyurethane foams, it is known to employ dispersions of reinforcing polymer particles in a polyether polyol in order to obtain higher load-bearing and good cell opening. Similarly, the use of reinforcing fibers and fillers is common in noncellular polyurethanes as well.

Due to the high cost of the reinforcing agents, and the processing difficulties imposed by their use, it is desirable to use the smallest amount thereof which provides adequate reinforcement, or even avoid their use altogether. In addition, it is always desirable to further improve the properties of polyurethanes.

It would therefore be desirable to provide a polyurethane and/or polyurea polymer having improved physical properties. It would also be desirable to provide a precursor material which, when reacted to form a polyurethane and/or polyurea polymer, provides improved properties, especially load bearing and/or tensile properties.

In one aspect, this invention is a liquid prepolymer composition containing free isocyanate groups and which is the reaction product of a stoichiometric excess of a polyisocyanate and an active hydrogen-containing compound which contains an internal rigid polyaromatic grouping.

In another aspect, this invention is a polyurethane and/or polyurea polymer prepared in the reaction of an active hydrogen-containing composition

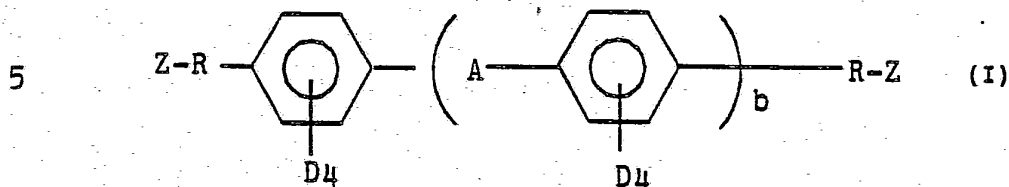
with a liquid prepolymer composition containing free isocyanate groups and which comprises the reaction product of a stoichiometric excess of a polyisocyanate with an polyaromatic active hydrogen-containing  
5 compound which contains an internal rigid polyaromatic grouping.

The applicants have found that the use of a prepolymer composition of this invention to prepare a  
10 polyurethane or polyurea provides substantially improved physical properties, particularly load-bearing and/or tensile properties in flexible polyurethane foam.

15 In this invention, a polyisocyanate-terminated prepolymer composition is used to prepare a polyurethane or polyurea polymer. The prepolymer composition is the reaction product of a stoichiometric excess of a polyisocyanate and an active hydrogen-  
20 containing compound which contains an internal rigid polyaromatic grouping (hereinafter "rigid precursor"). The internal rigid polyaromatic grouping advantageously has an aspect ratio of at least 2.4. Preferably, the  
25 internal rigid polyaromatic grouping has an aspect ratio of at least 6.4 or can aggregate with other like groups to form a nematic, twisted nematic (cholesteric), or smectic ordering (i.e., liquid crystalline).

30 The rigid precursor compounds used herein are polyphenylene compounds which are soluble in a polyisocyanate. These polyphenylene compounds are advantageously as represented by the structure 1

35



10 wherein each D is independently an inert substituent group which, when ortho to the -A- linkage, can form a cyclic structure with the -A- linkage and the aromatic rings, b is a number from 1 to 10, preferably 1 to 3, more preferably 1 to 2, each Z is independently an

15 active hydrogen-containing group, preferably hydroxyl, primary amine or secondary amine, each R is independently a divalent radical which is inert to the reaction of the isocyanate-reactive polyphenylene compound with a polyisocyanate, and A is a covalent

20 bond, a cycloaliphatic diradical,  $-\text{CH}_2\text{CH}_2-$  or a rigid linking group, or forms a cyclic structure with the aromatic rings and the groups D ortho to the -A- linkage. Preferably, each R is an oxyalkylene or

25 polyoxyalkylene diradical. More preferably, each R is an oxypropylene polyoxypropylene, oxyethylene or polyoxyethylene diradical. Most preferably, each R is an oxyalkylene polyoxyalkylene group containing from 1 to 4 repeating oxyethylene or oxypropylene units.

30 Suitable groups A include, for example, a covalent bond, a cycloaliphatic group,  $-\text{N}=\text{N}-$ ,  $-\text{COO}-$ ,

O  
↑

35  $-\text{N}=\text{N}-$ ,  $-\text{C}=\text{C}-$ ,  $-\text{C}\equiv\text{C}-$ ,  $-\text{N}=\text{C}-$ ,  $-\text{NHCO}-$ ,  $-\text{NHCOO}-$ ,  $-\text{N}=\text{C}=\text{N}$  and a heterocyclic group. In describing the groups D as inert, it is meant that the groups D do not undesirably

react with the polyisocyanate, undesirably interfere with the reaction of the polyisocyanate with an active hydrogen-containing compound, or destroy the rigid character of the rigid precursor compound. Exemplary such groups D include hydrogen, inertly substituted lower alkyl or halogen. Most preferably, the groups D are selected such that the rigid precursor compound is symmetrical. The groups D which are ortho to the -A-linkage can form, together with the -A- linkage, a cyclic structure, particularly a C<sub>5</sub>-C<sub>6</sub> cycloaliphatic structure. Examples of such rigid precursor compounds include adducts of bisphenol with from 2 to 10 moles of propylene oxide and/or ethylene oxide, adducts of 3,5,3',5'-tetramethylbiphenol with from 2 to 10 moles of propylene oxide and/or ethylene oxide and adducts of 3,5,3',5'-tetrahalobiphenol with from 2 to 10 moles of propylene oxide and/or ethylene oxide.

The rigid precursor compound can be reacted with a polyisocyanate to form an isocyanate-terminated prepolymer containing an internal rigid moiety. This is advantageously accomplished by combining a stoichiometric excess of the polyisocyanate with the rigid precursor compound. Advantageously from 1 to 50, preferably from 5 to 40, more preferably from 5 to 25 parts by weight of the rigid precursor compound are combined with 100 parts by weight of the polyisocyanate and caused to react until all of the active hydrogen-containing groups in the rigid precursor compound have reacted. The resulting prepolymer product is a solution or colloidal dispersion of the prepolymer in the polyisocyanate. In making this prepolymer, it is preferred to use a substantially difunctional

polyisocyanate, although higher functionality polyisocyanates may also be used.

5 In reacting the rigid precursor compound with the polyisocyanate, it may be desired to heat the mixture slightly, or to use a catalyst to speed the reaction. This is particularly true when the rigid precursor compound is hydroxyl-terminated. Mild temperatures, such as from 30 to 100°C, are usually  
10 sufficient. Suitable catalysts include the usual urethane catalysts, including tertiary amine and organometallic catalysts described below.

15 The polyisocyanate used herein is any which has properties suitable for preparing the desired polyurethane. These polyisocyanates include those having aromatically bound isocyanate groups as well as those which contain isocyanate groups bound to  
20 aliphatic carbon atoms. In general, aromatic polyisocyanates are preferred over the aliphatic polyisocyanates, as the rigid precursor materials and reaction products thereof with the polyisocyanate are generally more soluble in the aromatic polyisocyanates.

25 Aromatic polyisocyanates which are particularly useful herein include, for example, 2,4- and/or 2,6-toluene diisocyanate, diphenylmethanediisocyanate, p-phenylene diisocyanate, polymethylenepolyphenylpoly-  
30 isocyanates and mixtures thereof. Also useful are polymeric derivatives of diphenylmethanediisocyanate as well as prepolymers or quasi-prepolymers thereof.

35 Particularly useful aliphatic polyisocyanates include, for example, the hydrogenated derivatives of the foregoing aromatic polyisocyanates, as well as



hexamethylene diisocyanate, isophoronediiisocyanate and 1,4-cyclohexane diisocyanate.

5 In addition, prepolymers and quasi-prepolymers of the foregoing polyisocyanates having an -NCO content of 0.5 to 30 percent by weight are useful herein.

10 A polyurethane is prepared from the polyisocyanate composition of this invention by reacting it with at least one active hydrogen-containing compound. The polyisocyanate is advantageously present in an amount sufficient to provide in the reaction mixture from 70 to 500, preferably from 80 to 150, and more preferably from 95 15 to 120 isocyanate groups per 100 active hydrogen-containing groups. Higher amounts of the polyisocyanate can be used when the formation of an isocyanurate-containing polymer is desired.

20 In general, noncellular polyurethane and/or polyurea elastomers (those having an unfilled density of at least 0.8 g/cc) are prepared by reacting a relatively high equivalent weight active hydrogen- 25 containing compound (preferably 800 to 3000 molecular weight) and a chain extender compound with a polyisocyanate. The chain extender compound advantageously has an equivalent weight of from 31 to 250 and a functionality of from 2 to 4, preferably 2. 30 The chain extender is preferably a glycol or a diamine, with C<sub>2</sub>-C<sub>6</sub> alkylene glycols and sterically hindered aromatic diamines being preferred. In preparing noncellular or microcellular elastomers, a conventional casting process, particularly a solventless casting 35 process, or a reaction injection molding process can be employed. Suitable casting techniques are described,

for example, in U.S. Patent No. 4,556,703. Reaction injection molding techniques are described, for example, in Sweeney, F. M., Introduction to Reaction Injection Molding, Technomics, Inc., 1979. Suitable formulations for use in RIM processes are described, for example in U.S. Patent Nos. 4,269,945, 4,218,610, 4,297,444 and 4,530,941. In these formulations substitution of all or a portion of one or more of the active hydrogen-containing compounds with a liquid crystalline polyol or a liquid crystal dispersion having a similar equivalent weight functionality and reactivity is made.

In preparing elastomeric polyurethane and/or polyurea polymers, either a one-shot or two-shot (i.e. prepolymer) process can be employed. In the two-shot process, all or most of the relatively high equivalent weight active hydrogen-containing compound is reacted with an excess of a polyisocyanate to form an isocyanate-terminated prepolymer, which is then reacted with the chain extender and any remaining high equivalent weight material. In the one-shot process, most or all of the relatively high equivalent weight material is mixed with the chain extender and the mixture is reacted with the polyisocyanate. However, certain prepolymers and quasi-prepolymers may be employed as the polyisocyanate component even in a one-shot process. Preferably, the polyurethane and/or polyurea polymer is cellular, i.e. has an unfilled density of less than 0.8 g/cc. More preferably, the polyurethane and/or polyurea is a flexible polyurethane foam. Such flexible polyurethane foam is advantageously prepared by reacting a relatively high equivalent weight polyol with the polyisocyanate

composition of this invention in the presence of a blowing agent. In preparing flexible polyurethane foams, it is advantageously to also employ a surfactant to stabilize the foaming reaction mass and to  
5 compatibilize the various components of the reaction mixture, and to employ various catalysts for both the urethane forming and blowing reactions. In addition, a crosslinker such as diethanolamine is often employed to promote rapid initial curing.

10  
In preparing flexible polyurethane foam, the major component of the active hydrogen-containing compound(s) used advantageously has an equivalent weight of from 800 to 3000 and an average functionality  
15 (defined herein as the number of active hydrogen-containing groups per molecule) of from 2 to 4, more preferably from 2 to 3.

20 Suitable blowing agent for preparing foams are well known and include, for example, water, low boiling halogenated alkanes such as methylene chloride; monochlorodifluoromethane, dichlorodifluoromethane and dichloromonofluoromethane, the so-called "azo" blowing  
25 agents, finely divided solids, as well as other materials which generate a gas under the conditions of the foaming reaction. Water, the halogenated methanes or mixtures thereof are preferred. When water is used as the blowing agent, 0.5 to 10, preferably from 1 to  
30 5 parts by weight are used per 100 parts of active hydrogen-containing compound(s). The halogenated alkanes are typically used in an amount of from 5 to 75 parts per 100 parts by weight of active hydrogen-containing compound(s). However, the use of varying  
35 amounts of blowing agents to achieve a desired density is well known in the art, and it may in some instances

be advantageous to use amount of blowing agents outside of the ranges mentioned before.

5           Suitable surfactants include the diverse  
silicone surfactants, preferably those which are block  
copolymers of a polysiloxane and a poly(alkylene  
oxide). Suitable such surfactants include, for  
example, Y-10184 surfactant, available from Union  
Carbide Corporation. Surfactants are used in an amount  
10 sufficient to stabilize the foaming reaction mixture  
against collapse until the foam is cured, and to  
promote the formation of a somewhat uniform cell  
structure. Typically, from 0.1 to 5, preferably from  
0.3 to 3 parts by weight of surfactant are employed per  
15 100 parts of active hydrogen-containing compound(s).

          Crosslinkers which are commonly employed in  
preparing flexible polyurethane foams include, for  
example, low equivalent weight alkanolamines such as  
20 ethanolamine, diethanolamine, triethanolamine,  
propanolamine, dipropanolamine, tripropanolamine,  
methyldiethanol amine and methyl dripropanol amine.  
Also useful are the alkylene glycols and low equivalent  
25 weight hydroxyl-terminated polyols such as glycerine  
and trimethylol propane. Such crosslinkers are  
generally used in minor amounts, preferably from 0.2 to  
10, more preferably from 0.5 to 5 parts per 100 parts  
of relatively high equivalent weight active hydrogen-  
30 containing compounds. Catalysts for prepared  
polyurethane and/or polyurea foams include organo-  
metallic catalysts and tertiary amine compounds. Of  
the organometallic catalysts, organotin catalysts are  
generally preferred. Suitable catalysts are described,  
35 for example, in U.S. Patent No. 4,495,081. When using  
such catalysts, an amount sufficient to increase the

rate of the urethane-forming (and foaming reactions, when a cellular polymer is formed) is used. Typically, from 0.001 to 0.5 part of an organometallic catalyst is used per 100 parts of active hydrogen-containing  
5 compound(s). Tertiary amine-containing compounds are used in an amount ranging from 0.1 to 3 parts per 100 parts of active hydrogen-containing material. When polyisocyanurate foams are produced, alkali metal  
10 compounds are useful trimerization catalysts.

The foam can be prepared in any convenient manner. The foam can be prepared by reacting the components in a closed mold, or by permitting the reacting components to freely rise. Processes for  
15 preparing polyurethane foams are described, for example, in U.S. Patent No. 4,451,588.

In addition to preparing flexible foams and noncellular elastomers, the polyisocyanate composition  
20 of this invention is useful in preparing rigid cellular and noncellular polyurethane and/or polyurea polymers methods for making such materials are described, for example, in U.S. Patent Nos. 4,579,844 and 4,569,951.  
25 Rigid polyurethane foams are advantageously prepared using active hydrogen-containing compounds having an equivalent weight of from 31 to 400 and an average functionality of from 3 to 16, preferably from 3 to 8. The polyurethane and/or polyurea polymers of this  
30 invention are useful, for example, as seating, cushioning, industrial elastomers, automobile fascia and bumers and thermal insulation.

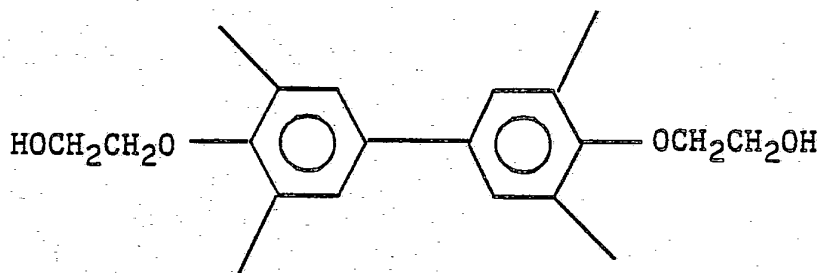
The following examples are provided to  
35 illustrate the invention, but are not intended to limit

the scope thereof. All parts and percentages are by weight unless otherwise indicated.

Example 1

5 A TDI prepolymer was prepared by adding to 100 parts TDI 10 parts of a rigid monomer having the structure

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and heating mildly until all of the hydroxyl groups have reacted. The resulting prepolymer was clear, indicating that the reaction product of this monomer and TDI is soluble in TDI. This prepolymer was then used as the sole polyisocyanate in the formation of a molded polyurethane foam (Sample No. 2). The foam was prepared by reacting the prepolymer at a 103 index with an active hydrogen-containing composition having a composition as indicated in Table 1 following.

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Table 1

	Component	Parts by weight
5	Polyol A <sup>1</sup>	60
	Copolymer Polyol A <sup>2</sup>	40
	Water	3.8
10	Silicone Surfactant <sup>3</sup>	1.6 cc
	Catalyst A <sup>4</sup>	0.3 cc
	Diethanolamine	1.7 cc
	Tertiary Amine Catalyst <sup>5</sup>	0.1 cc
15	Dimethyltindiaurate	0.005 cc
	<sup>1</sup> A 4800 molecular weight ethylene oxide-capped poly(propylene oxide triol).	
	<sup>2</sup> See note 1 of Table 1.	
	<sup>3</sup> DC-5043, available from Dow Corning Corporation	
20	<sup>4</sup> A 33 weight percent solution of triethylenediamine in dipropylene glycol	
	<sup>5</sup> bis(N,N-dimethylaminoethyl)amine	

25 The resulting foam Sample No. 1 a contained 3.27 weight percent of the rigid monomer and had properties as indicated in Table 2 following.

30 An additional foam was made in like manner, except the prepolymer was prepared using one-half the amount of the rigid monomer (Sample No. 2). Its properties are as indicated in Table 2. For comparison, a foam (comparative Sample No. A) was made using unmodified TDI as the polyisocyanate. Its properties are also as indicated in Table 2.

35

Table 2

Sample	1	2	A*
Density, lb/ft <sup>3</sup> (kg/m <sup>3</sup> )	2.05 (32.8)	1.96 (31.4)	1.95 (3.12)
Tensile Strength, psi (MPa) <sup>1</sup>	25 (0.17)	21.8 (0.15)	18 (0.12)
Elongation, % <sup>1</sup>	145	124	134
Tear Strength, pli (N/m) <sup>2</sup>	2.18 (381.5)	1.56 (273.0)	1.54 (269.5)
Resiliency, % (DB) <sup>3</sup>	45	47	55
ILD <sup>4</sup>			
25%	27	22	20
65%	74	60	54
return to 25%	20	17	16
% Hysteresis return <sup>5</sup>	75	79	82
Modulus <sup>6</sup>	2.74	2.70	2.79
Air Flow, ft <sup>3</sup> /min (m <sup>3</sup> /s) <sup>7</sup>	2.3 (1.1x10 <sup>-3</sup> )	2.1 (9.8x10 <sup>-4</sup> )	3.1 (1.5x10 <sup>-3</sup> )

\*Not an example of this invention.

<sup>1-5,7</sup> ASTM 3574-81

<sup>6</sup>Ratio of 65% ILD to 25% ILD

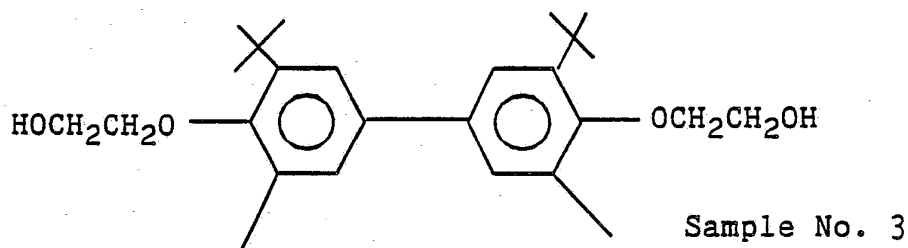


The data in Table 2 shows that significant improvements in load bearing, tear strength and tensile strength were achieved. In Sample No. 1, a substantial improvement in both tensile and elongation were obtained. Other properties were also very good.

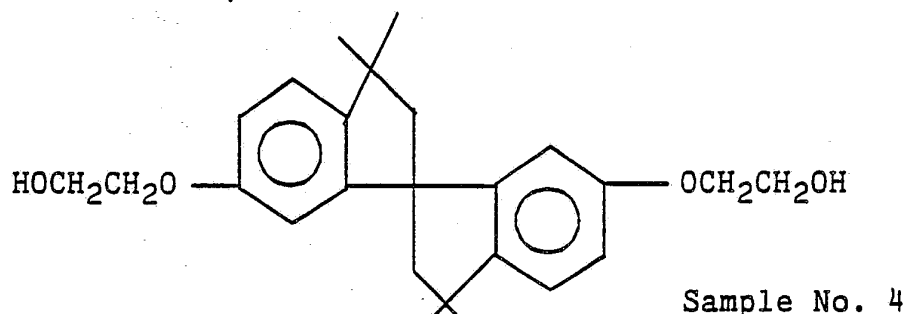
### Example 2

Three TDI polymers (sample Nos. 3 to 5) were prepared according to the procedure described in Example 1 by reacting 100 parts by weight TDI with 10 parts of rigid monomers represented by the structures:

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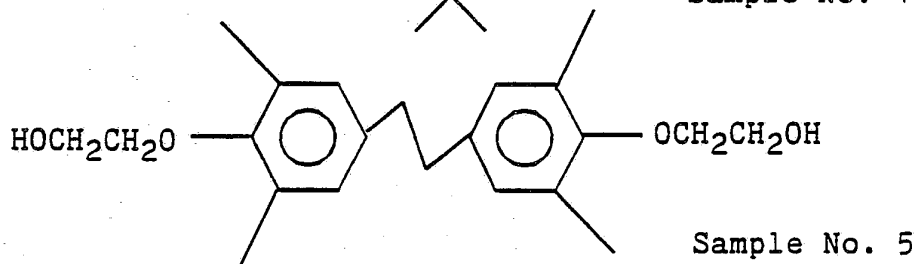


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Polyurethane foams were prepared each of these prepolymers according to the procedure described in

Example 1. The foams had properties as indicated in Table 3 following. For comparison, a foam was prepared using unmodified TDI as the polyisocyanate (comparative Sample B). Its properties are indicated in Table 3.

5 Substantial improvement in load bearing, tear strength and tensile strength are seen with this invention.

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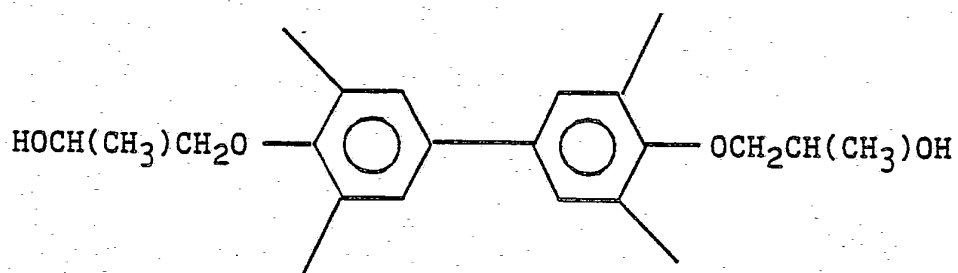
Table 3

Sample	3	4	5	B*
Density, lb/ft <sup>3</sup> (kg/m <sup>3</sup> )	2.25 (36.05)	2.19 (35.08)	2.24 (35.88)	2.15 (34.44)
Tensile Strength, psi (MPa) <sup>1</sup>	29.4 (0.20)	27.7 (0.19)	27.2 (0.19)	22.6 (0.16)
Elongation, % <sup>1</sup>	120	120	116	122
Tear Strength, pli (N/m) <sup>2</sup>	2.36 (413.0)	2.19 (383.2)	2.20 (385.0)	1.60 (280.0)
Resiliency, % (DB) <sup>3</sup>	40	40	42	55
ILD <sup>4</sup>				
25%	39	32	35	23
65%	108	89	97	66
return to 25%	24	22	23	18
% Hysteresis return <sup>5</sup>	63	67	67	77
Modulus <sup>6</sup>	2.77	2.78	2.77	2.87
Air Flow, ft <sup>3</sup> /min (m <sup>3</sup> /s) <sup>7</sup>	1.1 (5.2x10 <sup>-4</sup> )	1.3 (5.6x10 <sup>-4</sup> )	1.2 (5.6x10 <sup>-4</sup> )	2.0 (9.4x10 <sup>-4</sup> )

\* Not an example of this invention.  
 1-7-Same as notes 1-7 in Table 2.

Example 3

A TDI prepolymer Sample No. 6 was prepared according to the procedure described in Example 1 by reacting 100 parts by weight TDI with 10 parts of a rigid monomer represented by the structure:



The prepolymer was used to prepare a polyurethane foam according to the procedure described in Example 1. The foam had properties as indicated in Table 4 following. For comparison, a foam was prepared using unmodified TDI as the polyisocyanate (Comparative Sample C). Its properties are indicated in Table 4. Substantial improvement in load bearing and tensile strength are seen with this invention.

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Table 4

	<u>Sample</u>	<u>6</u>	<u>C*</u>
5	Density, lb/ft <sup>3</sup> (kg/m <sup>3</sup> )	2.3 (36.8)	2.11 (33.8)
	Tensile Strength, psi (MPa) <sup>1</sup>	28.5 (0.19)	21.7 (0.15)
	Elongation, %	117	117
	Tear Strength, pli (N/m) <sup>2</sup>	2.10 (368)	2.10 (368)
10	Resiliency, % (DB) <sup>3</sup>	42	51
	ILD <sup>4</sup>		
	25%	38	24
	65%	113	71
	return to 25%	25	19
15	% Hysteresis return <sup>5</sup>	66	79
	Modulus <sup>6</sup>	2.97	2.96
	Air Flow, ft <sup>3</sup> /min (m <sup>3</sup> /s) <sup>7</sup>	1.3 (6.1x10 <sup>-4</sup> )	1.8 (8.5x10 <sup>-4</sup> )

\*Not an example of this invention.

20 1-7-Same as notes 1-7 in Table 2.

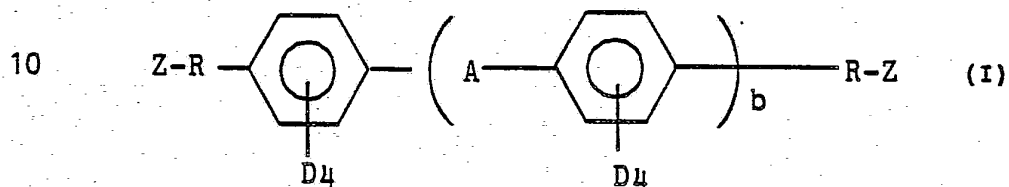
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1. A liquid prepolymer composition containing free isocyanate groups which comprises the reaction product of a stoichiometric excess of a polyisocyanate and a polyaromatic active hydrogen-containing compound which contains an internal rigid polyaromatic grouping.

2. The prepolymer composition of Claim 1 wherein said active polyaromatic hydrogen-containing compound is represented by the structure



15 wherein each D is independently an inert substituent group which, when ortho to the -A- linkage, can form a cyclic structure with the -A- linkage and the aromatic rings, b is a number from 1 to 10, each Z is independently an active hydrogen-containing group, each

20 R is independently a divalent radical which is inert to the reaction of the isocyanate-reactive polyphenylene compound with a polyisocyanate, and A is a covalent bond, a cycloaliphatic diradical, -CH<sub>2</sub>CH<sub>2</sub>- or a rigid

25 linking group, or forms a cyclic structure with the

aromatic rings and the groups D ortho to the -A-linkage.

5 3. The prepolymer composition of Claim 2 wherein from 1 to 50 parts of said polyaromatic active hydrogen-containing compound are used per 100 parts by weight polyisocyanate in preparing said composition.

10 4. The prepolymer composition of Claim 3 wherein said polyisocyanate is an aromatic polyisocyanate or an aliphatic polyisocyanate.

15 5. The prepolymer composition of Claim 4 wherein each D is hydrogen, lower alkyl or halogen, b is a number from 1 to 2, each Z is a hydroxyl, primary amine or secondary amine group, and each R is an oxyalkylene or polyoxyalkylene diradical.

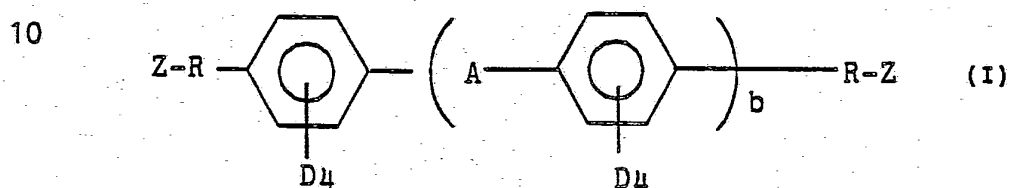
20 6. The prepolymer composition of Claim 5 wherein the groups D are chosen such that the polyaromatic active hydrogen-containing compound is symmetrical, and each R is an oxyalkylene or polyoxyalkylene group containing from 1 to 4 repeating oxyethylene or oxypropylene units.

25 7. The prepolymer composition of Claim 6 wherein the polyisocyanate comprises (1) 2,4- and/or 2,6-toluene diisocyanate; or (2) 2,4'- and/or 4,4'-diphenylmethanediisocyanate, or a derivative thereof.

30 8. A polyurethane and/or polyurea polymer prepared in the reaction of an active hydrogen-containing composition with a liquid prepolymer composition containing free isocyanate groups which  
35 comprises the reaction product of a stoichiometric excess of a polyisocyanate and a polyaromatic active

hydrogen-containing compound which contains an internal rigid polyaromatic grouping.

9. The polyurethane and/or polyurea polymer of Claim 8 wherein the active polyaromatic active hydrogen-containing compound is represented by the structure



15 wherein each D is independently an inert substituent group which, when ortho to the -A- linkage, can form a cyclic structure with the -A- linkage and the aromatic rings, b is a number from 1 to 10, each Z is

20 independently an active hydrogen-containing group, each R is independently a divalent radical which is inert to the reaction of the isocyanate-reactive polyphenylene compound with a polyisocyanate, and A is a covalent

25 linking group, or forms a cyclic structure with the aromatic rings and the groups D ortho to the -A- linkage.

30 10. The polyurethane and/or polyurea polymer of Claim 9 wherein the active hydrogen-containing composition comprises (1) a hydroxyl or primary or secondary amine-terminated polyether and the polyisocyanate is an aromatic polyisocyanate; or (2) a

35 relatively high equivalent weight active hydrogen-containing compound and a blowing agent.



11. The polyurethane and/or polyurea polymer of Claim 8, 9 or 10 which is a flexible foam or a rigid foam.

5           12. A process for preparing a liquid prepolymer composition containing free isocyanate groups which comprises reacting a stoichiometric excess of a polyisocyanate and a polyaromatic active hydrogen-containing compound which contains an internal rigid  
10 polyaromatic grouping.

          13. A process for preparing a polyurethane and/or polyurea polymer which comprises reacting an active hydrogen-containing composition with a liquid  
15 prepolymer composition containing free isocyanate groups which comprises the reaction product of a stoichiometric excess of a polyisocyanate and a polyaromatic active hydrogen-containing compound which  
20 contains an internal rigid polyaromatic grouping.

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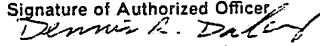
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# INTERNATIONAL SEARCH REPORT

International Application No.

PCT/US88/02291

<b>I. CLASSIFICATION OF SUBJECT MATTER</b> (if several classification symbols apply, indicate all) <sup>6</sup>		
According to International Patent Classification (IPC) or to both National Classification and IPC IPC(4): C08G 18/32, 18/48, 18/14, 18/38 U.S. Cl. 528/78, 79, 85; 521/159		
<b>II. FIELDS SEARCHED</b>		
Minimum Documentation Searched <sup>7</sup>		
Classification System	Classification Symbols	
U.S.	528/78, 79, 85; 521/159	
Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched <sup>8</sup>		
<b>III. DOCUMENTS CONSIDERED TO BE RELEVANT</b> <sup>9</sup>		
Category *	Citation of Document, <sup>11</sup> with indication, where appropriate, of the relevant passages <sup>12</sup>	Relevant to Claim No. <sup>13</sup>
X	U.S. A, 4,581,388 (RASSHOFER ET AL.) 08 APRIL 1986, SEE THE ENTIRE DOCUMENT.	1-13
A	U.S. A, 4,238,580 (LOUCKS ET AL) 09 DECEMBER 1980, SEE ENTIRE DOCUMENT.	1-13
A	U.S. A, 4,366,193 (LINDEN ET AL) 28 DECEMBER 1982, SEE ENTIRE DOCUMENT	1-13
A	U.S. A, 4,743,146 (HEFNER, JR.) 03 MAY 1988, SEE ENTIRE DOCUMENT.	1-13
A	U.S. A, 4,569,951 (NELSON) 11 FEBRUARY 1986, SEE ENTIRE DOCUMENT.	1-13
A	JP, B, 60-86113 (HITACHI) 15 MAY 1985, SEE ENTIRE DOCUMENT.	1-13
A	U.S. A, 3,925,296 (STONE ET AL) 09 DECEMBER 1975, SEE ENTIRE DOCUMENT.	1-13
<p>* Special categories of cited documents: <sup>10</sup></p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"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)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> <p>"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</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"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.</p> <p>"&amp;" document member of the same patent family</p>		
<b>IV. CERTIFICATION</b>		
Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report	
14 SEPTEMBER 1988	09 NOV 1988	
International Searching Authority	Signature of Authorized Officer	
ISA/US	 DENNIS R. DALEY	

## FURTHER INFORMATION CONTINUED FROM THE SECOND SHEET

Y	US, A, 4,701,475 (TURNER) 20 OCTOBER 1987, SEE ENTIRE DOCUMENT.	1-13
Y	US, A, 4,745,135 (THOMAS ET AL) 17 MAY 1988, (SEE ENTIRE DOCUMENT.	1-13
Y	US, A, 4,745,136 (THOMAS ET AL) 17 MAY 1988, SEE ENTIRE DOCUMENT.	1-13
Y	US, A, 4,745,137, (THOMAS ET AL) 17 MAY 1988, SEE ENTIRE DOCUMENT.	1-13

V.  OBSERVATIONS WHERE CERTAIN CLAIMS WERE FOUND UNSEARCHABLE <sup>1</sup>

This international search report has not been established in respect of certain claims under Article 17(2) (a) for the following reasons:

1.  Claim numbers \_\_\_\_\_, because they relate to subject matter <sup>12</sup> not required to be searched by this Authority, namely:

2.  Claim numbers \_\_\_\_\_, because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out <sup>13</sup>, specifically:

3.  Claim numbers \_\_\_\_\_, because they are dependent claims not drafted in accordance with the second and third sentences of PCT Rule 6.4(a).

VI.  OBSERVATIONS WHERE UNITY OF INVENTION IS LACKING <sup>2</sup>

This International Searching Authority found multiple inventions in this international application as follows:

I. Claims 1-7 and 12 drawn to a prepolymer composition; Class 528, subclass 79.

II. Claims 8-11 and 13 drawn to a polyurethane and/or polyurea polymer; Class 528, subclass 64.

1.  As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims of the international application.

2.  As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims of the international application for which fees were paid, specifically claims: **Telephonic practice**

3.  No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claim numbers:

4.  As all searchable claims could be searched without effort justifying an additional fee, the International Searching Authority did not invite payment of any additional fee.

Remark on Protest

The additional search fees were accompanied by applicant's protest.

No protest accompanied the payment of additional search fees.

PCT/US88/02291

Time Limit For Filing A Protest

Applicant is hereby given 15 days from the mailing date of this Search Report in which to file a protest of the holding of lack of unity of invention. In accordance with PCT Rule 40.2 applicant may protest the holding of lack of unity only with respect to group(s) paid for.