

(12) PATENT
(19) AUSTRALIAN PATENT OFFICE

(11) Application No. AU 199730928 B2
(10) Patent No. 722500

(54) Title
Process for producing hard polyurethane foams with low heat conductivity

(51)⁶ International Patent Classification(s)
C08G 018/40 C08J 009/14

(21) Application No: 199730928 (22) Application Date: 1997.05.28

(87) WIPO No: WO97/47673

(30) Priority Data

(31) Number (32) Date (33) Country
19623065 1996.06.10 DE

(43) Publication Date : 1998.01.07
(43) Publication Journal Date : 1998.03.05
(44) Accepted Journal Date : 2000.08.03

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(56) Related Art
JP 04-351620
AU 21546/97

OPI. DATE 07/01/98 APPLN. ID 30928/97
AOJP DATE 05/03/98 PCT NUMBER PCT/EP97/02767



AU9730928

<p>(51) Internationale Patentklassifikation ⁶ : C08G 18/40, C08J 9/14</p>		<p>A1</p>	<p>(11) Internationale Veröffentlichungsnummer: WO 97/47673</p> <p>(43) Internationales Veröffentlichungsdatum: 18. Dezember 1997 (18.12.97)</p>
<p>(21) Internationales Aktenzeichen: PCT/EP97/02767</p> <p>(22) Internationales Anmeldedatum: 28. Mai 1997 (28.05.97)</p> <p>(30) Prioritätsdaten: 196 23 065.9 10. Juni 1996 (10.06.96) DE</p> <p>(71) Anmelder (<i>für alle Bestimmungsstaaten ausser US</i>): BAYER AKTIENGESELLSCHAFT [DE/DE]; D-51368 Leverkusen (DE).</p> <p>(72) Erfinder; und</p> <p>(75) Erfinder/Anmelder (<i>nur für US</i>): McCULLOUGH, Dennis [US/DE]; Im Oberdödelsfeld 39, D-51069 Köln (DE). HEINEMANN, Torsten [DE/DE]; Andreas-Gryphius-Strasse 7, D-51065 Köln (DE). EISEN, Norbert [DE/DE]; Gerolsteiner Strasse 44, D-50937 Köln (DE). KLÄN, Walter [DE/DE]; August-Kekulé-Strasse 12, D-51373 Leverkusen (DE).</p> <p>(74) Gemeinsamer Vertreter: BAYER AKTIENGESELLSCHAFT; D-51368 Leverkusen (DE).</p>		<p>(81) Bestimmungsstaaten: AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, HU, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, TJ, TM, TR, TT, UA, UG, US, UZ, VN, ARIPO Patent (GH, KE, LS, MW, SD, SZ, UG), eurasisches Patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), europäisches Patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI Patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).</p> <p>Veröffentlicht <i>Mit internationalem Recherchenbericht.</i></p>	
<p>(54) Titel: PROCESS FOR PRODUCING HARD POLYURETHANE FOAMS WITH LOW HEAT CONDUCTIVITY</p> <p>(54) Bezeichnung: VERFAHREN ZUR HERSTELLUNG VON POLYURETHAN-HARTSCHAUMSTOFFEN MIT GERINGER WÄRMELEITFÄHIGKEIT</p> <p>(57) Abstract</p> <p>The description relates to a process for producing hard polyurethane foams with low heat conductivity from polyols and polyisocyanates, foaming agents and possibly foaming auxiliaries, in which the hard polyurethane foam is obtained by reacting: A. a polyol component containing 1. at least one polyester polyol of a molecular weight of 100 to 30,000 g/mol with at least two hydrogen atoms reactive to isocyanates, 2. at least two hydrogen atoms reactive to isocyanates and compounds containing at least one tertiary nitrogen atom and with a molecular weight of 150 to 12,500 g/mol, 3. compounds containing at least two hydrogen atoms reactive to isocyanates with a molecular weight of 150 to 12,500 g/mol, 4. catalysts, 5. water, 6. foaming agents and 7. possibly auxiliaries and/or additives; with: B. an organic and/or modified organic polyisocyanate with an NCO content of 20 to 48 % wt. In addition, cyclopentane-blown hard foams with low heat conductivity and their use as intermediate layers for composite components and for foam-filling hollow spaces are described.</p> <p>(57) Zusammenfassung</p> <p>Beschrieben wird ein Verfahren zur Herstellung von Polyurethan-Hartschaumstoffen mit geringer Wärmeleitfähigkeit aus Polyolen und Polyisocyanaten sowie Treibmitteln und gegebenenfalls Schaumhilfsmitteln, dadurch gekennzeichnet, dass der Polyurethan-Hartschaumstoff erhalten wird durch Umsetzung von (A) einer Polyolkomponente, enthaltend: 1) mindestens ein Polyesterpolyol vom Molekulargewicht 100 bis 30000 g/mol mit mindestens zwei gegenüber Isocyanaten reaktiven Wasserstoffatomen, 2) mindestens zwei gegenüber Isocyanaten reaktive Wasserstoffatome sowie mindestens ein tertiäres Stickstoffatom aufweisende Verbindungen vom Molekulargewicht 150 bis 12500 g/mol, 3) mindestens zwei gegenüber Isocyanaten reaktive Wasserstoffatome aufweisende Verbindungen vom Molekulargewicht 150 bis 12500 g/mol, 4) Katalysatoren, 5) Wasser, 6) Treibmittel und 7) gegebenenfalls Hilfs- und/oder Zusatzstoffe mit (B) einem organischen und/oder modifizierten organischen Polyisocyanat mit einem NCO-Gehalt von 20 bis 48 Gew.-%. Weiterhin werden mit Cyclopentan getriebene Hartschaumstoffe mit geringer Wärmeleitfähigkeit sowie deren Verwendung als Zwischenschicht für Verbundelemente sowie zum Ausschäumen von Hohlräumen beschrieben.</p>			

Process for the production of rigid polyurethane foams having low thermal conductivity

This invention relates to a novel process for the production of substantially 5 closed-cell rigid polyurethane foams.

Due to their low thermal conductivity, rigid polyurethane foams are used for 10 insulation applications in refrigeration and freezing appliances, in industrial equipment, tank farms, pipelines, shipbuilding and in the construction industry. A summary review of the production of rigid polyurethane foams and the use thereof is given in *Kunststoff-Handbuch*, volume 7 (*Polyurethane*), 2nd edition 1983, edited by Dr. Günter Oertel (Carl Hanser Verlag, Munich).

The thermal conductivity of a largely closed-cell rigid polyurethane foam is largely 15 dependent upon the nature of the blowing agent or cell gas used. Completely halogenated chlorofluorocarbons (CFCs), in particular trichlorofluoromethane (R11), which has particularly low thermal conductivity, had proved particularly suitable for this purpose. These substances are chemically inert and non-toxic. However, due to their elevated stability, completely halogenated chlorofluorocarbons reach the 20 stratosphere, where, due to their chlorine content, they play a part in breaking down the ozone present there (for example Molina, Rowland, *Nature* 249 (1974) 810; first interim report of the German Parliament's commission of enquiry, *Vorsorge zum Schutz der Erdatmosphäre* [precautions for the protection of the earth's atmosphere] of 02.11.1988, German Parliament, public relations department, Bonn).

25 Formulations containing a lower R11 concentration have been proposed in order to reduce the R11 content in rigid polyurethane foams.

It has also been proposed (for example EP 344 537, US patent 4 931 482) to use 30 partially fluorinated hydrocarbons (hydrofluoroalkanes) which still contain at least one carbon-hydrogen bond as a blowing agent. Substances from this class of compounds contain no chlorine atoms and thus have a ODP value (ozone depletion potential) of zero (by way of comparison: R11: ODP = 1). Typical representatives



of this class of substances are, for example: 1,1,1,4,4-hexafluorobutane (R356) or 1,1,1,3,3-pentafluoropropane (245fa).

It is furthermore known to use hydrocarbons, either pure or as a mixture (US 5 391 317), such as n- or i-pentane, 2,2-dimethylbutane, cyclopentane or cyclohexane as blowing agents. It is also known to use hydrocarbons in conjunction with water as blowing agents (EP 0 421 269).

It is moreover known that, by virtue of their chemical structure, unsubstituted 10 hydrocarbons are highly non-polar and thus mix very poorly with the polyols conventionally used in rigid foam production. Complete miscibility is, however, an important prerequisite for the conventional production technique in which the polyol and isocyanate components are mechanically foamed. In addition to the reactive 15 polyether- or polyesterpolyols, the polyol component also contains blowing agents and auxiliaries such as activators, emulsifiers and stabilisers in dissolved form. It is known that polyol formulations containing aminopolyethers exhibit particularly high alkane solubility (WO 94/03515).

It is also known that hydrocarbon-blown rigid foams have poorer thermal 20 conductivities than rigid foams blown with R11 or with reduced quantities of R11, which is due to the higher thermal conductivities of hydrocarbon gases. (Thermal conductivities of the gases at 20°C: R11: 8 mW/mK; cyclopentane: 10 mW/mK; n-pentane, 13 mW/mK; i-pentane, 13 mW/mK).

25 The object of the present invention was to provide hydrocarbon-blown rigid polyurethane foams which have thermal conductivities of the same low level as foams blown with reduced quantities of R11.

It has surprisingly been found that polyol formulations based on a certain polyol 30 mixture yield foams having thermal conductivities which are at the same, low level as foams blown with reduced quantities of R11, in particular if cyclopentane is used as the blowing agent.



The present invention accordingly provides a process for the production of rigid polyurethane foams having low thermal conductivity from polyols and polyisocyanates together with blowing agents and optionally foam auxiliaries, characterised in that the rigid polyurethane foam is obtained by reacting

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A. a polyol component containing

1. at least one polyesterpolyol of a molecular weight of 100 to 30000 g/mol having at least two isocyanate-reactive hydrogen atoms,

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2. polyols of a molecular weight from 150 to 12500 g/mol containing at least two isocyanate-reactive hydrogen atoms together with at least one tertiary nitrogen atom,

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3. polyols of a molecular weight from 150 to 12500 g/mol containing at least two isocyanate-reactive hydrogen atoms,

4. catalysts,

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5. 0.5-7% water related to the mass of component A,

6. alkanes and mixtures of alkanes as blowing agents and

25

7. optionally auxiliary substances and additives

with

- B. an organic and/or modified organic polyisocyanate having an NCO content of 20 to 48 wt. %

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It is surprising that the combination according to the invention of a polyesterpolyol with the stated aminopolyethers and a further polyol in the polyol component should result in hydrocarbon-blown foams with such a low thermal conductivity.



Polyol formulations according to the invention contain at least one polyesterpolyol of the molecular weight from 100 to 30000 g/mol, preferably of 150 to 10000 g/mol, particularly preferably of 200 to 600 g/mol, prepared from aromatic and/or aliphatic mono-, di- or tricarboxylic acids and polyols containing at least two 5 hydroxyl groups. Examples of dicarboxylic acids are phthalic acid, fumaric acid, maleic acid, azelaic acid, glutaric acid, adipic acid, suberic acid, terephthalic acid, isophthalic acid, decanedicarboxylic acid, malonic acid, glutaric acid, succinic acid and fatty acids such as stearic acid, oleic acid, ricinoleic acid. Both the pure mono-, di- or tricarboxylic acids and any desired mixtures thereof may be used. Instead of 10 the free mono-, di- and tricarboxylic acids, it is also possible to use the corresponding mono-, di- and tricarboxylic acid derivatives, such as for example mono-, di- and tricarboxylic acid esters of alcohols having 1 to 4 carbon atoms or mono-, di- and tricarboxylic anhydrides or triglycerides. The following are preferably used as 15 the alcohol component for esterification: ethylene glycol, diethylene glycol, triethylene glycol, tetraethylene glycol, 1,2- or 1,3-propanediol, 1,4-butanediol, 1,5-pentanediol, 1,6-hexanediol, 1,10-decanediol, glycerol, trimethylolpropane or mixtures thereof.

According to the invention, polyol formulations may also contain polyether esters, 20 as may, for example, be obtained by reacting phthalic anhydride with diethylene glycol and subsequently with ethylene oxide (EP-A 0 250 967).

Polyol formulations according to the invention contain at least one compound of the molecular weight from 150 to 12500 g/mol, preferably of 200 to 1500 g/mol, 25 containing at least two isocyanate-reactive hydrogen atoms, the molecules of which compound contain at least one tertiary nitrogen atom. These compounds are obtained by polyaddition of alkylene oxides, such as for example ethylene oxide, propylene oxide, butylene oxide, dodecyl oxide or styrene oxide, preferably propylene oxide or ethylene oxide, onto starter compounds. The starter compounds used are 30 ammonia or compounds containing at least one primary or secondary or tertiary amino group, such as for example aliphatic amines such as ethylenediamine, ethylenediamine oligomers (for example diethylenetriamine, triethylenetetramine or pentaethylenehexamine), ethanolamine, diethanolamine, triethanolamine, N-methyl-



or N-ethyl diethanolamine, 1,3-propylenediamine, 1,3- or 1,4-butylenediamine, 1,2-, 1,3-, 1,4-, 1,5-, 1,6-hexamethylenediamine, aromatic amines such as phenylene-diamines, tolylenediamines (2,3-tolylenediamine, 3,4-tolylenediamine, 2,4-tolylenediamine, 2,5-tolylenediamine, 2,6-tolylenediamine or mixtures of the stated isomers), 2,2'-diaminodiphenylmethane, 2,4'-diaminodiphenylmethane, 4,4'-diaminodiphenylmethane or mixtures of these isomers.

Polyol formulations according to the invention moreover contain at least one compound of the molecular weight from 150 to 12500 g/mol, preferably of 200 to 10 1500 g/mol, containing at least two isocyanate-reactive hydrogen atoms. These compounds are obtained by polyaddition of alkylene oxides, such as for example ethylene oxide, propylene oxide, butylene oxide, dodecyl oxide or styrene oxide, preferably propylene oxide or ethylene oxide, onto starter compounds. The starter compounds used are preferably water and polyhydric alcohols such as sucrose, 15 sorbitol, pentaerythritol, trimethylolpropane, glycerol, propylene glycol, ethylene glycol, diethylene glycol together with mixtures of the stated starter compounds. These polyols which are also to be used according to the invention advantageously allow the rigid polyurethane foams to achieve the mechanical properties which are conventionally required in practice.

20 Polyol formulations according to the invention contain an activator or an activator mixture, which results in a setting time of 20 to 50 s, preferably 25 to 45 s, particularly preferably of 27 to 40 s if foaming is performed at 20°C using a Hennecke HK 270 high pressure machine. The setting time extends from the time of mixing to 25 the moment from which a rod introduced into the foam draws fibres when withdrawn.

30 According to the invention, the catalysts conventional in polyurethane chemistry may be used. Examples of such catalysts are: triethylenediamine, N,N-dimethyl-cyclohexylamine, tetramethylenediamine, 1-methyl-4-dimethylaminoethylpiperazine, triethylamine, tributylamine, dimethylbenzylamine, N,N',N"-tris-(dimethylamino-propyl)hexahydrotriazine, dimethylaminopropylformamide, N,N,N',N"-tetramethyl-ethylenediamine, N,N,N',N"-tetramethylbutanediamine, tetramethylhexanediamine,



pentamethyldiethylenetriamine, tetramethyldiaminoethyl ether, dimethylpiperazine, 1,2-dimethylimidazole, 1-azabicyclo(3.3.0)octane, bis-(dimethylaminopropyl)urea, bis-(dimethylaminopropyl) ether, N-methylmorpholine, N-ethylmorpholine, N-cyclohexylmorpholine, 2,3-dimethyl-3,4,5,6-tetrahydropyrimidine, triethanolamine, diethanolamine, triisopropanolamine, N-methyldiethanolamine, N-ethyl-diethanolamine, dimethylethanolamine, tin(II) acetate, tin(II) octoate, tin(II) ethylhexoate, tin(II) laurate, dibutyltin diacetate, dibutyltin dilaurate, dibutyltin maleate, dioctyltin diacetate, tris-(N,N-dimethylaminopropyl)-s-hexahydrotriazine, tetramethylammonium hydroxide, sodium acetate, potassium acetate, sodium hydroxide or mixtures of these or similar catalysts.

Polyol formulations according to the invention contain 0.5 to 7.0 parts by weight, preferably 1.0 to 3.0 parts by weight of water per 100 parts by weight of polyol component A.

15 Alkanes such as cyclohexane, cyclopentane, i-pentane, n-pentane, n-butane, isobutane, 2,2-dimethylbutane and mixtures of the stated blowing agents are used according to the invention.

20 Aromatic polyisocyanates, as are for example described by W. Siefken in *Justus Liebigs Annalen der Chemie*, 562, pages 75 to 136, [are used], for example, as the isocyanate component, for example those of the formula



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in which

n means 2 to 4, preferably 2, and

30 Q means an aliphatic hydrocarbon residue having 2 to 18, preferably 6 to 10, C atoms, a cycloaliphatic hydrocarbon residue having 4 to 15, preferably 5 to 10, C atoms, an aromatic hydrocarbon residue having 8 to 15, preferably



8 to 13, C atoms, for example such polyisocyanates as are described in DE-OS 28 32 253, pages 10 to 11.

The industrially readily available polyisocyanates are generally particularly 5 preferred, for example 2,4- and 2,6-tolylene diisocyanate and any desired mixtures of these isomers ("TDI"), polyphenylpolymethylene polyisocyanates, as are produced by aniline/formaldehyde condensation and subsequent phosgenation ("crude MDI") and polyisocyanates containing carbodiimide groups, urethane groups, allophanate groups, isocyanurate groups, urea groups or biuret groups 10 ("modified polyisocyanates"), in particular modified polyisocyanate derived from 2,4- and 2,6-tolylene diisocyanate or from 4,4'- and/or 2,4'-diphenylmethane diisocyanate.

It is also possible to use prepolymers prepared from the stated isocyanates and 15 organic compounds having at least one hydroxyl group, such as for example polyol or polyester components containing 1 to 4 hydroxyl groups and of a molecular weight of 60 to 1400 g/mol.

Paraffins or fatty alcohols or dimethylpolysiloxanes together with pigments or dyes, 20 as well as stabilisers against ageing and weathering, plasticisers and substances having a fungistatic and bacteriostatic action, together with fillers such as barium sulphate, diatomaceous earth, carbon black or prepared chalk may also be used.

Further examples of substances optionally also used according to the invention such 25 as surface-active additives and foam stabilisers, together with cell regulators, reaction inhibitors, stabilisers, flame retardant substances, dyes and fillers, together with fungistatically and bacteriostatically active substances, together with details relating to the manner of use and mode of action of these additives are described in *Kunststoff-Handbuch*, volume VII, edited by Vieweg and Höchtl, Carl Hanser Verlag, Munich 1966, for example on pages 121 to 205, and 2nd edition 1983, 30 edited by G. Oertel (Carl Hanser Verlag, Munich).



According to the invention, foaming during foam production may also be performed in closed moulds. In this case, the reaction mixture is introduced into a mould. Mould materials which may be considered are metal, for example aluminium, or plastic, for example epoxy resin. The foamable reaction mixture foams in the mould and forms the moulding. Mould foaming may be performed in such a manner that the moulding has a cellular structure on its surface. It may, however, also be performed in such a manner that the moulding has a compact skin and a cellular core. According to the invention, the method used in the first case is to introduce a quantity of reaction mixture into the mould such that the resultant foam exactly fills the mould. The method used in the latter case involves introducing more foamable reaction mixture into the mould than is necessary to fill the mould cavity with foam. In the latter case, "overcharging" is thus used, such a process being known, for example, from US patents 3 178 490 and 3 182 104.

15 The present invention also provides the use of the rigid foams produced according to the invention as an interlayer for composite components and for filling cavities, especially in the production of refrigeration equipment.

20 The process according to the invention is preferably used for filling cavities in refrigeration and freezing appliances with foam. The foams may of course also be produced by slab foaming or using the *per se* known twin conveyor belt process.

25 The rigid foams obtainable according to the invention are used, for example, in the construction sector, and for insulating district heating pipes and transport containers.

30 The following examples are intended to illustrate the invention, but without restricting the scope thereof.

In all the Examples, the rigid polyurethane foams were produced at 20°C in a Hennecke HK 270 high pressure machine.



The setting times stated in the individual examples were determined in the following manner; the setting time extends from the time of mixing to the moment from which a rod introduced into the foam draws fibres when withdrawn.

5 Polyol A: Polypropylene oxide polyether of molecular weight 600 based on sucrose/glycerol

10 Polyol B: Polypropylene oxide polyether of molecular weight 1000 based on propylene glycol

15 Polyol C: Polypropylene oxide polyether of molecular weight 630 based on sucrose/propylene glycol

20 Polyol D: Polypropylene oxide polyether of molecular weight 370 based on glycerol

25 Polyol E: Polypropylene oxide polyether of molecular weight 345 based on ethylenediamine

30 Polyol F: Polypropylene oxide polyether of molecular weight 440 based on trimethylolpropane

35 Polyol G: Polyether ester of molecular weight 375 based on phthalic anhydride, diethylene glycol and ethylene oxide

40 Polyol H: Polypropylene oxide polyether of molecular weight 1120 based on triethanolamine

45 Polyol I: Polypropylene oxide polyether of molecular weight 560 based on o-tolylenediamine

50 Polyol K: Polypropylene oxide polyether of molecular weight 275 based on ethylenediamine



Example 1 (not according to the invention)

Formulation for rigid polyurethane foam

5 Component A

80 parts by weight of polyol A

20 parts by weight of polyol B

3.5 parts by weight of water

10 2.0 parts by weight of silicone stabiliser

3.5 parts by weight of activator mixture consisting of activator Desmopanid PV
(Bayer AG), activator Desmopanid 726b (Bayer AG) and
potassium acetate (25%) in diethylene glycol

15 100 parts by weight of component A are mixed at 20°C with 17 parts by weight of
CFC R11 and 145 parts by weight of crude MDI (Desmodur 44V20, Bayer AG) and
compacted to 32 kg/m³ in a closed mould.

Example 2 (not according to the invention)

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Formulation for rigid polyurethane foam

Component A

25 55 parts by weight of polyol C

25 parts by weight of polyol D

20 parts by weight of polyol E

2.0 parts by weight of water

2.0 parts by weight of silicone stabiliser

30 2.0 parts by weight of activator mixture consisting of activator Desmopanid PV
(Bayer AG) and activator Desmopanid 726b (Bayer AG)



100 parts by weight of component A are mixed at 20°C with 12 parts by weight of cyclopentane (Erdölchemie) and 151 parts by weight of crude MDI (Desmodur 44V20, Bayer AG) and compacted to 38 kg/m³ in a closed mould.

5 Example 3 (not according to the invention)

Formulation for rigid polyurethane foam

Component A

10 50 parts by weight of polyol A
40 parts by weight of polyol F
10 parts by weight of polyol G
2.0 parts by weight of water

15 2.0 parts by weight of silicone stabiliser
2.5 parts by weight of activator mixture consisting of activator Desmopan PV
(Bayer AG) and activator Desmopan 726b (Bayer AG)

100 parts by weight of component A are mixed at 20°C with 13 parts by weight of cyclopentane (Erdölchemie) and 148 parts by weight of crude MDI (Desmodur 44V20, Bayer AG) and compacted to 38 kg/m³ in a closed mould.

Example 4 (not according to the invention)

25 Formulation for rigid polyurethane foam

Component A

30 50 parts by weight of polyol C
 25 parts by weight of polyol E
 25 parts by weight of polyol H
 2.2 parts by weight of water
 2.0 parts by weight of silicone stabiliser



1.5 parts by weight of activator mixture consisting of activator Desmopan PV
(Bayer AG) and activator Desmopan 726b (Bayer AG)

100 parts by weight of component A are mixed at 20°C with 11 parts by weight of
5 i,n-pentane (8:3) and 142 parts by weight of crude MDI (Desmodur 44V20, Bayer
AG) and compacted to 36 kg/m³ in a closed mould.

Example 5 (not according to the invention)

10 Formulation for rigid polyurethane foam

Component A

15 55 parts by weight of polyol C
20 parts by weight of polyol D
25 parts by weight of polyesterpolyol Stepanol® 2352 (Stepan)
2.1 parts by weight of water
2.0 parts by weight of silicone stabiliser
1.5 parts by weight of activator mixture consisting of activator Desmopan PV
20 (Bayer AG) and activator Desmopan 726b (Bayer AG)

25 100 parts by weight of component A are mixed with 12 parts by weight of

cyclopentane (Erdölchemie). The mixture (component A + cyclopentane) becomes
turbid and separates immediately.

Example 6 (not according to the invention)

30 Formulation for rigid polyurethane foam

Component A

35 55 parts by weight of polyol C
20 parts by weight of polyol D



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25 parts by weight of polyesterpolyol Stepanpol® 2352 (Stepan)
2.3 parts by weight of water
2.0 parts by weight of silicone stabiliser
1.5 parts by weight of activator mixture consisting of activator Desmora

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pid PV (Bayer AG) and activator Desmora

pid 726b (Bayer AG)

100 parts by weight of component A are mixed with 11 parts by weight of i,n-pentane

(3:8). The mixture (component A + i,n-pentane) becomes turbid and separates

immediately.

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Example 7 (according to the invention)

Formulation for rigid polyurethane foam

15 Component A

40 parts by weight of polyol C
20 parts by weight of polyol I
15 parts by weight of polyol K
25 parts by weight of polyesterpolyol Stepanpol® 2352 (Stepan)
2.4 parts by weight of water
2.0 parts by weight of silicone stabiliser
1.4 parts by weight of activator Desmora

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pid PV (Bayer AG)

0.4 parts by weight of activator N,N',N"-tris-(dimethylaminopropyl)hexahydro-
25 triazine

100 parts by weight of component A are mixed at 20°C with 15 parts by weight of
cyclopentane (Erdölchemie) and 161 parts by weight of crude MDI (Desmodur
44V20, Bayer AG) and compacted to 34 kg/m³ in a closed mould.

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Example 8 (according to the invention)

Formulation for rigid polyurethane foam



Component A

20 parts by weight of polyol C
40 parts by weight of polyol I
5 15 parts by weight of polyol K
25 parts by weight of polyesterpolyol Stepanpol® 2352 (Stepan)
2.4 parts by weight of water
2.0 parts by weight of silicone stabiliser
1.4 parts by weight of activator Desmopan PV (Bayer AG)
10 0.4 parts by weight of activator N,N',N"-tris-(dimethylaminopropyl)hexahydro-
triazine

100 parts by weight of component A are mixed at 20°C with 15 parts by weight of cyclopentane (Erdölchemie) and 157 parts by weight of crude MDI (Desmodur 44V20, Bayer AG) and compacted to 34 kg/m³ in a closed mould.

Example 9 (according to the invention)

Formulation for rigid polyurethane foam

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Component A

10 parts by weight of polyol C
50 parts by weight of polyol I
25 15 parts by weight of polyol K
25 parts by weight of polyesterpolyol Stepanpol® 2352 (Stepan)
2.4 parts by weight of water
2.0 parts by weight of silicone stabiliser
0.5 parts by weight of activator Desmopan PV (Bayer AG)
30 0.5 parts by weight of activator dimethylaminopropylformamide
0.4 parts by weight of activator N,N',N"-tris-(dimethylaminopropyl)hexahydro-
triazine



100 parts by weight of component A are mixed at 20°C with 17 parts by weight of cyclopentane (Erdölchemie) and 170 parts by weight of MDI prepolymer (E577, Bayer AG) and compacted to 36 kg/m³ in a closed mould.

5 Example 10 (according to the invention)

Formulation for rigid polyurethane foam

Component A

10 40 parts by weight of polyol C
10 parts by weight of polyol G
50 parts by weight of polyol I
2.5 parts by weight of water
15 2.0 parts by weight of silicone stabiliser
0.5 parts by weight of activator Desmopan PV (Bayer AG)
1.6 parts by weight of activator Desmopan 726b (Bayer AG)

20 100 parts by weight of component A are mixed at 20°C with 13 parts by weight of cyclopentane (Erdölchemie) and 135 parts by weight of crude MDI (Desmodur 44V20, Bayer AG) and compacted to 35 kg/m³ in a closed mould.

Example 11 (according to the invention)

25 Formulation for rigid polyurethane foam

Component A

30 20 parts by weight of polyol C
45 parts by weight of polyol I
15 parts by weight of polyol K
20 parts by weight of polyesterpolyol Stepanpol® 2352 (Stepan)
2.4 parts by weight of water



2.0 parts by weight of silicone stabiliser

1.2 parts by weight of activator Desmopan PV (Bayer AG)

0.4 parts by weight of activator N,N',N"-tris-(dimethylaminopropyl)hexahydro-triazine

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100 parts by weight of component A are mixed at 20°C with 13 parts by weight of i,n-pentane (3:8) and 151 parts by weight of MDI prepolymer (Desmodur 44V20, Bayer AG) and compacted to 35 kg/m³ in a closed mould.

10 The test values shown in the Table were obtained from the foam slabs produced in Examples 1 to 11.

Example	Phase stability of component A containing blowing agent	Setting time of foam (s)	Thermal conductivity (mW/mK) to DIN 52616, 24°C
1	clear, stable mixture	50	19.6
2	clear, stable mixture	50	21.5
3	clear, stable mixture	29	21.6
4	clear, stable mixture	50	23.7
5	turbid, separated mixture	--	--
6	turbid, separated mixture	--	--
7	clear, stable mixture	25	19.9
8	clear, stable mixture	25	19.7
9	clear, stable mixture	31	19.9
10	clear, stable mixture	27	19.9
11	clear, stable mixture	28	22.0

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Example 1 shows a typical result for an R11-reduced system.



Examples 2 and 3 are prior art cyclopentane-blown systems having standard thermal conductivities.

5 Although Example 3 contains a polyesterpolyether and an activator mixture according to the invention, which results in a setting time of 29 s, a standard thermal conductivity is found.

Example 4 is a prior art i,n-pentane-blown system.

10 Examples 5 and 6 contains no amine-started polyols; the polyol formulation is thus not phase-stable with regard to cyclopentane and cannot be foamed using conventional techniques.

15 Examples 7 to 10 show that, using the process according to the invention with cyclopentane as the blowing agent, foams are obtained having the same low thermal conductivity as foams blown with reduced quantities of R11.

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Example 11 shows that foams having low thermal conductivities are also obtained using the process according to the invention with i,n-pentane as the blowing agent.

Throughout this specification and the claims which follow, unless the context requires otherwise, the word "contain", or variations such as "contains" or "containing", will be understood to imply the inclusion of a stated integer or group of integers or steps but not the exclusion of any other integer or group of integers or steps.



The claims defining the invention are as follows:

1. Process for the production of rigid polyurethane foams having low thermal conductivity from polyols and polyisocyanates together with blowing agents and optionally foam auxiliaries, characterised in that the rigid polyurethane foam is obtained by reacting

A. a polyol component containing

10 1. at least one polyesterpolyol of a molecular weight of 100 to 30000 g/mol having at least two isocyanate-reactive hydrogen atoms,

15 2. polyols of a molecular weight from 150 to 12500 g/mol containing at least two isocyanate-reactive hydrogen atoms together with at least one tertiary nitrogen atom,

20 3. polyols of a molecular weight from 150 to 12500 g/mol containing at least two isocyanate-reactive hydrogen atoms,

25 4. catalysts,

5. 0.5-7% water related to the mass of component A,

6. alkanes and mixtures of alkanes as blowing agents and

7. optionally auxiliary substances and additives

with

30 B. an organic and/or modified organic polyisocyanate having an NCO content of 20 to 48 wt. %.



2. Process for the production of rigid polyurethane foams according to claim 1, characterised in that the polyesterpolyol (1) used is a polyester of a molecular weight of 100 to 30000 g/mol prepared from aromatic and/or aliphatic mono-, di- and tricarboxylic acids and polyols containing at least two hydroxyl groups.

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3. Process for the production of rigid polyurethanes foams according to claim 1 or 2, characterised in that the component (2) used is an o-tolylenediamine-started polyether based on 70 to 100 wt. % of 1,2-propylene oxide and 0 to 30 wt. % of ethylene oxide.

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4. Process for the production of rigid polyurethane foams according to claim 1, characterised in that the component (2) used is an ethylenediamine-started polyether based on 50 to 100 wt. % of 1,2-propylene oxide and 0 to 50 wt. % of ethylene oxide.

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5. Process for the production of rigid polyurethane foams according to claim 1, characterised in that the component (2) used is a triethanolamine-started polyether based on 50 to 100 wt. % of 1,2-propylene oxide and 0 to 50 wt. % of ethylene oxide.

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6. Process for the production of rigid polyurethane foams according to claim 1, characterised in that component (3) contains a sucrose-started polyether based on 70 to 100 wt. % of 1,2-propylene oxide and 0 to 30 wt. % of ethylene oxide.

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7. Process for the production of rigid polyurethane foams according to claim 1, characterised in that component (3) contains a sorbitol-started polyether based on 70 to 100 wt. % of 1,2-propylene oxide and 0 to 30 wt. % of ethylene oxide.

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8. Process for the production of rigid polyurethane foams according to claim 1, characterised in that component (3) contains a trimethylolpropane-started



polyether based on 70 to 100 wt. % of 1,2-propylene oxide and 0 to 30 wt. % of ethylene oxide.

9. Process for the production of rigid polyurethane foams according to claim 5, characterised in that component (3) contains a glycerol-started polyether based on 70 to 100 wt. % of 1,2-propylene oxide and 0 to 30 wt. % of ethylene oxide.

10. Process for the production of rigid polyurethane foams according to claim 10, characterised in that the blowing agent (6) used is cyclopentane or n- and/or i-pentane.

11. Process for the production of rigid polyurethane foams according to claim 15, characterised in that the blowing agent (6) used contains mixtures of c-pentane and/or n-butane and/or isobutane and/or 2,2-dimethylbutane.

12. Process for the production of rigid polyurethane foams according to claim 20, characterised in that the blowing agent (6) used contains mixtures of n- and/or i-pentane and/or cyclopentane and/or cyclohexane.

13. Use of the rigid polyurethane foams obtained according to anyone of claims 1 to 12 as an interlayer for composite components or for filling cavities with foams.



14. Processes for the production of rigid polyurethane foams or uses of the rigid polyurethane foams produced thereby, substantially as hereinbefore described with reference to the Examples.

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15. Rigid polyurethane foams produced by the process according to anyone of claims 1-13.

DATED this 26th day of May, 2000

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