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<p>(54) Title: POLYURETHANE/POLYUREA ELASTOMERS</p> <p>(57) Abstract</p> <p>Polyurethane/urea elastomers having an isocyanate equivalent index below 100, preferably from 15 to 80; containing an effective amount of polyisocyanate component, and an effective amount of an isocyanate reactive component comprising at least one polyamine and at least one polyol, wherein said elastomer contains from 1 to 60 equivalent percent amine per isocyanate equivalent.</p>		

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POLYURETHANE/POLYUREA ELASTOMERSBackground of the InventionField of the Invention

5           The invention relates to polymeric elastomers which can be used as encapsulants, sealants, end seals, gaskets, and dams for telecommunications and electrical devices.

10                           Description of the Related Art

Elastomers and sealants containing polyurethanes and polyurethane/ureas are well known in the art.

U.S. Pat. No. 5,064,494, (Duck, et al.) discloses a sealant composition made from a polyol based isocyanate prepolymer and a heat activatable blocked complexed amine. The materials are cured by briefly heating to above 120°C and subsequently moisture cured.

U.S. Pat. No. 5,061,749 (Ito and Hayashi) discloses a polyol based isocyanate prepolymer and a vinyl polymer containing a hydrolyzable siloxy group. The material is stated to be useful as a sealing material when formulated with proper fillers and plasticizers.

U.S. Pat. No. 5,053,465 (Waddill) discloses sealers comprising a polyol based blocked isocyanate prepolymer epoxy resin blend cured with a polyether polyamine.

U.S. Pat. No. 5,034,435 (Squiller) discloses aqueously dispersed polyol based blocked isocyanate-terminated prepolymer epoxy compositions which are mixed with aliphatic polyamines to form a sealant.

U.S. Pat. No. 4,346,205 (Hiles) discloses energy-absorbing polyurethane foams and elastomer compositions having low compression characteristics comprising a flexible polyurethane of essentially linear structure containing unsaturated hydroxyl groups. The foams are the reaction product of substantially linear polyols having hydroxyl end groups and an aromatic isocyanate in less than stoichiometric amount. The elastomers are taught to have a Shore OO hardness of 50 or less.

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U.S. Pat. No. 4,476,258 (Hiles) discloses polyurethane elastomer compositions having a density from about 0.4 to about 1 gm/cc, a compression set of less than about 5%, and a recovery time of from about 10 to about 100 milliseconds. The elastomers are formed by reaction of a urethane-forming component containing at least four urethane-forming reactive sites and an elasticizing polyol selected from diols and triols and a diisocyanate in less than stoichiometric amounts. The materials are stated to have a Shore 00 hardness of about 20 to about 70. Various additives and fillers are disclosed including hollow glass spheres.

U.S. Pat. No. 4,722,946, (Hostettler) discloses non-liquid, energy-absorbing polyurethane foams and elastomers which are derived from reacting a mixture of linear and branched polyols having a linear to branched ratio of 1.0 to about 1.18, a polyisocyanate and, optionally, a blowing agent, under polyurethane-forming conditions at an isocyanate index of from about 65 to about 85. It is specifically stated that isocyanate indices below 65 do not give a product with useful consistency. It is further disclosed that the elastomers disclosed in the above Hiles patents could not be duplicated, but provided liquid materials which are not usable for the purposes intended.

U.S. Pat. No. 4,980,386 (Tiao and Tiao) discloses a method for the manufacture of shock attenuating low rebound polyurethane foams in which polyols are reacted with polyisocyanates having a functionality of at least 2.3 at an isocyanate index of from about 65 to about 85.

U.S. Pat. No. 5,010,117 (Herrington, et al.) discloses that polyurethane/polyurea foams prepared using polymer polyols with low levels of mono-functional impurities and water as the blowing agent provide improved mechanical properties. Useful polyisocyanate indices were disclosed to be 60 to about 200, preferably about 95 to about 110. It was specifically stated that

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with lower indices, insufficient curing occurs, which causes the foam to have poor properties.

U.S. Pat. No. 4,833,176 (Wolf and Kogelnik) discloses a process for the preparation of flexible  
5 polyurethane foams at an isocyanate index below 70, preferably 40-60, with 5-15 parts water and compounds containing at least two isocyanate reactive compounds.

It has now been discovered that useful viscoelastic elastomers can be obtained at isocyanate indices below 65  
10 and even at extremely low isocyanate indices, e.g., 15 to 50, when a polyamine is included in the isocyanate reactive mixture. Surprisingly, useful elastomers can be produced with a completely branched, or a completely linear isocyanate reactive component as well as a mixture  
15 of linear and branched materials. It has also been surprisingly discovered that certain physical properties can be maintained or even increased as the isocyanate index decreases by a proper balancing of the nature and reactivity of the isocyanate reactive component. By  
20 balancing these factors, and including at least one polymeric amine, elastomers may be prepared having viscoelastic characteristics ranging from firm elastomers to jelly-like sealants, as desired for varying applications.

25

#### Summary of the Invention

The invention provides polyurethane/urea elastomers having an isocyanate equivalent index below 100, preferably from 15 to 80, containing an effective  
30 amount of polyisocyanate component, and an effective amount of isocyanate reactive material, comprising at least one polyamine and at least one polyol, wherein said elastomer contains from 1 to 199 equivalent percent active amine hydrogen per isocyanate equivalent. The  
35 elastomers are useful as encapsulants, sealants, end seals, gaskets and the like.

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Suitable polyols and polyamines have molecular weights of from 400 to 100,000, preferably from 400 to 20,000, most preferably from 800 to 6,000. Useful polyamines may have primary or secondary amine groups.

5 Useful polymer polyols contain high molecular weight polyadducts or polycondensates, or polyhydroxyl compounds modified by vinyl polymerization can also be utilized. Suitable polymer polyols contain from 5 to 60 percent polymer dispersions in polyols.

10 One highly preferred elastomers of the invention also contains from 10 to 60 volume percent lightweight microspheres.

As used herein, these terms have the following meanings.

15 1. The term "elastomer" refers to a rubbery material which, when deformed, will return to approximately original dimensions in a relatively short time.

20 2. The term "isocyanate index" and "NCO-index" as used herein refer to the ratio of NCO groups over reactive hydrogen atoms present in a polyurethane formulation given as a percentage:

$$\text{NCO-index} = \frac{(\text{NCO})}{(\text{active hydrogen})} \times 100$$

25

In other words, the NCO-index expresses the percentage of isocyanate actually used in a formulation with respect to the amount of isocyanate theoretically required for reacting with the amount of isocyanate reactive hydrogen used in a formulation.

30 The expression "active hydrogen atoms" as used here for the purpose of calculating the isocyanate index refers to the total of hydroxyl and amine hydrogen atoms present in the reactive compositions in the form of polyols and polyamines. This means that for the purpose of calculating the isocyanate index one hydroxyl group is considered to comprise one active hydrogen and one

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primary amine group is considered to comprise two active hydrogens. The Zerewitnoff test used to determine active hydrogen is described in Journal of the American Chemical Society, Volume 49, page 3181 (1927).

5           3. The term "isocyanate reactive material" means a compound or blend of compounds containing active hydrogen atoms.

          4. The terms "equivalent weight" and "molecular weight" as used throughout the present specification  
10 refer to equivalent weight values that may be calculated by measuring the content of functional groups per weight of sample, and the molecular weight values that may be calculated from the aforementioned equivalent weight and the theoretical functionality of the compound (i.e., by  
15 the total number of hydrogen atoms attached to an oxygen atom and/or a nitrogen atom).

          5. The term "polyol" means a substance containing at least two hydroxyl groups attached to a single molecule.

20           6. The term "polyamine" means a substance containing at least two primary or secondary amino groups attached to a single molecule.

          7. The term "essentially inert" as used herein means that the plasticizer does not become cross-linked  
25 into the polyurethane/polyurea reaction product.

          8. The term "non-exuding" as used herein means that the plasticizer has the ability to become and remain blended with the polyurethane/polyurea reaction product. Many excellent plasticizers experience some blooming, or  
30 a slight separation from the solid, especially at higher temperatures, and over lengthy storage times. These plasticizers are still considered to be "substantially non-exuding".

          Percents, ratios and parts described herein are by  
35 weight unless otherwise specifically stated.

Detailed Description of the Invention

Useful organic elastomers comprise at least one isocyanate component. Suitable isocyanate components include any isocyanate having the required functionality.

- 5 The isocyanate should be present in sufficient amount to provide an isocyanate index of below 100, more preferably below 80, most preferably below 65. Equivalents for each component can be calculated by dividing the actual weight (in parts) of each component by the equivalent weight.
- 10 The isocyanate reactive component is a blend of compounds containing isocyanate reactive groups, the blend including at least one polyamine and at least one polyol, and may be completely linear, completely branched or a mixture thereof.

- 15 The term isocyanate also includes isocyanate-terminated prepolymers. Polyisocyanates may be linear or branched, aliphatic, cycloaliphatic, araliphatic, heterocyclic or aromatic, or any combination of such polyisocyanates. Particularly suitable polyisocyanates
- 20 correspond to the formula



- in which n is an integer of from 2 to 4, and Q is selected from an aliphatic hydrocarbon radical containing from 2 to 100 carbon atoms, and zero to 50 heteroatoms; a
- 25 cycloaliphatic hydrocarbon radical containing from 4 to 100 carbon atoms and zero to 50 heteroatoms; an aromatic hydrocarbon radical or heterocyclic aromatic radical containing from 6 to 15 carbon atoms and zero to 10 heteroatoms, and an araliphatic hydrocarbon radical
- 30 containing from 8 to 100 carbon atoms and zero to 50 heteroatoms. The heteroatoms that can be present in Q include non-peroxidic oxygen, sulfur, non-amino nitrogen, halogen, silicon, and non-phosphino phosphorus.

- Examples of polyisocyanates include ethylene
- 35 diisocyanate, 1,4-tetramethylene diisocyanate, 1,6-hexamethylene diisocyanate, trimethylhexamethylene diisocyanate, 1,12-dodecane diisocyanate, cyclobutane-



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1,3-diisocyanate, cyclohexane-1,3 and 1,4-diisocyanate and mixtures thereof, 1-isocyanato-3,3,5-trimethyl-5-isocyanatomethyl cyclohexane, 2,4- and 2,6-hexahydrotolylene diisocyanate and mixtures thereof,  
5 hexahydro-1,3 -and/or -1,4- phenylene diisocyanate, hexahydro-2,4'-and/or 4,4'-diphenylmethane diisocyanate, 1,3-and 1,4-phenylene diisocyanate, 2,4- and 2,6-tolylene diisocyanate and mixtures thereof, diphenylmethane-2,4'-and/or 4,4'-diisocyanate, naphthylene-1,5-diisocyanate,  
10 C<sub>36</sub> dimer acid diisocyanate (DDI) and the reaction products of four equivalents of the aforementioned isocyanate-containing compounds with compounds containing two isocyanate-reactive groups.

Also useful are e.g., triphenyl methane-4,4',4"-  
15 triisocyanate, polyphenyl polymethylene polyisocyanates of the type obtained by condensing aniline with formaldehyde, followed by phosgenation, (British Pat. Nos. 874,430 and 848,671), m- and p-isocyanatophenyl sulphonyl isocyanates, perchlorinated aryl  
20 polyisocyanates, polyisocyanates containing carbodiimide groups, norbornane diisocyanates, polyisocyanates containing allophanate groups, polyisocyanates containing isocyanurate groups, polyisocyanates containing urethane groups, polyisocyanates containing acrylated urea groups,  
25 polyisocyanates containing biuret groups, polyisocyanates produced by telomerization reactions, polyisocyanates containing ester groups, reaction products of the above-mentioned diisocyanates with acetals, polyisocyanates containing polymeric fatty acid esters, and araliphatic  
30 polyisocyanates. It is also possible to use mixtures of any of the above-mentioned polyisocyanates.

Preferred polyisocyanates include hexamethylene diisocyanate, the isocyanurate and the biuret thereof; 1-isocyanato-3,3,5-trimethyl-5-isocyanatomethyl cyclohexane  
35 (isophorone diisocyanate); the tolylene diisocyanates and isocyanurates thereof; the mixed isocyanurate of tolylene diisocyanate and hexamethylene diisocyanate; the reaction

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product of 1 mol of trimethylol propane and 3 mols of tolylene diisocyanate, crude diphenyl methane diisocyanate, dimer acid diisocyanate (DDI) and 4,4'-methylene-bis (cyclohexyl diisocyanate).

5           Blocked polyisocyanates may also be included. Illustrative of these materials are 4-nonylphenol blocked isocyanate prepolymers available as Desmocap™ from Miles.

          Suitable polyamines are those known in the art which contain more than one primary or secondary amino group  
10          capable of reacting with isocyanate groups and have molecular weights from 400 to 100,000, preferably 800 to 20,000, with functionality from 2 to 6, preferably 2 to 3.

          Examples include polyoxyalkylene polyamines derived  
15          from the amination of polyether polyols with the majority of the hydroxyl groups replaced by amine groups; polyamidoamines derived from dimerized fatty acids; amine terminated polybutadienes; amine terminated polytetrahydrofuran; amine terminated polybutadiene-  
20          acrylonitrile copolymers; amine terminated polyethers obtained by hydrolysis of isocyanate prepolymers or by hydrogenation of cyanoethylated polyoxpropylene ethers, polyamines containing urea or amide or urethane moieties in their backbone; cyanoethylated amine terminated  
25          polyoxypropylene ethers; polysiloxanes containing amino groups; tetramethylene oxide-di-aminobenzoates; polyethers containing aromatic amine end groups; Lewis acid-blocked primary or secondary aliphatic or aromatic amine groups, and mixtures thereof.

30          Useful classes of polyamines include:

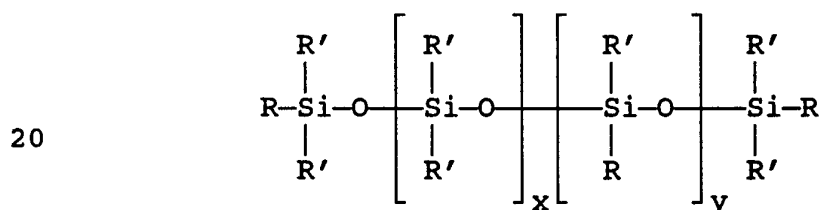
          a) aminopolyethers. Other suitable polyamines include those containing urea or amide or urethane or ester moieties in their backbones. Illustrative of these materials are the polyoxyalkylene polyamines available as  
35          Jeffamine™ from Texaco.

          (b) Polyamines containing aliphatic or cycloaliphatic organic compounds, such as

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polyamidoamines, amine-terminated polyalkadienes, and hydrogenated derivatives of the polyalkadiene polymer. In addition, amine terminated polyalkadiene copolymers with acrylonitrile or methacrylonitrile in the polymer backbone can be utilized. Illustrative of the above materials are the amine-terminated butadiene/acrylonitrile copolymers available as Hycar™ from BF Goodrich.

(c) Aminoalkyl terminated polydiorganosiloxanes, including polysiloxanes having a molecular weight of 400 to 100,000 which contain from 0.01 to 6 percent, preferably 0.05 to 1% by weight of nitrogen in the form of primary or secondary amino groups. Polysiloxane-containing amino groups include those having structural units corresponding to the following formula:



wherein R represents an amino group containing alkyl or aryl radical containing primary, secondary or tertiary amino groups and having a total of 2 to 20 carbon atoms

R' independently represent alkyl groups containing 1 to 6 carbon atoms, vinyl groups or phenyl groups

Y representing whole or (on a statistical average) fractional number of 0 to 4

X representing a whole or (on a statistical average) fractional number of 10 to 1400

Illustrative of these materials is the difunctional aminopropyl-terminated polydimethylsiloxane formed by reaction of amino propyltrialkoxysilane with octamethyl cyclotetrasiloxane.

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(d) Polyethers containing aromatic amine end groups including anthranilic acid esters, groups containing urea or urethane or amide or ester moieties in their backbone. Illustrative of the above materials are the  
5 polytetramethyleneoxide-di-p-aminobenzoates available as Polamine™ from Air Products.

Polyols useful in the invention are liquid or quasi-liquid polyols, with functionality from 2 to 8, with di- or trifunctional polyols being preferred. Useful polyols  
10 have molecular weights of 400 to 50,000, preferably 800 to 20,000.

Suitable polyols may be selected from polyether polyols based on ethylene oxide, propylene oxide, butylene oxide, tetrahydrofuran, epichlorohydrin or  
15 mixtures thereof, ricinoleic acid derivatives, e.g., castor oil; polyester polyols, polyamide or polyesteramide polyols; tertiary amine containing polyols, e.g., ethoxylated or propoxylated amides or amines; polyalkadiene polyols derived from butadiene  
20 polymers or copolymers, and hydrogenated derivatives thereof; polyacetals, polycarbonates containing hydroxyl groups; polyhydroxyl (meth)acrylic resins, polythioether polyols, polymer polyols, and the like.

Suitable classes of polyols include:

25 (a) Polyethers containing at least 2, generally 2 to 8, preferably 2 or 3 hydroxyl groups. The general term polyether polyols also includes polymers referred to as amine-based or amide-based polyols. When propylene oxide and ethylene oxide are utilized to prepare the  
30 polyether polyol, it is preferred that the oxypropylene content thereof be at least 60 weight percent, more preferably at least 70 weight percent and most preferably at least 80 weight percent. The ethylene oxide is most preferably present in the form of terminal  
35 poly(oxyethylene) blocks, constituting 10 to 20 weight percent of the polyether. Illustrative examples are the polypropylene oxide glycols, polypropylene oxide triols

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or ethylene-oxide-capped polypropylene oxide triols available either under the Arcol™ or Pluracol™ trade names.

(b) Esters of ricinoleic acid with polyhydric  
5 alcohols containing at least 2 hydroxyl groups, including mono, di-, and polyesters of ricinoleic acid. One naturally occurring triglyceride of ricinoleic acid is castor oil, which has an average functionality of about 2.7. Suitable interesterification products may also be  
10 prepared from castor oil and substantially non-hydroxyl-containing, naturally occurring triglyceride oils. Illustrative of the above materials is castor oil available from United Catalysts.

(c) Polyalkadiene polyols, prepared from dienes  
15 including unsubstituted, 2-substituted or 2,3-disubstituted 1,3-dienes of up to 12 carbon atoms. Preferably, the diene has up to 6 carbon atoms and the substituents in the 2-and/or 3-position may be hydrogen, alkyl groups having 1 to 4 carbon atoms, substituted  
20 aryl, unsubstituted aryl, halogen and the like. Typical of such dienes are 1,3-butadiene, isoprene, chloroprene, 2-cyano-1,3-butadiene, 2,3-dimethyl-1,2-butadiene, and the like. Hydrogenated derivatives may also be used. A hydroxyl terminated polybutadiene is available from ARCO  
25 Chemicals under the designation "Poly-bd R-45HT" and hydroxyl terminated polyisoprenes are available under the "LIR" trade name from Kennedy and Klim.

(d) Polyesters containing hydroxyl groups, e.g., reaction products of polyhydric, preferably dihydric and,  
30 optionally, trihydric alcohols with poly-basic, preferably dibasic, carboxylic acid.

Examples of suitable polyhydric alcohols are ethylene glycol, 1,2- and 1,3-propylene glycol, 1,4-and 2,3-butylene glycol, 1,6-hexanediol, 1,8-octanediol,  
35 neopentyl glycol, 1,4-bis-hydroxymethylcyclohexane, 2-methyl-1,3-propanediol, glycerol, trimethylol propane, 1,2,6-hexanetriol, 1,2,4-butanetriol, trimethylol ethane,

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pentaerythritol, quinitol, mannitol, sorbitol, formitol, methyl glycoside, diethylene glycol, triethylene glycol, tetraethylene glycol and higher polyethylene glycols, dipropylene glycol and higher polypropylene glycols, 5 dibutyl glycol and higher polybutylene glycols. The polyesters may contain terminal carboxyl groups. Polyesters of lactones, e.g., epsilon-caprolactone, or polyesters of hydroxycarboxylic acids, e.g., omegahydroxycaproic acid, may also be used.

10 (e) Polythioethers, particularly the condensation products of thiodiglycol alone and/or with other glycols, dicarboxylic acids, formaldehyde, aminocarboxylic acids or amino alcohols. Depending on the co-components, the products can be, for example, polythio mixed ethers, 15 polythioether esters or polythioether ester amides.

(f) Suitable polyacetals, including the compounds obtainable from glycols, such as diethylene glycol, triethylene glycol, 4,4'-diethoxydiphenyldimethylmethane, hexanediol and formaldehyde. Polyacetals suitable for 20 use in accordance with the present invention may also be obtained by polymerizing cyclic acetals such as trioxane.

(g) Polycarbonates containing hydroxyl groups,

(h) Polyhydroxy (meth)acrylic resins, which are polymers and copolymers of mono esters of (meth)acrylic 25 acid and polyhydric alcohols, useful for making polyester polyols (see (a), *infra*), e.g., homopolymers and copolymers of hydroxyethyl (meth)acrylate, hydroxypropyl (meth)acrylate, and the like. Illustrative of such compounds are G-cure™ acrylic resin available from Henkel 30 Corp., Minneapolis, MN, Desmophen™ A resins available from Mobay Corp., Pittsburgh, PA, and hydroxyl functional Acryloid™ resins, available from Rohm and Haas, Philadelphia, PA.

(i) Polyester amides and polyamides, including the 35 predominantly linear condensates.

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(j) Polyhydroxyl compounds already containing urethane or urea groups and optionally modified natural polyols, such as carbohydrates, for example, starch.

(k) Modified polyhydroxyl compounds, and modified  
5 derivatives thereof.

(l) Polyhydroxyl compounds containing high molecular weight polyadducts and polycondensates or prepolymers in a finely dispersed or dissolved form, e.g., a dispersion polymer polyol, a grafted copolymer  
10 polyol, a solution polymer polyol, or blends thereof. Polyhydroxyl compounds can also be modified by vinyl polymers of the type obtained, for example, by polymerizing styrene and acrylonitrile in the presence of polyethers. Plastics having particularly good flameproof  
15 properties are obtained by using polyether polyols modified by graft polymerization with vinyl phosphonic acid esters and, optionally (meth)acrylonitrile, (meth)acrylamide or hydroxyl functional (meth)acrylic acid esters. Polyhydroxyl compounds into which carboxyl  
20 groups have been introduced by radical graft polymerization with unsaturated carboxylic acids and, optionally, other olefinically unsaturated monomers may be used particularly advantageously in combination with mineral fillers. Also suitable are melamine, urea or  
25 urea/melamine blend particles dispersed in a polyol. Regardless of the specific polyol used, it is generally preferred to use polyols containing primary hydroxy groups. Mixtures of polymer dispersions and conventional polyols may be employed.

30 Illustrative examples of polymer polyols include Multranol™ 9151 and 9238, available from Miles Chemical Corporation; Arcol™ 34-28 and 24-32, available from Arco Corporation, and Pluracol™ 994 and 637, available from BASF Agtiengesellschaft.

35 Besides the above polyols and polyamines, lower molecular weight, reactive, chain-extending or crosslinking compounds having molecular weights of 400 or

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less and containing at least two isocyanate-reactive hydrogen atoms can also be employed. The amount of chain extending agent required varies with the desired crosslink density in the cured form. Useful examples  
5 include polyhydric alcohols, alkanol amines, primary or secondary aliphatic, cycloaliphatic, aromatic, araliphatic or heterocyclic amines, low molecular weight amine-initiated polyether polyols, ricinoleic derivatives, hydroxyl containing organophosphates, poly-  
10 (oxyalkylene)amines, substituted hydrazines and hydrazides, and mixtures thereof.

Suitable aromatic amine chain extenders include the sterically hindered aromatic polyamines, preferably diamines, which contain linear or branched alkyl  
15 substituents or halogen or similar substituents in the ortho position to the amino groups. Aromatic polyamines also include amines in which the amino group is attached to heterocyclic radicals of aromatic character. Examples include 1-methyl-3,5-diethyl-2,6-diamino benzene; 4,4'-  
20 methylene bis(2-chloroaniline); 4,4'-diamino-diphenyl sulfone; isobutyl-3,5-diamino-4-chlorobenzoate, NaCl blocked methylene bis(aniline).

In addition, aliphatic amine-containing chain extenders can be employed. Such compounds include  
25 ethylene diamine, methylene-bis(cyclohexyl amine), N,N'-ditertiary-butyl ethylenediamine, amino ethyl piperazine, meta-tetramethylenexylene diamine, and the like. Illustrative of the above materials is 5-amino-1,3,3'-trimethyl cyclohexane-methenamine (isophorone diamine)  
30 Vestamin™ available from Huls.

Low molecular weight hydroxyl terminated compounds can be utilized as chain extenders. Examples of such polyols are N,N-bis (2-hydroxypropylaniline, 1,6-hexanediol tripropyleneglycol, trimethylol propane, 1,4-  
35 dihydroxyl cyclohexane, diethanolamine, 1,4-bis (hydroxyethylpiperazine, and the like. It is also possible to use diols containing additional groups, for



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example, bis-(2-hydroxypropyl)-isophthalate, polycaprolactone glycol, 1,6-hexamethylene-bis-(2-hydroxyethylurethane), 4,4'-diphenylmethane-bis-(2-hydroxyethyl urea), ethylene glycol mono-ricinoleate, 5 and the like. Illustrative of the above materials are diethyl-N,N-bis(2-hydroxyethyl) amino methylphosphonate, Fyrol™, available from Akzo; pentaerythritol mono-ricinoleate, Conacure™ available from Conap; propylene oxide adduct of trimethylolpropane, Pluracol™, available 10 from BASF; and polyethylene or polypropylene oxide adducts of ethylene diamine, also available under the Pluracol™ or Quadrol™ trade name.

Preferred elastomers may also contain a plasticizing system having one or more extenders or plasticizers. The 15 plasticizing system is preferably selected so as to be essentially inert with polyurethane/polyurea reaction products and substantially non-exuding.

Useful plasticizers include aliphatic, naphthenic, and aromatic petroleum based hydrocarbon oils; cyclic 20 olefins (such as polycyclopentadiene), vegetable oils (such as linseed oil, soybean oil, sunflower oil, and the like); saturated or unsaturated synthetic oils; polyalphaolefins (such as hydrogenated polymerized decene-1), hydrogenated terphenyls, pine oil or coal tar 25 or other terpene derivatives, polypropylene oxide mono and di-esters, cyclopentadiene copolymers with fatty acid esters, phosphate esters and mono-, di-, and poly-esters, (such as trimellitates, phthalates, benzoates, fatty acid ester derivatives, castor oil derivatives, fatty acid 30 ester alcohols, dimer acid esters, glutarates, adipates, sebacates, polymeric polyesters, rosin esters, acrylate esters, epoxidized fatty acid esters, and the like) and mixtures thereof.

Flame retardency of the elastomers can be improved 35 by the use of halogen and/or phosphorus containing compounds, for example, halogenated phosphate or polyphosphate esters, halogenated organic phosphonates,

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and halogenated hydrocarbons. These flame retardants can be employed along with hydroxyalkyl phosphonate esters and/or appropriate fillers to impart the desired degree of fire retardancy. Illustrative of the above materials  
5 are polyalphaolefins available from Emery Chemical under the Emery trade name, tri-octyl trimellitate available from Nuodex under the Nuoplaz™ trade name, glyceryl tri(acetyl ricinoleate) available under the Flexricin™ trade name from CasChem, trixylenenylphosphate available  
10 from FMC under the Kronitex™ trade name, and soybean oil from Spencer-Kellogg.

Any conventional catalyst used in the preparation of polyurethanes may be employed herein. To facilitate the reaction from 0.005% to 5.0%, preferably 0.05 to 2.5% by  
15 weight of the total reactants of catalyst is added. Suitable catalysts include organometallic chelates, alcoholates, phenolates, and salts of organic acids, tertiary amines, organic tin compounds, bicyclic amidines, silaamines, acidic metal salts of strong acids,  
20 tertiary phosphines, alkali and alkali earth metal hydroxides, and the like, and combinations thereof.

Exemplary organometallic catalysts include catalytically active compounds of tin, iron, mercury, bismuth, zinc, manganese, lead, copper, cobalt, titanium,  
25 antimony, cadmium, aluminum, nickel, cerium, vanadium, and the like. Illustrative of the above compounds would be stannous octoate, bismuth neodecanoate, lead naphthenate, phenylmercuric benzoate, lead ethylhexanoate, and ferric acetyl acetonate. Suitable  
30 organic tin compounds include tin (II) salts of carboxylic acids such as tin ethylhexanoate and tin laurate and the tin (IV) compounds, such as dibutyl tin dilaurate, dibutyl tin oxide, dimethyl-tin (IV)-bis-thiolauryl, dibutyl tin-bis-thioglycolic acid octyl  
35 ester, and the like.

Useful tertiary amines include, for example, N-methyl morpholine, bis(2-dimethylaminoethyl) ether, 1-

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methyl-4-dimethylaminoethyl piperazine, dimethyl benzylamine, triethylamine, 1,8-diazabicyclo(5,4,0)-undec-7-ene (DBU) and salts thereof, 1,4-diazabicyclo(2,2,2) octane, triethylene diamine, and the like.

Preferred elastomers of the invention also contain hollow microspheres made of silicate, phenolic, glass, epoxy, vinylidene chloride copolymers, flyash, carbon, clay and the like. They must be roughly spherical, ranging in particle size from 0.5 to 300 microns. The microspheres may be glass, e.g., Scotchlite™, available from Minnesota Mining and Manufacturing Company (3M); polymeric, e.g., Expancel™ 551DE, available from Nobel Industries, UCAR microballoons, available from Union Carbide Corp., and Dualite™ M6001AE, available from Pierce and Stevens Corp.; or ceramic, e.g., Zeeosphere™ X-40, manufactured by Zeelan Industries. Such microspheres may also be treated with a coupling or wetting agent such as a silane, e.g., 3-glycidoxypropyl trimethoxy silane, or an organo-chromium or titanium or zirconium complex to enable the resin to effectively wet the microspheres.

Additional fillers or combinations of fillers may also be present, such as glass fibers, graphite fibers, fibrous materials emanating from an organic polymer, carbon black, mica, aluminum oxide hydrates, various silicates or carbonates or clays, fumed silica and the like. The term "filler" is used herein to include all solid additives including particulate matter or fibrous matter, present in the composition. Illustrative of the above materials is a fumed silica available under the trade name Cab-O-Sil™ from Cabot.

In one embodiment, expandable sealants may be made from compositions of the invention by adding expandable microspheres to the composition. The sealant may be a one-part sealant which is activated by the application of heat, or it may be a two-part sealant which exotherms

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upon reaction, providing the necessary heat to cause expansion of the microsphere. Such sealants are especially useful as sealants in devices which have heated process steps. The unexpanded encapsulant can be placed against one side of an area to be filled prior to the heated process step. As the device is heated, the elastomer sealant will expand to fill the area as desired. In one application, the elastomer is placed inside an automobile body where sealing is desired. A small amount is placed in a bead against the wall or seam. When the automobile is subjected to heat during the painting process, the seal will expand to fill the area and seal the seam.

Expandable microspheres useful in such an embodiment include those available as Expancel™ "WU" or "DU" microspheres from Nobel Industries, (designating whether the unexpanded microspheres are wet or dry), including Expancel™ 642 DU, 820 DU, 820WU and the like, providing the Expancel™ "WU" grades are dried before use to remove the moisture.

Although the crosslinking reactions to prepare the elastomeric compositions of the present invention are preferably conducted at or near ambient temperature, it should be obvious to one skilled in the art that the reaction rate may be accelerated, if desired, by the application of elevated temperatures, or if rendered necessary by the use of blocked isocyanates or expandable microspheres.

It is also possible to add other additives, such as wetting agents, UV absorbers, mold release agents, drying agents, such as molecular sieves, fungicides, oxidation preventatives or any other additive as necessary. As oxidation preventatives, there can be used hindered phenols, for example, Irganox™ 1010, Tetrakis methylene(3,5-di-tert-butyl-4-hydroxyhydro-cinnamate)methane, and Irganox™ 1076, Octadecyl 8 (3,5-

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tert-butyl-4-hydroxyphenol) propionate, all available from the Ciba-Geigy Company.

The above mentioned ingredients are not to be construed as conclusive of all acceptable materials  
5 useful in the compositions of the invention.

In order to make elastomers of the invention, the isocyanate reactive blend is mixed together, and the catalyst is added. Other additives, fillers and the catalyst are mixed into the blend. The isocyanate is  
10 then added to the blend and the elastomer is then cured.

Elastomers of the present invention are useful as sealants, end seals, coatings, vibration dampening devices, sound attenuation devices, bushings, sleeves, gaskets and the like. Elastomers having low viscosities  
15 are also useful as encapsulants and the like, especially in the electronics and telecommunications fields, e.g., in electrical and signal transmission devices.

In use for signal transmission devices, the elastomer is molded into the desired configuration or  
20 poured into a protective housing, and cured under the conditions required for the specific isocyanate component and isocyanate-reactive component used.

The following examples are for illustrative purposes only, and are not limiting to the scope of the invention.  
25 Where a particular test was not run in a particular example, this is indicated by a dashed line.

#### Test Methods

##### Shore OO Hardness

30 Shore OO hardness was tested according to the American Society of Test Methods, Test Method "D2240".

##### Tensile Strength and Elongation

Tensile Strength and elongation were measured  
35 according to ASTM Test Method "D-412".

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One-Quarter Cone Hardness

Hardness was tested using ASTM Test Method "D1403".

Heat Aging

5           Dry heat aging was tested by heating a thin polymer slab for 18 hours on a Teflon™ coated plate to 104.4°C (220°F) in a vented oven. Syneresis or its absence was observed visually, and dumbbells were then cut for elongation testing.

10

Glossary

The following glossary lists the commercially available components used in the following examples. The function of each component is also listed. Function of  
15 the component is defined as follows:

	<u>Function</u>	<u>Abbreviation</u>
	Isocyanate	I
	Blocked isocyanate	BI
20	Polyamine crosslinking agent	PACA
	Alcohol Crosslinking Agent	ACA
	Plasticizer	P
	Polymer Polyol Crosslinking Agent	PPCA
	Microsphere filler	M
25	Microsphere filler, expanding	MEF
	Filler	F
	Catalyst	C
	Antioxidant	A

MATERIAL	DESCRIPTION	AVERAGE EQUIVALENT WEIGHT	SOURCE	FUNCTION
Vestanat PDI	Isophorone-diisocyanate (3-isocyanato methyl -3, 5, 5, - trimethylcyclohexyl - isocyanate).	111	Huls	I
Mondur CD	Carbodiimide derivative of 4, 4' - diphenylmethane diisocyanate	144	Miles	I
Arco LHT-34	Polypropylene oxide adduct of glycerol, 5000 molecular weight triol	1660	Arco	ACA
Arco PPG 2025	Polypropylene oxide glycol, 2000 molecular weight diol	1000	Arco	ACA
Pluracol PEP500	Polypropylene oxide adduct of pentaerythritol, 500 molecular weight tetrol	125	BASF	ACA
USP Castor Oil	Vegetable oil of 70% glycerin triricinolein and 30% glycerol diricinolein mono-oleate or monolinoleate and hydroxy functionality of about 2.7	344	United Catalyst	ACA
Poly bd R45HT	Hydroxyl terminated polybutadiene (60% trans-1,4,20% cis-1,4, and 20% 1,2-vinyl) with average molecular weight of 2900 and hydroxyl functionality of about 2.5	1200	Atochem	ACA
Arco PPG425	Polypropylene oxide glycol, 425 molecular weight diol	213	Arco	ACA
Pluracol TP440	Polypropylene oxide adduct of trimethylolpropane 423 molecular weight diol	141	BASF	ACA
BiCat 8	Bismuth/Zinc Neodecanoate	N/A	Shephard	C
Polycat SA-102	2-Ethyl hexanoic acid salt of DBU (1,8-diazo-bicyclo (5.4.0) undecene-7)	N/A	Air Products	C
Polycat 33-LV	33% solution of 1,4-diazobicyclo(2.2.2) octane	N/A	Air Products	C
Dabco T-12	Dibutyl tin dilaurate	N/A	Air Products	C
Quadrol	Tetrakis (2-hydroxyl propyl) ethylene diamine with average molecular weight of 292 and four secondary hydroxyls	72.9	BASF	ACA

MATERIAL	DESCRIPTION	AVERAGE EQUIVALENT WEIGHT	SOURCE	FUNCTION
Hatcol DOP	Di-2 ethylhexyl phthalate	N/A	Hatco	P
Desmocap 11A	100% solids 4-nonylphenol blocked isocyanate prepolymer with 2.6 average functionality with 2.4% available isocyanate	1750	Miles	BI
Desmocap 12A	100% solids 4-nonylphenol blocked isocyanate prepolymer with 2.0 average functionality with 1.7% available isocyanate	2470	Miles	BI
Cyanamid TMXDI (meta)	Meta-tetramethylxylene diisocyanate-	122	Cyanamid	I
Isonate 143L	Uretonimine modified diphenyl-methane diisocyanate	179	Dow	I
Conacure AH-35	Hydroxyl terminated tetrafunctional polyol based on castor oil	202	Conap	ACA
Fyrol 6	Diethyl N,N-bis(2-hydroxyethyl) amino methylphosphonate	127	Akzo	ACA
LIR-503	Hydroxyl functional liquid polyisoprene with an average functionality of about 2.5 and an average molecular weight of about 25,000	10,000	Kennedy and Klim	ACA
Desmodur W	4, 4' methylene-bis(cyclohexyl) isocyanate, hydrogenated MDI or H <sub>12</sub> MDI	132	Miles	I
Jeffamine D2000	Polypropylene oxide diamine of about 2000 molecular weight	514	Texaco	PACA
Jeffamine T3000	Polypropylene oxide triamine of about 3000 molecular weight	500	Texaco	PACA
Jeffamine T5000	Polypropylene oxide triamine 5000 molecular weight	833	Texaco	PACA
Polamine 1000	Polytetramethylene oxide-di-p-aminobenzoate. Average molecular weight of about 1200	334	Air Products	PACA
Polamine 650	Polytetramethylene oxide-di-p-aminobenzoate. Average molecular weight of about 820	205	Air Products	PACA
PDMS Diamine	Polydimethylsiloxane diamine. Average molecular weight of about 20,000	5000	3M	PACA



MATERIAL	DESCRIPTION	AVERAGE EQUIVALENT WEIGHT	SOURCE	FUNCTION
Vestamin IPD	Isophorone diamine (cyclohexane-methenamine, 5-amino-1,3,3-trimethyl) Average molecular weight about 170.4	42.6	Huls	PACA
Hycar 1300 x 21	Difunctional secondary amine terminated butadiene acrylonitrile copolymer. Average molecular weight of about 2400	1200	BF Goodrich	PACA
Multranol 9151	Polyurea dispersion in ethylene oxide capped polypropylene oxide triol	2003	Miles	PPCA
Multranol 9283	Polyurea dispersion in ethylene oxide capped polypropylene oxide triol - Polymer polyol	2003	Miles	PPCA
Arcol Polymer Polyol 24-32	Dispersion of 10% polyacrylonitrile/10% polystyrene in ethylene oxide capped polypropylene oxide diol	1753	Arcol	PPCA
Arcol Polymer Polyol 34-28	Dispersion of 11% polyacrylonitrile/10% polystyrene in ethylene oxide capped polypropylene oxide triol	2003	Arcol	PPCA
Pluracol Polyol 973	Dispersion of 30% polyacrylonitrile/polystyrene in ethylene oxide capped polypropoxylated glycerin triol - polymer polyol	2244	BASF	PPCA
Pluracol P1010	Polypropylene oxide diol	525	BASF	ACA
Pluracol 355	Polyethylene oxide capped ethylene diamine -Tetrol	125	BASF	ACA
Arcol PPG - 1025	Polypropylene oxide glycol - Diol	494	Arcol	ACA
Arcol Polyol 11-27	Ethylene oxide capped polypropylene oxide triol	2078	Arcol	ACA
Arcol LHT 42	Polypropylene oxide triol	1385	Arcol	ACA
Arcol LHT 28	Polypropylene oxide triol	2003	Arcol	ACA
Irganox 1076	Octadecyl 8(3,5-t-butyl-4-hydroxyphenyl) propionate - antioxidant	N/A	Ciba-Geigy	A
Soybean Oil	Supreme soybean oil	N/A	Spencer-Kellogg	P

MATERIAL	DESCRIPTION	AVERAGE EQUIVALENT WEIGHT	SOURCE	FUNCTION
Flexiclin P-8	Glyceryl tri(acetyl ricinoleate)	N/A	CasChem	P
Escopol R-020	Polycyclopentadiene	N/A	Exxon	P
Emery 2900	Dioctyl dimerate	N/A	Emery	P
LVI 450	Napthenic oil, aniline pt 195	N/A	Shell	P
Kronitex TXP	Trixylenylphosphate	N/A	FMC	P
Scotchlite™ GB B23/500	Hollow glass microspheres of particle size 10-200 microns having a density (by water displacement) of about 0.23 gm/cc	N/A	3M Co.	M
Dualite M6001AE	Hollow composite polymeric microspheres coated with calcium carbonate of 50 micron particle size having a density of about 0.13 gm/cc	N/A	Pierce and Stevens	M
Expancel 551 DE	Hollow expanded microspheres composed of vinylidene chloride/acrylonitrile copolymer of 30 microns having a density of 0.02 - 0.036 gm/cc	N/A	Nobel Ind.	M
Expancel 551 DU	Hollow unexpanded microspheres composed of a vinylidene chloride/acrylonitrile copolymer of 10 microns, containing a blowing agent, isobutane, that expands to 35 microns at 142-150°C	N/A	Nobel Ind.	MEF
Expancel 461 DU	Hollow unexpanded microspheres composed of a vinylidene chloride/acrylonitrile copolymer of 10 microns, containing a blowing agent, isobutane, that expands to 35 microns at 144-152°C	N/A	Nobel Ind.	MEF
Cab O Sil M5	Fumed silica	N/A	Cabot	F
DDI 1410	Aliphatic diisocyanate based on C36 dimerized fatty acid	300	Henkel	I

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ExamplesElastomer Making Procedure

The same general procedure was followed for all of the examples. The isocyanate reactive blend was prepared and mixed from the stated polyamines, polyols, catalysts, microspheres, fillers, etc. The isocyanate was then added to the blend, and the reactants were quickly mixed mechanically and poured into a mold. The materials were then cured under one of several conditions. Cure "A" denotes that materials were cured overnight at ambient room temperature.

In cure "B" some molds were heated for one and one half hours at 76.7°C (170°F) to speed the curing, and then allowed to sit overnight.

Finally, for Cure "C", used in examples 13-18, which involved blocked isocyanates, the molds were placed in a vented oven and heated for forty-five minutes at 124°C (256°F).

All microspheres or fillers were dried at least 18 hours at 71.1°C (160°F).

Comparative Examples C1-C7

In U.S. Pat No. 4,722,946, it was taught that only liquid products or those with "chewing gum" consistency are obtained at isocyanate indices below 100 with polyisocyanates and isocyanate reactive mixtures comprising linear polyols. Products were made using the elastomer making procedure listed above. Even with the use of branched polyols, only liquid or "chewing gum" consistency products were obtained at isocyanate indices below 65. (See examples 8, 15, 20, 33, and 43.) Solid viscoelastomers were not produced at isocyanate indices below the limits.

In order to confirm the results, the comparative examples C1-C7 in Table I were produced. Isocyanate-reactive mixtures were reacted with both aromatic and aliphatic polyisocyanates using various catalysts at

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isocyanate indices of 50 or below. The various polyols used in these experiments had functionalities ranging from 2 to 4, and thus were linear and branched, with primary and secondary alcohols having varying molecular weights. None of the comparative examples yielded solid elastomers, rather viscous liquids were formed in all cases.

#### Examples 1-37

Examples 1-37 were made according to the above described procedure. In contrast to the foregoing comparative examples, surprisingly useful viscoelastic elastomers were obtained at isocyanate indices below 65 and even at very low isocyanate indices when a polyamine was included in the isocyanate reactive mixture. Useful polyamine-containing elastomers were produced not only with completely branched isocyanate reactive mixtures, but also with completely linear isocyanate reactive mixtures, and isocyanate reactive mixtures containing both linear and branched compounds.

Elasticity remained even after dry heat aging of the elastomers at 104°C, and no syneresis occurred under those conditions. Elastomers containing hollow microspheres yielded lightweight elastomers.

As can be seen in Table II, Example 1, when a polyamine was included with the same polyol ingredients as Comparative Example C2 of Table I, (Example 8 of U.S. Pat. No. 4,722,946), a hard elastomer having a Shore 00 hardness of above 60 resulted. Likewise, a similar value for hardness was obtained with a diamine and polymer polyol in Example 2. The linear/branched NH and OH ratios by equivalent for Examples 1 and 2 were below 1.00/0.50.

Example 3 demonstrates an elastomer from a completely linear isocyanate reactive mixture having an isocyanate index of 40. Again a solid elastomer having good properties was formed, rather than a viscous liquid as the prior art would indicate from such as system.

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Example 4 was produced with an all branched isocyanate reactive mixture having the polyamine added to the identical polyol ingredients of Comparative Example C4. Elastomers were also formed from a polymeric amine and the polyol ingredients of Comparative Examples 3 and 5 and the properties are demonstrated as Examples 5 and 6 in Table II.

Tables III to VIII show elastomers made from varying systems in order to demonstrate the broad nature of the invention. Elastomers are formed from completely linear isocyanate reactive components in Examples 16 and 18 having isocyanate indices of 24. Various amines are utilized; the usefulness of aliphatic primary diamines is shown in Examples 7, 10, 11, 15, 16, 18, 21 and 28 at varying isocyanate indices from 25 to 50. Aliphatic secondary amines are utilized in Examples 30 and 37. Examples 1, 2, 3, 8, and 33 use aromatic diamines. Polydimethylsiloxane diamines were used in Examples 9 and 13. Examples of aliphatic triamines are Nos. 4, 5, 6, 12, 14, 17, 19, 20, 22-27, 29, 31, 32, 34 and 35. These examples have isocyanate indices ranging from 13 to 82.

The Examples also demonstrate the range of polyisocyanates useful in systems of the invention. Aliphatic polyisocyanates are used in Examples 3-12, and 19-37. Examples 1, 2, 13-18, and 34 use aromatic polyisocyanates, and blocked isocyanates are used in Examples 13-18.

Likewise, non-amine isocyanate-reactive components have been varied. Difunctional and trifunctional polymer polyols are employed in Examples 2, 3, 7, 10, 12-21, 23-27, and 30-33. Examples 9, 11 and 21 utilized a tetrol in the formulations.

Varying plasticizers, microspheres and the like were also utilized throughout the examples. Hard elastomeric materials were produced with an isocyanate index as low as 20 and useful sealing materials were produced below that value with compositions of this invention.

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Unexpanded hollow polymeric microspheres (Expancel 551 DU in Example 16 and Expancel 461 DU in Example 17) were also expanded during a heat cure with blocked isocyanates to give an expanding sealant as described earlier.

- 5 Example 16 expanded twenty percent and Example 17 expanded twenty-five percent.



TABLE II

Components	1	2	3	4	5	6
Mondur CD	20.7	8.8	---	---	---	---
Vestanat IPDI	---	---	---	5.5	8.5	8.1
Desmodur N-3200	---	---	4.9	---	---	---
Arcol PPG2025	35.7	---	---	---	39.9	53.8
Pluracol TP440	11.9	---	---	---	---	---
Multranol 9151	---	63.1	---	---	---	---
Pluracol 1010	---	13.8	---	---	---	---
Arcol Polymer Polyol 24-32	---	---	85.5	---	---	---
Poly bd R45HT	---	---	---	73.7	---	---
Pluracol PEP550	---	---	---	---	---	3.3
Polamine 650	29.7	12.3	---	---	---	---
Polamine 1000	---	---	7.6	---	---	---
Jeffamine T3000	---	---	---	18.8	34.5	32.8
Castor Oil	---	---	---	---	15.1	---
BiCat 8	0.2	0.1	0.15	0.3	0.3	0.3
Irganox 1076	1.8	1.9	1.85	1.7	1.7	1.7
Isocyanate Index	54.6	52.2	39.8	50.0	50.1	50.0
NH and OH Ratio linear/branched (by equivalent)	1.0/0.5	1.0/0.4	All linear	All branched	1.0/2.8	1.0/1. 7
Cure	A	A	A	A	B	A
Hardness, Shore 00	61.6	59.0	35.0	32.0	22.2	15.0
Hardness, 1/4 Cone	12.2	8.6	18.6	20.9	32.8	36.7
Density, gm/cc	0.89	1.02	0.98	0.81	0.94	0.96
Tensile Strength, N/cm <sup>2</sup> (psi)	53.3 (75.8)	113.3 (161.2)	91.7 (130.5)	14.1 (20.0)	19.8 (28.2)	9.3 (13.2)
% Elongation, Initial	918.4	383.7	429.5	314.9	687.2	813.5
Tear Strength, N/cm (lb/in)	32.6 (18.6)	68.6 (39.2)	37.3 (21.3)	8.2 (4.7)	9.3 (5.3)	4.6 (2.6)
After dry heat aging -18 hrs., 104.4°C, % Elongation -18 hrs., 104.4°C, Syneresis	673.8 None	629.2 None	420.4 None	256.0 None	746.6 None	--- ---



TABLE III

Components	7	8	9	10	11	12
Desmodur-W	5.0	---	---	5.7	6.0	3.7
Vestanat IPDI	---	5.2	3.2	---	---	---
Jeffamine D2000	12.1	---	---	17.2	22.7	---
Polamine 1000	---	14.0	---	---	---	---
PDMS diamine	---	---	14.4	---	---	---
Jeffamine T3000	---	---	---	---	---	9.0
Pluracol 973	57.8	---	---	58.3	---	42.7
Pluracol P1010	13.1	---	---	---	---	---
Castor Oil	---	17.0	36.8	13.8	---	---
Multranol 9151	---	51.8	32.8	---	---	---
Quadrol	---	---	0.8	---	1.6	---
Arcol PPG 1025	---	---	---	---	57.7	---
Acrol LHT 42	---	---	---	---	---	39.6
BiCat 8	0.5	0.3	0.3	0.15	0.15	0.15
Irganox 1076	1.5	1.7	1.7	1.85	1.85	1.85
3M GB B23/500	10.0	10.0	10.0	---	10.0	---
Expancel 551DE	---	---	---	3.0	---	3.0
Isocyanate Index	50.6	39.9	21.0	43.0	24.7	42.7
NH and OH Ratio; linear/branched (by equivalent)	1.0/0.5	1.0/1.8	1.0/46.7	1.0/1.9	1.0/0.1	All Branched
Cure	A	B	B	B	B	B
Hardness, Shore 00	52.0	31.6	58.6	54.4	44.9	38.3
Hardness, 1/4 cone	21.0	28.5	19	9.3	12.8	12.7
Density, gm/cc	0.72	0.65	0.71	0.56	0.75	0.57
Tensile Strenght, N/cm <sup>2</sup> (psi)	14.9 (21.2)	11.4 (16.2)	23.3 (33.1)	64.5 (91.8)	17.5 (24.9)	26.2 (37.3)
% Elongation, Initial	844.6	439.5	180.2	262.5	236.7	244.0
Tear Strength, N/cm (lb/in)	14.9 (8.5)	12.4 (7.1)	22.8 (13.0)	45.9 (26.2)	10.5 (6.0)	17.9 (10.2)
After dry heat aging -18hrs., 104.4°C, % Elongation -18 hrs., 104.4° C, Syneresis	---	---	283.4 None	272.1 None	384.9 None	257.8 None

TABLE IV

Components	13	14	15	16	17	18
Desmocap 11A	26.1	---	23.0	24.8	29.6	23.0
Desmocap 12A	---	50.0	---	---	---	---
PDMS diamine	14.9	---	---	---	---	---
Vestamin IPD	---	0.2	---	0.2	---	0.2
Jeffamine T3000	---	16.2	---	---	8.3	---
Jeffamine D2000	---	---	12.1	10.7	---	9.9
Castor Oil	20.1	---	---	---	10.6	---
Multranol 9151	26.9	---	---	---	---	---
Arcol Polymer Polyol 24-32	---	21.6	---	59.3	---	54.9
Pluracol 973	---	---	59.9	---	45.5	---
BiCat 8	0.5	0.5	0.5	0.5	0.5	0.5
Irganox 1076	1.5	1.5	1.5	1.5	1.5	1.5
3M GB B23/500	10.0	10.0	---	---	---	10.0
Expancel 551 DE	---	---	3.0	---	---	---
Expancel 551 DU	---	---	---	3.0	---	---
Expancel 461 DU	---	---	---	---	4.0	---
Isocyanate Index	19.9	41.0	25.8	23.6	25.0	23.5
NH and OH Ratio; linear/branched (by equivalent)	1.0/24.1	1.0/0.5	1.0/1.1	All linear	All branched	All linear
Cure	C	C	C	C	C	C
Hardness, Shore 00	48.2	53.4	25.5	30.4	48.8	46.0
Hardness, 1/4 cone	24.8	10.6	17.7	16.1	9.0	13.5
Density, gm/cc	0.73	0.72	0.57	0.8	0.79	0.70
Tensile Strength, N/cm <sup>2</sup> (psi)	15.5 (22.1)	49.6 (70.5)	31.9 (45.4)	100.9 (143. 5)	61.2 (87.1)	48.2 (68.5)
% Elongation, Initial	288.3	716.2	573.0	924.5	728.5	889.2
Tear Strength, N/cm (lb/in)	19.4 (11.1)	28.5 (16.3)	30.6 (17.5)	47.8 (27.3)	41.7 (23.8)	24.9 (14.2)
After dry heat aging -18 hrs., 104.4°C, % Elongation -18 hrs., 104.4° C, Syneresis	345.1 None	691.3 None	798.5 None	925.1 None	606.4 None	--- None

TABLE V

Components	19	20	21	22	23	23
Vestanat IPDI	3.0	2.4	4.8	--	5.8	4.9
Cyanamid TMXDI (Meta)	--	--	--	4.6	--	--
Jeffamine T5000	14.4	11.5	--	31.4	--	--
Jeffamine D2000	--	--	8.6	--	--	--
Jeffamine T3000	--	--	--	--	8.8	8.9
Castor Oil	33.4	45.1	38.3	12.8	15.0	15.1
Pluracol 973	41.2	33.0	--	--	--	--
Pluracol 355	--	--	2.2	--	--	--
Multranol 9151	--	--	34.1	--	--	--
Arcol Polymer Polyol 34-28	--	--	--	--	58.4	59.1
Arcol Polyol 11-27	--	--	--	39.2	--	--
BiCat 8	0.2	0.5	0.2	0.15	0.15	0.15
Irganox 1076	1.8	1.5	1.8	1.85	1.85	1.85
Dualite M6001AE	6.0	6.0	--	--	--	--
3M GB B23/500	--	--	10.0	10.0	10.0	10.0
Isocyanate Index	20.3	13.5	26.5	40.2	57.8	48.4
NH and OH Ratio; linear/branched (by equivalent)	All branched	All branched	1.0/8.5	All branched	All branched	All branched
Cure	B	B	A	B	B	B
Hardness, Shore 00	21.1	--	33.0	51.2	70.8	69.8
Hardness, 1/4 cone	22.4	82.3	25.5	18.6	9.0	8.6
Density, gm/cc	0.64	--	0.65	0.69	0.68	0.67
Tensile Strength, N/cm <sup>2</sup> (psi)	17.6 (25.1)	--	22.3 (31.7)	8.9 (12.6)	62.0 (88.2)	91.8 (130.6)
% Elongation, Initial	493.0	--	541.6	440.4	214.6	305.8
Tear Strength, N/cm (lb/in)	11.7 (6.7)	--	17.0 (9.7)	8.9 (5.1)	49.7 (28.4)	55.9 (31.9)
After dry heat aging - 18 hrs., 104.4°C, % Elongation - 18 hrs., 104.4° C, Syneresis	--	--	526.1 None	919.3 None	294.8 None	169.6 None

TABLE VI

Components	25	26	27	28	29	30
Vestanat IPDI	4.0	3.0	2.1	---	---	---
Desmodur W	---	---	---	1.4	---	---
DDI 1410	---	---	---	---	9.6	11.5
Jeffamine T3000	8.9	9.1	9.1	---	---	---
Jeffamine D2000	---	---	---	3.5	---	---
Jeffamine T5000	---	---	---	---	11.9	---
Hycar 1300 x 21	---	---	---	---	---	9.2
Castor Oil	15.4	15.5	15.7	---	---	16.1
Arcol Polymer Polyol 34-28	59.7	60.4	61.1	---	---	51.
LIR 503	---	---	---	58.8	---	---
Arcol LHT-28	---	---	---	28.3	---	---
Poly bd R45HT	---	---	---	---	65.6	---
Fyrol 6	---	---	---	---	0.9	---
BiCat 8	0.2	0.2	0.2	0.15	0.6	0.15
Irganox 1076	1.8	1.8	1.8	1.85	1.4	1.85
3M GB B23/500	10.0	10.0	10.0	---	10.0	10.0
Dualite M6001AE	---	---	---	6.0	---	---
Isocyanate Ratio	39.0	28.9	20.0	45.1	41.1	47.9
NH and OH Ratio linear/branched (by equivalent)	All branched	All branched	All branched	1.0/5.7	1.0/10.1	1.0/9.4
Cure	B	B	B	B	B	B
Hardness, Shore 00	69.6	48.0	---	12.8	---	63.6
Hardness, 1/4 cone	8.4	15.9	115	38.8	47.4	9.9
Density, gm/cc	0.68	0.67	---	---	0.59	0.71
Tensile Strength, N/cm <sup>2</sup> (psi)	78.1 (111.1)	35.9 (51.1)	---	---	8.6 (12.2)	49.6 (70.5)
% Elongation, Initial	271.2	421.6	---	---	538.1	372.8
Tear Strength, N/cm (lb/in)	51.0 (29.1)	25.5 (14.9)	---	---	6.7 (3.8)	44.8 (26.5)
After dry heat aging -18 hrs., 104.4°C, % Elongation	423.5	508.2	---	---	356.2	408.2
-18 hrs., 104.4°C, Syneresis	None	None	---	---	None	None

TABLE VII

Components	31	32	33	34	35
DDI 1410	6.3	5.3	---	5.0	6.1
Vestanat IPDI	---	---	3.7	---	---
Isonate 143L	---	---	---	0.4	---
Jeffamine T3000	6.5	6.5	---	---	---
Polamine 650	---	---	2.7	---	---
Jeffamine T5000	---	---	---	6.5	6.8
Vestamin IPD	---	---	---	---	0.2
Polybd R45HT	22.7	23.0	---	17.6	16.5
Multranol 9238	34.5	35.2	53.5	---	---
Castor Oil	---	---	10.1	---	---
BiCat 8	0.4	0.2	0.4	0.8	0.8
Irganox 1076	1.6	1.8	1.6	1.1	1.1
3M GB B23/500	10.0	10.0	10.0	10.0	10.0
Cab O Sil M5	---	---	---	3.0	3.0
Soybean Oil	10.8	10.8	---	---	---
Emery 3006	7.2	7.2	---	22.2	---
Flexicin P-8	---	---	18.0	---	---
Nuodex 6959	---	---	---	33.4	---
Escopol R-020	---	---	---	---	27.7
Emory 2900	---	---	---	---	27.8
Isocyanate Ratio	42.2	35.1	48.1	82.4	75.1
NH and OH Ratio linear/branched (by equivalent)	All branched	All branched	1.0/0.2	All branched	1.0/0.2
Cure	B	B	A	B	B
Hardness, Shore 00	19.2	---	49.3	30.6	13.4
Hardness, 1/4 cone	30.1	86.0	17.8	21.5	28.1
Density, gm/cc	0.62	---	0.64	0.63	0.61
Tensile Strength, N/cm <sup>2</sup> (psi)	19.2 (27.3)	---	23.8 (33.9)	15.7 (22.3)	9.6 (13.6)
% Elongation	843.7	---	510.9	134.8	388.9
Tear Strength, N/cm (lb/in)	9.1 (5.2)	---	20.8 (11.9)	12.6 (7.2)	8.4 (4.8)
After dry heat aging-18 hrs., 104.4°C, % Elongation -18 hrs., 104.4°C, Syneresis	801.1 None	---	726.5 None	136.8 None	375.0 None

TABLE VIII

Components	36	37
DDI 1410	6.5	6.5
Hycar 1300 x 21	5.2	5.2
Poly bd R45HT	17.8	17.8
Conacure AH35	0.3	0.3
BiCat 8	0.8	0.8
Irganox 1076	1.1	1.1
3M GB B23/500	10.0	10.0
Drapex 429	36.8	---
Shell LVI 450	18.5	18.5
Kronitex TXP	---	36.8
Isocyanate Ratio	97.0	97.0
NH and OH Ratio linear/branched (by equivalent)	1.0/3.8	1.0/3.8
Cure	B	B
Hardness, Shore 00	47.4	18.8
Hardness, 1/4 cone	14.6	35.5
Density, gm/cc	0.66	0.67
Tensile Strength, N/cm <sup>2</sup> (psi)	31.6 (45.0)	17.6 (25.1)
% Elongation	158.2	153.8
Tear Strength, N/cm (lb/in)	25.0 (14.3)	15.9 (9.1)
After dry heat aging -18 hrs., 104.4°C, % Elongation	150.1	140.0
-18 hrs., 104.4°C, Syneresis	None	None

What is Claimed is:

1. A flexible polyurethane\urea elastomer comprising a reaction product of:

- 5 a) from 1% to 55% of a polyisocyanate component having the formula  $Q(NCO)_n$ , wherein n is an integer from about 2 to about 4, and Q is selected from the group consisting of an aliphatic hydrocarbon radical containing from about 2 to about 100 carbon atoms, and up to 50 heteroatoms; a cycloaliphatic hydrocarbon radical containing from 4 to 100 carbon atoms and zero to 50 heteroatoms; an aromatic hydrocarbon radical or heterocyclic aromatic radical containing from 6 to 15 carbon atoms and zero to 10 heteroatoms, and an araliphatic hydrocarbon radical containing from 8 to 100 carbon atoms and zero to 50 heteroatoms,
- 10
- 15
- 20 b) from 45% to 99% of an isocyanate reactive component, containing from at least one polyamine selected from the group consisting of those polyamines which contain more than one primary or secondary amino group capable of reacting with isocyanate groups, said polyamine having a molecular weight of from 400 to 100,000, and at least one polyol selected from the group consisting of liquid or quasi-liquid polyols having a functionality of from 2 to 8, said reaction product having an isocyanate index of less than 100, and from 0.005% to 5% of a catalyst for the reaction of said polyisocyanate component and said isocyanate reactive component,
- 25
- 30

wherein said elastomer contains from 1 to 199 equivalent percent active amine hydrogen per isocyanate equivalent.

- 35 2. A flexible elastomer according to claim 1 wherein said polyisocyanate is selected from the group consisting of 1-isocyanato-3,3,5-trimethyl-5-isocyanato

methyl cyclohexane (isophorone diisocyanate), dimer acid diisocyanate, 2,4'diphenyl methane diisocyanate and carbodiimide derivatives thereof, 4,4'diphenyl methane diisocyanate and carbodiimide derivatives thereof

5

3. A flexible elastomer according to claim 2 wherein said polyisocyanate component further comprises a polyurethane prepolymer having blocked isocyanate groups wherein said prepolymer is prepared from  
10 poly(oxypropylene)diol or poly(oxypropylene)triol and toluene diisocyanate.

4. A flexible elastomer according to claim 1 wherein said polyamine comprises from about 2 to about  
15 40% of said composition, and is selected from the group consisting of aminopolyethers, polyamidoamines, polyoxyalkylene polyamines, amine-terminated butadiene/acrylonitrile copolymers, aminoalkyl terminated polydiorganosiloxanes, polytetramethylene oxide-di-  
20 aminobenzoates, polyethers containing aromatic amine end groups and amine-terminated polyethers containing a moiety selected from urea, amide, ester and urethane moieties in the polymer backbone.

25 5. A flexible elastomer according to claim 4 wherein said polyamine is selected from polyoxyalkylene polyamines, amine-terminated butadiene/acrylonitrile copolymers, aminoalkyl terminated polydiorganosilxanes, and polytetramethylene oxide-di-p-amino benzoates.

30

6. A flexible elastomer according to claim 1 wherein said polyol comprises from about 10% to about 80% of said composition, and is selected from the group consisting of polyether polyols based on ethylene oxide,  
35 propylene oxide, butylene oxide, tetrahydrofuran, epichlorohydrin or mixtures thereof, ricinoleic acid derivatives, polyester polyols, polyamide or



polyesteramide polyols; tertiary amine containing polyols, propoxylated amides or amines; polyalkadiene polyols derived from butadiene polymers or copolymers, and hydrogenated derivatives thereof; polyacetals, 5 polycarbonates containing hydroxyl groups; polyhydroxyl (meth)acrylic resins, polythioether polyols and polymer polyols.

7. A flexible elastomer according to claim 6 10 wherein said polyol is selected from the group consisting of a polypropylene oxide polyol, a polypropylene oxide/polyethylene oxide polyol, a polybutadiene polyol, a polymer polyol and castor oil.

8. A flexible elastomer according to claim 7 15 comprising wherein said polyol is a polymer polyol containing of a polymer polyol, wherein said polyol contains from 1 to 60% by weight of fine polymer particles of a graft copolymer containing poly(alkylene 20 oxide) polyol and a group selected from styrene and acrylonitrile.

9. A flexible elastomer according to claim 1 25 comprising from 5% to 95% of at least one plasticizer selected from the group consisting of polyalphaolefins, cyclic polyolefins, petroleum oils, vegetable oils, naphthenic oils, paraffinic oils, synthetic oils, phosphate esters, monoesters, diesters, polyesters, rosin esters, pine oil, coal tar, glyceryl- 30 tri(acetylricinoleate) and mixtures thereof.

10. A flexible elastomer according to claim 1 35 further comprising from 10 to 60 volume percent hollow microspheres selected from the group consisting of glass microspheres, expanded and unexpanded polymeric microspheres, and ceramic microspheres.

11. A sealant for a signal conducting device comprising a flexible polyurethane/urea elastomer according to claim 1.

5           12. A sealant according to claim 15 wherein said reaction product is extended with at least from 5 to 95 percent of a plasticizer, forming a plasticized sealant which is substantially nonexuding.

10           13. A signal transmission component comprising a signal transmission device, and an elastomer according to claim 1, said elastomer being a dielectric elastomer.

15           14. A signal transmission component wherein said device comprises  
a) an outer closure member capable of enclosing a cable splice, said cable splice having at least one set of wires penetrating said splice, and  
b) a means for sealing said outer closure  
20           comprising an endseal composed of a flexible polyurethane/urea elastomer according to claim 1, said endseal being positioned between said outer closure and said at least one set of wires, said endseal having means formed therein for passage of  
25           said wires.

15. An electrical transmission device comprising an electrically transmissive component and a flexible polyurethane/urea elastomer according to claim 1.

**INTERNATIONAL SEARCH REPORT**

PCT/US 93/05309

International Application No

<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			
Int.Cl. 5	C08G18/48; C08G18/69;	C08G18/50; C08G18/61;	C08G18/40; H01B3/30; C08G18/60 C08J9/32
<b>II. FIELDS SEARCHED</b>			
Minimum Documentation Searched <sup>7</sup>			
Classification System	Classification Symbols		
Int.Cl. 5	C08G ;	C08J ;	H01B
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<sup>9</sup></b>			
Category <sup>o</sup>	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	US,A,3 979 364 (R.L. ROWTON) 7 September 1976 see claims 1-4,9-11 see column 2, line 24 - line 40 see column 4, line 24 - line 42 see column 6, line 4 - column 7, line 11 ---		1-7
X	US,A,3 892 820 (HACHIRO GOTO ET AL.) 1 July 1975 see claims 1,4 see column 2, line 35 - line 54 see column 5, line 27 - line 39 ---		1-7
X	EP,A,0 421 220 (MOBAY) 10 April 1991 see claims 1,8 see page 3, line 28 - page 4, line 17 ---		1-8
-/--			
<p><sup>o</sup> 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	
06 OCTOBER 1993		1993 10 06	
International Searching Authority		Signature of Authorized Officer	
EUROPEAN PATENT OFFICE		VAN PUYMBROECK M. A.	

III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)		
Category °	Citation of Document, with indication, where appropriate, of the relevant passages	Relevant to Claim No.
X	EP,A,0 362 647 (MOBAY) 11 April 1990 see claims 1,8 see column 3, line 41 - column 4, line 47 ---	1-8
A	FR,A,1 358 187 (THE GENERAL TIRE & RUBBER CO.) 2 March 1964 see page 1, right column, paragraph 3 see page 2, right column, paragraph 2 - page 3, right column, paragraph 3 see page 4, right column, paragraph 4 - page 5, left column, paragraph 1 ---	1
A	EP,A,0 288 067 (ASAHI GLASS CO.) 26 October 1988 see claims 1-3 see page 5, line 11 - page 6, line 40 see page 8, line 37 - line 46 -----	1

**ANNEX TO THE INTERNATIONAL SEARCH REPORT  
ON INTERNATIONAL PATENT APPLICATION NO.**

US 9305309  
SA 76322

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report. The members are as contained in the European Patent Office EDP file on  
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