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(72) EISEN, Norbert, DE
(72) HEINEMANN, Torsten, DE
(72) MCCULLOUGH, Dennis, US
(72) KLÄN, Walter, DE
(71) BAYER AKTIENGESELLSCHAFT, DE

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(54) **PROCEDE DE PRODUCTION DE MOUSSES RIGIDES DE POLYURETHANNE EXPANSEES AUX HYDROCARBURES**

(54) **METHOD OF PRODUCING HYDROCARBON-EXPANDED RIGID POLYURETHANE FOAMS**

(57) L'invention concerne un procédé de production de mousses rigides de polyuréthanne à partir de polyols et de polyisocyanates, ainsi que d'agents d'expansion, et le cas échéant, d'auxiliaires de moussage. Ce procédé est caractérisé en ce que la mousse rigide de polyuréthanne est obtenue par réaction de (A) un composant polyol comportant en moyenne 3 atomes d'hydrogène, contenant: (1) 60 à 100 % de polyéthers et/ou de polyesters comportant au moins 2 groupes hydroxyle, présentant un poids moléculaire compris entre 250 et 1500, et une tension interfaciale de 6 à 14 mN/m par rapport à l'isopentane et/ou au n-pentane utilisé(s) comme agent d'expansion; (2) de l'isopentane et/ou du n-pentane servant d'agent d'expansion; (3) de l'eau; (4) et éventuellement des auxiliaires et additifs; avec (B) un polyisocyanate présentant une teneur en NCO comprise entre 20 et 48 % en poids et, par rapport à l'isopentane et/ou au n-pentane utilisé(s) comme agent d'expansion, une tension interfaciale de 4,0 à 8 mN/m.

(57) Described is a method of producing rigid polyurethane foams from polyols and polysiocyanates plus foaming agents and, optionally, foaming auxiliaries. The method is characterized in that the foam is obtained by reacting: A) a polyol component with an average of at least three hydrogen atoms and containing 1) 60 to 100 % of polyethers and/or polyesters with at least two hydroxyl groups, a molecular weight of 250 to 1,500 and an interfacial tension of 6 to 14 mN/m with respect to the iso-and/or n-pentane used as the foaming agent, 2) iso- and/or n-pentane as the foaming agent, 3) water and optionally 4) auxiliaries and additives with B) a polyisocyanate with an NCO content of 20 to 48 % by weight and with an interfacial tension of 4.0 to 8 mN/m with respect to the iso- and/or n-pentane used as the foaming agent.

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(71) Anmelder *(für alle Bestimmungsstaaten ausser US)*: BAYER AKTIENGESELLSCHAFT [DE/DE]; D-51368 Leverkusen (DE).

(72) Erfinder; und
(75) Erfinder/Anmelder *(nur für US)*: EISEN, Norbert [DE/DE]; Gerolsteinerstrasse 44, D-50937 Köln (DE). HEINEMANN, Torsten [DE/DE]; Andreas-Gryphius-Strasse 7, D-51065 Köln (DE). McCULLOUGH, Dennis [US/DE]; Im Oberiddelsfeld 39, D-51069 Köln (DE). KLÄN, Walter [DE/DE]; August-Kekulé-Strasse 12, D-51373 Leverkusen (DE).

(74) Gemeinsamer Vertreter: BAYER AKTIENGESELLSCHAFT; D-51368 Leverkusen (DE).

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(54) Title: METHOD OF PRODUCING HYDROCARBON-EXPANDED RIGID POLYURETHANE FOAMS

(54) Bezeichnung: VERFAHREN ZUR HERSTELLUNG KOHLENWASSERSTOFF-GETRIEBENER POLYURETHAN-HARTSCHAUMSTOFFE

(57) Abstract

Described is a method of producing rigid polyurethane foams from polyols and polyisocyanates plus foaming agents and, optionally, foaming auxiliaries. The method is characterized in that the foam is obtained by reacting: A) a polyol component with an average of at least three hydrogen atoms and containing 1) 60 to 100 % of polyethers and/or polyesters with at least two hydroxyl groups, a molecular weight of 250 to 1,500 and an interfacial tension of 6 to 14 mN/m with respect to the iso-and/or n-pentane used as the foaming agent, 2) iso- and/or n-pentane as the foaming agent, 3) water and optionally 4) auxiliaries and additives with B) a polyisocyanate with an NCO content of 20 to 48 % by weight and with an interfacial tension of 4.0 to 8 mN/m with respect to the iso- and/or n-pentane used as the foaming agent.

(57) Zusammenfassung

Beschrieben wird ein Verfahren zur Herstellung von Polyurethan-Hartschaumstoffen aus Polyolen und Polyisocyanaten sowie Treibmitteln und gegebenenfalls Schaumhilfsmitteln, dadurch gekennzeichnet, daß der Polyurethan-Hartschaumstoff erhalten wird durch Umsetzung von A) einer im Mittel mindestens 3 Wasserstoffatome aufweisenden Polyolkomponente, enthaltend 1. 60 bis 100 % von mindestens 2 Hydroxylgruppen aufweisenden Polyethern und/oder Polyestern vom Molekulargewicht 250 bis 1.500, die gegenüber i- und/oder n-Pentan als Treibmittel eine Grenzflächenspannung von 6 bis 14 mN/m aufweisen, 2. i- und/oder n-Pentan als Treibmittel, 3. Wasser und 4. gegebenenfalls Hilfs- und Zusatzstoffen mit B) einem Polyisocyanat mit einem NCO-Gehalt von 20 bis 48 Gew.-%, welches gegenüber i- und/oder n-Pentan als Treibmittel eine Grenzflächenspannung von 4,0 bis 8 mN/m aufweist.

A process for preparing hydrocarbon-blown polyurethane rigid foams

It is known that polyurethane rigid foams can be blown with low-boiling alkanes. Cyclic alkanes are used to advantage here because they make an outstanding contribution to the thermal conductivity of the expanded material due to their low gaseous thermal conductivity. Cyclopentane is preferably used.

The beneficial properties when used as an insulator in domestic refrigerators have to be compared with a disadvantageous commercial situation. Thus, a specific quality of polystyrene inner container has to be used, as a result of the solvent properties of cyclopentane.

Furthermore, cyclopentane has the disadvantage, due to its relatively high boiling point of 49°C, that it condenses at low temperatures such as are conventional during the use of polyurethane rigid foams as insulators in domestic refrigerators. Due to the undesired condensation of the blowing agent, a reduced pressure is produced in the cells which again has to be offset by an elevated foam strength or increased density.

Compared with the acyclic homologous pentane compounds, n-pentane and i–pentane, cyclopentane incurs higher manufacturing costs. n-pentane or i-pentane blown systems have been known for some time in the field of polyurethane rigid foams. However, the higher gaseous thermal conductivities, as compared with cyclopentane,which result in poorer thermal insulation capacity of the corresponding expanded systems is a disadvantage.

The object of the present invention was to develop a n-pentane or i-pentane blown rigid foam in which the disadvantages mentioned above are overcome and in particular in which low thermal conductivities are produced.

Surprisingly, it has now been found that polyol formulations based on specific polyethers and polyisocyanates, which have a specific surface tension with respect to

n–pentane or i-pentane as blowing agent, produce expanded materials with particularly low thermal conductivities.

The invention provides a process for preparing polyurethane rigid foams from polyols and polyisocyanates as well as blowing agents and optionally foam auxiliary agents, characterised in that the polyurethane rigid foam is obtained by reacting

A) a polyol component with on average at least 3 hydrogen atoms, containing

1. 60 to 100 % of polyethers and/or polyesters with at least 2 hydroxyl groups and a molecular weight of 250 to 1,500, which have a surface tension of 6 to 14 mN/m with respect to i-pentane and/or n-pentane as blowing agent,

2. i-pentane and/or n-pentane as blowing agent,

3. water and

4. optionally auxiliary agents and additives

with

B) a polyisocyanate with an NCO-content of 20 to 48 wt.% which has a surface tension of 4.0 to 8 mN/m with respect to i-pentane or n-pentane as blowing agent.

Polyol formulations according to the invention preferably contain polyethers with a molecular weight of 250 to 1,500, obtained by the polyaddition of 70 to 100 wt.% of ethylene oxide and 0 to 30 wt.% of propylene oxide to starter compounds.

Preferred compounds are sorbitol started polyethers with a molecular weight of 500 to 1,400 based on 70 to 100 wt.% of ethylene oxide and 0 to 30 wt.% of 1,2-propylene

oxide; sucrose started polyethers with a molecular weight of 500 to 1,400 based on 70 to 100 wt.% of ethylene oxide and 0 to 30 wt.% of 1,2-propylene oxide; trimethylolpropane started polyethers with a molecular weight of 250 to 850 based on 70 to 100 wt.% of ethylene oxide and 0 to 30 wt.% of 1,2-propylene oxide; glycerine started polyethers with a molecular weight of 250 to 850 based on 70 to 100 wt.% of ethylene oxide and 0 to 30 wt.% of 1,2-propylene oxide; o-toluylene-diamine started polyethers with a molecular weight of 250 to 850 based on 70 to 100 wt.% of ethylene oxide and 0 to 30 wt.% of 1,2-propylene oxide.

According to the invention the polyol formulations preferably contain polyesters with a molecular weight of 200 to 600 formed from aromatic and aliphatic dicarboxylic acids and polyols containing at least 2 hydroxyl groups. Examples of dicarboxylic acids are phthalic acid or phthalic anhydride, terephthalic acid, isophthalic aid, malonic acid and succinic acid. The following are preferably used as the alcohol component for esterification: ethylene glycol, di, tri or tetraethylene glycol or mixtures thereof.

Polyol formulations according to the invention may also contain polyether-esters, such as are obtainable by the reaction of phthalic anhydride with diethylene glycol and then with ethylene oxide (EP-A 0 250 967).

Polyethers and polyesters according to the invention preferably have a surface tension of 6 to 14 mN/m, in particular 10 to 13, with respect to n-pentane and/or i-pentane.

In polyol formulations, these products are preferably present in a proportion of 60 to 100%, preferably 80 to 90%.

Polyisocyanates are preferably prepolymers with terminal NCO groups.

The isocyanate components are, e.g. aromatic polyisocyanates such as are described, for instance, by W. Siefkin in Justus Liebigs Annalen der Chemie, 562, pages 75 to 136, for example those of the formula

$$Q(NCO)_n$$

in which

n is 2 to 4, preferably 2 and

Q represents an aliphatic hydrocarbon group with 2 to 18, preferably 6 to 10, carbon atoms, a cycloaliphatic hydrocarbon group with 4 to 15, preferably 5 to 10, carbon atoms, an aromatic hydrocarbon group with 8 to 15, preferably 8 to 13, carbon atoms, e.g. polyisocyanates like those which are described in DE-OS 2 832 253, pages 10 to 11.

Industrially readily accessible polyisocyanates are generally particularly preferred, e.g. 2,4 and 2,6-toluylene diisocyanate and any mixture of these isomers ("TDI), polyphenylpolymethylene polyisocyanates such as can be prepared by aniline/formaldehyde condensation and subsequent phosgenation (crude "MDI") and polyisocyanates with carbodiimide groups, urethane groups, allophanate groups, isocyanurate groups, urea groups or biuret groups ("modified polyisocyanates"), in particular modified polyisocyanates which are derived from 2,4 and 2,6-toluylene diisocyanate or from 4,4' and/or 2,4'-diphenylmethane diisocyanate.

Starting components for the prepolymers are organic compounds with at least one hydroxyl group.

Polyol or polyester components with a molecular weight of 60 to 1,400 and containing 1 to 4 hydroxyl groups are preferred.

Polyesters with a molecular weight of 200 to 600 based on aromatic and/or aliphatic dicarboxylic acids and polyethers with a molecular weight of 60 to 1,400, obtained by the polyaddition of 70 to 100 wt.% of ethylene oxide and 0 to 30 wt.% of 1,2–propylene oxide to starter compounds such as ethylene glycol, trimethylolpropane and glycerine are preferred.

Products produced from phthalic anhydride with diethylene glycol and/or ethylene glycol are particularly preferred.

Polyether-esters with a molecular weight of 300 to 450, such as are obtainable by the reaction of phthalic anhydride with diethylene glycol and subsequently with ethylene oxide are also particularly preferred (EP-A 0 250 967).

Prepolymers according to the invention preferably have a surface tension of 4.5 to 8 mN/m, in particular of 5 to 7 mN/m, with respect to n-pentane and/or i–pentane.

Paraffins or fatty alcohols or dimethylpolysiloxanes as well as pigments or colorants, also stabilisers against the effects of ageing and weathering, plasticisers and anti-fungal or anti-bacterial substances as well as fillers such as barium sulphate, kieselguhr, carbon black or prepared chalk, may also be incorporated.

Further examples of optionally incorporated surface active additives and foam stabilisers, as well as cell regulators, reaction retardants, stabilisers, flame inhibiting substances, colorants and fillers as well as anti-fungal and anti-bacterial substances for use according to the invention and details about the use and effects of these additives are described in Kunststoff-Handbuch, vol. VII, published by Vieweg and Höchtlen, Carl-Hanser-Verlag, Munich, 1966, e.g. on pages 121 to 205.

When preparing a foam, according to the invention the foaming procedure may also be performed in closed moulds. In this case the reaction mixture is introduced into a mould. Suitable mould materials are metals, e.g. aluminium, or plastics, e.g. epoxide resin. The foamable reaction mixture foams in the mould and forms the moulded item. The mould-foaming procedure may be performed in such a way that the moulded item has a cellular structure at its surface. It may also be performed, however, in such a way that the moulded item has a solid skin and a cellular core. According to the invention, the procedure in the first case is to introduce sufficient foamable reaction mixture into the mould for the foam produced to just fill the mould. The mode of operation in the last-mentioned case comprises introducing more foamable reaction mixture into the mould than is required to fill the interior of the mould with foam. In the latter case, therefore, the process uses "overcharging", a type of procedure which is known, e.g. from US-PS 3 178 490 and 3 182 104.

The invention also provides use of the rigid foam prepared according to the invention as an intermediate layer for laminated elements and for filling the hollow spaces in domestic refrigerators with foam.

The process according to the invention is preferably used for filling the hollow cavities in refrigerator and freezer housings with foam.

Obviously, expanded materials may also be produced by block foaming or by the double transport method which is known per se.

The rigid foams obtainable according to the invention are used, for instance, in the building industry and for the insulation of long-distance energy pipes and containers.

The following examples are intended to explain the invention without, however, restricting its scope.

The surface tension was determined by the conditions in appendix V of the Directive described in the Official Journal of the European Community in accordance with Directive 92/69/EWG (17th amendment to Directive 67/548/EWG) with the OECD ring method, taking the GLP into account.

Example 1 (comparison example)

Formulation for polyurethane rigid foam

Component A:

50 parts by wt. sucrose (80 wt.%) and propylene glycol (20 wt.%) started polyether with a molecular weight of 600, obtained by anionic polyaddition using 1,2-propylene oxide (surface tension with respect to n-pentane: 4.4 mN/m)

25 parts by wt. trimethylolpropane started polyether with a molecular weight of 430, obtained by anionic polyaddition using 1,2-propylene oxide (surface tension with respect to n-pentane: 1.3 mN/m)

25 parts by wt. propylene glycol started polyether with a molecular weight of 1,000, obtained by anionic polyaddition using 1,2-propylene oxide (surface tension with respect to n-pentane: 0.8 mN/m)

2.5 parts by wt. water

2.0 parts by wt. foam stabiliser, B 8423 (from Goldschmidt)

2.0 parts by wt. activator, Desmorapid 726b (Bayer AG)

Component B:

125 parts by wt. crude MDI (NCO content = 31.5 wt.%)
(surface tension with respect to n-pentane 3.3 mN/m)

100 parts by wt. of component A were mixed with 11 parts by wt. of n-pentane and 125 parts by wt. of component B using a stirrer (2,000 rpm) at 20°C and compressed in a closed mould at 34 kg/m^3.

Example 2 (comparison example)

Formulation for polyurethane rigid foam

Component A

100 parts by wt.	sorbitol started polyether with a molecular weight of 640, obtained by anionic polyaddition using ethylene oxide (surface tension with respect to n-pentane: 12.4 mN/m)
2.5 parts by wt.	water
2.0 parts by wt.	foam stabiliser, B 8423 (from Goldschmidt)
2.0 parts by wt.	activator, Desmorapid 726b (Bayer AG)

Component B:

168 parts by wt.	crude MDI (NCO content = 31.5 wt.%) (surface tension with respect to n-pentane 3.3 mN/m)

100 parts by wt. of component A were mixed with 11 parts by wt. of n-pentane and 168 parts by wt. of component B using a stirrer (2,000 rpm) at 20°C. An expanded material could not be obtained due to the structure collapsing.

Example 3 (comparison example)

Formulation for polyurethane rigid foam

Component A

50 parts by wt. sucrose (80 wt.%) and propylene glycol (20 wt.%) started polyether with a molecular weight of 600, obtained by anionic polyaddition using 1,2-propylene oxide (surface tension with respect to n-pentane: 4.4 mN/m)

25 parts by wt. trimethylolpropane started polyether with a molecular weight of 430, obtained by anionic polyaddition using 1,2-propylene oxide (surface tension with respect to n-pentane: 1.3 mN/m)

25 parts by wt. propylene glycol started polyether with a molecular weight of 1,000, obtained by anionic polyaddition using 1,2-propylene oxide (surface tension with respect to n-pentane: 0.8 mN/m)

2.5 parts by wt. water

2.0 parts by wt. foam stabiliser, B 8423 (from Goldschmidt)

2.0 parts by wt. activator, Desmorapid 726b (Bayer AG)

Component B:

146 parts by wt. prepolymer with an NCO content of 27 wt.%, obtained by reacting 92 wt.% of crude MDI (NCO content = 31.5 wt.%) with 8 wt.% of polyether-ester with a molecular weight of 370 based on phthalic anhydride, diethylene glycol and ethylene oxide.

100 parts by wt. of component A were mixed with 11 parts by wt. of n-pentane and 146 parts by wt. of component B using a stirrer (2,000 rpm) at 20°C and compressed in a closed mould at 34 kg/m^3.

Example 4 (according to the invention)

Formulation for polyurethane rigid foam

Component A

100 parts by wt. sorbitol started polyether with a molecular weight of 640, obtained by anionic polyaddition using ethylene oxide (surface tension with respect to n-pentane: 12.4 mN/m)

2.5 parts by wt. water

2.0 parts by wt. foam stabiliser, B 8423 (from Goldschmidt)

2.0 parts by wt. activator, Desmorapid 726b (Bayer AG)

Component B

196 parts by wt. prepolymer with an NCO content of 27 wt.%, obtained by reacting 92 wt.% of crude MDI (NCO content = 31.5 wt.%)

with 8 wt.% of polyether-ester with a molecular weight of 370 based on phthalic anhydride, diethylene glycol and ethylene oxide (surface tension with respect to n-pentane 5 mN/m)

100 parts by wt. of component A were mixed with 11 parts by wt. of n-pentane and 196 parts by wt. of component B using a stirrer (2,000 rpm) at 20°C and compressed in a closed mould at 34 kg/m^3.

Example 5 (according to the invention)

Component A

80 parts by wt. sorbitol started polyether with a molecular weight of 640, obtained by anionic polyaddition using ethylene oxide (surface tension with respect to n-pentane: 12.4 mN/m)

20 parts by wt. polyether-ester with a molecular weight of 370 based on phthalic anhydride, diethylene glycol and ethylene oxide (surface tension with respect to n-pentane: 12.3 mN/m)

2.5 parts by wt. water

2.0 parts by wt. foam stabiliser, B 8423 (from Goldschmidt)

2.0 parts by wt. activator, Desmorapid 726b (Bayer AG)

Component B

193 parts by wt. prepolymer with an NCO content of 25.5 wt.%, obtained by reacting 90 wt.% of crude MDI (NCO content = 31.5 wt.%)

with 10 wt.% of polyether-ester with a molecular weight of 355 based on phthalic anhydride and diethylene glycol (surface tension with respect to n-pentane 6.4 mN/m)

100 parts by wt. of component A were mixed with 11 parts by wt. of n-pentane and 193 parts by wt. of component B using a stirrer (2,000 rpm) at 20°C and compressed in a closed mould at 34 kg/m^3.

The test figures in the following Table were obtained for the foam sheets prepared in examples 1 to 5.

Example	Thermal conductivity [mW/mK] according to DIN 52616, 24°C
1	24
2	collapsed
3	23.3
4	20.5
5	20.0

As can be seen from examples 4 and 5, n-pentane blown PUR rigid foams with much lower thermal conductivities can be obtained by combining polyethers and polyisocyanates according to the invention.

Claims

1. A process for preparing polyurethane rigid foams from polyols and polyisocyanates as well as blowing agents and optionally foam auxiliary agents, characterised in that the polyurethane rigid foam is obtained by reacting

   A) a polyol component with on average at least 3 hydrogen atoms, containing

      1. 60 to 100 % of polyethers and/or polyesters with at least 2 hydroxyl groups and a molecular weight of 250 to 1,500, which have a surface tension of 6 to 14 mN/m with respect to i-pentane and/or n-pentane as blowing agent,

      2. i-pentane and/or n-pentane as blowing agent,

      3. water and

      4. optionally auxiliary agents and additives

   with

   B) a polyisocyanate with an NCO-content of 20 to 48 wt.% which has a surface tension of 4.0 to 8 mN/m with respect to i-pentane or n–pentane as blowing agent.

2. A process for preparing polyurethane rigid foams according to Claim 1, characterised in that a polyether with a molecular weight of 250 to 1,500,

obtainable by the polyaddition of 70 to 100 wt.% of ethylene oxide and 0 to 30 wt.% of propylene oxide to starter compounds, is used.

3. A process for preparing polyurethane rigid foams according to Claim 2, characterised in that a sorbitol started polyether with a molecular weight of 500 to 1,400 based on 70 to 100 wt.% of ethylene oxide and 0 to 30 wt.% of 1,2-propylene oxide is used.

4. A process for preparing polyurethane rigid foams according to Claim 2, characterised in that a sucrose started polyether with a molecular weight of 500 to 1,400 based on 70 to 100 wt.% of ethylene oxide and 0 to 30 wt.% of 1,2-propylene oxide is used.

5. A process for preparing polyurethane rigid foams according to Claim 2, characterised in that a trimethylolpropane started polyether with a molecular weight of 250 to 850 based on 70 to 100 wt.% of ethylene oxide and 0 to 30 wt.% of 1,2-propylene oxide is used.

6. A process for preparing polyurethane rigid foams according to Claim 2, characterised in that a glycerine started polyether with a molecular weight of 250 to 850 based on 70 to 100 wt.% of ethylene oxide and 0 to 30 wt.% of 1,2-propylene oxide is used.

7. A process for preparing polyurethane rigid foams according to Claim 2, characterised in that an o-toluylene diamine started polyether with a molecular weight of 250 to 850 based on 70 to 100 wt.% of ethylene oxide and 0 to 30 wt.% of 1,2-propylene oxide is used.

8. A process for preparing polyurethane rigid foams according to Claim 1, characterised in that a polyester with a molecular weight of 200 to 600,

formed from aromatic and aliphatic dicarboxylic acids and polyols with at least 2 hydroxyl groups, is used.

9. A process for preparing polyurethane rigid foams according to Claim 1, characterised in that a prepolymer with an NCO content of 20 to 33 wt.% and with terminal NCO groups, which has been obtained by reacting

1. 4,4'-diphenylmethane diisocyanate, optionally in a mixture with the 2,4 and 2,2-isomers and 0 to 30 wt.% of higher functional fractions, with

2. a polyether with a molecular weight of 60 to 1,400 obtained by the polyaddition of 70 to 100 wt.% of ethylene oxide and 0 to 30 wt.% of 1,2-propylene oxide,

is used as the polyisocyanate.

10. A process for preparing polyurethane rigid foams according to Claim 1, characterised in that a prepolymer with an NCO content of 20 to 33 wt.% and with terminal NCO groups, which has been obtained by reacting

1. 4,4'-diphenylmethane diisocyanate, optionally in a mixture with the 2,4 and 2,2-isomers and 0 to 30 wt.% of higher functional fractions, with

2. a polyester with a molecular weight of 200 to 600 based on aromatic and aliphatic dicarboxylic acids and polyols with at least 2 hydroxyl groups,

is used as the polyisocyanate.

11. A process for preparing polyurethane rigid foams according to Claim 1, characterised in that a prepolymer with an NCO content of 25 to 45 wt.% and with terminal NCO groups which has been obtained by reacting

1. toluylene diisocyanate, optionally a mixture of the 2,4 and 2,6-isomers and 0 to 30 wt.% of higher functional fractions, with

2. a polyether with a molecular weight of 60 to 1,400 obtained by the polyaddition of 70 to 100 wt.% of ethylene oxide and 0 to 30 wt.% of 1,2-propylene oxide to starter compounds,

was used as the polyisocyanate.

12. A process for preparing polyurethane rigid foams according to Claim 1, characterised in that a prepolymer with an NCO content of 25 to 45 wt.% and with terminal NCO groups, which has been obtained by reacting

1. toluylene diisocyanate, optionally a mixture of the 2,4 and 2,6-isomers and 0 to 30 wt.% of higher functional fractions, with

2. a polyester with a molecular weight of 200 to 600 based on aromatic and aliphatic dicarboxylic acids and polyols with at least 2 hydroxyl groups,

is used as the polyisocyanate.