



Europäisches Patentamt
European Patent Office
Office européen des brevets



Publication number: **0 312 365 B1**

12

EUROPEAN PATENT SPECIFICATION

45 Date of publication of patent specification: 10.08.94 51 Int. Cl.⁵: C08G 18/10, C08G 18/78

21 Application number: 88309615.8

22 Date of filing: 13.10.88

54 **Polyisocyanate compositions.**

30 Priority: 16.10.87 GB 8724348
09.09.88 GB 8821186

43 Date of publication of application:
19.04.89 Bulletin 89/16

45 Publication of the grant of the patent:
10.08.94 Bulletin 94/32

84 Designated Contracting States:
AT BE CH DE ES FR GB GR IT LI NL SE

56 References cited:
EP-A- 0 000 194 DE-A- 2 062 068
DE-A- 2 737 670 FR-A- 2 352 011
US-A- 3 420 800 US-A- 3 832 311

CHEMICAL ABSTRACTS, vol. 70, no. 6, 10th
February 1969, pages 1-2, abstract
no.20347s, Columbus, Ohio, US; I.A. ZHAR-
KOVA et al.: "Determination of allophanateg-
roups in polyurethane prepolymers by infra-
red spectroscopy"

73 Proprietor: ICI AMERICAS INC.
Concord Pike & New Murphy Road
Wilmington Delaware 19897 (US)

Proprietor: IMPERIAL CHEMICAL INDUSTRIES

PLC
Imperial Chemical House,
Millbank
London SW1P 3JF (GB)

72 Inventor: Cassidy, Edward Francis
rue J. Vanderlinden 28
B-1180 Ukkel (BE)
Inventor: Gillis, Herbert Russell
Mechelsesteenweg 146
B-1960 Sterrebeek (BE)
Inventor: Leenslag, Jan Willem
Beekstraat 10
B-3055 Neerijse (BE)
Inventor: Parfondry, Alain
avenue J. Bordet 66-12
B-1140 Evere (BE)

74 Representative: Leherte, Georges Maurice
Lucien Marie et al
ICI Group Patents Services Dept.
PO Box 6
Shire Park
Bessemer Road
Welwyn Garden City Herts. AL7 1HD (GB)

Note: Within nine months from the publication of the mention of the grant of the European patent, any person may give notice to the European Patent Office of opposition to the European patent granted. Notice of opposition shall be filed in a written reasoned statement. It shall not be deemed to have been filed until the opposition fee has been paid (Art. 99(1) European patent convention).

EP 0 312 365 B1

Description

This invention relates to isocyanate terminated prepolymers useful in the production of mouldings by the reaction injection moulding process and in the production of foams and to reaction systems containing said compositions.

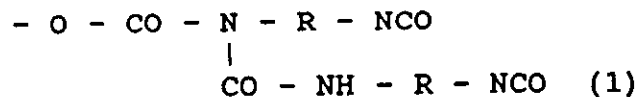
One of the more important methods of making isocyanate based cellular or non-cellular elastomers is the technique known as reaction injection moulding (RIM) whereby two highly reactive liquid streams are impingement mixed and rapidly injected into a mould cavity. The two streams generally comprise a polyisocyanate or derivative thereof, usually known as the "A" component, and an isocyanate reactive stream, known as the "B" component, commonly containing polyol and/or polyamine reactants.

It has now been found that allophanate-modified isocyanate-terminated prepolymers are useful in the production of RIM elastomers and can be processed on conventional equipment to give elastomers having a high level of physical properties. The prepolymers are also useful in the production of foams.

Accordingly, the present invention provides an allophanate-modified isocyanate-terminated prepolymer obtainable by reacting a polymeric polyol having a nominal average hydroxyl functionality of from 2 to 3 and an average hydroxyl equivalent weight of from 1000 to 3000 with at least 5 equivalents, per hydroxyl equivalent, of a diphenylmethane diisocyanate isomer or mixtures thereof optionally together with a minor proportion of higher functionality polyphenylene polymethylene polyisocyanates, the product containing allophanate groups in a ratio with respect to urethane groups of at least 1:4.

Unless otherwise stated, the expressions "equivalent weight" and "molecular weight" as used throughout the present specification refer to the equivalent weight values as may be calculated by measuring the content of functional groups per weight of polymer sample, and to the molecular weight values as may be calculated from the thus obtained equivalent weight and the theoretical functionality of the polymers.

The prepolymers of the invention may be regarded as allophanate polyisocyanates in which a significant proportion of the isocyanate groups are present in terminal groups of the formula :



wherein R represents a divalent hydrocarbon radical, for example a methylene-bis-phenylene radical.

Especially useful prepolymers contain at least two groups of Formula 1 separated one from another by a chain of more than 70 atoms, preferably more than 100 atoms.

In this connection, references to the number of atoms present in a chain indicate the number of atoms present in the backbone of a chain but not hydrogen atoms or other substituents attached to backbone atoms. Thus, in a poly(propylene oxide) chain, the carbon and oxygen atoms constituting the backbone of the chain are counted but not the attached hydrogen atoms or the atoms present in the methyl substituents.

Organic polyisocyanates which may be used in the preparation of the prepolymers of the invention include the available MDI isomers, that is to say 4,4'-diphenylmethane diisocyanate, 2,4'-diphenylmethane diisocyanate and mixtures thereof. Whilst diisocyanates are the preferred polyisocyanates for use in the preparation of the polyisocyanate compositions, mixtures of diisocyanates with minor proportions of higher functionality polyisocyanates may be used if desired. Thus, MDI variants such as uretonimine-modified MDI may be used.

The starting materials for use in the preparation of the prepolymers are polymeric polyols having average nominal hydroxyl functionalities of 2 to 3 and average hydroxyl equivalent weights in the range from 1000 to 3000. Suitable polyols and methods for their preparation have been fully described in the prior art and, as examples of such polyols, there may be mentioned polyesters, polyesteramides, polythioethers, polycarbonates, polyacetals, polyolefins, polysiloxanes and, especially, polyethers.

Polyether polyols which may be used include products obtained by the polymerisation of a cyclic oxide, for example ethylene oxide, propylene oxide or tetrahydrofuran in the presence, where necessary, of polyfunctional initiators. Suitable initiator compounds contain a plurality of active hydrogen atoms and include water and polyols, for example ethylene glycol, propylene glycol, diethylene glycol, cyclohexane dimethanol, resorcinol, bisphenol A, glycerol, trimethylolpropane or 1,2,6-hexanetriol. Mixtures of initiators and/or cyclic oxides may be used.

Especially useful polyether polyols include polyoxypropylene diols and triols and poly(oxyethylene-oxypropylene) diols and triols obtained by the simultaneous or sequential addition of ethylene and

propylene oxides to di- or trifunctional initiators as fully described in the prior art. Mixtures of the said diols and triols can be particularly useful. Other useful polyether polyols include polytetramethylene glycols obtained by the polymerisation of tetrahydrofuran.

5 Polyester polyols which may be used include hydroxyl-terminated reaction products of polyhydric alcohols such as ethylene glycol, propylene glycol, diethylene glycol, 1,4-butanediol, bis(hydroxyethyl) terephthalate, glycerol, trimethylolpropane or polyether polyols or mixtures of such polyhydric alcohols, and polycarboxylic acids, especially dicarboxylic acids or their ester-forming derivatives, for example succinic, glutaric and adipic acids or their dimethyl esters, sebacic acid, phthalic anhydride, tetrachlorophthalic anhydride or dimethyl terephthalate or mixtures thereof.

10 Polyesteramides may be obtained by the inclusion of aminoalcohols such as ethanolamine in polyesterification mixtures. Polyesters obtained by the polymerisation of lactones, for example caprolactone, in conjunction with a polyol, may also be used.

Polythioether polyols which may be used include products obtained by condensing thiodiglycol either alone or with other glycols, alkylene oxides, dicarboxylic acids, formaldehyde, amino-alcohols or aminocarboxylic acids.

15 Polycarbonate polyols which may be used include products obtained by reacting diols such as 1,3-propanediol, 1,4-butanediol, 1,6-hexanediol, diethylene glycol or tetraethylene glycol with diaryl carbonates, for example diphenyl carbonate, or with phosgene.

20 Polyacetal polyols which may be used include those prepared by reacting glycols such as diethylene glycol, triethylene glycol or hexanediol with formaldehyde. Suitable polyacetals may also be prepared by polymerising cyclic acetals.

Suitable polyolefin polyols include hydroxy-terminated butadiene homo- and copolymers and suitable polysiloxane polyols include polydimethylsiloxane diols and triols.

25 In preparing the prepolymers, the polyisocyanate and the alcohol may be reacted together using conditions that have been fully described in the prior art for the production of urethane prepolymers (see "Polyurethanes Handbook" Ed. G. Oertel, Carl Hanser Verlag, Munich (1985), p. 20). Thus, one or more polyisocyanates may be reacted with one or more polyols under substantially anhydrous conditions at temperatures between 50° and 110° C, optionally in the presence of catalysts, until the formation of urethane groups by reaction between the isocyanate groups and the hydroxyl groups is substantially complete. Reaction between the urethane groups and the excess of polyisocyanate is then allowed to take place so that at least 20 %, preferably at least 50 %, and optionally up to 100 % of the initially formed urethane groups are converted to allophanate groups. The conversion of urethane groups to allophanate groups may be assisted by catalysis. Suitable catalysts are known in the polyurethane art and include tin compounds such as dibutyltin dilaurate and sulphonic acids.

35 It is preferable to avoid those catalysts which under the conditions of prepolymer formation, promote competing isocyanate reactions such as trimerisation. (see "Polyurethanes Handbook", Ed. G. Oertel, Carl Hanser Verlag, Munich (1985), pages 79-81).

In preparing the prepolymers, the polyisocyanate and the alcohol are suitably reacted in such proportion that the initial NCO/OH is at least 5:1.

40 One convenient method of preparing the prepolymers involves adding the alcohol gradually to the total amount of organic polyisocyanate so as to minimise chain extension.

The prepolymers of the invention are of particular value in the production of moulded elastomers by the RIM technique, the compositions being reacted as "A" components, optionally in conjunction with other polyisocyanates or variants thereof, with suitable "B" components, that is to say isocyanate-reactive materials.

45 Thus, in a further aspect of the present invention, there is provided a reaction system for use in making a reaction injection moulded elastomer, said system comprising the following components which are placed in separate containers :

50 (A) an allophanate-modified isocyanate-terminated prepolymer obtainable by reacting a polymeric polyol having a nominal average hydroxyl functionality of from 2 to 3 and an average hydroxyl equivalent weight of from 1000 to 3000 with at least 5 equivalents, per hydroxyl equivalent, of a diphenylmethane diisocyanate isomer or mixtures thereof optionally together with a minor proportion of higher functionality polyphenylene polymethylene polyisocyanates, the product containing allophanate groups in a ratio with respect to urethane groups of at least 1:4, and

55 (B) an isocyanate-reactive component.

Valuable reaction systems for use in making a reaction injection moulded elastomer are systems comprising the following components which are placed in separate containers :

(A) an allophanate-modified isocyanate-terminated prepolymer obtainable by reacting a polymeric polyol having a nominal average hydroxyl functionality of from 2 to 3 and an average hydroxyl equivalent weight of from 1000 to 3000 with at least 5 equivalents, per hydroxyl equivalent, of a diphenylmethane diisocyanate isomer or mixtures thereof optionally together with a minor proportion of higher functionality polyphenylene polymethylene polyisocyanates, the product containing allophanate groups in a ratio with respect to urethane groups of at least 1:4, and

(B) an isocyanate-reactive composition comprising :

(i) an aromatic polyamine chain extender having an aromatically bound primary and/or secondary amine functionality of from 2 to 3.0, an average molecular weight of from 100 to 400 and wherein at least 50 mole per cent of the species comprising said polyamine are diamines, and,

(ii) an amino-, imino-, enamino- and/or hydroxyl-functional polyether having an average of from 1.1 to 5 isocyanate-reactive groups per molecule and an average molecular weight of from 1000 to 10,000.

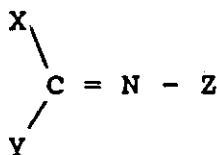
Component B of the reaction systems of the invention, the isocyanate-reactive component, may contain the usual ingredients of such components, for example soft block components, chain extenders and mixtures thereof. Typical soft block components include polyols, polyamines, iminofunctional compounds, enamine-containing compounds and mixtures thereof having equivalent weights of at least 500, preferably at least 750, whilst typical chain extenders include compounds of the same classes having equivalent weights below 500.

Polyols having equivalent weights of at least 500 which may be present in Component B include the polymeric polyols described above in relation to the preparation of the polyisocyanate composition. Preferred polyols include the above mentioned polyoxypropylene and poly(oxyethylene-oxypropylene) diols and triols and mixtures thereof.

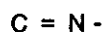
Polyamines having equivalent weights of at least 500 which may be present in Component B include amino-terminated polythioethers, polyesters, polyesteramides, polycarbonates, polyacetals, polyolefins, polysiloxanes and, especially, polyethers. Polyether polyamines which may be used include products obtained by the reductive amination of polyether polyols as described, for example, in US Patent No. 3,654,370, or by the cyanoethylation of polyols followed by hydrogenation. Poxoxypropylene and poly(oxyethylene-oxypropylene) diamines and triamines and mixtures thereof are preferred. Preferred equivalent weights are in the range from 500 to 5000, especially 1000 to 3000.

Imino-functional compounds which may be present in Component B are imino-functional compounds capable of reacting directly with polyisocyanates without prior cleavage of the C=N bond to form a monomeric byproduct. Suitable imino-functional compounds include imino-functional polyether resins having molecular weights of at least 1000, preferably 2000 to 8000 and an average imino functionality of at least 1, preferably from 2 to 4.

"Imino-functional" as used herein means that a reactant contains the grouping :



wherein X, Y and Z are chemical moieties which collectively form the rest of said compound and are each independently selected from hydrogen and organic radicals which are attached to the imino unit :



of said compound through N, C, O, S, Si or P, the central carbon atom of said imino unit being bonded to three atoms.

In the above structure, neither the carbon nor the nitrogen atom of the imino unit should be incorporated within an aromatic or other fully conjugated ring or ring system. It is preferred that Z is attached to the imino unit through carbon and that X and Y are independently H or organic radicals attached through C, N or O. It is most preferred that X, Y and Z are attached through saturated atoms, preferably aliphatic carbon atoms.

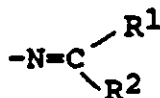
The range of imino functional reagents which may be used in the invention is not limited by or to any particular chemistry for the preparation of said reagents. For example, imine terminated aliphatic polyethers

may be made by a number of different routes. Specifically, the amine groups (-NH₂) of an aliphatic amine-terminated polyether can be prereacted with an aldehyde (RCH₂CHO) or a ketone (R¹-CO-R²) to form, respectively, the corresponding aldimine

5 -N=CHCH₂R

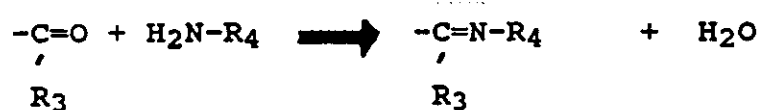
or the corresponding ketimine

10



wherein R, R¹, and R² are hereinafter defined, or the aldehyde and/or ketone groups, of an aldehyde and/or ketone-terminated polyether, can be prereacted with an aliphatic primary mono-amine to form, respectively, the corresponding aldimine and/or ketimine-terminated polyethers:

20



wherein: R₃ = H or alkyl, R₄ = H or alkyl.

25

Many types of imino-functional compounds are useful in this invention, including (but not limited to) those listed in Table A, following :

30

35

40

45

50

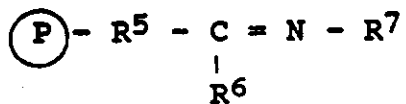
55

TABLE A

5

TYPE

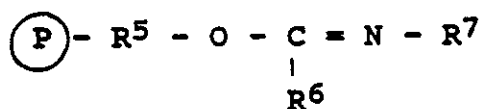
10



Simple imine

15

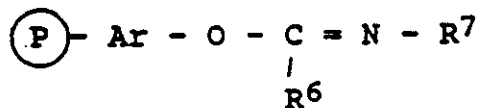
20



Imino ester

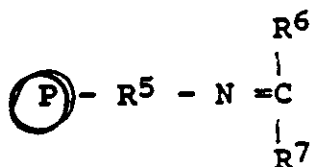
25

30

Imino ester
(aromatic)

35

40



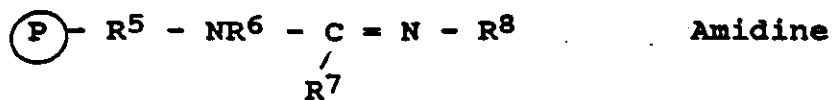
Simple imine

45

50

55

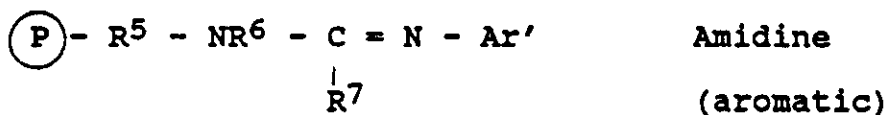
5



10

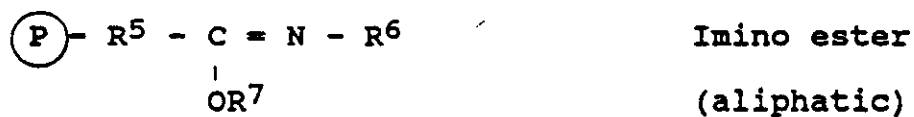


15



20

25



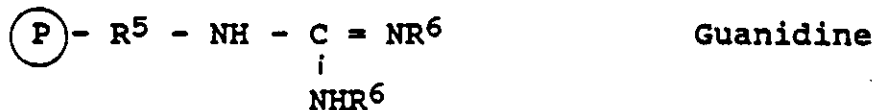
30

35



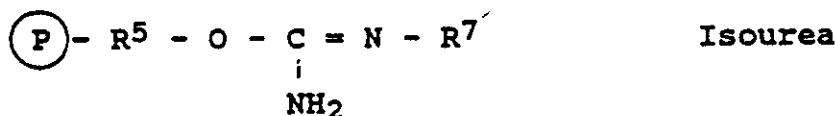
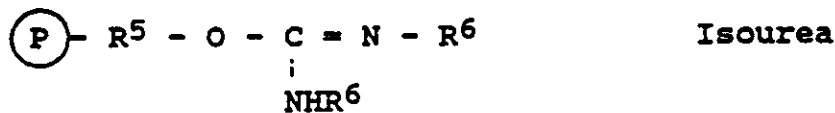
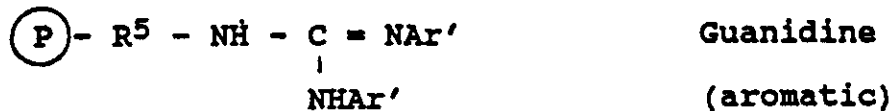
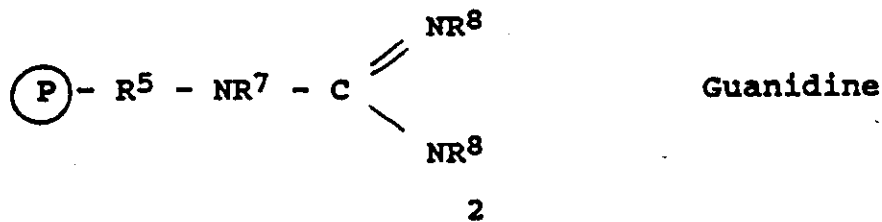
40

45



50

55



35 wherein:

R^5 and Ar are divalent aliphatic and aromatic organic linking groups, respectively;

$\textcircled{\text{P}}$ represents a polyether or hydrocarbon chain or radical, to which said imino (C=N) functional group is attached as indicated by the drawings.

R^6 is H or a monovalent organic aliphatic group of 1 to 10 carbons;

40 R^7 and R^8 are monovalent aliphatic organic groups of 1 to 10 carbon atoms, and

Ar is a monovalent aromatic organic group of 6 to 18 carbon atoms.

These stated groups are well known in the art. Thus R_5 may in particular be propylene, Ar methoxyphenylene, R_6 propyl, R_7 propyl, R_8 propyl and Ar methoxyphenyl.

45 It is noted that in the above formulas any two of the three substituents attached to the imino unit can be incorporated as members of a non-aromatic 5 or 6 membered ring. The ring can be carbocyclic or heterocyclic depending, of course, on the particular substituents so incorporated and on whether the carbon or the nitrogen atom (or both) of the imino unit are also incorporated.

50 When aromatic groups are present in the imino unit it is preferable that they be attached to the carbon atom of said unit and it is most preferred that said aromatic group bear electron donating substituents such as hydroxy, alkoxy N,N-dialkyl-amino etc.

The preparation of these imino functional groups in both cyclic and acyclic forms is well known in the literature. Isoureas are generally prepared by the reaction of an alcohol with a carbodiimide in the presence of a suitable catalyst. The alcohol component may be aliphatic, as described in E. Schmidt, F. Moosmüller, Lieb. Ann. Chem. 597, 235, (1956), or aromatic as in E. Vowinkel, Chem. Ber., 96, 1702, (1963). The catalyst employed in these reactions are frequently chloride salts of copper, such as the use of copper (I) chloride in E. Vowinkel, I. Buthe, Chem. Ber., 107, 1353, (1974), or copper (II) chloride, as in E. Schmidt, E. Dabritz, K. Thulke, Lieb. Ann. Chem., 685, 161, (1965).

However the reaction can also be carried out by the addition of an alkaline metal to the alcohol component

as exemplified by the use of sodium metal in H.G. Khorana, *Canad. J. Chem.* **32**, 261, 1953.

Guanidines can be prepared by the reaction of an amine with a carbodiimide in a manner similar to that outlined in the references cited above.

Alternatively alkylguanidines may be prepared by the reaction of an alkylamine salt with dicyandiamide as in E.A. Werner, *J. Chem. Soc.*, **121**, 1790, (1922). In yet another method s-methylthiourea sulphate is combined with an alkylamine as described in "Heterocyclic Chemistry", A. Albert, Althone Press, London, 1968.

A general review of the preparation of imidates is given in "The Chemistry of amidines and imidates", Ed. S. Patai, chapter 9, "Imidates including cyclic imidates", D.G. Neilson, John Wiley, London, 1975. This work includes references to the preparation of the analogous thioimidates. The preparation of acyclic imidates by the combination of an aliphatic or aromatic nitrile with an alcohol under acidic or basic conditions is described in F.C. Schaefer, G.A. Peters, *J. Org. Chem.*, **26**, 412, (1961).

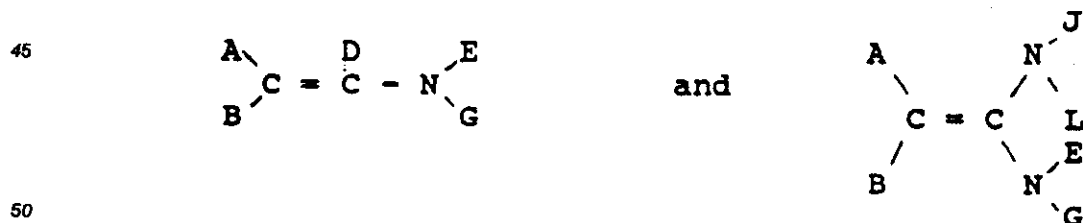
The preparation of cyclic imidates, such as oxazolines and dihydro-1,3-oxazines, by the Ritter reaction (addition of 1,3-diols or epoxides to a nitrile under acid catalysis) is described in "Advances in heterocyclic chemistry", Vol. 6, Ed. A.R. Katritzky, A.R. Boulton, Section II.A, "Heterocyclic synthesis involving nitrilium salts and nitriles under acidic conditions", F. Johnson, R. Madronero, Academic Press, New York, 1966 and references therein. In addition this text teaches the preparation of thioimidates such as thiazolines and dihydro-1,3-thiazines. Methods for the preparation of oxazolines and oxazines are also described in US 3630996 to D. Tomalia, US 3640957 to D. Tomalia and R.J. Thomas, in H. Witte, W. Seeliger, *Angew. Chem. Int. Ed.*, 1972, 287 and in US 3813378 to H. Witte and W. Seeliger.

A general review of the preparation of amidines is given in "The Chemistry of amidines and imidates", Ed. S. Patai, chapter 7, "Preparation and synthetic uses of amidines". The general class of five membered ring amidines known as imidazolines can be prepared in a manner similar to that outlined above by the combination of a nitrile containing compound with ethylenediamine in the presence of an acid catalyst. Alternatively these materials can be prepared by the combination of ethylenediamine with carboxylic acids under dehydrating conditions. Other methods for the preparation of these materials include the combination of ethylenediamine with thioamides or with an imino ether hydrochloride. These procedures are described in "The Chemistry of Heterocyclic compounds : Imidazole and its Derivatives", Part I, Ed. A. Weissberger, author K. Hofman, Interscience Publishers, New York, 1953 and references therein. Particularly useful for the preparation of imidazoline terminated softblocks from cyanoethylated polyether polyols would be the method outlined in US 4006247 to H.P. Panzer.

The preparation of the homologous tetrahydropyrimidines can be achieved in a similar manner by the use of 1,3-propanediamine as the diamine component. Specific methods are described in "The Chemistry of Heterocyclic Compounds : The Pyrimidines, Supplement I", Ed. A. Weissberger and E.C. Taylor, author D.J. Brown, Interscience Publishers, New York, 1953.

The preparation of an imine can be achieved by any of a number of well documented procedures. In particular, these materials can be obtained by the combination of a primary amine with an aldehyde or a ketone under dehydrating conditions. This and numerous alternative methods are contained in "The Chemistry of the Carbon-Nitrogen Double Bond", Ed. S. Patai, Interscience Publishers, London, 1970 and references therein.

Enamine-containing compounds which may be present in Component B include compounds having the structures



wherein each of A, B, D, E, G, J and L, independently, represents hydrogen or an optionally substituted hydrocarbon radical, any of A, B and D and, independently, any of E, G, J and L optionally being joined together to form one or more carbocyclic or heterocyclic rings.

In many preferred enamino-functional compounds, E, G, J and L are not hydrogen. It is also preferred that not both of A and B are hydrogen. Especially useful enamino-functional compounds contain two or more enamino groups as a result of any of A, B, D, E, G, J and/or L being a radical terminating in one or

more enamino groups.

Preferred enamino-functional compounds include enamino-functional polyether resins having molecular weights of at least 1000, preferably 2000 to 8000 and an average enamine functionality of at least 1.1, preferably from 2 to 4.

5 Suitable enamino-functional compounds may be obtained in known manner by reacting a carbonyl compound containing at least one alpha-hydrogen atom, for example an aliphatic, cyclo-aliphatic or araliphatic aldehyde or ketone such as acetaldehyde, propionaldehyde, isobutyraldehyde, caproaldehyde, cyclohexyl aldehyde, acetone, methyl ethyl ketone, benzyl methyl ketone, cyclopentanone, cyclohexanone, trimethylcyclohexanone, mixtures of these and the like with a secondary amine, for example a secondary
10 amino-terminated polymer such as a polyether.

General techniques for the synthesis of enamines have been described in, for example, Org. Coatings and Plastics Chem., 44, 151 and 157, (1981), ACS-PMSE preprints, August/September 1983, 456 and 461, and US Patents 4,342,841 and 4,552,945.

15 Polyols having equivalent weights below 500 which may be present as chain extenders in the B Components of the reaction systems of the invention include simple non-polymeric diols such as ethylene glycol and 1,4-butanediol.

Polyamines having equivalent weights below 500 which may be used as chain extenders include aliphatic, cycloaliphatic or araliphatic polyamines containing two or more primary and/or secondary amino groups and, especially, aromatic polyamines.

20 Aromatic polyamines useful as chain extenders in the reaction systems of the invention particularly include diamines, especially those having molecular weights from 100 to 400, preferably between 122 and 300.

Suitable diamines have been fully described in the prior art and include 3,5-diethyl-2,4-toluenediamine, 3,5-diethyl-2,6-toluenediamine, DETDA which is a mixture of about 80 % by weight of 3,5-diethyl-2,4-toluenediamine and about 20 % by weight of 3,5-diethyl-2,6-toluenediamine, 1,3,5-triethyl-2,6-diaminobenzene, 2,4-diaminotoluene, 2,6-diaminotoluene, 2,4'-diaminodiphenylmethane, 4,4'-diaminodiphenylmethane, 3,3'-dimethyl-5,5'-diethyl-4,4'-diaminodiphenylmethane, 3,3',5,5'-tetraisopropyl-4,4'-diaminodiphenylmethane and the like and mixtures thereof.

30 Imino-functional and/or enamine-containing compounds suitable as chain extenders typically have molecular weights below 1000, especially between 100 and 600 and functionalities between 1 and 3, preferably 1 to 2. In other respects, for example structure and functionality, they may have the characteristics of the higher molecular weight imino-functional or enamine-containing compounds described above.

40 Examples of preferred imino-functional compounds for use as chain extenders in the reaction systems of the invention include simple aldimines and/or ketimines such as may be obtained by reacting aldehydes, for example formaldehyde, acetaldehyde, propionaldehyde, n-butyraldehyde, isobutyraldehyde, heptaldehyde, alpha-methylvaleraldehyde, beta-methylvaleraldehyde, caproaldehyde, isocaproaldehyde or cyclohexyl aldehyde and mixtures thereof or ketones, for example acetone, methyl ethyl ketone, methyl n-propyl ketone, methyl isopropyl ketone, diethyl ketone, benzyl methyl ketone or cyclo-hexanone and mixtures thereof with primary amines, especially aliphatic diamines. Examples of suitable amines include
40 hexamethylene diamine, menthane diamine, isophorone diamine, xylylene diamine, 2-methylpentamethylene diamine, polyoxyalkylene diamines and/or triamines and mixtures of such amines. Primary mono-amines may also be used either alone or together with diamines.

45 Examples of suitable enamine-containing chain extenders are described in US Patents 4,342,841 and 4,552,945. Other examples include the bis-enamines formed by reacting piperazine with simple carbonyl compounds such as acetone, methyl ethyl ketone, cyclohexanone and the like.

Particularly valuable reaction systems for use in the RIM process comprise the following components which are placed in separate containers :

50 (A) an allophanate-modified isocyanate-terminated prepolymer obtainable by reacting a polymeric polyol having a nominal average hydroxyl functionality of from 2 to 3 and an average hydroxyl equivalent weight of from 1000 to 3000 with at least 5 equivalents, per hydroxyl equivalent, of a diphenylmethane diisocyanate isomer or mixtures thereof optionally together with a minor proportion of higher functionality polyphenylene polymethylene polyisocyanates, the product containing allophanate groups in a ratio with respect to urethane groups of at least 1:4 and,

(B) an isocyanate-reactive composition comprising :

55 (i) a chain extender comprising :

(a) 0-100 % of an aromatic polyamine having an aromatically bound primary and/or secondary amine functionality of from 2 to 3.0, an average molecular weight of from 100 to 400 and wherein at least 50 mole per cent of the species comprising said polyamine are diamines, and,

correspondingly,

(b) 100-0 % of an imino- and/or enamino-functional aliphatic compound having from about 1 to about 3 isocyanate-reactive imino and/or enamine groups per molecule and a molecular weight less than 1000, and

5 (ii) an imino- and/or enamino-functional polyether having an average of from 1.1 to 5 isocyanate-reactive imino and/or enamine groups per molecule and an average molecular weight of from 1000 to 10,000 and wherein said imino and/or enamine groups constitute at least 50 mole per cent of the isocyanate-reactive groups in said polyether and at least 50 mole per cent of said imino- and/or enamino-functional polyether species contain 2 or more imino and/or enamine groups per molecule.

10 The reaction systems of the present invention may further contain other conventional ingredients of such systems such as internal mould release agents, catalysts, surfactants, blowing agents, fillers (which may be reinforcements), plasticizers, fire retardants, coupling agents, and the like.

Suitable internal mold release agents include, for example, copper stearate, Zinc stearate and a dimethyl polysiloxane with organic acid groups which is commercially available as Dow-Corning Q2-7119
15 from Dow-Corning Corporation. Other organo-polysiloxanes bearing organic hydroxyl groups (instead of acids) can also be used. A specific example of a very effective, hydroxy functional, polysiloxane internal mold release additive is L-412T (available from Goldschmidt AG). The amount of internal mold release agent used can be from 0.001 to 5.0 percent by weight of the total reactants (i.e. total polymer).

Catalysts are generally not required during the preparation of polyureas by RIM. Catalysts may,
20 however, be used if desired. Suitable catalysts include, for example, tertiary amines or organotin compounds, such as dibutyltin dilaurate, dibutyltin diacetate, diethyltin diacetate, dihexyltin diacetate, di-2-ethylhexyltin oxide, stannous octoate, stannous oleate, or a mixture thereof.

Tertiary amine catalysts include trialkylamines which include, for example, triethylamine; heterocyclic amines such as N-alkylmorpholines which include, for example, N-methylmorpholine, N-ethylmorpholine;
25 2,2'-bis(dimethyl-amino)diethyl ether; 1,4-dimethylpiperazine, triethylenediamine, and aliphatic polyamines such as N,N, N',N'-tetramethyl-1,3-butanediamine, or alkanolamines such as N-methyl diethanolamine. The amount of catalyst used will generally be less than 5 percent by weight of the total reactants, preferably less than 1%. Combinations of tertiary amine and organotin catalysts are frequently used in the art. Isocyanurate catalysts, such as alkali and/or alkaline earth metal salts of carboxylic acids, may also be
30 added to the formulations of the invention.

Suitable surfactants include for example, sodium salts of castor oil sulfonates; alkali metal or ammonium salts of sulfonic acids such as dodecyl benzene sulfonic acid; and polyether siloxanes having a structure such that a copolymer of ethylene oxide and propylene oxide is attached to a polydimethyl siloxane radical.
35 The amount of surfactant used is less than 2 percent by weight of the total reactants, preferably less than 1%.

Suitable blowing agents include, for example, dissolved or dispersed gases such as air, CO₂, N₂O, or nitrogen, and low boiling halogenated hydrocarbons such as methylene chloride and trichloromonofluoromethane. The amount of blowing agent used is preferably less than 4 percent by weight of the total reactants.

40 Suitable fillers include fiberglass reinforcement fibers, particularly those having lengths of from 1/16 inch (0.16 cm) to 1/2 inch (1.27 cm) and milled glass fibers having a length of 1/16 inch (0.16 cm), 1/8 inch (0.32 cm) or 1/4 inch (0.64 cm) and the like. Shorter fibers are always preferred for ease of processing when they are incorporated as part of the "A" or "B" component streams. Other particularly suitable fillers are mica, fumed silica, flake glass, Wollastonite, calcium carbonate, carbon black, and the like.

45 The products of the present invention can be shaped into useful articles such as automobile fascias, or panels, by the reaction injection molding (RIM) process, which is performed in a RIM machine. RIM machines are well known in the art and include those supplied by Admiral Equipment Corp., Akron, Ohio by Cincinnati Milacron Corp., Cincinnati, Ohio, by Battenfeld GmbH, Meinerzhagen, West Germany and by Krauss-Maffei GmbH, West Germany.

50 The reagents may be blended in a suitable container and agitated at a temperature from 20 °C to 100 °C. It is preferred to mix and process the ingredients of component (B) at or near ambient (20 °C) temperature.

The "A" and "B" Components are placed in separate containers, which are generally equipped with agitators, of the RIM machine wherein the temperature of the "A" Component is 20 °C to 125 °C. It is preferred that the isocyanate temperature used for processing and mixing be below 50 °C, particularly if the isocyanate contains a catalyst or latent catalyst for the imine-isocyanate reaction. The temperature of the
55 "B" Component can be between 20 °C to 80 °C, but is preferably 20 °C to 40 °C.

The "A" Component and "B" Component are impingement mixed in a forced mix head such as, for example, a Krauss-Maffei mix head. The "A" and "B" Components are pumped to the mix head by a

metering pump, for example, a Viking Mark 21A, at a discharge pressure from 4.8×10^6 Pa (700 psi) to 34.5×10^6 Pa (5000 psi). It is sometimes necessary to maintain the component streams (A and B) within the pistons (or pumps), mix head, and all conduits connecting these components, at temperatures comparable to those which prevail within the storage tanks. This is often done by heat-tracing and/or by independent recirculation of the components.

The amounts of the "A" and the "B" Components pumped to the mix head is measured as the ratio by weight of the "A" Component to the "B" Component wherein the ratio is from 9:1 to 1:9, preferably from 3:1 to 1:3, depending upon the reactants used and the isocyanate index desired. It is preferred that a weight ratio be employed which yields a ratio of isocyanate equivalents in stream (A) to isocyanate-reactive functional groups in stream (B) between 0.70 and 1.90, preferably 0.90 to 1.30, more preferably 0.95 to 1.20. This ratio of equivalents is known as the index and is often expressed as a percentage. The expression "isocyanate-reactive-functional-groups" are defined herein to include imine groups, primary and/or secondary amine groups (aromatic or aliphatic), hydroxyl groups, enamine groups, ketene aminal groups, mercapto(-SH) groups and carboxylic acids, said groups being organically bound.

Either or both streams may contain up to 40% or its weight in solid fillers or reinforcements. In a preferred embodiment, each stream contains at least 70% by weight of reactive species, not more than 30% by weight of fillers and/or reinforcements, and not more than 10% of other optional additives.

The impingement mixed blend of "A"/"B" streams is injected into a mold at a velocity from 0.136 kg/sec. (0.3 lb./sec.) to 31.75 kg./sec.(70 lb./sec.), preferably 2.27 to 9.07 kg/sec. (5 to 20 lb./sec.). The mold is heated to a temperature from 20 °C to 250 °C. Suitable molds are made of metal such as aluminum or steel, although other materials can be used if they can withstand the processing conditions and wear. Usually an external mold release agent is applied before the first molding. These are usually soaps or waxes which are solid at the mold temperature employed.

A molded polymer article is formed after the impingement mixture is in the mold from 1 second to 30 seconds, preferably 5 to 20 seconds. The mold is then opened and the molded product is removed from the mold. The molded product may be post cured by placing the product in an oven having a temperature between 50 °C and 250 °C for a time from one-half hour to 3 hours.

Although not essential to the successful practice of this invention, it is within the scope of the invention to incorporate reactive ingredients into the reaction systems of the invention, in minor amounts, which are different from the types of reactants specifically described herein.

The individual components of the reaction systems are desirably stored and processed under an inert atmosphere such as dry air or nitrogen.

The formulations of the invention are processed at an isocyanate index between 0.70 and 1.90, preferably between 0.95 and 1.20; with the proviso that, if a catalyst for the conversion of isocyanate to isocyanurate groups is present, the index may extend up to 15. Examples of suitable isocyanurate catalysts include alkali metal salts of carboxylic acids, for example, potassium 2-ethylhexoate.

The prepolymers of the invention may also be reacted with isocyanate-reactive components, for example polyols, in the presence of the usual blowing agents, catalysts, surfactants and the like to form foams having densities of from 10 to 400 kg/m³.

The invention is illustrated but not limited by the following Examples in which all parts, percentages and ratios are by weight unless otherwise indicated. In the Examples, Flexural Modulus was determined by ASTM D790; Impact (falling weight) was determined by ASTM D3029-84.

Example 1

Prepolymer 1 was prepared by reacting 43.9 parts of polypropylene glycol 2000 with 56.1 parts of an 80/20 mixture of 4,4'- and 2,4'-diphenylmethane diisocyanates in the presence of 0.002 part of dibutyltin dilaurate at 115 °C for 2 hours. The allophanate containing prepolymer so obtained had an NCO content of 14.1 %.

Example 2

A series of elastomer products were prepared on a Battenfeld SHK-65 machine, by reacting the prepolymer of example 1 with a number of "B" components, using the RIM technique. As "B" components use was made of the following isocyanate reactive compositions :

Amine composition A :

40 pbw of Jeffamine*D 2000
 10 pbw of Jeffamine*D 400
 5 50 pbw of DETDA

Imine composition B :

40 pbw of the cyclohexanone imine of Jeffamine*T 5000
 10 15 pbw of the cyclohexanone imine of Jeffamine*D 400
 45 pbw of DETDA

Imine composition C :

15 70 pbw of the cyclohexanone imine of Jeffamine*T 5000
 30 pbw of DETDA

The relative amounts of prepolymers ("A" Component) and isocyanate reactive compositions ("B" Component) are stated in the following Table 1A. The temperature of the mold was maintained at approximately 90° C.

20 The properties of the elastomer products thus obtained are indicated in the following Table 1B.

TABLE 1

25 Preparation of elastomer products by the RIM techniqueA : Amounts of "A" and "B" Components

Example No.	2a	2b	2c
30 Component "A" (parts by weight)	prepolymer 1 204	prepolymer 1 223	prepolymer 1 183
Component "B" (parts by weight)	Amine comp. A 100	Amine comp. A 100	Imine comp. B 100

35

B : Properties of the elastomer products obtained

Example No.	2a	2b	2c
40 Density (kg/m ³)	1131	1138	1134
Flexural Modulus (MPa)	763	709	657
Hardness (Shore D)	71	71	70
45 Tensile Strength (kPa)	32703	29371	29857
Elongation at break (%)	117	117	107
Impact			
at 20° C (J)	68	48	50
50 at -20° C (J)	54	48	50

55

* "Jeffamine" is a trade mark for polyether diamines and triamines marketed by Texaco.

TABLE 1 (Continuation)

A : Amounts of "A" and "B" Components

Example No.	2d	2e	2f
Component "A" (parts by weight)	prepolymer 1 200	prepolymer 1 129	prepolymer 1 119
Component "B" (parts by weight)	Imine comp. B 100	Imine comp. C 100	Imine comp. C 100

B : Properties of the elastomer products obtained

Example No.	2d	2e	2f
Density (kg/m ³)	1137	1125	1110
Flexural Modulus (Eflex MPa)	636	402	381
Hardness (Shore D)	69	65	66
Tensile Strength (kPa)	28300	23111	23900
Elongation at break (%)	93	135	153
Impact at 20° C (J)	70	83	66
at -20° C (J)	51	60	64

30 **Claims**

1. An allophanate-modified isocyanate-terminated prepolymer obtainable by reacting a polymeric polyol having a nominal average hydroxyl functionality of from 2 to 3 and an average hydroxyl equivalent weight of from 1000 to 3000 with at least 5 equivalents, per hydroxyl equivalent, of a diphenylmethane diisocyanate isomer or mixtures thereof optionally together with a minor proportion of higher functionality polyphenylene polymethylene polyisocyanates, the product containing allophanate groups in a ratio with respect to urethane groups of at least 1:4.
2. A prepolymer according to claim 1 wherein the ratio is at least 1:1.
3. A prepolymer according to claim 1 wherein the polymeric polyol is a polyether polyol.
4. A prepolymer according to claim 2 wherein the polyether polyol is a polyoxypropylene diol or triol or a poly(oxyethylene-oxypropylene) diol or triol.
5. A reaction system for making a reaction injection moulded elastomer, said system comprising the following components which are placed in separate containers :
 - (A) a prepolymer as defined in claim 1, and
 - (B) an isocyanate-reactive component.
6. A reaction system according to claim 5 wherein the isocyanate-reactive component comprises an aromatic polyamine.
7. A reaction system according to claims 5 and 6 comprising :
 - (A) a prepolymer as defined in claim 1, and
 - (B) an isocyanate-reactive composition comprising :
 - (i) an aromatic polyamine chain extender having an aromatically bound primary and/or secondary amine functionality of from 2 to 3.0, an average molecular weight of from 100 to 400 and wherein

at least 50 mole per cent of the species comprising said polyamine are diamines, and,
 (ii) an amino-, imino-, enamino- and/or hydroxyl-functional
 polyether having an average of from 1.1 to 5 isocyanate-reactive groups per molecule and an
 average molecular weight of from 1000 to 10,000.

5

8. A reaction system according to claim 5 comprising :

- (A) a prepolymer as defined in claim 1, and
 (B) an isocyanate-reactive composition comprising :

10

(i) a chain extender comprising :

(a) 0-100 % of an aromatic polyamine having an aromatically

bound primary and/or secondary amine functionality of from 2 to 3.0, an average molecular
 weight of from 100 to 400 and wherein at least 50 mole per cent of the species comprising
 said polyamine are diamines, and,

15

(b) 100-0 % of an imino- and/or enamino-functional aliphatic compound having from 1 to 3
 isocyanate-reactive imino and/or enamine groups per molecule and a molecular weight less
 than 1000, and

20

(ii) an imino- and/or enamino-functional polyether having an average of from 1.1 to 5 isocyanate-
 reactive imino and/or enamine groups per molecule and an average molecular weight of from
 1000 to 10,000 and wherein said imino and/or enamine groups constitute at least 50 mole per
 cent of the isocyanate-reactive groups in said polyether and at least 50 mole per cent of said
 imino- and/or enamino-functional polyether species contain 2 or more imino and/or enamine
 groups per molecule.

9. The use of a prepolymer according to claims 1-4 for preparing a reaction injection moulded elastomer.

25

Patentansprüche

30

1. Allophanatmodifiziertes Präpolymer mit Isocyanatende, erhältlich durch Umsetzung eines polymeren
 Polyols mit einer nominellen mittleren Hydroxyfunktionalität von 2 bis 3 und einem mittleren Hydroxyä-
 quivalentgewicht von 1.000 bis 3.000 mit mindestens fünf Äquivalenten pro Hydroxyäquivalent eines
 Diphenylmethandiisocyanatisomers oder dessen Mischungen, ggf. zusammen mit einem geringen
 Anteil an Polyphenylenpolymethylen-diisocyanaten höherer Funktionalität, wobei das Produkt Allopha-
 natgruppen in einem Verhältnis von mindestens 1:4 in Bezug auf Urethangruppen enthält.

35

2. Präpolymer nach Anspruch 1, wobei das Verhältnis mindestens 1:1 ist.

3. Präpolymer nach Anspruch 1, wobei das polymere Polyol ein Polyetherpolyol ist.

40

4. Präpolymer nach Anspruch 2, wobei das Polyetherpolyol ein Polyoxypropylendiol oder -triol oder ein
 poly(oxyethylen-oxypropylen)diol oder -triol ist.

5. Reaktionssystem zur Herstellung eines Reaktionsspritzguß-Elastomers, wobei das System die folgen-
 den Komponenten umfaßt, die in getrennte Behälter gegeben werden:

45

(A) ein Präpolymer nach Anspruch 1, und

(B) eine isocyanatreaktive Komponente.

6. Reaktionssystem nach Anspruch 5, wobei die isocyanatreaktive Komponente ein aromatisches Polya-
 min umfaßt.

50

7. Reaktionssystem nach Anspruch 5 oder 6, umfassend:

(A) ein Präpolymer nach Anspruch 1, und

(B) eine isocyanatreaktive Zusammensetzung, umfassend:

55

(i) einen aromatischen Polyaminkettenerweiterer mit einer aromatisch gebundenen primären
 und/oder sekundären Aminfunktionalität von 2 bis 3,0, einem mittleren Molekulargewicht von 100
 bis 400 und wobei mindestens 50 Mol% der das Polyamin aufweisenden Spezies Diamine sind,
 und

(ii) einen amino-, imino-, enamino- und/oder hydroxyfunktionellen Polyether mit einem Mittel von
 1,1 bis 5 isocyanatreaktiven Gruppen pro Molekül und einem mittleren Molekulargewicht von

1.000 bis 10.000.

8. Reaktionssystem nach Anspruch 5, umfassend:

(A) ein Präpolymer nach Anspruch 1, und

(B) eine isocyanatreaktive Zusammensetzung, umfassend:

(i) einen Kettenerweiterer, umfassend:

(a) 0 bis 100 % eines aromatischen Polyamins mit einer aromatisch gebundenen primären und/oder sekundären Aminfunktionalität von 2 bis 3,0, einem mittleren Molekulargewicht von 100 bis 400 und wobei mindestens 50 Mol% der das Polyamin umfassenden Spezies Diamine sind, und

(b) 100 bis 0 % einer imino- und/oder enaminfunktionellen aliphatischen Verbindung mit 1 bis 3 isocyanatreaktiven Imino- und/oder Enamingruppen pro Molekül und einem Molekulargewicht unter 1.000 und

(ii) einen imino- und/oder enaminfunktionellen Polyether mit einem Mittel von 1,1 bis 5 isocyanatreaktiven Imino- und/oder Enamingruppen pro Molekül und einem mittleren Molekulargewicht von 1.000 bis 10.000 und wobei die Imino- und/oder Enamingruppen mindestens 50 Mol% der isocyanatreaktiven Gruppen in dem Polyether ausmachen und mindestens 50 Mol% der imino- und/oder enaminfunktionellen Polyetherspezies zwei oder mehr Imino- und/oder Enamingruppen pro Molekül enthalten.

9. Verwendung eines Präpolymers nach Anspruch 1 bis 4 zur Herstellung eines Reaktions-spritzguß-Elastomers.

Revendications

1. Prépolymère à terminaison isocyanate et modification allophanate, pouvant être obtenu par réaction d'un polyol polymérique possédant une fonctionnalité hydroxyle moyenne nominale de 2 à 3 et un poids équivalent d'hydroxyle moyen de 1000 à 3000 avec au moins 5 équivalents, par équivalent d'hydroxyle, d'un isomère de diisocyanate de diphenylméthane ou de mélanges de tels isomères facultativement en association avec une petite proportion de polyphénylène-polyméthylène-polyisocyanates de plus haute fonctionnalité, le produit contenant des groupes allophanate en un rapport de ces groupes aux groupes uréthane au moins égal à 1:4.

2. Prépolymère suivant la revendication 1, dans lequel le rapport est au moins égal à 1:1.

3. Prépolymère suivant la revendication 1, dans lequel le polyol polymérique est un polyéther-polyol.

4. Prépolymère suivant la revendication 2, dans lequel le polyéther-polyol est un polyoxypropylène-diol ou -triol ou un polyoxyéthylène-oxypropylène-diol ou -triol.

5. Formulation réactionnelle pour la préparation d'un élastomère moulé par injection-réaction, ladite formulation comprenant les constituants suivants qui sont placés dans des récipients distincts :

(A) un prépolymère répondant à la définition suivant la revendication 1, et

(B) un constituant réactif avec les isocyanates.

6. Formulation réactionnelle suivant la revendication 5, dans laquelle le constituant réactif avec les isocyanates comprend une polyamine aromatique.

7. Formulation réactionnelle suivant les revendications 5 et 6, comprenant :

(A) un prépolymère répondant à la définition suivant la revendication 1, et

(B) une composition réactive avec les isocyanates, comprenant :

(i) un agent d'allongement de chaîne du type polyamine aromatique possédant une fonctionnalité amine primaire et/ou secondaire à liaison aromatique de 2 à 3,0, un poids moléculaire moyen de 100 à 400, au moins 50 moles % des entités constituant ladite polyamine consistant en diamines, et

(ii) un polyéther à fonctionnalité amino, imino, énamino et/ou hydroxyle, possédant un nombre moyen de 1,1 à 5 groupes réactifs avec les isocyanates par molécule et ayant un poids moléculaire moyen de 1000 à 10 000.

8. Formulation réactionnelle suivant la revendication 5, comprenant :

(A) un prépolymère répondant à la définition suivant la revendication 1, et

(B) une composition réactive avec les isocyanates, comprenant :

(i) un agent d'allongement de chaîne comprenant :

(a) 0 à 100 % d'une polyamine aromatique possédant une fonctionnalité amine primaire et/ou secondaire à liaison aromatique de 2 à 3,0, un poids moléculaire moyen de 100 à 400, au moins 50 moles % des entités formant ladite polyamine consistant en diamines, et

(b) 100 à 0 % d'un composé aliphatique à fonctionnalité imino et/ou énamino ayant 1 à 3 groupes imino et/ou énamino réactifs avec les isocyanates par molécule et un poids moléculaire inférieur à 1000, et

(ii) un polyéther à fonctionnalité imino et/ou énamino ayant un nombre moyen de 1,1 à 5 groupes imino et/ou énamino réactifs avec les isocyanates par molécule et un poids moléculaire moyen de 1000 à 10 000, lesdits groupes imino et/ou énamino constituant au moins 50 moles % des groupes réactifs avec les isocyanates dans ledit polyéther, et au moins 50 moles % desdits polyéthers à fonctionnalité imino et/ou énamino contenant 2 ou plus de 2 groupes imino et/ou énamino par molécule.

9. Utilisation d'un prépolymère suivant les revendications 1 à 4 pour la préparation d'un élastomère moulé par injection-réaction.

REGISTER ENTRY FOR EP0312365

European Application No EP88309615.8 filing date 13.10.1988

Priorities claimed:

16.10.1987 in United Kingdom - doc: 8724348

09.09.1988 in United Kingdom - doc: 8821186

Designated States BE CH DE ES FR GB GR IT LI NL SE AT

Title POLYISOCYANATE COMPOSITIONS.

Applicants/Proprietors

ICI AMERICAS INC, /Concord Pike & New Murphy Road, Wilmington Delaware
19897, United States of America [ADP No. 50483916001]

IMPERIAL CHEMICAL INDUSTRIES PLC, Imperial Chemical House Millbank, London
SW1P 3JF, United Kingdom [ADP No. 52287612001]

Inventors

EDWARD FRANCIS CASSIDY, rue J. Vanderlinden 28, B-1180 Ukkel, Belgium
[ADP No. 56489305001]

HERBERT RUSSELL GILLIS, Mechelsesteenweg 146, B-1960 Sterrebeek, Belgium
[ADP No. 55977672001]

JAN WILLEM LEENSLAG, Beekstraat 10, B-3055 Neerijse, Belgium
[ADP No. 55977706001]

ALAIN PARFONDRIY, avenue J. Bordet 66-12, B-1140 Evere, Belgium
[ADP No. 55998421001]

Classified to
C08G C07C

Address for Service

IMPERIAL CHEMICAL INDUSTRIES PLC, ICI Group Patents, Group Patents
Services Dept, PO Box 6, Shire Park, Bessemer Road, WELWYN GARDEN CITY,
Hertfordshire, AL7 1HD, United Kingdom [ADP No. 00000935001]

EPO Representative

GEORGES MAURICE LUCIEN MARIE LEHERTE, Imperial Chemical Industries PLC
Legal Department: Patents P.O. Box 6, Welwyn Garden City Herts. AL7 1HD,
United Kingdom [ADP No. 50887769001]

Publication No EP0312365 dated 19.04.1989

Publication in English

Examination requested 24.04.1990

Patent Granted with effect from 10.08.1994 (Section 25(1)) with title
POLYISOCYANATE COMPOSITIONS.

16.10.1989 EPO: Search report published on 15.11.1989

Entry Type 25.11 Staff ID.

Auth ID. EPT

- 05.10.1993 IMPERIAL CHEMICAL INDUSTRIES PLC, ICI Group Patents, Group Patents Services Dept, PO Box 6, Shire Park, Bessemer Road, WELWYN GARDEN CITY, Hertfordshire, AL7 1HD, United Kingdom [ADP No. 00000935001] registered as address for service
Entry Type 8.11 Staff ID. ER2 Auth ID. AA
- 08.07.1994 Notification from EPO of change of Applicant/Proprietor details from
ICI AMERICAS INC, Concord Pike & New Murphy Road, Wilmington Delaware 19897, United States of America [ADP No. 50483916001] to
IMPERIAL CHEMICAL INDUSTRIES PLC, Imperial Chemical House Millbank, London SW1P 3JF, United Kingdom [ADP No. 52287612001]
ICI AMERICAS INC, Concord Pike & New Murphy Road, Wilmington Delaware 19897, United States of America [ADP No. 04515607002]
Entry Type 25.14 Staff ID. RD06 Auth ID. EPT
- 08.07.1994 Notification from EPO of change of EPO Representative details from
GEORGES MAURICE LUCIEN MARIE LEHERTE, Imperial Chemical Industries PLC Legal Department: Patents P.O. Box 6, Welwyn Garden City Herts. AL7 1HD, United Kingdom [ADP No. 50887769001] to
GEORGES MAURICE LUCIEN MARIE LEHERTE, ICI Group Patents Services Dept. PO Box 6 Shire Park Bessemer Road, Welwyn Garden City Herts. AL7 1HD, United Kingdom [ADP No. 50887769001]
Entry Type 25.14 Staff ID. RD06 Auth ID. EPT
- 22.08.1994 Notification of change of Address For Service name and address of
IMPERIAL CHEMICAL INDUSTRIES PLC, ICI Group Patents, Group Patents Services Dept, PO Box 6, Shire Park, Bessemer Road, WELWYN GARDEN CITY, Hertfordshire, AL7 1HD, United Kingdom [ADP No. 00000935001] to
ICI POLYURETHANES, Everslaan 45, B-3078 Everberg, Belgium [ADP No. 06613715001]
dated 19.07.1994. Official evidence filed on GB2245361
Entry Type 7.1 Staff ID. NM Auth ID. EO
- 19.02.1996 Notification of change of Address For Service address of
ICI POLYURETHANES, Everslaan 45, B-3078 Everberg, Belgium [ADP No. 06613715001] to
INTELLECTUAL PROPERTY DEPARTMENT, PO Box 90, ICI Materials, Wilton, Cleveland, TS90 8JE, United Kingdom [ADP No. 06934954001]
dated 16.02.1995. Written notification filed on EP0434216
Entry Type 7.3 Staff ID. SA2 Auth ID. AA

**** END OF REGISTER ENTRY ****

OA80-01
EP

OPTICS - PATENTS

05/09/96 11:07:57
PAGE: 1

RENEWAL DETAILS

PUBLICATION NUMBER EP0312365

PROPRIETOR(S)

IMPERIAL CHEMICAL INDUSTRIES PLC, Imperial Chemical House, Millbank,
London SW1P 3JF, United Kingdom

ICI AMERICAS INC., Concord Pike & New Murphy Road, Wilmington
Delaware 19897, United States of America

DATE FILED 13.10.1988

DATE GRANTED 10.08.1994

DATE NEXT RENEWAL DUE 13.10.1996

DATE NOT IN FORCE

DATE OF LAST RENEWAL 14.09.1995

YEAR OF LAST RENEWAL 08

STATUS PATENT IN FORCE

**** END OF REPORT ****