

This invention relates to an isocyanate-terminated prepolymer and a process for its use in manufacturing polyurethane article, particularly flexible polyurethane foam.

Polyurethane foams are generally prepared by intimately mixing under reaction conditions a substance containing isocyanate groups with a substance containing groups bearing isocyanate-reactive hydrogen atoms. The substance containing isocyanate-reactive hydrogen atoms is generally a polyalcohol and can be an amine or imine-terminated polyether polyol, a polyester polyol or especially a conventional polyether polyol. The isocyanate is generally an organic polyisocyanate, especially an aromatic polyisocyanate such as toluene diisocyanate or a (poly) methylene-bridged polyisocyanate such as methylene diphenyldiisocyanate (MDI).

When preparing flexible, open-celled, polyurethane foam it is advantageous to employ polyisocyanates or polyisocyanate compositions which comprise a significant amount of a diisocyanate, thereby limiting the cross-linking within the polymer network and providing for desirable physical properties such as elongation. Especially desirable due to the physical properties of the resulting foam is the use of 4,4'-methylene diphenyldiisocyanate in the manufacture of polyurethane foam.

In the case of methylene-bridged diisocyanates such as methylene diphenyldiisocyanate (MDI) and especially the 4,4'-isomer, processing problems in the preparation of the foam may be encountered. The 4,4'-isomer is a solid at room temperature and therefore when used in a relative pure state, requires that the preparation of the foam be conducted at elevated temperatures. To overcome this problem, it is known from the art to operate with blends of poly- and/or diisocyanates comprising 4,4'-MDI, see for example, U.S. Patent 4,256,849. An alternative means of overcoming this processing inconvenience is to prepare an isocyanate-terminated prepolymer from the 4,4'-MDI thereby reducing its tendency to solidify at room or low temperatures.

Isocyanate-terminated prepolymers are generally prepared by reaction of a large molar excess of a suitable isocyanate with an active hydrogen-containing compound. Such active hydrogen-containing compounds are usually difunctional or trifunctional compounds of various molecular weights, and especially polyether polyols. The selection of the active hydrogen-containing compound is made in consideration of the physical properties desired for the resulting foam. For example, when preparing flexible polyurethane foams known as "cold-cure" foams use of a polyether polyol comprising oxyethylene residues is desirable. The foams are identified as "cold-cure" foams because when removed from the mold the requirement to heat the foam to accelerate the curing of the polymer is no longer necessary. Such "cold-cure" foam can generally be handled in a relatively short period of time without any significant risk of deformation.

Patent publication EP 22,617, describes a process for the manufacture of "cold-cure" flexible polyurethane foams by reacting an organic polyisocyanate composition comprising a prepolymer prepared from the reaction of methylene diphenyldiisocyanate with a polyoxyalkylene diol or triol containing from at least 50 weight percent, randomly distributed, oxyethylene residues and having a hydroxyl equivalent weight of from 1000 to 2000. While such a prepolymer essentially overcomes the processing problems associated with 4,4'-MDI and provides for a foam with acceptable physical properties it is desirable to improve further the foam properties to meet with more demanding industrial requirements. Particularly, it is desired to improve elongation properties while maintaining overall acceptable physical properties such as the extent of cell opening within the foam.

To this effect, the preparation of isocyanate-terminated prepolymers from alternative polyoxyalkylene polyols and their subsequent use in the manufacture of polyurethane foam has been investigated.

Surprisingly, it has now been found that to obtain improvement of the foam properties, particularly elongation, it is necessary to select the polyoxyalkylene polyol both in consideration of its hydroxyl equivalent weight and also its oxyethylene content.

In a first aspect, this invention is an isocyanate-terminated prepolymer prepared by reacting a polyisocyanate comprising 4,4'-methylene diphenyldiisocyanate in from at least 40 weight percent with a polyoxyalkylene polyol, wherein the polyol has an average functionality of from 2 to 4 and a hydroxyl equivalent weight of from 2200 to 3500 and contains oxyethylene residues in an amount of from 40 to 68 percent by weight.

In a second aspect, this invention is a process for the preparation of a polyurethane foam by intimately mixing under reaction conditions components comprising

(a) polyisocyanate composition containing an isocyanate-terminated prepolymer prepared by reacting a polyisocyanate comprising 4,4'-methylene diphenyldiisocyanate in an amount of at least 40 weight percent with a polyoxyalkylene polyol, wherein the polyol has an average functionality of from 2 to 4 and a hydroxyl equivalent weight of from 2200 to 3500 and contains oxyethylene residues in an amount of from 40 to 68 percent by weight; and

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(b) an active hydrogen-containing composition comprising (1) a high equivalent weight isocyanate-reactive material, (2) a blocking agent, and (3) a catalyst for promoting the formation of urethane groups wherein component (a) is present in an amount to provide from 0.6 to 1.3 isocyanate groups per active hydrogen atom present in component (b).

5 In yet a third aspect, this invention is an opened-celled polyurethane foam having an average density of from 10 to 250 kilograms per cubic meter prepared according to the above process.

The isocyanate-terminated prepolymer of this invention may be characterized as having an isocyanate content of from 5 to 31 weight percent, preferably 10, more preferably 15, yet more preferably 25 and most preferably 28 weight percent and up to 31 weight percent.

10 The isocyanate-terminated prepolymer of this invention is prepared by contacting under reaction conditions a polyisocyanate with a polyoxyalkylene polyol. The polyoxyalkylene polyol used in the preparation of the prepolymer has an average functionality of from 2 to 4, preferably from 2 to 3 and most preferably has an average functionality of 3. By "average functionality" it is understood the number of isocyanate-reactive sites per molecule, in the case of polyols, hydroxyl groups, capable of reacting with
15 isocyanate groups.

The polyoxyalkylene polyol is further characterized in that it has a hydroxyl equivalent weight of from 2200 to 3500 and contains oxyethylene residues in an amount of from 40 to 68 percent by weight.

Preferably the hydroxyl equivalent weight of the polyol is 2300 and more preferably 2400 and up to 3200, more preferably up to 2800.

20 The oxyethylene residue content of the polyol preferably is 55 and more preferably 58 and most preferably 60 up to 65, more preferably up to 64 percent by weight. An oxyethylene content of the polyol outside these ranges when eventually incorporated into a polyurethane foam may not provide for the desired property characteristics of the resulting foam.

The distribution of the oxyethylene residues within the polyol may be as one or a plurality of oxyethylene blocks either internally or terminally situated on the polyoxyalkylene chain, or alternatively in a random manner throughout the entirety of the polyoxyalkylene chain of the polyol, or combinations thereof.

The remaining part of the polyoxyalkylene chain when not constituted by oxyethylene residues comprises oxypropylene, oxybutylene residues or mixtures thereof, but especially of oxypropylene residues. Such residues being obtained from reaction of the alkylene oxides, propylene oxide, and butylene oxide
30 respectively. A convenient and preferred source of oxyethylene residues is ethylene oxide. Residues from other oxides may also be present.

Methods of preparing the above described polyoxyalkylene polyols are well known in the art and generally comprise the base-catalyzed addition of the alkylene oxide(s), especially ethylene oxide and propylene oxide, to a di-, tri-, or tetrafunctional initiator at elevated temperatures and pressures.

35 Suitable initiators include difunctional compounds such as water, ethylene glycol, propylene glycol and higher oxyalkylene adducts thereof, bis-(4-hydroxyphenyl)-2,2-propane and glycol adducts of phthalic anhydride; trifunctional compounds such as trimethylolpropane, hexanetriol and especially glycerine; and tetrafunctional compounds such as ethylenediamine and pentaerythritol.

The preferred initiators due to ready availability and convenient processing are water, ethylene glycol, propylene glycol, glycerine and their higher oxyalkylene adducts, especially preferred is glycerine.

The polyisocyanate used to prepare the prepolymer consists essentially of a methylene diphenyldiisocyanate or a polymethylene polyphenyl polyisocyanate or mixtures thereof, wherein the polyisocyanate comprises an amount of at least 40 weight percent of the isomer 4,4'-methylene diphenyldiisocyanate (MDI). Preferably the polyisocyanate comprises 45, more preferably 52, and most preferably from 60 and
45 up to 98, more preferably up to 90 weight percent 4,4'-MDI.

When not constituted by 4,4'-MDI, the remaining part of the polyisocyanate used in reaction to prepare the prepolymer can comprise 2,4'-MDI, 2,2'-MDI, polymethylene polyphenyl polyisocyanates or mixtures thereof. When present, advantageously the 2,4'-MDI does not constitute more than 50 weight percent of the isocyanate used to prepare the prepolymer and the polymethylene polyphenyl polyisocyanate not more
50 than 50 weight percent.

In a preferred embodiment of this invention, the polyoxyalkylene polyol, preferably a triol, is reacted with a polyisocyanate consisting essentially of 4,4'-MDI, 2,4'-MDI and polymethylene polyphenyl polyisocyanate wherein the percent by weight ratio of the 4,4'-MDI to 2,4'-MDI based on total weight of polyisocyanate present is from 40:40 to 90:10, preferably from 50:30 to 75:10, and more preferably from
55 50:25 to 65:12 percent, the remainder being the polymethylene polyphenyl polyisocyanate.

Exemplary of such a preferred polyisocyanate for use in preparing the prepolymer is that obtained by blending 4,4'-MDI and 2,4'-MDI in a 70:30 weight ratio with a crude methylene diphenyldiisocyanate composition such as, for example, VORANATE™ M220 available from The Dow Chemical Company, and



containing polymethylene polyphenyl polyisocyanate (approximately 57.5 weight percent), 4,4'-MDI (40 weight percent) and 2,4'-MDI (2.5 weight percent). Combining the 70:30, 4,4'-2,4'-MDI blend with VORANATE™ M220 in for example a 60:40 weight ratio provides a polyisocyanate suitable for use in manufacturing the prepolymer consisting essentially of 4,4'-MDI (58 percent), 2,4' (19 percent) and polymethylene polyphenyl polyisocyanate (23 percent). Such a prepolymer obtained from the preferred polyisocyanate is also suitable for immediate use in the preparation of a flexible polyurethane foam without, for example, any subsequent blending with other polyisocyanates.

In a less preferred embodiment, the polyoxyalkylene polyol may be reacted with a polyisocyanate consisting essentially of 4,4'-MDI and 2,4'-MDI to provide a prepolymer which if subsequently desired may be blended with other isocyanates including crude methylene diphenyldiisocyanate.

When preparing the prepolymer the relative amount of polyoxyalkylene polyol to polyisocyanate is such to provide for a resulting prepolymer having the above mentioned isocyanate content. In preparing the prepolymer the above described polyoxyalkylene polyol optionally may also be used in combination with other isocyanate-reactive substances conventionally used in the preparation of isocyanate-terminated prepolymers. When used in combination with other conventional isocyanate reactive substances the above-described polyoxyalkylene polyol is present in an amount of from 1 to 99 weight percent of the total isocyanate reactive mixture used to prepare the isocyanate-terminated prepolymer. Preferably the polyoxyalkylene polyol is present in from at least 10 and more preferably in from at least 20 weight percent. Such conventional substances include for example ethylene glycol, propylene glycol, and higher molecular weight adducts thereof such as obtained by reaction with C₂ to C₄ alkylene oxide, and not falling within the above description of the polyoxyalkylene polyol. Exemplary of higher molecular weight adducts are polyoxypropylene glycols having a molecular weight of from 134 to 2000 such as, for example, those designated as VORANOL™ P400, VORANOL™ P1010 and VORANOL™ P2000 all available from The Dow Chemical Company. Other conventional isocyanate reactive substances also include oxyalkylene adducts of initiators as given for the above-described polyoxyalkylene polyol.

The prepolymer may be prepared by using conditions that have been described in the prior art for such preparations. Typically, the prepolymer can be prepared by the controlled addition of the polyol to the isocyanate while continuously mixing. The rate of addition of the polyol to the isocyanate advantageously is such so as to maintain, if necessary with heating or cooling, a reaction temperature of from 45°C to 90°C, preferably from 60°C to 80°C.

In the second aspect of this invention, there is provided a process for the preparation of polyurethane foam by intimately mixing under reaction conditions components comprising

- (a) the prepolymer as described hereinabove optionally as part of a polyisocyanate composition; and
- (b) an active hydrogen-containing composition comprising (1) a high equivalent weight isocyanate-reactive material, (2) a blowing agent, and (3) a catalyst for promoting the formation of urethane groups wherein component (a) is present in an amount to provide from 0.6 to 1.3 isocyanate groups per active hydrogen atom present in component (b).

The high equivalent weight isocyanate-reactive material present in component (b) is a compound containing from 2 to 8, preferably from 2 to 4 isocyanate-reactive, hydrogen atoms, per molecule and which has an average equivalent weight of from 500 to 3,000 and preferably from 800 to 2,500. Typical high equivalent weight isocyanate-reactive materials include polyamines, polyester polyols and especially polyether polyols. The polyether polyol, may be a polyoxypropylene or a poly(oxypropylene-oxyethylene) polyol or a mixture thereof. Such polyether polyols are well known in the art and many being commercially available. The poly(oxypropylene-oxyethylene) polyol include oxyethylene capped polyoxypropylene polyols and other random or block products obtained by reacting ethylene and propylene oxide with active hydrogen-containing initiators.

Suitable high equivalent weight isocyanate-reactive material for use in preparing the polyurethane foams are polyether polyols, generally diols and triols having an average hydroxyl equivalent weight of from 500 to 3,000 and preferably from 800 to 2,500. Exemplary of such polyether polyols are those sold by The Dow Chemical Company under the trademark VORANOL™ and include, for example, VORANOL™ 4711, VORANOL™ 6001, VORANOL™ 3322 and VORANOL™ 1421. Other suitable polyols include PHD-, PIPA- or SAN-type copolymer polyols such as, for example, VORANOL™ CP-8020.

The blowing agent contained within component (b) is present in an amount to provide the resulting polyurethane foam with an overall density of from 10 to 250 kilograms per cubic meter, preferably 15, more preferably 25, and most preferably 30 and preferably up to 100, more preferably up to 80 kilograms per cubic meter.



In a preferred embodiment of this invention the blowing agent comprises water. Water reacts with isocyanate moieties leading to generation of carbon dioxide, the so generated nascent carbon dioxide functions as a blowing agent providing for a cellular structure to the polyurethane.

Typically, the amount of water present providing for sufficient blowing capacity to result in foams with the desired densities is from 1.0 to 7 parts by weight per 100 parts by weight of component (b), based on total weight of all constituents present in component (b). Advantageously, such amounts of water are preferably 2.5, more preferably 3.5 and up to 6, more preferably up to 5.5 parts by weight.

The blowing requirement for preparing foams of the desired density can be provided for in its entirety by use of water. However, in addition to water, small amounts of physical blowing agents may be present when necessary to achieve the desired density. Exemplary of such physical blowing agents which may be present include, for example, methylene chloride, trichlorofluoromethane, dichlorotrifluoroethane, chlorodifluoroethane; hydrocarbons such as pentane and hexane; and entrained gases such as air nitrogen and carbon dioxide.

Suitable catalysts which may be used in the process of this invention to promote the formation of urethane groups include tertiary amines and organometallic compounds especially tin compounds. Exemplary of suitable catalysts are tertiary amine compounds including N,N-dimethylcyclohexylamine, N,N-dimethylbenzylamine, N,N-dimethanolamine, bis(dimethylaminoethyl)ether and 1,4-diazobicyclo[2.2.2]octane; are tin compounds including stannous octoate and dibutyltin dilaurate. Combinations of amine and/or tin compounds as catalyst may advantageously be employed in the process.

In the process of this invention component (a) is present in an amount sufficient to provide from 0.6 to 1.3 isocyanate groups per isocyanate-reactive hydrogen atom present in both component (b). Preferably, the amount of component (a) is such so as to provide from 0.8 up to 1.15, more preferably up to 1.05 isocyanate groups per active hydrogen atom. The amount of isocyanate present may also be expressed in terms of an "isocyanate-reaction index". In this case, an isocyanate-reaction index of 100 corresponds to a ratio of 1 isocyanate group per isocyanate-reactive hydrogen atom.

Other conventional components which optionally, but advantageously are present in the process, include surfactants such as, for example, siloxane-oxyalkylene copolymers such as products sold under the trademark Tegostab by Th. Goldschmidt including B-4113 and B-4690; chain extending agents such as, for example, ethylene glycol, 1,4-butanediol, diethanolamine, diisopropanolamine and polyamine; fillers; fire-retardants, for example, melamine; pigments and dyes.

The components of the foam-forming reaction may be mixed together in any convenient manner, for example, by using any of the mixing equipment described in the prior art for the purpose. If desired non inter-reactive components may be preblended so as to reduce the number of component streams which require intimate mixing with each other. It is generally advantageous to use a two-stream system whereby one stream normally comprises prepolymer and optionally any additional polyisocyanate, while the second stream normally comprises all other components of the reaction mixture and which essentially do not interreact prior to mixing with the isocyanate stream.

The process of the invention and the isocyanate-terminated prepolymer is particularly useful in the preparation of polyurethane foams especially "cold-cure" foams. Such foams are suitable for many application areas including upholstery, sound and vibration damping and cushioning.

Use of the prepolymers of this invention in the preparation of polyurethane foams provides for foams exhibiting an enhanced degree of elongation compared to foams obtained from reaction of art known prepolymers.

The invention is illustrated by the following Examples in which all parts and percentages are by weight, unless otherwise stated.

Prepolymers are prepared according to the procedure further described and evaluated by preparing flexible polyurethane foam therefrom using the polyol formulation given below. The polyurethane foam is prepared by intimately mixing the isocyanate, prepolymer, with the polyol formulation using a high pressure foaming machine.

Polyol Formulation	
100 parts	glycerine-initiated polyoxypropylene-oxyethylene (15% cap) polyol; molecular weight 6000
3.75 parts	water
0.8 part	triethylenediamine (33% in dipropylene glycol)
0.15 part	Catalyst NIAX-A1 supplied by Union Carbide Co.
0.8 part	Surfactant, Tegostab B4113 supplied by Th Goldschmidt Ag.



Physical properties of the resulting molded foams obtained by mixing reaction components under high pressure conditions and introducing the reacting mass into a mold thermostated to 50 °C are reported. Test procedures employed to measure the physical properties as reported are for tensile strength and elongation - DIN 53571; compression load deflection (CLD)- DIN 53577; and for indentation load deflection (ILD)- DIN 53576.

Prepolymer 1

An isocyanate-terminated prepolymer having an isocyanate content of 29 weight percent is prepared by reacting 11.1 parts of a polyoxyethylene-oxypropylene triol (hydroxyl equivalent weight 2463; oxyethylene content 61 percent, randomly distributed) with 100 parts of an isocyanate blend constituted of 4,4'-MDI (58 percent), 2,4'-MDI (19 percent) and polymethylene polyphenyl polyisocyanate (23 percent).

The polyol is added to the isocyanate blend while continuously mixing at a rate such to maintain a reaction temperature of between 65 °C to 70 °C. When the entire amount of the polyol has been added the resulting reaction mixture is stirred at the same temperature for an additional hour to ensure completion of reaction.

Properties of foams obtained by reacting the so prepared prepolymer with the identified polyol formulation are given hereinabove.

	Foam 1	Foam 2	Foam 3
Isocyanate Reaction Index	90	100	110
Free-rise density (kg·m ⁻³)	36	36	/
Molded density (kg·m ⁻³)	44.4	44.9	45.2
Elongation (%)	143	133	119
Tensile Strength (kPa)	117	138	181
CLD (kPa)	3.56	4.44	6.43
ILD (N)	150	195	260

Prepolymer 2

An isocyanate-terminated prepolymer having an isocyanate content of 29 weight percent is prepared according to the same procedure as for Prepolymer 1, by reacting 11.0 parts of a polyoxyethylene-oxypropylene triol (hydroxyl equivalent weight 2270; oxyethylene content 59 percent, randomly distributed) with 100 parts of an isocyanate blend constituted of 4,4'-MDI (58 percent), 2,4'-MDI (19 percent) and polymethylene polyphenyl polyisocyanate (23 percent).

Properties of foams obtained by reacting the so prepared prepolymer with the identified polyol formulation are given hereinabove.

	Foam 4	Foam 5	Foam 6
Isocyanate Reaction Index	90	100	110
Molded density (kg·m ⁻³)	44.7	44.4	44.5
Elongation (%)	130	125	118
Tensile Strength (kPa)	134	152	180
CLD (kPa)	4.34	5.41	6.44

Comparative Prepolymer A

A comparative prepolymer having an isocyanate content of 29 weight percent is prepared, by the same procedure as for Prepolymer 1, by reacting 10.8 parts of a polyoxyethylene-oxypropylene triol (hydroxyl equivalent weight 1670; oxyethylene content 72 percent, randomly distributed) with 100 parts of an isocyanate blend constituted of 4,4'-MDI (58 percent), 2,4'-MDI (19 percent) and polymethylene polyphenyl polyisocyanate (23 percent).



	Foam A*	Foam B*	Foam C*
Isocyanate Reaction Index	90	100	110
Free-rise density (kg:m ³)	38	/	/
Molded density (kg:m ³)	45.7	45.6	45.5
Elongation (%)	120	115	99
Tensile Strength (kPa)	122	140	159
CLD (kPa)	3.81	4.77	5.89
ILD (N)	150	190	240

* Not an example of this invention

Comparative Prepolymer B

A comparative prepolymer having an isocyanate content of 29 weight percent is prepared, by the same procedure as for Prepolymer 1, by reacting 11.1 parts of a polyoxyethylene-oxypropylene triol (hydroxyl equivalent weight 2670; oxyethylene content 70 percent, randomly distributed) with 100 parts of an isocyanate blend constituted of 4,4'-MDI (58 percent), 2,4'-MDI (19 percent) and polymethylene polyphenyl polyisocyanate (23 percent).

	Foam D*	Foam E*
Isocyanate Reaction Index	90	100
Molded density (Kg:m ³)	47.8	46.8
Elongation (%)	117	103
Tensile Strength (kPa)	118	143
CLD (kPa)	4.12	5.08

* Not an example of this invention.

Foams 1 to 6 show the enhanced elongation performance that can be obtained with the prepolymers of this invention relative to comparative prepolymers.

Prepolymer 3

An isocyanate-terminated prepolymer having an isocyanate content of 29 weight percent is prepared according to the procedure as given for Prepolymer 1, only this example, 11.1 parts of a polyoxyethyleneoxyalkylene triol (hydroxyl equivalent weight 2635; oxyethylene content 61 percent equally distributed as an internal oxyethylene block and as a terminal oxyethylene block) are reacted with the same polyisocyanate blend.

Comparative Prepolymer C

A comparative prepolymer having an isocyanate content of 29 weight percent is prepared by the same procedure as for Prepolymer 1, by reacting 10.9 parts of a polyoxyethylene-oxypropylene triol (hydroxyl equivalent weight 1954; oxyethylene content 64 percent, randomly distributed) with 100 parts of an isocyanate blend constituted of 4,4'-MDI (58 percent), 2,4'-MDI (19) percent and polymethylene polyphenyl polyisocyanate (23 percent).

The following table presents physical properties of foams obtained by reacting the prepolymers 1, 3 and C with the polyol formulation presented hereinabove. Foams are prepared in this instance using a low pressure mixing dispensing unit.

The data obtained clearly indicates the advantageous elongation performance that can be obtained with the prepolymers of this invention.

