



(86) Date de dépôt PCT/PCT Filing Date: 2003/10/08
(87) Date publication PCT/PCT Publication Date: 2004/05/06
(85) Entrée phase nationale/National Entry: 2005/04/18
(86) N° demande PCT/PCT Application No.: EP 2003/011107
(87) N° publication PCT/PCT Publication No.: 2004/037882
(30) Priorité/Priority: 2002/10/21 (102 48 949.1) DE

(51) Cl.Int.⁷/Int.Cl.⁷ C08G 18/10, C08G 18/48, C08G 18/42
(71) Demandeur/Applicant:
BAYER MATERIALSCIENCE AG, DE
(72) Inventeurs/Inventors:
MICHELS, ERHARD, DE;
NEFZGER, HARTMUT, DE;
SCHLEIERMACHER, STEPHAN, DE
(74) Agent: FETHERSTONHAUGH & CO.

(54) Titre : POLYURETHANES-ELASTOMERES, LEUR PROCEDE DE PRODUCTION ET LEUR UTILISATION
(54) Title: POLYURETHANE ELASTOMERS, METHOD FOR THE PRODUCTION THEREOF AND USE OF THE SAME

(57) **Abrégé/Abstract:**

The invention relates to polyurethane elastomers having a defined cross-linkage density, to a method for producing said elastomers using special polyether ester polyols, and to the use of the same, especially for producing microcellular and massive polyurethane elastomer parts.



ABSTRACT

The invention relates to polyurethane elastomers having a defined cross-linkage density, to a method for producing said elastomers using special polyether ester polyols, and to the use of the same, especially for producing microcellular and massive polyurethane elastomer parts.

Polyurethane elastomers, process for the preparation thereof and use thereof

5 The invention relates to polyurethane elastomers having a defined node density, a process for the preparation thereof with utilisation of specific polyetherester polyols, and the use thereof, in particular for the production of microcellular and solid polyurethane elastomer components.

10 Various processes for preparing polyurethanes which comprise in the so-called soft segment both polyether groups and polyester groups simultaneously have already been described in the past.

15 A variant (Plominska-Michalak, B.; Lisoska, R.; Balas, A. *Journal of Elastomers and Plastics* (26) 1994 327-334) resides in reacting a polyether-based NCO prepolymer with a polyester polyol. In the resulting polyurethane elastomer abrasion is reduced, the long-term flexural strength at room temperature and -15°C is improved, and the viscosity of the NCO prepolymer is lowered by comparison with a polyester-based NCO prepolymer. However, it is disadvantageous that problem-free mixing of the components becomes more difficult owing to the great difference
20 in viscosity between the reaction components. A further disadvantage is the inherent risk of microphase separations in the so-called soft segment of the polyurethane elastomer, which impair the end properties.

25 Another variant (DE-A 199 27 188) proposes physical mixing of polyethers and polyesters in the polyol formulation. In this way polyurethanes can be obtained which have improved oil resistance compared with that of pure polyether polyurethanes. The inadequate storage life of the polyol formulations is disadvantageous because the low compatibility of polyesters and polyethers brings about macroscopic demixing after a relatively short time. Users of such a system
30 experience undesirable difficulties in terms of storage and logistics.

The previously mentioned disadvantages are circumvented with separation-stable polyetherester polyols which can be prepared by discontinuous synthesis processes:

insertion in polyethers, alkoxylation of a polyester with alkylene oxide, polycondensation with alkylene oxide, two-stage and single-stage polycondensation.

5 In practice, however, it emerges that such polyetherester polyols do not afford PUs having generally good long-term flexural strength, in particular if they have been exposed to hydrolytic ageing.

10 In US-A 5 436 314 (insertion in polyethers) carboxylic acids or carboxylic acid anhydrides are reacted with polyether polyols in the presence of strong Brönsted acids, and polyetherester polyols having randomly distributed ester groups are obtained. However, these products do not have polymethylene segments of different lengths, though they contribute substantially to the good properties of many polyesters. The metal salts of strong Brönsted acids furthermore contaminate the polyetheresters and diminish the hydrolytic stability of their ester bonds, such that
15 the utilisation thereof in, for example, shoe soles results in inferior materials.

When alkoxyating a polyester with alkylene oxide, polyesters are first prepared, which are then alkoxyated with alkylene oxide. This is a widespread method which results in 3-block copolymers, the polyester-block-polyether polyols. An inherent
20 disadvantage of the process is that the block structure of the polyether-block-polyester polyols, created with such an outlay, is not in transesterification equilibrium. For this reason they may rearrange at elevated temperature and lose their constitutional structure. This has an undesirable effect on their storage stability.

25 In DE-A 198 58 104 a polyester-carboxylic acid is synthesised in the first stage from ring esters, alcohols and carboxylic acids, and in the subsequent step is alkoxyated with ethylene oxide or propylene oxide, preferably without additional catalysts. The products serve as raw materials for rigid foams. Here, they reduce shrinkage, increase strength and reduce the tendency to crystallise. These advantages can,
30 however, be realised only when at least one polyol component or one isocyanate has a number average functionality markedly greater than 2, which enables a highly cross-linked polyurethane system to be constructed. As is generally known in the art, microcellular elastomers having good properties such as, for example, good long-

term flexural strength cannot be obtained in this way. The ring esters from which the polyester polyols of the first synthesis step are synthesised are furthermore not preparable without increased outlay, because they must first be obtained from mixtures of linear and cyclic esters by extraction or distillation, a major
5 disadvantage of this process.

In US-A 4 487 853 acid semiesters are prepared as an intermediate, by esterification of polyether polyols with carboxylic acid anhydrides, followed by ethoxylation with catalysis provided by amines or tin compounds, with polyester-co-polyether polyols
10 being obtained which are low in ester-groups and have a high proportion of terminal primary hydroxyl groups. However, it is disadvantageous that the ether groups are utilised in a very high excess vis-à-vis ester groups, such that the advantages of typical polyetherester polyols or polyester-block-polyether polyols are not fully realised. Dicarboxylic acid anhydrides, which are generally costly, must furthermore
15 be used as educts for the synthesis of adipic acid esters, which constitute important raw materials for polyurethane elastomers.

Double metal cyanide catalysts are utilised in WO 200127185. They enable ether blocks to be started on polyesterols with few by-products and unsaturated terminal
20 groups. The products have good miscibility with ethers and esters which the specification recommends as surface-active agents or phase promoters. However, a disadvantage emerges that polyethers having a large number of terminal primary hydroxyl groups are known not be preparable with double metal cyanide catalysts, because the ethylene oxide polymerisation starts on a small number of hydroxyl
25 functions where it constructs high molecular weight polyethylene oxide units. For this reason the polyester-block-polyether polyols presented in WO 200127185 have only limited use in polyol formulations, specifically when polyols having a majority of secondary hydroxyl groups of low reactivity suffice for the application. This limitation is a major disadvantage for many applications.

30

In DE-A 21 10 278 (polycondensation with alkylene oxide) polyether polyol, carboxylic acid anhydride and alkylene oxide react in a one-pot process to give polyetherester polyol having randomly distributed polyether units. Because of the

nature of the process the alkylene oxides form only derivatised dimethylene bridges. Longer carbon bridges, such as are utilised in butanediol esters or hexanediol esters, are lacking. Costly adipic acid anhydride must moreover be utilised in this process.

5 In DE-A 34 37 915 (two-stage polycondensation) a polyether polyol is reacted with a carboxylic acid or a carboxylic acid anhydride or a carboxylic acid ester to give a polyester-carboxylic acid which in a second step reacts with aliphatic alcohols to give the actual polyetherester polyol. Disadvantages in this case are, on the one hand, the multi-stage process and, on the other, the costly carboxylic acid derivatives. A
10 similar process is described in DE-A 34 37 915. In this case, a traditional polyester polycarboxylic acid is not constructed from polyether polyols, but is reacted with polyether polyols and aliphatic alkanols.

According to EP-A 0 601 470 (single-step polycondensation) polycarboxylic acids,
15 alkanediol mixtures and polyether polyols are condensed to give randomly distributed polyetherester polyols having a ratio of ether groups to ester groups in the polyetherester polyol of from 0.3 to 1.5. The particular advantage of this process resides in the fact that polyurethane flexible foams having reduced fogging can be prepared with these polyetherester polyols. The polyetherester polyols are here
20 reacted with polyisocyanates.

The object of the present invention was therefore to provide microcellular polyurethanes which have improved long-term flexural properties both at room temperature and at -15°C and also following hydrolytic ageing (at 70°C and 95%
25 atmospheric humidity for 7 days).

It has surprisingly been found that polyetherester polyols comprising alkane polyol mixtures and specific polyether polyols, whereof the number average functionality is from 1.9 to 2.5, preferably 1.95 to 2.1 and particularly preferably 2.001 to 2.08, and
30 whereof the ratio of ether groups to ester groups can preferably vary from 0.3 to 2.5, preferably 0.6 to 2.0 and particularly preferably 0.9 to 1.5, react with polyisocyanates to give hydrolysis-resistant polyurethane elastomers which have very good long-term flexural strength both before and after hydrolytic ageing,

provided that the node density of the polyurethane elastomers is from 0.1 mole/kg to 0.0001 mole/kg, preferably 0.08 to 0.001 mole/kg, particularly preferably 0.04 to 0.01 mole/kg.

5 The term "node density of the polyurethane elastomers" (unit: [mole/kg]) is understood as the number of trivalent permanent chemical cross-linking sites of the polyurethane elastomer in moles per kilogram of PU elastomer. For this purpose the amounts of substance of all the molecules of those starting raw materials of the polyurethane elastomer which have a functionality greater than 2 are included. In
10 order to be able to treat all cross-linking sites as trifunctional cross-linking sites, the functionalities of higher-functional molecular species are weighted differently: trifunctional molecules are weighted at 1, tetrafunctional molecules at 2, pentafunctional molecules at 3, hexafunctional molecules at 4, and so on. In accordance with this definition a polyurethane prepared from the equivalently-
15 foamed components polyester diol, 1,4-butanediol, triethanolamine, pentaerythritol with a mixture of 1.21 wt.% 2,4'-diphenylmethane diisocyanate and 98.79 wt.% 4,4'-diphenylmethane diisocyanate would have an elastomer node density of 0.69 mole/kg, as can be seen from the calculation given as an example in the Table below.

20

Table: Example of calculation of elastomer node density

Component	Mass [g]	Molecular weight [g/mol]	Amount of substance [mole]	Functionality	Weighted trifunctional cross-linking points per molecule	Cross-linking points [mole/100g]	Cross-linking points [mole/kg]
Polyester diol	35.47	3032.43	0.0117	2	0	0.000	0.00
1,4-Butanediol	8.87	90.12	0.0984	2	0	0.000	0.00
Triethanolamine	4.43	149.20	0.0297	3	1	0.030	0.30
Pentaerythritol	2.66	136.20	0.0195	4	2	0.039	0.39
MDI*	48.57	250.75	0.1937	2	0	0.000	0.00
Total	100.00					Total cross-linking points = elastomer node density [mole/kg] 0.69	

* Mixture of 1.21 wt.% 2,4'-diphenylmethane diisocyanate and 98.79 wt.% 4,4'-diphenylmethane diisocyanate

5

The present invention therefore provides polyurethane elastomers which have a node density of from 0.1 mole/kg to 0.0001 mole/kg, preferably 0.08 to 0.001 mole/kg, particularly preferably 0.04 to 0.01 mole/kg, obtainable by reacting

- 10 a) at least one polyetherester polyol having a number average molecular weight of from 1000 g/mol to 6000 g/mol, preferably 2500 g/mol to 5000 g/mol, a number average functionality of from 1.9 to 2.5, preferably 1.95 to 2.1 and particularly preferably 2.001 to 2.08, and a ratio of ether groups to ester groups of the polyetherester of from 0.3 to 2.5, preferably 0.6 to 2.0,
- 15 particularly preferably 0.9 to 1.5,

which is obtainable by polycondensation from

- 20 a1) at least one or a plurality of dicarboxylic acids having up to 12 carbon atoms and/or derivatives thereof,
- a2) at least one or a plurality of polyether polyols having a number average molecular weight of from 1000 g/mol to 6000 g/mol, preferably 2500 g/mol to 5000 g/mol, an average functionality of from 1.7 to 2.5 as well as a 70% to 100% primary OH group content, preferably an 85% to 96% primary OH group content, and
- 25

- 5 a3) at least one or a plurality of polyols having a number average molecular weight of from 18 to 750 g/mol, preferably 18 g/mol to 400 g/mol, particularly preferably 62 g/mol to 200 g/mol, a number average functionality of from 2 to 8 and having at least 2 terminal (primary) OH groups per molecule,
- 10 b) optionally polymer polyols which have OH numbers of from 10 to 149 and average functionalities of from 1.7 to 4, preferably 1.8 to 3.5 and which comprise from 1 to 50 wt.%, preferably 1 to 45 wt.%, fillers, in relation to the polymer polyol,
- 15 c) low molecular weight chain extenders having average functionalities of from 1.8 to 2.1 and having a number average molecular weight of from 18 g/mol to 750 g/mol, preferably 18 g/mol to 400 g/mol, particularly preferably 62 g/mol to 200 g/mol, and/or cross-linking agents having average functionalities of from 2.2 to 8, preferably 2.5 to 4, and having a number average molecular weight of from 18 g/mol to 750 g/mol, preferably 18 g/mol to 400 g/mol, particularly preferably 62 g/mol to 200 g/mol,
- 20 in the presence of
- d) optionally catalysts,
- e) optionally blowing agents and
- f) optionally additives,
- 25 with
- g) at least one polyisocyanate selected from the group comprising
- 30 g1) organic polyisocyanates,
- g2) modified polyisocyanates and

g3) NCO prepolymers based on g1) and/or g2) and a polyol x),

wherein the polyol x) is selected from the group comprising

- 5 x1) polyester polyols,
 x2) polyetherester polyols and
 x3) mixtures of x1) and x2),

g4) as well as mixtures of g1), g2) and g3).

10

The term "polyetherester polyol" is understood to signify a compound which has ether groups, ester groups and OH groups.

15

The polyetherester polyols a) which are to be used according to the invention have a number average molecular weight of from 1000 g/mol to 6000 g/mol, preferably 2500 g/mol to 5000 g/mol, a number average hydroxyl functionality of from 1.9 to 2.5, preferably 1.95 to 2.1 and particularly preferably 2.001 to 2.08, and a ratio of ether groups to ester groups of from 0.3 to 2.5, preferably 0.6 to 2.0 and particularly preferably 0.9 to 1.5.

20

25

Organic dicarboxylic acids a1) having up to 12 carbon atoms are suitable for the preparation of the polyetherester polyols, preferably aliphatic dicarboxylic acids having 4 to 6 carbon atoms, which are used either individually or in mixture. Examples which might be named are suberic acid, azelaic acid, decanedicarboxylic acid, maleic acid, malonic acid, phthalic acid, pimelic acid and sebacic acid, as well as in particular glutaric acid, fumaric acid, succinic acid and adipic acid. Anhydrides thereof as well as esters and semiesters thereof with low molecular weight monofunctional alcohols having 1 to 4 carbon atoms are examples of derivatives of these acids which may be utilised.

30

As the component a2) for the preparation of the polyetherester polyols, polyether polyols are utilised which are obtained by the alkoxylation of starter molecules, preferably polyhydric alcohols. The starter molecules are at least bifunctional, but

may optionally also comprise higher-functional, in particular trifunctional, starter molecule contents. The alkoxylation is normally effected in two steps. Alkoxylation first takes place with preferably propylene oxide or less preferably 1,2-butylene oxide or less preferably 2,3-butylene oxide in the presence of basic catalysts or double metal cyanide catalysts, and is followed by ethoxylation with ethylene oxide. The ethylene oxide content of the polyether polyol is from 10 wt.% to 40 wt.%, preferably 15 wt.% to 35 wt.%.

The component a3) preferably embraces diols having primary OH groups and number average molecular weights of ≤ 750 g/mol, preferably from 18 g/mol to 400 g/mol, particularly preferably 62 g/mol to 200 g/mol; such as, for example 1,2-ethanediol, 1,3-propanediol, 1,4-butanediol, 1,5-pentenediol, 1,5-pentanediol, neopentyl glycol, 1,6-hexanediol, 1,7-heptanediol, 1,8-octanediol, 1,10-decanediol, 2-methyl-1,3-propanediol, 2,2-dimethyl-1,3-propanediol, 3-methyl-1,5-pentanediol, 2-butyl-2-ethyl-1,3-propanediol, 2-butene-1,4-diol and 2-butene-1,4-diol, ether diols such as diethylene glycol, triethylene glycol, tetraethylene glycol, dibutylene glycol, tributylene glycol, tetrabutylene glycol, dihexylene glycol, trihexylene glycol, tetrahexylene glycol and oligomer mixtures of alkylene glycols, such as diethylene glycol.

Alongside the diols, polyols having number average functionalities of > 2 to 8, preferably 2.1 to 5, particularly preferably 3 to 4, may also be co-used, for example, 1,1,1-trimethylolpropane, triethanolamine, glycerol, sorbitan and pentaerythritol as well as polyethylene oxide polyols which have average molecular weights of less than 750 g/mol, preferably from 18 g/mol to 400 g/mol, particularly preferably 62 g/mol to 200 g/mol and are started on triols or tetraols.

Each member of the diols group may be utilised alone or in combination with other diols and polyols. The diols and polyols may also be added subsequently to a polyester polyol, even if they are not reacted thereby or are not reacted until the polycondensation equilibrium is reached in the esterification reaction. The relative quantity of polyols utilised is limited by the given number average hydroxyl functionality of the polyetherester polyol a).

Polymer-modified polyols, in particular graft polymer polyols based on polyethers, polyesters or polyetheresters, are suitable as the polymer polyols b). Suitable graft components are in particular those based on styrene and/or acrylonitrile, which have
5 been prepared by in situ polymerisation of acrylonitrile, styrene or preferably mixtures of styrene and acrylonitrile, for example in a ratio by weight of from 90 : 10 to 10 : 90, preferably 70 : 30 to 30 : 70. Polyol dispersions which comprise as the disperse phase – normally in quantities of from 1 to 50 wt.%, preferably 1 to 45 wt.%, in relation to polymer polyol fillers, for example inorganic fillers,
10 polyureas (PHDs), polyhydrazides, polyurethanes comprising bound tert.-amino groups, and/or melamine are also suitable as the component b).

In order to prepare the polyurethane elastomers according to the invention low molecular weight bifunctional chain extenders, cross-linking agents having number
15 average functionalities of from 2.2 to 8 or mixtures of chain extenders and cross-linking agents are used additionally as the component c).

Such chain extenders and cross-linking agents c) are utilised in order to modify the mechanical properties, in particular the hardness, of the polyurethane elastomers.
20 Suitable chain extenders are compounds such as are described under component a3), as well as diesters of terephthalic acid with glycols having 2 to 4 carbon atoms, such as, for example, terephthalic acid-bis-2-hydroxyethyl ester or terephthalic acid-bis-4-hydroxybutyl ester, hydroxyalkylene ethers of hydroquinone or resorcinol, such as, for example, 1,4-di-(β -hydroxyethyl) hydroquinone or 1,3-(β -hydroxyethyl)
25 resorcinol, N-alkyldialkanolamines having 2 to 12, carbon atoms, for example N-methyl- and N-ethyl diethanolamine. In addition to the cross-linking agents named under component a3), cross-linking agents are, for example, triols, tetraols, oligomeric polyalkylene polyols, aromatic and aliphatic amines and diamines having a functionality of from 2.2 to 8, preferably 3 to 4, which normally have molecular
30 weights of ≤ 750 g/mol, preferably 18 to 400 g/mol, particularly preferably 62 to 200 g/mol.

The relative quantity of polyene and tetraols utilised is limited by the given node density of the polyurethane elastomers according to the invention in combination with the average hydroxyl functionality of the polyetherester polyol a).

- 5 The compounds of the component c) may be utilised in the form of mixtures or individually. Mixtures of chain extenders and cross-linking agents are also usable.

As the component d) amine catalysts such as are current among those skilled in the art may be utilised, for example tertiary amines such as triethylamine, tributylamine,
10 N-methylmorpholine, N-ethylmorpholine, N,N,N',N'-tetramethyl ethylenediamine, pentamethyl diethylenetriamine and higher homologues, 1,4-diazabicyclo-[2,2,2]-octane, N-methyl-N'-dimethylaminoethyl piperazine, bis(dimethylaminoalkyl)-piperazine, N,N-dimethylbenzylamine, N,N-dimethylcyclohexylamine, N,N-diethylbenzylamine, bis(N,N-diethylaminoethyl) adipate, N,N,N',N'-tetramethyl-1,3-
15 butanediamine, N,N-dimethyl- β -phenylethylamine, bis(dimethylaminopropyl) urea, bis(dimethylaminopropyl)amine, 1,2-dimethylimidazole, 2-methylimidazole, diazabicycloundecene, monocyclic and bicyclic amidines, bis(dialkylamino) alkyl ethers such as, for example, bis(dimethylaminoethyl) ether, as well as tertiary amines having amide groups (preferably formamide groups). The following are also
20 considered as the catalysts: Mannich bases prepared from secondary amines, which are known per se, such as dimethylamine, and aldehydes, preferably formaldehyde, or ketones such as acetone, methyl ethyl ketone, or cyclohexanone and phenols such as phenol, N-nonylphenol or bisphenol A. Tertiary amines having hydrogen atoms which are Zerewitinoff-active vis-à-vis isocyanate groups, as a catalyst are, for
25 example, triethanolamine, triisopropanolamine, N-methyldiethanolamine, N-ethyldiethanolamine, N,N-dimethylethanolamine, reaction products thereof with alkylene oxides such as propylene oxide and/or ethylene oxide, as well as secondary-tertiary amines. Silaamines having carbon-silicon bonds may furthermore be utilised as catalysts, for example 2,2,4-trimethyl-2-silamorpholine and 1,3-
30 diethylaminomethyl tetramethyldisiloxane. Nitrogenous bases such as tetraalkylammonium hydroxides, furthermore hexahydrotriazines, are further considered. The reaction between NCO groups and Zerewitinoff-active hydrogen atoms is also greatly accelerated by lactams and azalactams.

Compact polyurethane elastomers, for example polyurethane shoe outer soles, can be produced in the absence of moisture and physically or chemically acting blowing agents.

5

For the preparation of microcellular polyurethane elastomers water is preferably used as the blowing agent e), which reacts in situ with the isocyanate component g) with formation of carbon dioxide and amino groups which for their part react further with further isocyanate groups to give urea groups, and act in this instance as chain
10 extenders.

Where water is added to the polyurethane formulation in order to adjust the desired density, this is normally used in quantities of from 0.001 to 3.0 wt.%, preferably 0.01 to 2.0 wt.% and in particular 0.05 to 1.0 wt.%, in relation to the weight of the
15 components a) to f).

Gases or highly volatile inorganic or organic substances which vaporise under the influence of the exothermic polyaddition reaction and preferably have a boiling point at standard pressure within the range -40 to 120°C, preferably -30 to 90°C,
20 being physical blowing agents, may be utilised as the blowing agent e) in place of water or preferably in combination with water. Acetone, ethyl acetate, halogen-substituted alkanes or perhalogenated alkanes such as R134a, R141b, R365mfc, R245fa, and further n-butane, iso-butane, iso-pentane, n-pentane, cyclopentane, n-hexane, iso-hexane, cyclohexane, n-heptane, iso-heptane or diethyl ether, for
25 example, are considered as organic blowing agents, and air, CO₂ or N₂O, for example, are considered as inorganic blowing agents. A blowing action can also be obtained by the addition of compounds which decompose at temperatures above room temperature with separation of gases, for example of nitrogen and/or carbon dioxide, such as azo compounds, for example azodicarbonamide or azo-bis-
30 isobutyric acid nitrile, or salts such as ammonium bicarbonate, ammonium carbamate or ammonium salts of organic carboxylic acids, for example monoammonium salts of malonic acid, boric acid, formic acid or ethanoic acid. Further examples of blowing agents, as well as details regarding the use of blowing

agents, are described in R. Vieweg, A. Höchtlen (ed.): "Kunststoff-Handbuch", Vol. VII, Carl-Hanser-Verlag, Munich, 3rd edition, 1993, pp. 115 to 118 and 710 to 715.

5 The quantity which it is expedient to utilise of solid blowing agents, low-boiling liquids or gases, which in each case may be utilised individually or in the form of mixtures, for example as liquid or gas mixtures or as gas-liquid mixtures, is naturally dependent on the density sought and the quantity of water utilised. The necessary quantities can be readily determined experimentally. Solid, liquid and/or
10 gas quantities of from 0.01 to 35 wt.%, preferably 0.1 to 6 wt.%, in each case in relation to the weight of the components a) to f), normally deliver satisfactory results. The gas, for example, air, carbon dioxide, nitrogen and/or helium, can be introduced both by way of the higher molecular weight polyhydroxyl compounds a) and b) and also by way of the compounds d) and f) and also by way of the
15 polyisocyanates g).

The reaction mixture for the preparation of the compact or cellular polyurethane elastomers may optionally be provided with additives f). Examples which might be named are surface-active additives such as emulsifiers, foam stabilisers, cell
20 regulators, flame retardants, nucleating agents, oxidation retardants, stabilisers, lubricants and mould release agents, dyes, dispersion aids and pigments. The sodium salts of castor oil sulfonates or salts of fatty acids with amines such as oleic acid diethylamine or stearic acid diethanolamine, for example, are considered as the emulsifiers. Alkali metal salts or ammonium salts of sulfonic acids such as, for
25 instance, of dodecylbenzenesulfonic acid or dinaphthylmethane disulfonic acid or of fatty acids such as ricinoleic acid or of polymeric fatty acids may also be co-used as surface-active additives. Polyether siloxanes, specifically water-soluble representatives, are above all considered as the foam stabilisers. These compounds are generally constructed such that a copolymer of ethylene oxide and propylene
30 oxide is combined with a polydimethylsiloxane radical. Polysiloxane-polyoxyalkylene copolymers having multiple branchings by way of allophanate groups are particularly attractive. Other organopolysiloxanes, oxyethylated alkylphenols, oxyethylated fatty alcohols, paraffin oils, castor oil acid esters or

ricinoleic acid esters, sulfonated castor oil, peanut oil and cell regulators such as paraffins, fatty alcohols and polydimethyl siloxanes are also suitable. In order to improve the emulsifying action, the dispersion of the filler, the cell structure and/or in order to stabilise it, oligomeric polyacrylates having polyoxyalkylene radicals and fluoroalkane radicals as side groups are furthermore suitable. The surface-active substances are normally employed in quantities of from 0.01 to 5 parts by weight, in relation to 100 parts by weight of the higher molecular weight polyhydroxyl compounds a) and b). Reaction retardants, antistatic agents such as, for example, Catafor[®]Ca 100, may be added, and further, pigments or dyes and flame retardants which are known per se, and further, stabilisers against the effects of ageing and weathering, plasticisers and fungistats and bacteriostats.

Further examples of surface-active additives and foam stabilisers, as well as cell regulators, reaction retardants, stabilisers, flame-retardant substances, plasticisers, dyes and fillers as well as fungistats and bacteriostats which are optionally co-used, as well as details regarding the mode of use and action of these additives are described in R. Vieweg, A. Höchtlen (ed.): "Kunststoff-Handbuch", Vol. VII, Carl-Hanser-Verlag, Munich, 3rd edition, 1993, pp. 118 to 124.

Aliphatic, cycloaliphatic, araliphatic, aromatic and heterocyclic polyisocyanates corresponding to the formula



in which $n = 2$ to 7 , preferably 2 , and Q denotes an aliphatic hydrocarbon radical having 2 to 18 , preferably 6 to 10 , C atoms, a cycloaliphatic hydrocarbon radical having 4 to 15 , preferably 5 to 10 , C atoms, an aromatic hydrocarbon radical having 6 to 15 , preferably 6 to 13 , C atoms, or an araliphatic hydrocarbon radical having 8 to 15 , preferably 8 to 13 , C atoms, are suitable as the component g1); the following are suitable, for example: 1,4-tetramethylene diisocyanate, 1,6-hexamethylene diisocyanate (HDI), 1,12-dodecane diisocyanate, cyclobutane-1,3-diisocyanate, cyclohexane-1,3-diisocyanate and cyclohexane-1,4-diisocyanate, 1-isocyanato-3,3,5-trimethyl-5-isocyanatomethyl cyclohexane (IPDI), 2,4- and 2,6-

hexahydrotolylene diisocyanate, hexahydro-1,3- and -1,4-phenylene diisocyanate, perhydro-2,4'-diphenylmethane diisocyanate, perhydro-4,4'-diphenylmethane diisocyanate, 1,3- and 1,4-phenylene diisocyanate, 1,4-naphthalene diisocyanate (1,4-NDI), 1,5-naphthalene diisocyanate (1,5-NDI), 1,4-durene diisocyanate (DDI),
5 4,4'-stilbene diisocyanate, 3,3'-dimethyl-4,4'-biphenylene diisocyanate (TODI), 2,4- and 2,6-tolylene diisocyanate (TDI), diphenylmethane-2,4'-diisocyanate, diphenylmethane-2,2'-diisocyanate and diphenylmethane-4,4'-diisocyanate (MDI) and polynuclear representatives of the diphenylmethane diisocyanate series. The named compounds and isomers thereof may in each case be utilised individually or
10 in the form of mixtures.

The industrially readily accessible polyisocyanates, for example 2,4- and 2,6-tolylene diisocyanate, naphthylene-1,5-diisocyanate, 4,4'-diphenylmethane diisocyanate, 2,4'-diphenylmethane diisocyanate, 2,2'-diphenylmethane diisocyanate
15 and polyphenyl polymethylene polyisocyanates, as prepared by aniline-formaldehyde condensation followed by phosgenation ("raw MDI"), are preferably utilised, wherein the polyisocyanates may be utilised individually or in the form of mixtures.

20 Mixtures of 4,4'-diphenylmethane diisocyanate, 2,4'-diphenylmethane diisocyanate are particularly preferred.

The following are considered as the modified isocyanates g2), for example: polyisocyanates having carbodiimide groups, such as, for example, bis(4,4'-
25 diphenylmethane) carbodiimide, polyisocyanates having allophanate groups, polyisocyanates having isocyanurate groups, polyisocyanates having urethane groups, polyisocyanates having acylated urea groups, polyisocyanates having biuret groups, polyisocyanates prepared by telomerisation reactions, reaction products of the aforementioned isocyanates with acetals, and polyisocyanates comprising
30 polymeric fatty acid esters.

Modified polyisocyanates such as are derived from 2,4- and/or 2,6-tolylene diisocyanate, from 4,4'- and/or 2,4'-diphenylmethane diisocyanate or from naphthylene-1,5-diisocyanate, and mixtures thereof are particularly preferred.

- 5 The polyester polyols x2) are prepared by condensation of one or more dicarboxylic acids a1) with at least one or a plurality of polyols of the components a3), c) and/or other short-chain polyols y) and with at least one or a plurality of long-chain polyols of the components a2) or z).
- 10 The polyetherester polyols x2) may be identical to the polyetherester polyols a). They may, however, also be prepared based on polyether polyols or mixtures of a plurality of polyether polyols z) having a number average molecular weight of from 1000 g/mol to 6000 g/mol, preferably 2500 g/mol to 5000 g/mol, and having an average functionality of from 1.7 to 2.5 and less than 70% primary OH groups.
- 15 These polyether polyols z) are obtained by alkoxylation of starter molecules, preferably alcohols. The starter molecules are at least bifunctional, but may optionally also comprise higher-functional, in particular trifunctional, starter molecule contents. The alkoxylation takes place in two steps. Alkoxylation with propylene oxide, 1,2-butylene oxide or 2,3-butylene oxide first takes place with
- 20 basic catalysis or with double metal cyanide catalysis, and ethoxylation optionally follows. The ethylene oxide content of the polyether is between 0 wt.% and 10 wt.%.

- As the component y), cross-linking agents and chain extenders such as are described
- 25 under c) and/or polyols having an average hydroxyl functionality of from 2 to 8, having one or two secondary hydroxyl groups and number average molecular weights of less than 750 g/mol may be utilised. They include saturated and unsaturated aliphatic diols such as 1,2-propanediol, 1,2-butanediol, 1,3-butanediol, ether diols such as dipropylene glycol, tripropylene glycol, tetrapropylene glycol, di-
- 30 1,2-butylene glycol, tri-1,2-butylene glycol, tetra-1,2-butylene glycol, di-1,3-butylene glycol, tri-1,3-butylene glycol, tetra-1,3-butylene glycol and oligomer mixtures thereof.

In addition to the diols, polypropylene oxide polyols started on triols or tetraols can also be used, for example 1,1,1-trimethylolpropane, triethanolamine, glycerol and pentaerythritol having average molecular weights of less than 750 g/mol.

5 Each compound from the diols group may be utilised alone or in combination with further diols and/or polyhydric polyols. These diols or polyols can also be added subsequently to a polyester polyol, even if as a result they are not reacted or are not reacted until the polycondensation equilibrium has been reached in the esterification
10 reaction. The relative quantity of polyols utilised is limited by the given number average hydroxyl functionality of the polyetherester polyol x2) and the given node density for the polyurethane elastomer.

The polyester polyols x1) are prepared by condensation of one or more dicarboxylic acids a1) with at least one polyol or a plurality of polyols according to a3), c) and/or
15 y).

The present invention also provides a process for the preparation of the polyurethane elastomers according to the invention, which is characterised in that

20 a) at least one polyetherester polyol having a number average molecular weight of from 1000 g/mol to 6000 g/mol, having a number average functionality of from 1.9 to 2.5 and a ratio of ether groups to ester groups of the polyetherester of from 0.3 to 2.5,

25 which is obtainable by polycondensation from

a1) at least one or a plurality of dicarboxylic acids having up to 12 carbon atoms and/or derivatives thereof,

30 a2) at least one or a plurality of polyether polyols having a number average molecular weight of from 1000 g/mol to 6000 g/mol, having an average functionality of from 1.7 to 2.5 and a primary OH group content of from 70% to 100% and

5 a3) at least one or a plurality of polyols having a number average molecular weight of from 18 to 750 g/mol, a number average functionality of from 2 to 8 and at least 2 terminal OH groups per molecule,

10 b) optionally polymer polyols which have an OH number of from 10 to 149 and average functionalities of from 1.7 to 4, and which comprise from 1 to 50 wt.% fillers, in relation to the polymer polyol,

15 c) low molecular weight chain extenders having average functionalities of from 1.8 to 2.1 and having a number average molecular weight of from 18 to 750 g/mol and/or cross-linking agents having average functionalities of from 2.2 to 8 and having a number average molecular weight of from 18 to 750 g/mol,

is reacted in the presence of

20 d) optionally catalysts,
e) optionally blowing agents and
f) optionally additives

with

25 g) at least one polyisocyanate selected from the group comprising

g1) organic polyisocyanates,
g2) modified polyisocyanates,
g3) NCO prepolymers based on g1) and/or g2) and a polyol x),

30

wherein the polyol x) is selected from the group comprising

x1) polyester polyols,

- 19 -

- x2) polyetherester polyols and
- x3) mixtures of x1) and x2),

g4) and mixtures of g1), g2) and/or g3).

5

In order to prepare the polyetherester polyols a) or x2), the organic, for example aromatic and preferably aliphatic, polycarboxylic acids and/or derivatives and polyols are preferably polycondensed in catalyst-free manner or in the presence of esterification catalysts, expediently in an atmosphere of inert gases such as, for example, nitrogen, helium, argon, in solution and also in the melt at temperatures of
10 from 150 to 300°C, preferably 180 to 230°C, optionally at reduced pressure to the desired acid value which is advantageously less than 10, preferably less than 1.

According to a preferred preparation process the esterification reaction is run at
15 standard pressure until no more condensate forms. Catalyst can then be added. The reaction is completed at a pressure of less than 500 mbar, preferably from 2 to 150 mbar. Iron catalysts, cadmium catalysts, cobalt catalysts, lead catalysts, zinc catalysts, antimony catalysts, magnesium catalysts, titanium catalysts and tin catalysts, for example, in the form of metal oxides or metal salts are considered as
20 the esterification catalysts. The polycondensation may, however, also be carried out in the presence of diluents and/or entraining agents such as, for example, benzene, toluene, xylene or chlorobenzene, in order to bring about azeotropic separation of the water of condensation. Mixtures of the named agents are likewise usual.

25 In order to prepare the polyester polyols x1) the organic polycarboxylic acids and/or derivatives thereof are preferably utilised with polyhydric alcohols, advantageously in a quantitative ratio such that the hydroxyl groups are at all times present in numerical excess vis-à-vis carboxyl groups or carboxyl derivatives.

30 The polyurethane elastomers according to the invention are preferably prepared by the prepolymer process, wherein expediently the prepolymer g3) is obtained by reacting at least one polyol or a plurality of polyols x) with at least one or a plurality

of isocyanates g1) and optionally modified isocyanates g2) as well as optionally short-chain polyols a3) and/or y) and/or c).

5 In order to prepare the solid or microcellular polyurethane elastomers according to the invention, isocyanates g) comprising the component g1) with optionally the component g2) or preferably the NCO prepolymer g3) are preferably reacted with at least one polyetherester polyol a) and low molecular weight chain extenders and/or cross-linking agents c) optionally with the addition of catalysts d), blowing agents e) and additives f).

10

In order to prepare the polyurethane elastomers according to the invention the components are reacted in quantities such that the equivalent ratio of the NCO groups of the isocyanate g) to the sum of the hydrogen atoms of the components a), b), c), d) and f), which are reactive to isocyanate groups, as well as any chemically
15 acting blowing agents e) which may be utilised, is from 0.8 : 1 to 1.2 : 1, preferably 0.95 : 1 to 1.15 : 1 and in particular 1.00 : 1 to 1.05 : 1.

According to the invention all the components, taking account of their isocyanate functionalities and hydroxyl functionalities, are furthermore combined such that the
20 resulting polyurethane elastomer has a node density of between 0.1 mole/kg and 0.0001 mole/kg, preferably between 0.001 and 0.08 mole/kg, particularly preferably between 0.01 and 0.04 mole/kg.

The polyurethane elastomers according to the invention are preferably utilised in the
25 production of shoe components, in particular shoe soles.

The invention will be explained in further detail by reference to the Examples which follow.

Examples

The polyurethane elastomer was obtained by equivalent reaction of a polyol formulation α and an NCO prepolymer β (average functionality 2.01). The compositions of the polyol formulation α and the NCO prepolymer β can be seen in Table 2. The physical properties of the polyurethane elastomers according to the invention are listed in Table 3.

The general directions for preparing the polyetherester polyols are described taking polyetherester polyol C as an example:

4662 g (53.7 mole) of a hydroxy-functionalised polyether P (hydroxyl number 28; number average hydroxyl functionality 1.81; primary hydroxyl groups 90 mol.% (propylene glycol as the starter; 68.7 wt.% propylene oxide; 29.4 wt. ethylene oxide)), 426 g (4 mole) diethylene glycol, 417 g (4.8 mole) ethylene glycol, 767 g (8.8 mole) 1,4-butanediol, 15 g (0.1 mole) trimethylolpropane and 2461 g (16.8 mole) adipic acid were heated to a melt in a 10-litre four-necked round flask equipped with a stirrer, packed column, descending condenser and thermometer as well as a vacuum pump and heating mantle, with nitrogen being passed through the apparatus. Heating to 180°C was continued until no further water separated out. 200 mg tin(II) chloride were then added, a vacuum was applied slowly, and the temperature was raised to 200°C. Stirring continued for 2 hours at 200°C and 5 mbar in order to complete the reaction. A polyetherester having an acid value of 0.3, a hydroxyl number of 34.6 and a viscosity of 930 mPa.s at 75°C was obtained. The starting compounds as well as the physical data of the polyetherester polyols and the polyester polyols can be seen in Table 1.

The polyurethane test pieces were prepared such that the polyol formulation α at 55°C was mixed with a toothed mixer at 3000 rpm in a low-pressure foaming unit with the NCO prepolymer β at 40°, the mixture was poured into an aluminium hinged mould (200 x 140 x 10 mm) temperature-controlled at 50°C, the hinged mould was closed, and the polyurethane elastomer was demoulded after 3.5 minutes.

Following 24 hours' storage the Shore A hardness in accordance with DIN 53 505 was determined by means of blue gel on the polyurethane elastomer slabs thus obtained. The stab-type crack growth in accordance with DIN 53 522 of a 2 mm wide stab through the bending line of test pieces (2 cm x 15 cm x 1 cm) backed with a Texon strip was furthermore determined after 30,000 bending cycles. The results are set out in Table 3. The flexing endurance tests were performed at room temperature and at -15°C. Test pieces were additionally aged for 7 days at 95% atmospheric humidity and 70°C, dried for 24 hours at 70°C, reconditioned for a further 24 hours at room temperature, after which they underwent a flexing endurance test at room temperature. Abrasion was determined in accordance with DIN 53516, and the fuel resistance was determined in accordance with EN 344.

Table 1: Polyetherester polyols C, E to O, as well as polyester polyols A, B and D

	Component a3)										
	Hydroxyl number [mg KOH/g]	Acid value [mg KOH/g]	Viscosity ^{75°C} [mPa.s]	Molecular weight [g/mol]	Number average hydroxyl functionality	Ethylene glycol [wt.%]	1,4-butanediol [wt.%]	Diethylene glycol [wt.%]	Trimethylolpropane [wt.%]	Polyether P [wt.%]	Adipic acid [wt.%]
A	29.0	0.5	2800	3869	2.000	0.2076	0.1291	-	-	-	0.663
B	37.0	0.7	1900	3032	2.000	0.2085	0.1300	-	-	-	0.661
C	34.6	0.3	930	3303	2.037	0.0481	0.0883	0.0403	0.0017	0.5379	0.284
D	35.7	0.6	1900	3201	2.037	0.1006	0.1888	0.0861	0.0016	-	0.623
E	35.0	0.6	1350	3265	2.037	0.1082	0.0993	0.0453	0.0016	0.3024	0.443
F	38.3	0.4	830	2984	2.037	-	0.1524	0.0695	0.0017	0.4642	0.312
G	37.0	0.4	1330	3089	2.037	0.0503	0.1846	0.0421	0.0016	0.2813	0.440
H	37.50	0.3	960	3047	2.037	0.0939	-	0.0787	0.0017	0.5249	0.301
I	39.1	0.3	1070	2923	2.037	0.0583	0.1069	0.0976	0.0017	0.3254	0.410
J	34.7	0.4	1180	3293	2.037	0.0749	0.1374	-	0.0017	0.4185	0.368
K	37.2	0.4	1160	3131	2.076	0.0653	0.1198	0.0536	0.0033	0.3651	0.393
L	36.5	0.4	1160	3074	2.000	0.0667	0.1219	0.0544	-	0.3643	0.393
M	31.3	0.8	1430	3651	2.037	0.0670	0.1185	0.0538	0.0012	0.3623	0.397
N	40.4	0.3	920	2829	2.037	0.0659	0.1209	0.0549	0.0018	0.3675	0.389
O	38.90	0.8	1040	2942	2.040	0.0655	0.1231	0.0545	0.0016	0.3650	0.390

Table 2: Compositions of polyol formulations α and the prepolymer β

Polyol formulation α		NCO prepolymer β	
Component	[wt.%]	Component	[wt.%]
Butanediol	13.01	Desmodur® 44M	46.32
Diazabicyclooctane	0.56	Desmodur® CD	4.96
Triethanolamine	0.19	Polyol A	48.72
Water	0.32		100.00
Foam stabiliser	0.09		
Polyols B to O	85.83	Desmodur®: Isocyanate, commercially available from Bayer AG	
	100.00		

Table 3: Properties of the polyurethane elastomer test specimens having a density of 600 kg/m³

Test	Polyol in polyol formulation α	Average functionality of polyol formulation α	Hardness (Shore A)	Long-term flexural strength at room temp.			Long-term flexural strength at -15°C			Long-term flexural strength at room temp. following hydrolytic ageing			Abrasion [ng]	Fuel resis-tance	Swelling [%]	Node density [mole/kg]
				Stab-type crack growth after 30,000 bends	Break at n bends	n bends	Stab-type crack growth after 30,000 bends	Break at n bends	n bends	Stab-type crack growth after 30,000 bends	Break at n bends	n bends				
				No. of x	Widening [mm]	No. of y	n bends	No. of x	Widening [mm]	No. of y	n bends	No. of x	Widening [mm]	No. of y	n bends	
B	2.0085	64	0	4	22,500	2	4.7	3	21,667	0	4,185	4	78	1	0.0177	
C	2.0142	63	4	0	3.0	3	4.4	1	30,000	3	30,000	1	92	6	0.0229	
D	2.0143	62	0	4	11,300	0		4	16,300	4		0	42	1	0.0231	
E	2.0142	61	0	4	20,000	0		4	27,500	4		0	68	1	0.0230	
F	2.0145	62	3	1	30,000	3	5.0	1	25,000	4		0	70	7	0.0234	
G	2.0144	61	0	4	22,500	0		3	23,300	4		0	62	3	0.0232	
H	2.0149	61	4	0		4	2.2	0		3		1	94	6	0.0237	
I	2.0148	60	4	0		4	4.0	0		4		0	86	4	0.0235	
J	2.0142	62	4	0		4	1.2	0		4		0	68	5	0.0229	
K	2.0203	61	0	4	30,000	3	9.9	1	30,000	4		0	62	4	0.0286	
L	2.0085	60	4	0		4	0.6	0		0	13,800	4	66	5	0.0177	
M	2.0138	60	4	0		4	1.1	0	5,000	0		4	95	4	0.0224	
N	2.0148	61	2	2	30,000	3	6.1	1	30,000	4		0	75	4	0.0237	
O	2.0146	64	4	0		4	3.5	0		0	17,675	4	68	4	0.0235	

* Comparison

The letters "x" and "y" when added give the number of test strips which underwent a flexing endurance test. "x" designates the number of test strips having stab-type crack growth and "y" the number of test strips which broke.

Claims

1. Polyurethane elastomers which have a node density of from 0.1 mole/kg to 0.0001 mole/kg, obtainable by reacting

5

a) at least one polyetherester polyol having a number average molecular weight of from 1000 g/mol to 6000 g/mol, a number average functionality of from 1.9 to 2.5 and a ratio of ether groups to ester groups of the polyetherester of from 0.3 to 2.5,

10

which is obtainable by polycondensation from

a1) at least one or a plurality of dicarboxylic acids having up to 12 carbon atoms and/or derivatives thereof,

15

a2) at least one or a plurality of polyether polyols having a number average molecular weight of from 1000 g/mol to 6000 g/mol, an average functionality of from 1.7 to 2.5 as well as a 70% to 100% primary OH group content, and

20

a3) at least one or a plurality of polyols having a number average molecular weight of from 18 to 750 g/mol, a number average functionality of from 2 to 8 and having at least 2 terminal OH groups per molecule,

25

b) optionally polymer polyols which have an OH number of from 10 to 149 and average functionalities of from 1.7 to 4 and which comprise from 1 to 50 wt.% fillers, in relation to the polymer polyol,

30

c) low molecular weight chain extenders having average functionalities of from 1.8 to 2.1 and having a number average molecular weight of from 18 to 750 g/mol and/or cross-linking agents having average

functionalities of from 2.2 to 8 and having a number average molecular weight of from 18 to 750 g/mol,

in the presence of

5

- d) optionally catalysts,
- e) optionally blowing agents and
- f) optionally additives,

10

with

- g) at least one polyisocyanate selected from the group comprising

15

- g1) organic polyisocyanates,
- g2) modified polyisocyanates,
- g3) NCO prepolymers based on g1) and/or g2) and a polyol x),

wherein the polyol x) is selected from the group comprising

20

- x1) polyester polyols,
- x2) polyetherester polyols and
- x3) mixtures of x1) and x2),

- g4) and mixtures of g1), g2) and/or g3).

25

2. Polyurethane elastomers according to claim 1, characterised in that the polyisocyanate g1) is 4,4'-diphenylmethane diisocyanate, 2,4'-diphenylmethane diisocyanate or a mixture thereof.

30

3. Polyurethane elastomers according to claim 1, characterised in that the polyol a3) is selected from the group comprising 1,4-butanediol, 1,2-ethanediol, diethylene glycol, hexanediol, trimethylolpropane, sorbitan, pentaerythritol, triethanolamine and glycerol.

4. Process for the preparation of the polyurethane elastomers according to claims 1 to 3, characterised in that
- 5 a) at least one polyetherester polyol having a number average molecular weight of from 1000 g/mol to 6000 g/mol, a number average functionality of from 1.9 to 2.5 and a ratio of ether groups to ester groups of the polyetherester of from 0.3 to 2.5,
- 10 which is obtainable by polycondensation from
- a1) at least one or a plurality of dicarboxylic acids having up to 12 carbon atoms and/or derivatives thereof,
- 15 a2) at least one or a plurality of polyether polyols having a number average molecular weight of from 1000 g/mol to 6000 g/mol, an average functionality of from 1.7 to 2.5 as well as a 70% to 100% primary OH group content, and
- 20 a3) at least one or a plurality of polyols having a number average molecular weight of from 18 to 750 g/mol, a number average functionality of from 2 to 8 and having at least 2 terminal OH groups per molecule,
- 25 b) optionally polymer polyols which have an OH number of from 10 to 149 and average functionalities of from 1.7 to 4 and which comprise from 1 to 50 wt.% fillers, in relation to the polymer polyol,
- 30 c) low molecular weight chain extenders having average functionalities of from 1.8 to 2.1 and having a number average molecular weight of from 18 g/mol to 750 g/mol and/or cross-linking agents having average functionalities of from 2.2 to 8 and having a number average molecular weight of from 18 g/mol to 750 g/mol,

in the presence of

- 5
- d) optionally catalysts,
 - e) optionally blowing agents and
 - f) optionally additives,

with

- 10
- g) at least one polyisocyanate selected from the group comprising

- g1) organic polyisocyanates,
- g2) modified polyisocyanates,
- g3) NCO prepolymers based on g1) and/or g2) and a polyol x),

15

wherein the polyol x) is selected from the group comprising

- x1) polyester polyols,
- x2) polyetherester polyols and
- 20 x3) mixtures of x1) and x2),

20

- g4) and mixtures of g1), g2) and/or g3).

25

5. Use of the polyurethane elastomers according to claims 1 to 3 for the production of elastomeric mouldings, in particular shoe soles having densities within the range 180 to 1200 kg/m³.

30

6. Elastomeric mouldings for industrial articles and consumer goods, in particular shoe soles produced from polyurethane elastomers according to claims 1 to 3.