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(54) Title: POLYISOCYANURATE RESIN FOAM HAVING HIGH COMPRESSIVE STRENGTH, LOW THERMAL CONDUCTIVITY, AND HIGH SURFACE QUALITY

(54) Bezeichnung: POLYISOCYANURATHARTSCHAUMSTOFF MIT HOHER DRUCKFESTIGKEIT, GERINGER WÄRMELEITFÄHIGKEIT UND HOHER OBERFLÄCHENGÜTE

(57) Abstract: The present invention relates to a process for producing polyisocyanurate resin foams, in which method: (a) aromatic polyisocyanate, (b) compounds reactive to isocyanate groups, containing at least one polyetherol (b1) and/or polyesterol (b2), wherein the number average content of hydrogen atoms of the components (b1) and (b2) that are reactive with isocyanate is at least 1.7, (c) catalyst, (d) blowing agent, (e) flame retardant, (f) optionally auxiliary agents and additives and (g) optionally compounds which have aliphatic, hydrophobic groups and are not covered by the definition of the compounds (a) to (f) are mixed to form a reaction mixture and are allowed to cure to form polyisocyanurate resin foam, wherein blowing agent (d) contains at least one aliphatic, halogenated hydrocarbon compound (d1), made up of 2 to 5 carbon atoms, at least one hydrogen atom and at least one fluorine and/or chlorine atom, and the compound (d1) contains at least one carbon-carbon double bond, and contains a hydrocarbon compound having 4 to 8 carbon atoms (d2), and the molar proportion of halogenated hydrocarbon compound (d1) is between 20 and 60 mol.% and the molar proportion of hydrocarbon compound (d2) is between 40 and 80 mol.%, in each case based on the total content of the blowing agent (d1) and (d2), and the components (b) to (f) can contain compounds having aliphatic, hydrophobic groups and the content of aliphatic, hydrophobic groups is at most 4.0 wt.%, based on the total weight of components (b) to (g), and the mixing to form a reaction mixture takes place with an isocyanate index of at least 240. The present invention further relates to a polyisocyanurate resin foam which can be obtained in accordance with a method according to the invention.

(57) Zusammenfassung: Die vorliegende Erfindung betrifft ein Verfahren zur Herstellung von Polyisocyanurathartschaumstoffen, bei dem man (a) aromatisches Polyisocyanat, (b) gegenüber Isocyanatgruppen reaktive Verbindungen, enthaltend mindestens ein Polyetherol (b1) und/oder Polyesterol (b2), wobei der zahlenmittlere Gehalt an mit Isocyanat reaktiven Wasserstoffatomen der Komponente (b1) und (b2) mindestens 1,7 beträgt, (c) Katalysator, (d) Treibmittel, (e) Flammschutzmittel (f) gegebenenfalls Hilfs- und Zusatzstoffe und (g) gegebenenfalls Verbindungen mit aliphatischen, hydrophoben Gruppen, die nicht unter die Definition der Verbindungen (a) bis (f) fallen, zu einer Reaktionsmischung vermischt und zum Polyisocyanurathartschaumstoff aushärten lässt, wobei Treibmittel (d) mindestens eine aliphatische, halogenierte Kohlenwasserstoffverbindung (d1), aufgebaut aus 2 bis 5 Kohlenstoffatomen, mindestens einem Wasserstoffatom und mindestens einem Fluor und/oder Chloratom und die Verbindung (d1) mindestens eine Kohlenstoff-Kohlenstoff-Doppelbindung enthält, und eine Kohlenwasserstoffverbindung mit 4 bis 8 Kohlenstoffatomen (d2) enthält und der molare Anteil von halogenierter Kohlenwasserstoffverbindung (d1) zwischen 20 und 60 mol% und der molare Anteil von Kohlenwasserstoffverbindung (d2) zwischen 40 und 80 mol-%, jeweils bezogen auf den Gesamtgehalt der Treibmittel (d1) und (d2), beträgt, und die Komponenten (b) bis (f) Verbindungen mit aliphatischen, hydrophoben Gruppen enthalten können und der Gehalt an aliphatischen, hydrophoben Gruppen, bezogen auf das Gesamtgewicht der Komponenten (b) bis (g), maximal 4,0 Gew.-% beträgt und die Vermischung zur Reaktionsmischung bei einem Isocyanatindex von mindestens 240 erfolgt. Weiter betrifft die vorliegende Erfindung einen Polyisocyanurathartschaumstoff, erhältlich nach einem erfindungsgemäßen Verfahren.

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[Fortsetzung auf der nächsten Seite]

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— *mit internationalem Recherchenbericht (Artikel 21 Absatz 3)*

POLYISOCYANURATE RESIN FOAM HAVING HIGH COMPRESSIVE STRENGTH, LOW THERMAL CONDUCTIVITY, AND HIGH SURFACE QUALITY

The present invention relates to a process for producing polyisocyanurate foams, wherein (a) aromatic polyisocyanate, (b) isocyanate-reactive compounds comprising at least one polyetherol (b1) and/or polyesterol (b2), wherein the number-average content of isocyanate-reactive hydrogen atoms of components (b1) and (b2) is at least 1.7, (c) catalyst, (d) blowing agents, (e) flame retardants, (f) optionally auxiliary and additive substances and (g) optionally compounds having aliphatic hydrophobic groups and not falling under the definition of compounds (a) to (f) are mixed to afford a reaction mixture and allowed to cure to afford a rigid polyisocyanurate foam, wherein blowing agent (d) comprises at least one aliphatic halogenated hydrocarbon compound (d1) composed of 2 to 5 carbon atoms, at least one hydrogen atom and at least one fluorine and/or chlorine atom and compound (d1) comprises at least one carbon-carbon double bond and a hydrocarbon compound having 4 to 8 carbon atoms (d2) and the molar proportion of halogenated hydrocarbon compound (d1) is between 20 and 60 mol% and the molar proportion of hydrocarbon compound (d2) is between 40 and 80 mol%, in each case based on the total content of the blowing agents (d1) and (d2), and components (b) to (f) may comprise compounds having aliphatic hydrophobic groups and the content of aliphatic hydrophobic groups, based on the total weight of components (b) to (g), is not more than 4.0% by weight and the mixing to afford the reaction mixture is carried out at an isocyanate index of at least 240. The present invention further relates to a rigid polyisocyanurate foam obtainable by a process according to the invention.

Rigid polyurethane foams or rigid polyisocyanurate foams are often used as insulation material for thermal insulation. The foams are especially employed in composite elements having at least one outer layer. The production of composite elements from in particular metallic outer layers and a core of isocyanate-based foams, typically polyurethane (PUR) or polyisocyanurate (PIR) foams, often referred to as sandwich elements, on continuously operating double belt lines is currently practiced on a large scale. In addition to sandwich elements for refrigerated warehouse insulation, elements for forming façades of a very wide variety of buildings or as roof elements are becoming ever more important.

Essential requirements of polyurethane or polyisocyanurate foams are a low thermal conductivity, good mechanical properties and good flame retardancy. The thermal insulation properties of closed cell rigid foams depend on numerous factors, in particular on the average cell size and the thermal conductivity of the cell gases. In the production of sandwich elements, the foam surfaces, in particular the foam underside, should also ideally be free from defects.

In the past, chlorofluorocarbons (CFCs) were used in large quantities as physical blowing agents for the production of polyisocyanate-based rigid foams, particularly due to their very low thermal conductivity. Their ozone-depleting potential (ODP) within the stratosphere has long been known and the use of CFCs is thus no longer permitted by regulatory regimes. The hydroochlorofluorocarbons (HCFCs), especially R141b, initially appeared to be a promising alternative to CFCs, but this class of substances also has an ozone-depleting effect and their use has therefore been prohibited. Alternative blowing agents likewise having a low thermal conductivity, such as hydrofluorocarbons (HFCs), have virtually no ozone-depleting effect but are typically potent greenhouse gases and therefore have a high GWP (global warming potential), as a result of which the use of use HFCs as physical blowing agents for production of polyurethane or polyisocyanurate foams is also disadvantageous.

Due to the above-described disadvantages of the CFCs and HFCs hydrocarbons are often used as physical blowing agents for producing polyisocyanate-based rigid foams today. Pentane isomers, which are very often used as physical blowing agents in the continuous and discontinuous production of rigid foam composite elements, are of central importance here. For the continuous production of polyurethane or polyisocyanurate sandwich elements, the use of n-pentane as physical blowing agent has become established over time, in particular for economic reasons.

To achieve improved processability of the polyurethane or polyisocyanurate reaction mixtures in cojunction with hydrocarbons, polyol components obtained by incorporating hydrophobic compounds into polyol structures were developed. Thus for example EP 2804886 describes the incorporation of fatty acid structures into polyester polyols. It is thus possible to employ for example pure fatty acids or fatty acid derivatives, for example vegetable oils, as reactants in polyester or polyether polyol production. The fatty acid derivatives are incorporated into the resulting polyester polyols via a transesterification reaction during the polycondensation. Another option for hydrophobizing polyester polyols is for example the use of dimeric fatty acids as units for polyester synthesis (EP 3140333) or the use of hydrophobic alkyl alcohols, for example nonylphenol, or fatty alcohols and derivatives thereof. EP 2820059 describes the production of such polyetherols through the use of proportions of fatty acids or fatty acid derivatives in starter components used for alkoxylation. In addition to the incorporation of hydrophobic structures in polyols, improved processability of hydrocarbon-blown polyurethane or polyisocyanurate-containing reaction mixtures can also be achieved by directly employing hydrophobic compounds such as for example vegetable oils, fatty acids, fatty acid derivatives or fatty alcohols in polyol components. Thus for example EP 1023351 describes the additive use

of hydrophobic compounds such as for example carboxylic acids (especially fatty acids), carboxylic acid esters (especially fatty acid esters) and alkyl alcohols (especially fatty alcohols) in polyol resin mixtures for producing polyurethane- or polyisocyanurate-containing rigid foams. EP 3294786 describes for example the use of alkoxylated vegetable oils in polyol resin mixtures for producing rigid foams. EP 0742241 describes the use of a hydrophobic compatibilizer, for example nonylphenol, for improving the processability of hydrocarbon-blown polyol components.

Switching from n-pentane to the physical blowing agent cyclopentane does make it possible to produce rigid foams having low thermal conductivities from polyurethane or polyisocyanate reaction mixtures but the change to cyclopentane also brings about a severe deterioration in mechanical foam properties, in particular compressive strength and dimensional stabilities.

The change from non-flammable CFCs and HFCs to flammable hydrocarbons demands a significant increase in the flame retardant contents in the reaction components to achieve comparable flame retardancies of the rigid foams. Increasing the flame retardant quantities is undesirable for eco-toxicological reasons. In a direct comparison with CFCs and HFCs the hydrocarbons also have markedly higher thermal conductivity values, which is why the sole use of hydrocarbons as physical blowing agents for production of rigid foams having improved thermal insulation characteristics is likewise disadvantageous.

Non-flammable hydrofluoroolefins (HFOs), such as hydrofluoropropenes or hydrochlorofluoropropenes, are suitable candidates to replace HFCs since they have a very low ODP and GWP as well as low thermal conductivity. Their use in reaction mixtures for producing closed-cell rigid polyurethane or polyisocyanurate foams is described in numerous patent publications. These include the following specifications: EP 2154223, EP 2739676, EP 2513023, US 20180264303, US9738768, US 2013/0149452, US 20150322225.

Among the compounds of the HFO blowing agents especially 1-chloro-3,3,3-trifluoropropene [1233zd(E))] and 1,1,1,4,4,4-hexafluoro-2-butene [1336mzz (Z)] have acquired commercial importance in recent years. One disadvantage of these blowing agents is that they can severely reduce the storage stability of polyol components when stored with specific amine catalysts and silicone-containing foam stabilizers. In the production of continuous sandwich elements the problem of storage stability can be overcome if for example either the amine catalysts, the foam stabilizers or the HFO blowing agents are metered into the reaction mixture as separate components; with further options for improving storage stability including the use of specific catalysts and specific foam stabilizers.

In addition to the disadvantage of storage stability it has also been shown that the use of 1-chloro-3,3,3-trifluoropropene in particular brings about a deterioration in the compressive strength of the foam, as is also the case with cyclopentane. The use of excessive amounts of 1,1,1,4,4,4-hexafluoro-2-butene often results to a decline in foam quality under the outer layers, especially in the continuous double belt process.

WO2019096763 describes a polyurethane foam sandwich element for thermal insulation and a process for producing the sandwich element. The blowing agent for producing the polyurethane foam comprises cis-1,1,1,4,4,4-hexafluoro-2-butene (HFO-1336mzz-Z) and cyclopentane. The polyurethane foam composite panel according to the present invention good insulation performance and mechanical strength. Isocyanurate foams, in particular foams at an isocyanate index of above 220, are not disclosed.

Examples 1 and 2 from WO2018218102 describe rigid polyurethane foams produced using potassium octoate (Dabco® K15), a flame retardant (TMCP) and a mixture of HFO-1336mzz(Z)(cis-1,1,1,4,4,4 -hexafluoro-2-butene) and cyclopentane in a molar ratio of 50:50 or 25:75. The polyol employed is Stepanpol PS 2352, a hydrophobic polyesterol comprising a proportion of 7% by weight of fatty acid and 2.5% by weight of nonylphenol.

It is also known that polyisocyanurate foams are more fire resistance than polyurethane foams.

In sample 3 of example 2, WO2016184433 describes production of a polyurethane foam using potassium octoate, a flame retardant and a mixture of HCFO-1233zd and cyclopentane in a molar ratio of about 35:65. The polyol employed is the sugar-based polyetherol GR 835G from Sinopec having an OH number of 450 mg KOH/g. This results in an isocyanate index of 210.

It is accordingly an object of the present invention to improve the profile of the abovementioned properties and in particular to develop a novel process which may be used for producing rigid polyisocyanurate foams and makes it possible to produce optimized rigid foams which have high flame retardancy and significantly reduced thermal conductivity and exhibit very good mechanical compressive strengths despite improved thermal insulation properties. It is a further object of the invention to develop a process which is suitable for producing polyisocyanurate sandwich elements, in particular in a continuous production process, and which affords sandwich elements having very low thermal conductivities, a high compressive strength and a high flame retardancy as well as excellent foam surface qualities, in particular facing the lower outer layer.

This object is achieved by a process for producing rigid polyisocyanurate foams, wherein (a) aromatic polyisocyanate, (b) isocyanate-reactive compounds comprising at least one polyetherol (b1) and/or polyesterol (b2), wherein the number-average content of isocyanate-reactive hydrogen atoms of components (b1) and (b2) is at least 1.7, (c) catalyst, (d) blowing agents, (e) flame retardants, (f) optionally auxiliary and additive substances and (g) optionally compounds having aliphatic hydrophobic groups and not falling under the definition of compounds (a) to (f) are mixed to afford a reaction mixture and allowed to cure to afford a rigid polyisocyanurate foam, wherein blowing agent (d) comprises at least one aliphatic halogenated hydrocarbon compound (d1) composed of 2 to 5 carbon atoms, at least one hydrogen atom and at least one fluorine and/or chlorine atom and compound (d1) comprises at least one carbon-carbon double bond and a hydrocarbon compound having 4 to 8 carbon atoms (d2) and the molar proportion of halogenated hydrocarbon compound (d1) is between 20 and 60 mol% and the molar proportion of hydrocarbon compound (d2) is between 40 and 80 mol%, in each case based on the total content of the blowing agents (d1) and (d2), and components (b) to (f) may comprise compounds having aliphatic hydrophobic groups and the content of aliphatic hydrophobic groups, based on the total weight of components (b) to (g), is not more than 4.0% by weight and the mixing to afford the reaction mixture is carried out at an isocyanate index of at least 240. The present invention further relates to a rigid polyisocyanurate foam obtainable by a process according to the invention.

A rigid polyisocyanurate foam is generally understood to mean a foam which comprises both urethane and isocyanurate groups. In the context of the invention the term rigid polyurethane foam is to be understood as also encompassing rigid polyisocyanurate foam, wherein production of polyisocyanurate foams is based on an isocyanate index of at least 180. The isocyanate index is to be understood as meaning the ratio of isocyanate groups to isocyanate-reactive groups multiplied by 100. An isocyanate index of 100 corresponds to an equimolar ratio of the employed isocyanate groups of component (a) to the isocyanate-reactive groups of components (b) to (g).

Rigid polyisocyanurate films according to the present invention exhibit a compressive stress at 10% compression of not less than 80 kPa, preferably not less than 120 kPa, particularly preferably not less than 140 kPa. Furthermore, the isocyanate-based rigid foam has a closed-cell content of more than 80%, preferably more than 90%, according to DIN ISO 4590. Further details about rigid polyisocyanurate foams according to the invention may be found in “Kunststoffhandbuch, Band 7, Polyurethane”, Carl Hanser Verlag, 3rd edition, 1993, chapter 6, in particular chapter 6.2.2 and 6.5.2.2.

It is essential to the present invention that components (b) to (g) comprise 0% to not more than 4.0% by weight, i.e. 0% to 4% by weight, preferably from 0% to 3.5% by weight and in particular 0.1% to 3.0% by weight, of aliphatic hydrophobic groups, based on the total weight of components (b) to (g). In the context of the present invention, a hydrophobic group is to be understood as meaning an aliphatic hydrocarbon group having preferably more than 6, particularly preferably more than 8 and less than 100 and in particular at least 10 and at most 50, directly adjacent carbon atoms. The adjacent carbon atoms may be bonded not only through carbon-carbon single bonds but also through carbon-carbon double bonds. The carbon atoms of the hydrophobic group are directly bonded to one another and not interrupted by heteroatoms for example. By contrast, hydrogen atoms of the hydrocarbons may be substituted, for example by halogen atoms, OH groups or carboxylic acid groups. It is preferable when the hydrocarbons of the hydrophobic groups according to the invention are not substituted.

If compounds having hydrophobic groups are employed these may be a portion of any of the compounds (b) to (f) or employed as separate compounds comprising hydrophobic groups (g). To calculate the proportion of the hydrophobic groups it is exclusively the weight of the hydrophobic group that is used and any substituents distinct from hydrogen, such as OH groups or halogen groups, are not taken into account in calculating the proportion.

The polyisocyanates (a) are the aromatic polyfunctional isocyanates known in the art. Such polyfunctional isocyanates are known and may be produced by methods known per se. The polyfunctional isocyanates may in particular also be used in the form of mixtures, so that component (A) in this case comprises different polyfunctional isocyanates. Polyisocyanate (a) is a polyfunctional isocyanate having two (hereinbelow also referred to as diisocyanates) or more than two isocyanate groups per molecule.

The isocyanates (a) are in particular selected from the group consisting of aromatic polyisocyanates, such as 2,4- and 2,6-toluene diisocyanate and the corresponding isomer mixtures, 4,4'-, 2,4'- and 2,2'-diphenylmethane diisocyanate and the corresponding isomer mixtures, mixtures of 4,4'- and 2,4'-diphenylmethane diisocyanates, polyphenylpolymethylene polyisocyanates, mixtures of 4,4'-, 2,4'- and 2,2'-diphenylmethane diisocyanates and polyphenylpolyethylene polyisocyanates (crude MDI) and mixtures of crude MDI and toluene diisocyanates.

Particularly suitable are 2,2'-, 2,4'- or 4,4'-diphenylmethane diisocyanate (MDI) and mixtures of two or three of these isomers, 1,5-naphthylene diisocyanate (NDI), 2,4- and/or 2,6-toluene

diisocyanate (TDI), 3,3'-dimethyldiphenyl diisocyanate, 1,2-diphenylethane diisocyanate and/or p-phenylene diisocyanate (PPDI).

Often also employed are modified polyisocyanates, i.e. products obtained by chemical reaction of organic polyisocyanates and comprising at least two reactive isocyanate groups per molecule. Particular mention may be made of polyisocyanates comprising ester, urea, biuret, allophanate, carbodiimide, isocyanurate, uretdione, carbamate and/or urethane groups, often also together with unconverted polyisocyanates.

The polyisocyanates of component (a) particularly preferably comprise 2,2'-MDI or 2,4'-MDI or 4,4'-MDI or mixtures of at least two of these isocyanates (also known as monomeric diphenylmethane or MMDI) or oligomeric MDI, which consists of higher homologs of MDI having at least 3 aromatic nuclei and a functionality of at least 3, or mixtures of two or more of the abovementioned diphenylmethane diisocyanates or crude MDI obtained in the manufacture of MDI or preferably mixtures of at least one oligomer of MDI and at least one of the abovementioned low molecular weight MDI derivatives 2,2'-MDI, 2,4'-MDI or 4,4'-MDI (also referred to as polymeric MDI). The isomers and homologues of MDI are generally obtained by distillation of crude MDI.

In addition to dinuclear MDI (MMDI) polymeric MDI also comprises one or more polynuclear condensation products of MDI having a functionality of more than 2, in particular 3 or 4 or 5. Polymeric MDI is known and is often referred to as polyphenylpolymethylene polyisocyanate.

The average functionality of a polyisocyanate comprising polymeric MDI may vary in the range from about 2.2 to about 4, in particular from 2.4 to 3.8 and especially from 2.6 to 3.0. Such a mixture of MDI-based polyfunctional isocyanates having different functionalities is in particular the crude MDI obtained as an intermediate in the production of MDI.

Polyfunctional isocyanates or mixtures of two or more polyfunctional isocyanates based on MDI are known and are commercially available from BASF Polyurethanes GmbH under the trade names Lupranat® M20, Lupranat® M50, or Lupranat® M70.

Component (a) preferably comprises at least 70% by weight, particularly preferably at least 90% by weight and in particular 100% by weight, based on the total weight of component (a), of one or more isocyanates selected from the group consisting of 2,2'-MDI, 2,4'-MDI, 4,4'-MDI and oligomers of MDI. The content of oligomeric MDI is preferably at least 20 percent by weight,

particularly preferably from more than 30 percent by weight to less than 80 percent by weight, based on the total weight of component (a).

The viscosity of component (a) employed may vary over a wide range. The component (a) preferably has a viscosity of of 100 to 3000 mPa*s, particularly preferably of 100 to 1000 mPa*s, particularly preferably of 100 to 800 mPa*s, particularly preferably of 200 to 700 mPa*s and particularly preferably of 400 to 650 mPa*s at 25°C. The viscosity of component (a) may vary over a wide range.

Isocyanate-reactive compounds (b) employed may be any compounds having isocyanate-reactive groups known in polyurethane chemistry, preferably compounds having at least one hydroxyl group,-NH group, or NH_2 group or carboxylic acid group, preferably having at least one NH_2 or OH group and in particular at least one OH group. The functionality towards isocyanate groups may be in the range from 1 to 8, preferably 2 to 8. The isocyanate-reactive compounds include polyether polyols (b1), polyester polyols (b2) or mixtures thereof, preferably polyesterols (b2) or mixtures of polyetherols (b1) and polyesterols (b2). Polyetherols (b1) and polyesterols (b2) preferably have a number-average molecular weight of 150 to 15 000 g/mol, preferably 150 to 5000 g/mol and particularly preferably 200 to 2000 g/mol. In addition to polyetherols and polyesterols it is also possible to employ low molecular weight chain extenders and/or crosslinking agents known in polyurethane chemistry. Compounds (b) preferably have a number-average molecular weight of 62 to 15 000 g/mol. Compounds (b) preferably have a number-average functionality of at least 1.7, particularly preferably at least 2. According to the invention the polyetherols (b1) and/or polyesterols (b2) have a number-average functionality of at least 1.7, more preferably of at least 2.0.

Polyetherols (b1) are produced for example from epoxides, such as propylene oxide and/or ethylene oxide, or from tetrahydrofuran with hydrogen-active starter compounds, such as aliphatic alcohols, phenols, amines, carboxylic acids, water and compounds based on natural substances, such as sucrose, sorbitol or mannitol, using a catalyst. These may include basic catalysts or double-metal cyanide catalysts, as described for example in PCT/EP2005/010124, EP 90444 or WO 05/090440.

Polyesterols (b2) are produced, for example, from aliphatic or aromatic dicarboxylic acids and polyhydric alcohols, polythioether polyols, polyesteramides, hydroxyl-containing polyacetals and/or hydroxyl-containing aliphatic polycarbonates, preferably in the presence of an esterification catalyst. Further possible polyols are, for example, cited in “Kunststoffhandbuch, Band 7, Polyurethane”, Carl Hanser Verlag, 3rd Edition, 1993, Chapter 3.1.

According to the invention the isocyanate-reactive compounds (b) comprise a polyether polyol (b1) and/or a polyester polyol (b2), preferably a polyester polyol (b2), optionally in combination with a polyether polyol (b1). The weight fraction of polyetherol (b1) is preferably 0% to 30% by weight, particularly preferably 0% to 20% by weight and in particular 1% to 15% by weight, and of polyesterol (b2) is preferably 70% to 100%, particularly preferably 80% to 100% and in particular 85% to 99% by weight, in each case based on the total weight of polyetherol (b1) and polyesterol (b2). In the context of the present disclosure the terms “polyester polyol” and “polyesterol” are synonymous, as also are the terms “polyether polyol” and “polyetherol”.

The polyetherols (b1) are obtained by known processes, for example by anionic polymerization of alkylene oxides with addition of at least one starter molecule comprising 1 to 8, preferably 2 to 6, reactive hydrogen atoms in bonded form or a starter molecule mixture comprising, averaged over all starters present, 1.5 to 8, preferably 2 to 6, reactive hydrogen atoms in bonded form in the presence of catalysts. Fractional functionalities can be obtained by using mixtures of starter molecules with different functionality. The nominal functionality ignores effects on functionality due by way of example to side reactions. Employable catalysts include alkali metal hydroxides, such as sodium or potassium hydroxide or alkali metal alkoxides, such as sodium methoxide, sodium or potassium ethoxide or potassium isopropoxide, or in the case of cationic polymerization Lewis acids, such as antimony pentachloride, boron trifluoride etherate or Fuller's earth. It is also possible to use aminic alkoxylation catalysts, for example dimethylethanolamine (DMEOA), imidazole and imidazole derivatives. Employable catalysts also include double-metal cyanide compounds, so-called DMC catalysts.

Employed alkylene oxides are preferably one or more compounds having 2 to 4 carbon atoms in the alkylene radical, for example tetrahydrofuran, 1,2-propylene oxide, ethylene oxide, or 1,2- or 2,3-butylene oxide, in each case alone or in the form of mixtures. It is preferable to employ ethylene oxide and/or 1,2-propylene oxide, particularly preferably ethylene oxide.

Contemplated starter molecules include hydroxyl- or amine-containing compounds, for example ethylene glycol, diethylene glycol, triethylene glycol, 1,2-propanediol, 1,3-propanediol, bisphenol A, bisphenol F, glycerol, trimethylolpropane, pentaerythritol, sugar derivatives, such as sucrose, hexitol derivatives, such as sorbitol, methylamine, ethylamine, isopropylamine, butylamine, benzylamine, aniline, toluidine, toluenediamine (TDA), naphthylamine, ethylenediamine, methylenedianiline, 2,2’-diaminodiphenylmethane (2,2-MDA) 2,4’-diaminodiphenylmethane (2,4-MDA), 4,4’-diaminodiphenylmethane (4,4-MDA), diethylentriamine, 4,4’-methylenedianiline, 1,3-propanediamine, 1,6-hexanediamine,

ethanolamine, diethanolamine, triethanolamine and also other dihydric or polyhydric alcohols or monofunctional or polyfunctional amines or water. Since the highly functional compounds are often in solid form under the customary reaction conditions of alkoxylation, it is generally customary to effect alkoxylation thereof together with co-initiators. Examples of co-initiators are water, lower polyhydric alcohols, e.g. glycerol, trimethylolpropane, pentaerythritol, diethylene glycol, ethylene glycol, propylene glycol and homologs of these. Contemplated further co-initiators include for example: organic fatty acids or monofunctional fatty alcohols, fatty acid monoesters or fatty acid methyl esters, for example oleic acid, stearic acid, methyl oleate, methyl stearate or biodiesel, these serving to improve blowing agent solubility during production of rigid polyurethane foams.

Preferred starter molecules for production of the polyether polyols (b1) include sorbitol, sucrose, ethylenediamine, TDA, trimethylolpropane, pentaerythritol, glycerol, biodiesel, nonylphenol, ethylene glycol and diethylene glycol. Further preferred starter molecules include all starters or starter mixtures having an average overall functionality of ≤3, particularly preferably glycerol, trimethylolpropane, biodiesel, nonylphenol, ethylene glycol, diethylene glycol, propylene glycol and bisphenol A, in particular ethylene glycol, diethylene glycol and glycerol.

The polyether polyols employed in the context of component (b1) preferably have an average functionality of 1.5 to 6 and in particular of 2.0 to 4.0 and number-average molecular weights of preferably 150 to 3000 g/mol, particularly preferably of 150 to 1500 g/mol and in particular of 250 to 800 g/mol. The OH number of the polyether polyols of component (b1) is preferably 1200 to 50 mg KOH/g, preferably 600 to 100 mg KOH/g and in particular 300 to 150 mg KOH/g.

Suitable polyester polyols (b2) can be produced from organic dicarboxylic acids having from 2 to 12 carbon atoms, preferably aromatic, or from mixtures of aromatic and aliphatic dicarboxylic acids with polyhydric alcohols, preferably diols, having 2 to 12 carbon atoms, preferably 2 to 6 carbon atoms.

Dicarboxylic acids used can in particular comprise the following: succinic acid, glutaric acid, adipic acid, suberic acid, azelaic acid, sebacic acid, decanedicarboxylic acid, maleic acid, fumaric acid, phthalic acid, isophthalic acid and terephthalic acid. The dicarboxylic acids can be used here either individually or else in a mixture. It is also possible to use, instead of the free dicarboxylic acids, the corresponding dicarboxylic acid derivatives, for example dicarboxylic esters of alcohols having 1 to 4 carbon atoms or dicarboxylic anhydrides. Employed aromatic dicarboxylic acids or acid derivatives preferably comprise phthalic acid, phthalic anhydride, terephthalic acid and/or isophthalic acid in admixture or alone. Employed aliphatic dicarboxylic

acids are preferably dicarboxylic acid mixtures of succinic, glutaric and adipic acid in quantity ratios of for example 20 to 35 : 35 to 50 : 20 to 32 parts by weight, and in particular adipic acid. The polyesterols (b2) employed are particularly preferably exclusively those obtained using exclusively aromatic dicarboxylic acids or derivatives thereof. Preferably employed aromatic dicarboxylic acids are at least one compound selected from the group consisting of terephthalic acid, dimethyl terephthalate (DMT), polyethylene terephthalate (PET), phthalic acid, phthalic anhydride (PSA) and isophthalic acid, particularly preferably at least one compound from the group consisting of terephthalic acid, dimethyl terephthalate (DMT), polyethylene terephthalate (PET) and phthalic anhydride (PSA) and in particular from phthalic acid and/or phthalic anhydride.

Examples of di- and polyhydric alcohols, especially diols, are: monoethylene glycol, diethylene glycol, triethylene glycol, polyethylene glycol, 1,2- or 1,3-propanediol, dipropylene glycol, polyopropylene glycol, 1,4-butanediol, 1,5-pentanediol, 1,6-hexanediol, 1,10-decanediol, glycerol, trimethylolpropane and pentaerythritol and also alkoxylates of the same starters. It is preferable to employ monoethylene glycol, diethylene glycol, triethylene glycol, 1,2-or 1,3-propanediol, dipropylene glycol and ethoxylates of the same starters, for example ethoxylated glycerol, or mixtures of at least one of the aforementioned diols. Especially employed are monoethylene glycol, diethylene glycol, glycerol and ethoxylates of the same starters or mixtures of at least two of the aforementioned diols, especially diethylene glycol. It is also possible to employ polyester polyols derived from lactones, for example ε-caprolactone, or hydroxycarboxylic acids, for example ω-hydroxycaproic acid.

Production of the polyester polyols (b2) may comprise polycondensation of the aliphatic and aromatic polycarboxylic acids and/or derivatives and polyhydric alcohols in the absence of catalyst or preferably in the presence of esterification catalysts, advantageously in an atmosphere of inert gas such as nitrogen in the melt at temperatures of 150°C to 280ºC, preferably 180°C to 260ºC, optionally under reduced pressure until the desired acid number, which is advantageously less than 10, but preferably less than 2, has been reached. Suitable as esterification catalysts are, for example, iron, cadmium, cobalt, lead, zinc, antimony, magnesium, titanium and tin catalysts in the form of metals, metal oxides or metal salts. The polycondensation can, however, also be carried out in liquid phase in the presence of diluents and/or entraining agents, e.g. benzene, toluene, xylene or chlorobenzene, for azeotropic removal by distillation of the water of condensation.

To produce the polyester polyols (b2), the organic polycarboxylic acids and/or derivatives and polyhydric alcohols are advantageously polycondensed in a molar ratio of 1 : 1 to 2.2, preferably 1 : 1.05 to 2.1 and particularly preferably 1 : 1.1 to 2.0.

The obtained polyester polyols (b2) generally have a number-average molecular weight of 200 to 3000, preferably 300 to 1000 and in particular 400 to 800.

If component (b) comprises compounds having hydrophobic groups, the compounds comprise not only at least one hydrophobic group but also at least one isocyanate-reactive group, for example an acid group, an amino group or a hydroxyl group. These constituents may be the polyetherols (b1) or the polyesterols (b2) but, alternatively or in addition, separate compounds which comprise both one or more isocyanate-reactive groups and one or more hydrophobic groups may also be employed. If the hydrophobic groups are a constituent of the polyetherols (b1) or polyesterols (b2) these may be incorporated into the polyols (b1) or (b2) by known reactions such as transesterification or alkoxylation. The starting compounds having hydrophobic groups that are incorporated into polyols (b1) or (b2) generally have at least one group that can be esterified, transesterified, or alkoxylated, such as for instance a carboxylic acid group, a carboxylic ester group, a carboxamide group, a carboxylic anhydride group, a hydroxyl group or a primary or secondary amino group.

Compounds having hydrophobic groups of component (b), which do not fall under the definition of the polyetherols (b1) or polyesterols (b2) are for example hydroxyl-functional hydrophobic substances such as alkyl alcohols, fatty alcohols or hydroxyl-functionalized oleochemical compounds. Examples of such alkyl alcohols and fatty alcohols are octyl, nonyl, decyl, undecyl, dodecyl, oleyl, cetyl, isodecyl, tridecyl, lauryl and mixed C12-C14 alcohols, 2-ethylhexanol, alkylphenols having > 6 carbon atoms in the alkyl radical, for example nonylphenol, oxo alcohols having > 6 carbon atoms, obtainable by hydroformylation of α-olefins and further reactions, Guerbet alcohols having > 6 carbon atoms and mixtures of different alkyl and fatty alcohols.

If hydroxy-functional compounds having hydrophobic groups are employed it is preferable to use: castor oil, turkey red oil, hydroxyl-modified oils such as grapeseed oil, black cumin oil, pumpkin seed oil, borage seed oil, soybean oil, wheatgerm oil, rapeseed oil, sunflower oil, peanut oil, apricot kernel oil, pistachio kernel oil, almond oil, olive oil, macadamia nut oil, avocado oil, sea buckthorn oil, sesame oil, hazelnut oil, evening primrose oil, wild rose oil, hemp oil, safflower oil, walnut oil, fatty acid esters modified with hydroxyl groups, which esters are based on myristoleic acid, palmitoleic acid, oleic acid, vaccenic acid, petroselinic acid, gadoleic acid, erucic acid, nervonic acid, linoleic acid, linolenic acid, stearidonic acid, arachidonic acid,

timnodonic acid, clupanodonic acid or cervonic acid or mixtures of at least two of these compounds.

A further group of hydroxyl-functionalized oleochemical is obtainable by ring-opening of epoxidized fatty acid esters with simultaneous reaction with alcohols and optionally subsequent further transesterification reactions. The incorporation of hydroxyl groups into oils and fats is primarily achieved by epoxidation of the olefinic double bond comprised in these products, followed by the reaction of the epoxy groups formed with a mono- or polyhydric alcohol. The epoxide ring here becomes a hydroxyl group or, in the case of polyfunctional alcohols, a structure having a greater number of OH groups. Since oils and fats are typically glycerol esters, the abovementioned reactions are also accompanied by parallel transesterification reactions. The resulting compounds preferably have a molecular weight in the range between 500 and 1500 g/mol.

Hydrophobic group-comprising compounds (b) comprising amine groups are preferably to be understood as meaning compounds having between 7 and 40 carbon atoms. Examples include the fatty alkanolamines such as decylamine, dodecylamine, tetradecylamine and hexadecylamine.

Employable alkanolamides include for example fatty alkanolamides, for example fatty acid diethanolamide, lauric acid diethanolamide and oleic acid monoethanolamide.

As described, hydrophobic group-comprising compounds (b) can also be understood as meaning compounds comprising at least one carboxylic acid group, for example, mono- or bifunctional carboxylic acids, for example having 7-40 carbon atoms per molecule. Examples include: Dimer fatty acids or preferably fatty acids. Examples of fatty acids are caproic acid, caprylic acid, capric acid, lauric acid, myristic acid, palmitic acid, stearic acid, oleic acid, linoleic acid, linolenic acid, ricinoleic acid and mixtures thereof. The acids may be of either biological or petrochemical origin. An example of a suitable petrochemical acid is 2-ethylhexanoic acid for example.

The hydroxy-functionalized oleochemical compound, if present, is further preferably a polyesterol having a hydrophobic group (b2a). Production of the the polyester polyols (b2a) having a hydrophobic group preferably employs as hydrophobic starting compounds fatty acids, fatty acid derivatives or alkylphenol alkoxylates having ≥8 carbon atoms in the alkyl group.

The polyester polyols (b2) preferably comprise at least one polyesterol (b2a) obtainable by esterification of

(b2a1) 10 to 80 mol% of a dicarboxylic acid composition comprising

(b2a11) 20 to 100 mol%, based on the dicarboxylic acid composition, of one or more aromatic dicarboxylic acids or derivatives of same,

(b2a12) 0 to 80 mol%, based on the dicarboxylic acid composition, of one or more aliphatic dicarboxylic acids or derivatives of same,

(b2a2) 0 to 30 mol% of one or more fatty acids and/or fatty acid derivatives,

(b2a3) 2 to 70 mol% of one or more aliphatic or cycloaliphatic diols having 2 to 18 carbon atoms or alkoxylates of same,

(b2a4) 0 to 80 mol% of an alkoxylation product of at least one starter molecule having an average functionality of at least two,

in each case based on the total amount of components (b2a1) to (b2a4), wherein components (b2a1) to (b2a4) sum to 100 mol%.

A polyester polyol of component (b2) preferably has a number-average functionality of not less than 1.7, preferably of not less than 1.8, particularly preferably of not less than 2.0 and in particular of not less than 2.2, thus resulting in a higher crosslinking density of the polyurethane produced therewith and therefore in better mechanical properties of the polyurethane foam.

Component (b) can further comprise chain extenders and/or crosslinking agents, for example for modifying the mechanical properties, for example hardness. Employed chain extenders and/or crosslinking agents used are diols and/or triols and also aminoalcohols having molecular weights of less than 150 g/mol, preferably of 60 to 130 g/mol. Contemplated compounds include for example aliphatic, cycloaliphatic and/or araliphatic diols having 2 to 8, preferably 2 to 6, carbon atoms, for example ethylene glycol, 1,2-propylene glycol, diethylene glycol, dipropylene glycol, 1,3-propanediol, 1,4-butanediol, 1,6-hexanediol, o-, m-, p-dihydroxycyclohexane, bis(2-hydroxyethyl)hydroquinone. Likewise contemplated are aliphatic and cycloaliphatic triols such as glycerol, trimethylolpropane and 1,2,4- and 1,3,5-trihydroxycyclohexane.

Provided that chain extenders, crosslinking agents or mixtures thereof are used for production of the rigid polyurethane foams, these are advantageously employed in an amount of 0% to 15% by weight, preferably 0% to 5% by weight, based on the total weight of component (b). Component (b) preferably comprises less than 10% by weight and particularly preferably less than than 7% by weight and in particular less than 5% by weight of chain extenders and/or crosslinking agents.

Compounds used as catalysts (c) for production of the polyurethane foams in particular include compounds that greatly accelerate the reaction of the compounds comprising reactive hydroxyl groups of components (b) to (g) with the polyisocyanates (a).

It is advantageous to use basic polyurethane catalysts, for example tertiary amines, examples being triethylamine, tributylamine, dimethylbenzylamine, dicyclohexylmethylamine, dimethylcyclohexylamine, N,N,N',N'-tetramethyldiaminodiethyl ether, bis(dimethylaminopropyl)urea, N-methyl- or N-ethylmorpholine, N-cyclohexylmorpholine, N,N,N',N'-tetramethylethylenediamine, N,N,N,N-tetramethylbutanediamine, N,N,N,N-tetramethylhexane-1,6-diamine, pentamethyldiethylenetriamine, bis(2-dimethylaminoethyl) ether, dimethylpiperazine, N-dimethylaminoethylpiperidine, 1,2-dimethylimidazole, 1-azabicyclo[2.2.0]octane, 1,4-diazabicyclo[2.2.2]octane (Dabco), and alkanolamine compounds, for example triethanolamine, triisopropanolamine, N-methyl- and N-ethyldiethanolamine, dimethylaminoethanol, 2-(N,N-dimethylaminoethoxy)ethanol, N,N',N"-tris(dialkylaminoalkyl)hexahydrotriazines, e.g. N,N',N"-tris(dimethylaminopropyl)-s-hexahydrotriazine, and triethylenediamine. However, suitable catalysts also include metal salts, such as iron(II) chloride, zinc chloride, lead octoate and tin salts,vsuch as tin dioctoate, tin diethylhexoate, and dibutyltin dilaurate and also mixtures of tertiary amines and organotin salts.

Contemplated catalysts further include: amidines, for example 2,3-dimethyl-3,4,5,6-tetrahydropyrimidine, tetraalkylammonium hydroxides, for example tetramethylammonium hydroxide, alkali metal hydroxides, for example sodium hydroxide, and alkali metal alcoholates, for example sodium methanolate and sodium isopropanolate, alkali metal carboxylates, and also alkali metal salts of long-chain fatty acids having 8 to 20 carbon atoms and optionally having pendant OH groups.

Also contemplated as catalysts are incorporable amines, i.e. preferably amines having an OH, NH or NH_2 function, such as for example ethylenediamine, triethanolamine, diethanolamine, ethanolamine and dimethylethanolamine. Incorporable catalysts may be regarded either as compounds of component (c) or as compounds of component (b).

It is preferable to use 0.001 to 10 parts by weight of catalyst or of catalyst combination, based on 100 parts by weight of component (b). It is also possible to carry out the reactions without catalysis. In this case, it is usual to utilize the catalytic activity of amine-started polyols.

Contemplated catalysts for the trimerization reaction of the excess NCO groups with one another further include: catalysts that form isocyanurate groups, for example salts of ammonium ions or of alkali metals, especially ammonium carboxylates or alkali metal carboxylates, alone or in combination with tertiary amines. Formation of isocyanurate leads to flame-retardant PIR foams which are preferably used in rigid foam for technical applications, for example in the construction industry as insulation sheet or sandwich elements.

In a preferred embodiment the catalyst (c) comprises an amine catalyst having a tertiary amino group and an ammonium or alkali metal carboxylate catalyst. In a particularly preferred embodiment the catalyst (c) comprises at least one amine catalyst selected from the group consisting of pentamethyldiethylenetriamine and bis(2-dimethylaminoethyl) ether and at least one alkali metal carboxylate catalyst selected from the group consisting of potassium formate, potassium acetate and potassium 2-ethylhexanoate. It has surprisingly been found that use of these catalysts in the continuous production of sandwich elements, for example in a double belt, affords sandwich elements which have a particularly smooth foam surface facing the outer layer, in particular facing the lower outer layer. This results in sandwich panels having excellent adhesion of the foam to the outer layer and to flawless surfaces.

According to the invention the blowing agent (d) employed is a blowing agent mixture comprising at least one aliphatic halogenated hydrocarbon compound (d1) composed of 2 to 5 carbon atoms, at least one hydrogen atom and at least one fluorine and/or chlorine atom and a hydrocarbon compound having 4 to 8 carbon atoms (d2), wherein the compound (d1) has at least one carbon-carbon double bond.

Suitable compounds (d1) comprise trifluoropropenes and tetrafluoropropenes, such as (HFO-1234), pentafluoropropenes, such as (HFO-1225), chlorotrifluoropropenes, such as (HFO-1233), chlorotetrafluoropropenes and hexafluorobutenes, and also mixtures of one or more of these components. Preference is given to tetrafluoropropenes, pentafluoropropenes, chlorotrifluoropropenes and hexafluorobutenes, wherein the unsaturated, terminal carbon atom bears at least one chlorine or fluorine substituent. Examples include 1,3,3,3-tetrafluoropropene (HFO-1234ze); 1,1,3,3-tetrafluoropropene; 1,2,3,3,3-pentafluoropropene (HFO-1225ye); 1,1,1-trifluoropropene; 1,1,1,3,3-pentafluoropropene (HFO-1225zc); 1,1,2,3,3-pentafluoropropene (HFO-1225yc); 1-chloro-2,3,3,3-tetrafluoropropene (HFO-1224yd); 1,1,1,2,3-pentafluoropropene (HFO-1225yez); 1-chloro-3,3,3-trifluoropropene (HCFO-1233zd); 1,1,1,4,4,4-hexafluorobut-2-ene (HFO-1336mzz) or mixtures of two or more of these components.

Particularly preferred compounds (d1) are hydroolefins selected from the group consisting of trans-1-chloro-3,3,3-trifluoro-propene (HCFO-1233zd(E)), cis-1-chloro-2,3,3,3-tetrafluoropropene (HCFO-1224yd), trans-1,1,1,4,4,4-hexafluorobut-2-ene (HFO-1336mzz(E)), cis-1,1,1,4,4,4-hexafluorobut-2-ene (HFO-1336mzz(Z)) or mixtures of two or more of these components. Particular preference is given to trans-1-chloro-3,3,3-trifluoropropene (HCFO-1233zd(E)) which surprisingly leads to particularly flawless foam qualities on the lower outer layer in the continuous production process.

Examples of hydrocarbon compounds having 4 to 8 carbon atoms (d2) are compounds such as heptane, hexane and isopentane, preferably technical mixtures such as n- and isopentane, n- and isobutane and propane, cycloalkanes, such as cyclopentane and/or or cyclohexane, and in particular pentane isomers, such as n-pentane, isopentane and cyclopentane. The hydrocarbon compound (d2) preferably comprises at least 60 mol %, particularly preferably more than 70 mol % and in particular more than 80 mol % of cycloaliphatic hydrocarbon compounds.

Further physical blowing agents may be employed in addition to blowing agents (d1) und (d2). Suitable such agents in particular include liquids which are inert toward the employed isocyanates and have boiling points below 100°C, preferably below 50°C, at atmospheric pressure, so that they evaporate when subjected to the exothermic polyaddition reaction. Examples include ethers, such as furan, dimethyl ether and diethyl ether, ketones, such as acetone and methyl ethyl ketone, alkyl carboxylates such as methyl formate, dimethyl oxalate and ethyl acetate and halogenated hydrocarbons, such as methylene chloride, dichloromonofluoromethane, difluoromethane, trifluoromethane, difluoroethane, tetrafluoroethane, chlorodifluoroethane, 1,1-dichloro-2,2,2-trifluoroethane, 2,2-dichloro-2-fluoroethane and heptafluoropropane. It is also possible to use mixtures of these low-boiling-point liquids with one another and/or with other substituted or unsubstituted hydrocarbons. The proportion of physical blowing agent that does not fall under the definition of component (d1) or (d2) is preferably less than 30% by weight, particularly preferably less than 15% by weight, more preferably less than 5% by weight, in each case based on the total weight of the blowing agent component (d1) and (d2) and the further physical blowing agents. It is especially the case that no further physical blowing agent is used in addition to the blowing agent components (d1) and (d2).

Blowing agents used to produce the polyurethane foams according to the present invention also include chemical blowing agents. These react with isocyanate groups to form carbon dioxide and in the case of formic acid to form carbon dioxide and carbon monoxide. Suitable chemical blowing agents (d3) further comprise organic carboxylic acids, for example formic acid, acetic

acid, oxalic acid, and further carboxyl-containing compounds having < 6 carbon atoms and water.

It is preferable when no halogenated hydrocarbons are employed as blowing agent in addition to compounds (d1). The chemical blowing agents (d3) employed are preferably water, formic acid-water mixtures or formic acid, and particularly preferred chemical blowing agents are water or formic acid-water mixtures, in particular water-formic acid mixtures having a formic acid content of >70% by weight based on blowing agent (d3), resulting in improved outer layer adhesion and flawless foam surfaces under the lower outer layer.

When chemical blowing agents (d3) are employed they are preferably employed at less than 2% by weight, based on the total weight of components (b) to (g), preferably at 0.5 to 1.5% by weight.

According to the invention the molar proportion of halogenated hydrocarbon compounds (d1) is 20 to 60 mol%, preferably 25 to 55 mol% and particularly preferably 30 to 50 mol% and the molar proportion of hydrocarbon compound (d2) is between 40 and 80 mol%, preferably 45 and 75 mol% and particularly preferably 50 to 70 mol%, in each case based on the total content of the blowing agents (d1) and (d2).

The blowing agents (d) are preferably employed in amounts such that the free foam density of the obtained polyisocyanate-based rigid foams according to the invention is between 10 and 100 g/l, preferably between 20 and 75 g/l and in particular between 30 and 50 g/l.

The flame retardants (e) employed may generally be the flame retardants known from the prior art. Examples of suitable flame retardants are brominated esters, brominated ethers (Ixol) and brominated alcohols such as dibromoneopentyl alcohol, tribromoneopentyl alcohol and PHT-4-diol, and also chlorinated phosphates such as tris(2-chloroethyl) phosphate, tris(2-chloropropyl) phosphate (TCPP), tris(1,3-dichloropropyl) phosphate, tricresyl phosphate, tris(2,3-dibromopropyl) phosphate, tetrakis(2-chloroethyl) ethylenediphosphate, dimethyl methanephosphonate, diethyl diethanolaminomethylphosphonate, and also commercially available halogenated flame-retardant polyols. Other phosphates or phosphonates that may be employed as liquid flame retardants include diethyl ethanephosphonate (DEEP), triethyl phosphate (TEP), dimethyl propylphosphonate (DMPP), and diphenyl cresyl phosphate (DPC). Flame retardants having isocyanate-reactive groups are considered to belong both to the component of the flame retardants (e) and to component (b).

Flame retardants other than the aforementioned flame retardants that may be use to provide flame retardancy to the rigid polyurethane foams are inorganic or organic flame retardants such as red phosphorus, preparations comprising red phosphorus, aluminum oxide hydrate, antimony trioxide, arsenic oxide, ammonium polyphosphate and calcium sulfate, expandable graphite and cyanuric acid derivatives, for example melamine, and mixtures of at least two flame retardants, for example ammonium polyphosphates and melamine, and also optionally maize starch or ammonium polyphosphate, melamine and expandable graphite; aromatic polyesters can optionally also be used for this purpose.

Preferred flame retardants do not include any bromine. Particularly preferred flame retardants consist of atoms selected from the group consisting of carbon, hydrogen, phosphorus, nitrogen, oxygen and chlorine, more especially from the group consisting of carbon, hydrogen, phosphorus and chlorine.

Preferred flame retardants comprise no groups reactive toward isocyanate groups. The flame retardants are preferably liquid at room temperature. Particular preference is to TCPP, DEEP, TEP, DMPP and DPC and also oligomeric halogen-free flame retardants such as Fyrol® PNX (ICL) and Levagard® 2000 (Lanxess) and/or incorporable phosphorus-based flame retardants, such as Veriquel® R-100 (ICL) and Levagard® 2100 (Lanxess), in particular TCPP and TEP, yet more preference being given to TEP, which in continuous processing results in flawless foam surfaces under the lower outer layer and, in the event of fire, in reduced release of caustic combustion gases.

The proportion of the flame retardant (e) is generally 1% to 40% by weight, preferably 5% to 30% by weight, particularly preferably 8% to 25% by weight, based on the total weight of the components (b) to (g).

The reaction mixture for producing the polyurethane foams according to the invention may optionally be admixed with further auxiliaries and/or additives (f). These may include for example surface-active substances, foam stabilizers, cell regulators, fillers, light stabilizers, dyes, pigments, hydrolysis stabilizers and fungistatic and bacteriostatic substances.

Contemplated surface-active substances include for example compounds which are used to aid homogenization of the starting materials and are optionally also suitable for regulating the cell structure of the plastics. Examples include emulsifiers, such as the sodium salts of castor oil sulfates or of fatty acids and also salts of fatty acids with amines, for example diethylamine oleate, diethanolamine stearate, diethanolamine ricinoleate, salts of sulfonic acids, for example

alkali metal or ammonium salts of dodecylbenzene- or dinaphthylmethanedisulfonic acid and ricinoleic acid, such as siloxane-oxyalkylene copolymers and other organopolysiloxanes and dimethylpolysiloxanes. Also suitable for improving emulsifying action, cell structure and/or stabilization of the foam are oligomeric acrylates having polyoxyalkylene and fluoroalkane radicals as side groups. The surface-active substances are typically employed in amounts of 0.01 to 10 parts by weight based on 100 parts by weight of component (b).

Foam stabilizers employed may be customary foam stabilizers, for example those based on silicone, such as siloxane-oxyalkylene copolymers and other organopolysiloxanes.

Fillers, in particular reinforcing fillers, are to be understood as meaning the customary organic and inorganic fillers, reinforcers, weighting agents, agents for improving abrasion behavior in paints, coating compositions etc. that are known per se. Individual examples include: inorganic fillers such as silicatic minerals, for example phyllosilicates such as antigorite, serpentine, hornblends, amphiboles, chrysotile and talc, metal oxides, for example kaolin, aluminum oxides, titanium oxides and iron oxides, metal salts, for example chalk, barite, and inorganic pigments, for example cadmium sulfide and zinc sulfide, and also glass, etc. It is preferable to use kaolin (china clay), aluminum silicate and coprecipitates of barium sulfate and aluminum silicate, and also natural and synthetic fibrous minerals, for example wollastonite, and fibers of various lengths made of metal and in particular of glass; these can optionally have been sized. Contemplated organic fillers include for example: carbon, melamine, rosin, cyclopentadienyl resins and graft polymers, and also cellulose fibers, polyamide fibers, polyacrylonitrile fibers, polyurethane fibers and polyester fibers derived from aromatic and/or aliphatic dicarboxylic esters, and in particular carbon fibers.
The inorganic and organic fillers can be used individually or in the form of mixtures, quantities of these added to the reaction mixture advantageously being 0.5 to 50% by weight, preferably 1 to 40% by weight, based on the weight of components (a) to (f), where however the content of mats, nonwovens and wovens made of natural and synthetic fibers can reach up to 80% by weight, based on the weight of components (a) to (f).

Compounds (g) are preferably substances which are free-flowing at a temperature of 20°C and an ambient pressure of 1 bar. Examples of compounds (g) include carboxylic esters, such as lower alkanol esters of carboxylic acids, for example fatty acid ethyl esters or preferably fatty acid methyl esters, for example methyl caproate, methyl caprylate, methyl caprate, methyl laurate, methyl myristate, methyl palmitate, methyl oleate, methyl stearate, methyl linoleate, methyl linolenate and mixtures thereof, particularly preferably biodiesel.

It is preferably also possible to employ triglycerides, particularly preferably fats and oils, as compounds having hydrophobic groups (g), for example triglycerides, such as rapeseed oil, olive oil, corn oil, palm oil, pumpkin seed oil, sunflower oil, wheat seed oil, soybean oil, coconut oil, tall oil, cotton seed oil, grape seed oil, apricot kernel oil, safflower oil, avocado oil, macadamia oil, pistachio oil, almond oil, linseed oil, sesame oil, hazelnut oil, peanut oil, walnut oil, primrose oil, sea buckthorn oil, safflower oil, borage seed oil, black cumin oil, wild rose oil, tallow and mixtures thereof.

According to the invention production of the polyurethane foams is effected by mixing components (a) to (e) and, if present, (f) and (g) to afford a reaction mixture. Premixtures may also be produced to reduce complexity. These comprise at least one isocyanate component (A) comprising polyisocyanates (a) and a polyol component (B) comprising isocyanate-reactive compounds (b). All or some of the further components (c) to (g) may be added to isocyanate component (A) and polyol component (B) in whole or in part, wherein, due to the high reactivity of the isocyanates, in many cases the components (c) to (g) are often added to the polyol component to avoid side reactions. However, blowing agents (d1) in particular may also be admixed with the isocyanate component (A). The physical blowing agents (d1) and (d2) are preferably added to the reaction mixture in an extra stream and the remaining components (d) to (g) particularly preferably added to the polyol component (B). The reaction mixture is then allowed to react to afford the polyurethane foam. In the context of the present invention a reaction mixture is to be understood as meaning the mixture of the isocyanates (a) and the isocyanate-reactive compounds (b) at reaction conversions of less than 90% based on the isocyanate groups.

The mixing of the components to afford the reaction mixture is carried out at an isocyanate index of 240 to 1000, by preference at 240 to 800, preferably at 240 to 600, particularly preferably at 280 to 500 and in particular at 330 to 400. The starting components are mixed at a temperature of 15°C to 90°C, preferably 20°C to 60°C, in particular 20°C to 45°C. The reaction mixture can be mixed by mixing in high- or low-pressure metering machines.

The reaction mixture may be introduced into a mold, for example, to react. Discontinuous sandwich elements, for example, are produced by this technology.

The rigid foams according to the invention are preferably produced on continuously operating double belt lines. The polyol and isocyanate components are metered with a high-pressure apparatus and mixed in a mixing head. Catalysts and/or blowing agents may be metered into the polyol mixture beforehand using separate pumps. The reaction mixture is continuously

applied onto the outer layer. The lower layer with the reaction mixture and the upper outer are introduced into the double belt in which the reaction mixture foams and cures. After exiting the double belt, the continuous sheet is cut to the desired dimensions. This makes it possible to produce sandwich elements having metallic outer layers or having flexible outer layers.

The upper and lower outer layers employed, which may be identical or different, may be flexible or rigid outer layers which are typically employed in the double-belt process. These include metal outer layers, such as aluminum or steel, bitumen outer layers, paper, non-woven fabrics, plastic sheets such as polystyrene, plastic films such as polyethylene films or wood outer layers. The outer layers can also be coated, for example with a conventional coating or an adhesion promoter. It is particularly preferable to employ outer layers which are impermeable to the cell gas of the polyurethane foam.

Such processes are known and described, for example, in “Kunststoffhandbuch, volume 7, Polyurethane”, Carl Hanser Verlag, 3rd Edition 1993, Chapter 6.2.2 or EP 2234732.

The present invention finally provides a polyisocyanate-based rigid foam obtainable by a process according to the invention and a polyurethane sandwich element comprising such a polyisocyanate-based rigid foam according to the invention.

A polyisocyanate-based rigid foam according to the invention features exceptional mechanical properties, in particular exceptional compressive strength and exceptionally low thermal conductivities. The production of sandwich elements, in particular in the continuous double belt process, moreover affords sandwich elements having an exceptional surface quality of the polyisocyanate-based rigid foam, in particular facing the lower outer layer.

The invention is elucidated hereinbelow with reference to examples.

The following input materials were used to produce the reaction mixtures shown in Tables 1, 2 and 4:

Polyols:

Polyesterol 1: Esterification product of terephthalic acid, oleic acid, diethylene glycol and ethoxylated glycerol having a hydroxyl number of 535 mg KOH/g, a hydroxyl number of 244 mg KOH/g and a weight fraction of oleic acid of 15% in the end product. This results in a proportion of hydrophobic groups in the total weight of the polyesterol 1 of about 13.3% by weight based on the total weight of the polyesterol 1.

Polyesterol 2: Esterification product of phthalic anhydride, diethylene glycol and monoethylene glycol having a hydroxyl number of 240 mg KOH/g and a weight fraction of oleic acid of 0% in the end product.

Polyesterol 3: Esterification product of phthalic anhydride, soybean oil and diethylene glycol having a hydroxyl number of 194 mg KOH/g and a weight fraction of fatty acid of 3.7% in the end product. This results in a proportion of hydrophobic groups in the total weight of the polyesterol 3 of about 3.1% by weight based on the total weight of the polyesterol 3.

Polyester polyol 4: Esterification product of phthalic anhydride, glycerol, oleic acid and diethylene glycol having a hydroxyl number of 195 mg KOH/g and a weight fraction of oleic acid of 3.7% in the end product. This results in a proportion of hydrophobic groups in the total weight of the polyesterol 4 of about 3.3% by weight based on the total weight of the polyesterol 4.

Polyester polyol 5: Esterification product of phthalic anhydride, monoethylene glycol and diethylene glycol having a hydroxyl number of 215 mg KOH/g and a weight fraction of oleic acid of 15.8% in the end product. This results in a proportion of hydrophobic groups in the total weight of the polyesterol 5 of about 14.0% by weight based on the total weight of the polyesterol 5.

Polyetherol 1: Polyethylene glycol having a hydroxyl number of 188 mg KOH/g

Flame retardants:

TCPP: Tris(2-chloroisopropyl) phosphate having a chlorine content of 32.5% by weight and a phosphorus content of 9.5% by weight.

TEP: Triethyl phosphate having a phosphorus content of 17% by weight

Foam Stabilizers:

Tegostab® B 8443: Silicone-containing foam stabilizer from Evonik

Catalysts:

Catalyst A: Trimerization catalyst consisting of 36.2% by weight of potassium formate dissolved in 63.7% by weight of monoethylene glycol

Catalyst B: Catalyst consisting of 23.1% by weight of bis(2-dimethylaminoethyl) ether and 76.9% by weight of dipropylene glycol.

Chemical blowing agents:

Amasil 85 %: Formic acid solution (85% by weight in water)

Physical blowing agents:

Pentane S 80/20: Mixture of 80% by weight of n-pentane and 20% by weight of isopentane

Cyclopentane 70: Mixture of 70% by weight of cyclopentane and 30% by weight of isopentane

Cyclopentane 95: Mixture of 95% by weight of cyclopentane and 5% by weight of isopentane

Solstice® LBA: 1-chloro-3,3,3-trifluoropropene from Honeywell

Opteon™ 1100: (*Z*)-1,1,1,4,4,4-hexafluoro-2-butene from Chemours

Blowing agent mixture 1: Mixture of 55.88% by weight of cyclopentane 70 and 44.12% by weight of Solstice® LBA results in a blowing agent mixture comprising about 70 mol% of cyclopentane 70.

Blowing agent mixture 2: Mixture of 56.12% by weight of pentane S 80/20 and 43.88% by weight of Solstice® LBA results in a blowing agent mixture comprising about 70 mol% of pentane S 80/20.

Isocyanates:

Lupranat® M50: polymeric methylenediphenyl diisocyanate (PMDI) from BASF having a viscosity of approx. 550 mPa*s at 25°C.

The polyol components shown in Tables 1, 2 and 4 were produced from the abovementioned starting materials and reacted in the laboratory and on a high-pressure apparatus in a continuous double-belt process.

Laboratory foaming for establishing identical densities and fiber times (gel times):

The polyol components shown in table 1 were adjusted to identical fiber times of 53 s ± 2 s and cup foam densities of 44 kg/m³ ± 2 kg/m³ by variation of the physical blowing agents and

catalyst B. The amount of catalyst A was selected such that the finished foams for all settings comprised identical concentrations. The polyol components adjusted in this way were reacted with Lupranat® M50 in a mixing ratio such that the index for all settings was 330 ± 10. In this way, 80 g of reaction mixture were reacted in a paper cup by intensively mixing the mixture at 1400 rpm for 8 seconds using a laboratory stirrer.

The polyol components shown in table 2 were adjusted to identical fiber times of 53 s ± 2 s and cup foam densities of 42 kg/m³ ± 2 kg/m³ by variation of the physical blowing agents and catalyst B. The amount of catalyst A was selected such that the finished foams for all settings comprised identical concentrations. The polyol components adjusted in this way were reacted with Lupranat® M50 in a mixing ratio such that the index for all settings was 330 ± 10. In this way, 80 g of reaction mixture were reacted in a paper cup by intensively mixing the mixture at 1400 rpm for 8 seconds using a laboratory stirrer.

The polyol components shown in table 3 were adjusted to identical fiber times of 53 s ± 2 s and cup foam densities of 42 kg/m³ ± 2 kg/m³ by variation of the physical blowing agents and catalyst B. The amount of catalyst A was selected such that the finished foams for all settings comprised identical concentrations. The polyol components adjusted in this way were reacted with Lupranat® M50 in a mixing ratio such that the index for all settings was 210 ± 10. In this way, 80 g of reaction mixture were reacted in a paper cup by intensively mixing the mixture at 1400 rpm for 8 seconds using a laboratory stirrer.

The reaction mixtures thus adjusted to comparable densities and fiber times were subsequently used to produce rigid foam blocks, from which test specimens for thermal conductivity and compressive strength measurements were taken.
To produce the foam blocks for the thermal conductivity measurements 450 g of reaction mixture were reacted in a paper cup by intensively mixing the mixture at 1400 rpm for 6 seconds using a laboratory stirrer. The reaction mixture was then transferred into a box mold open at the top and having dimensions of 150 mm × 120 mm × 120 mm. The test specimens for the thermal conductivity measurements having directions of 200 mm x 200 mm x 30 mm were always taken from the center of the foam block in the rise direction of the foam.

Thermal conductivity was measured with a λ-Meter EP500e thermal conductivity meter from "Lambda Messtechnik GmbH Dresden" at an average temperature of 23°C. The thermal conductivity values reported in tables 1 and 2 are average values of a duplicate determination of two test specimens from two different but identically produced foam blocks.

9 test specimens having dimensions of 50 mm x 50 mm x 50 mm were additionally taken from the same foam blocks for determination of compressive strength according to DIN EN 826. Here too, the test specimens were always taken in the same way. Of the 9 test specimens, 3 test specimens were rotated such that the test was carried out counter to the rise direction of the foam (top). Of the 9 test specimens, 3 test specimens were rotated such that the test was carried out particular to the rise direction of the foam (in the x-direction). Of the 9 test specimens, 3 test specimens were rotated such that the test was carried out perpendicular to the rise direction of the foam (in the y-direction).

The 9 compressive strengths measured were then averaged and reported as values (compressive strength 3D) in tables 1 and 2.

Table 1: Laboratory experiments with cyclopentane 70 / Solstice® LBA mixtures

	Example	1	2	3	4	5	6 I
Polyol component	Polyester polyol 1 [parts by weight]	61.1	45.8		61.1	45.8	
	Polyester polyol 2 [parts by weight]	15.2	30.5	76.3	15.2	30.5	76.3
	Polyether polyol 1 [parts by weight]	7.8	7.8	7.8	7.8	7.8	7.8
	TCPP [parts by weight]	12	12	12	12	12	12
	Tegostab B 8443 [parts by weight]	2	2	2	2	2	2
Blowing agent component	Amasil 85% [parts by weight]	1.9	1.9	1.9	1.9	1.9	1.9
	Cyclopentane 70	X	X	X	0.0	0.0	0.0
	Blowing agent mixture 1	0.0	0.0	0.0	X	X	X
Properties	Hydrophobic fraction in components (b) to (g) [weight fraction]	8.1	6.1	0.0	8.1	6.1	0.0
	Thermal conductivity [mW/m·K]	21.3	21.0	20.8	21.1	19.9	19.6
	3D Compressive strength [MPa]	X	X	X	0.174	0.182	0.193

I: Inventive, X: Used

Table 2: Laboratory experiments with pentane S 80/20 / Solstice® LBA mixtures

	Example	7	8	9	10	11

Polyol Component	Polyester polyol 1 [parts by weight]	76.3	53.4	22.9		
	Polyester polyol 2 [parts by weight]		22.9	53.4	76.3	
	Polyester polyol 3 [parts by weight]					76.3
	Polyether polyol 1 [parts by weight]	7.8	7.8	7.8	7.8	7.8
	TCPP [parts by weight]	12	12	12	12	12
	Tegostab B 8443 [parts by weight]	2	2	2	2	2
Blowing agent component	Amasil 85% [parts by weight]	1.9	1.9	1.9	1.9	1.9
	Pentane S 80/20	X	X	X	X	X
Properties	Hydrophobic fraction in components (b) - (g) [weight fraction]	10.1	7.1	3.0	0	2.4
	Thermal conductivity [mW/m·K]	22.2	21.9	21.7	21.3	21.3
	3D Compressive strength [MPa]	0.189	0.200	0.215	0.217	0.225

	Example	12	13	14 I	15 I	16 I	17 I	18
Polyol Component	Polyester polyol 1 [parts by weight]	76.3	53.4	22.9				
	Polyester polyol 2 [parts by weight]		22.9	53.4	76.3			
	Polyester polyol 3 [parts by weight]					76.3		
	Polyester polyol 4 [parts by weight]						76.3	
	Polyester polyol 5 [parts by weight]							76.3
	Polyether polyol 1 [parts by weight]	7.8	7.8	7.8	7.8	7.8	7.8	7.8

	TCPP [parts by weight]	12	12	12	12	12	12	12
	Tegostab B 8443 [parts by weight]	2	2	2	2	2	2	2
Blowing agent component	Amasil 85% [parts by weight]	1.9	1.9	1.9	1.9	1.9	1.9	1.9
	Blowing agent mixture 2	X	X	X	X	X	X	X
Properties	Hydrophobic fraction in components (b) - (g) [weight fraction]	10.1	7.1	3.0	0.0	2.4	2.5	10.6
	Thermal conductivity [mW/m·K]	22.0	21.6	21.2	20.7	20.8	20.7	22.1
	3D Compressive strength [MPa]	0.187	0.193	0.212	0.211	0.214	0.210	0.195

I: Inventive, X: Used

Table 3: Laboratory experiments with pentane S 80/20 / Solstice® LBA mixtures at index of 210

__Example		19
Polyol Component	Polyester polyol 1 [parts by weight]	22.9
	Polyester polyol 2 [parts by weight]	53.4
	Polyether polyol 1 [parts by weight]	7.8
	TCPP [parts by weight]	12
	Tegostab B 8443 [parts by weight]	2
Blowing agent component	Amasil 85% [parts by weight]	1.9
	Blowing agent mixture 2	X
Properties	Hydrophobic fraction in components (b) - (g) [weight fraction]	9.6
	Thermal conductivity [mW/m·K]	22.3
	3D Compressive strength [MPa]	0.182

X: Used

Due to the lower thermal conductivity of the blowing agent Solstice® LBA compared to cyclopentane 70 and pentane S 80/20 it is unsurprising that the foams produced in the laboratory with blowing agent mixtures 1 and 2 also have a lower thermal conductivity. However, it was surprisingly found that the use of polyol components having a lower content of

hydrophobic groups in components (b) - (g) results in a markedly reduced thermal conductivity and a markedly improved compressive strength of the laboratory foams.

Foaming of the inventive polyol component from example 13 at a reduced index of 210 (example 19) results in a significant increase in the thermal conductivity and a significant reduction in the compressive strength of the foam.

Continuous production of sandwich elements by the double-belt process:

In addition to the laboratory foaming, composite elements of 80 mm in thickness were produced in the double-belt process. For production the polyol components specified below and temperature-controlled to 20°C ± 1°C, were reacted with Lupranat® M50, which had likewise been heated to 20°C ± 1°C. The amount of Lupranat® M50 was always chosen such that all rigid foams produced had an isocyanate index of 345±10.

Production of the composite elements employed as the lower outer layer either an aluminum foil of 0.05 mm in thickness heated to 35°C ± 2°C or an aluminum sheet of 0.5 mm in thickness heated to 40°C ± 2°C. Both top layers are industry standard and are also used in the conventional continuous production process process of sandwich panels. The temperature of the double belt was always 60°C ± 1°C.

To produce the composite elements of 80 mm in thickness the amount of catalyst B and of the physical blowing agent was selected such that the gel time of the reaction mixture was exactly 28 seconds and the contact time of the reaction mixture with the upper belt was exactly 23 seconds and the foam had an overall density of 38.0 ± 1.5 g/l.

For determination of thermal conductivities, compressive strengths and foam surfaces, sample specimens of 2.0 m in length and 1.25 m in width, from which the sample specimens required for the tests were always taken at the same sites, were taken after successful adjustment of the foamed parameters.

Determination of compressive strength of the sandwich foams:

After storage for 24 hours under standard climatic conditions further test specimens having dimensions of 100 mm x 100 mm x sandwich thickness were taken from the sample specimens using a band saw. The test specimens were taken at identical sites distributed over the width of the element (left, center, right) and the compressive strength of the foam was determined in accordance with the sandwich standard DIN EN ISO 14509-A.2 according to EN 826.

Determination of thermal conductivities of the sandwich foams:

After storage for 24 hours under standard climatic conditions further test specimens having dimensions of 200 mm x 200 mm x 30 mm were taken from the sample specimens using a band saw. The test specimens were taken in the center of the sandwich element thickness and sandwich element width.

Thermal conductivity was measured with a λ-Meter EP500e thermal conductivity meter from "Lambda Messtechnik GmbH Dresden" at an average temperature of 23°C. The thermal conductivity values reported in table 5 are average values of a duplicate determination of two test specimens.

Evaluation of foam surface after tear-off of lower outer layers:

After mechanical removal of the aluminum foil and the aluminum sheet, to which the liquid reaction mixture is directly applied in the double-belt process (lower outer layer), the foam surfaces were initially assessed and evaluated, where grade 1 represents the best foam surface and grade 5 represents the worst foam surface:

Table 4: Optical assessment of foam quality

	Aluminum foil	Profile sheet
Grade 1	Optically flawless (velvet skin)	Optically flawless (velvet skin)
Grade 2	Small push zones	Small push zones
Grade 3	Cavity depth: < 0.2 cm	Cavity depth: < 0.2 cm
Grade 4	Cavity depth: 0.3 - 0.6 cm	Cavity depth: 0.3 - 0.6 cm
Grade 5	Cavity depth: > 0.6 cm	Cavity depth: > 0.6 cm

Table 5: Double-belt experiments

	Example	19	20 I	21 I	22	23	24 I
Polyol component	Polyester polyol 2 [parts by weight]	63.7	63.7	63.7	63.7	63.7	63.7
	Polyether polyol 1 [parts by weight]	9.0	9.0	9.0	9.0	9.0	9.0
	TCPP [parts by weight]	25.3	25.3	25.3	25.3	25.3	25.3
	Tegostab B 8443 [parts by weight]	2.0	2.0	2.0	2.0	2.0	2.0

Blowing agent component	Amasil 85% [parts by weight]	1.6	1.6	1.6	1.6	1.6	1.6
	Cyclopentane 95 [parts by weight]	14.1	10.3	6.7	3.7	0	10.5
	Solstice® LBA [parts by weight]	0	6.2	12.5	18.9	24.9	0
	Opteon™ 1100 [parts by weight]	0	0	0	0	0	8.2
Proportion of Solstice LBA	mol of Solstice® LBA / (mol of Solstice® LBA + mol of cyclopentane 95)*100 [%]	0	24.4	50.1	73.3	100	0
Proportion of Opteon 1100	mol of Opteon™ 1100 / (mol of Opteon™ 1100 + mol of cyclopentane 95)*100 [%]	0	0	0	0	0	25.0
Properties	Proportion of hydrophobic groups in components (b) - (g) [weight fraction]	0	0	0	0	0	0
	Thermal conductivity [mW/mK]	18.9	18.2	18.3	18.6	18.6	18.3
	Compressive strength [MPa]	0.152	0.140	0.155	0.135	0.142	0.139
	Foam quality aluminum foil underside [1-5]	1	1	1	2	2	1
	Foam quality aluminum sheet underside [1-5]	2	2	2	3	3	2

	Example	25	26 I	27	28	29	30 I
Polyol component	Polyester polyol 1 [parts by weight]			63.7		63.7	
	Polyester polyol 2 [parts by weight]	63.7			63.7		
	Polyester polyol 3 [parts by weight]		63.7				78
	Polyether polyol 1 [parts by weight]	9.0	9.0	9.0	9.0	9.0	10
	TCPP [parts by weight]	25.3	25.3	25.3	25.3	25.3	

	TEP [parts by weight]						10
	Tegostab B 8443 [parts by weight]	2.0	2.0	2.0	2.0	2.0	2.0
Blowing agent component	Amasil 85% [parts by weight]	1.6	1.6	1.6	1.6	1.6	1.6
	Cyclopentane 95 [parts by weight]	3.5	10.3	10.3	0	0	11
	Pentane S 80/20 [parts by weight]		0	0	14.2	14.2	0
	Solstice® LBA [parts by weight]		6.2	6.2	0	0	6.8
	Opteon™ 1100 [parts by weight]	24.7					0
Proportion of Solstice LBA	mol of Solstice® LBA / (mol of Solstice® LBA + mol of cyclopentane 95)*100 [%]	0	24.4	24.4	0	0	24.6
Proportion of Opteon 1100	mol of Opteon™ 1100 / (mol of Opteon™ 1100 + mol of cyclopentane 95)*100 [%]	75.1	0	0	0	0	0
Properties	Hydrophobic fraction in components (b) - (g) [weight fraction]	0	2.0	8.5	0	8.5	2.4
	Thermal conductivity [mW/mK]	18.7	18.2	19.0	20.3	21.0	18.2
	Compressive strength [MPa]	0.148	0.150	0.095	0.170	0.130	0.145
	Foam quality aluminum foil underside [1-6]	3	1	1	4	1	1
	Foam quality aluminum sheet underside [1-6]	4	2	2	5	2	1

I: inventive

When using identical amounts of the identical blowing agent mixture it is apparent that in the double belt process too the use of the inventive polyol components having a small proportion of hydrophobic groups in components (b) - (g) (examples 20, 26 and 30) achieves a markedly reduced thermal conductivity and increased compressive strength of the produced foams relative to the polyol components having an elevated proportion of hydrophobic groups in

components (b) - (g) (example 27). However, the polyol components having a lower proportion of hydrophobic groups in components (b) – (g) do not show a continuous improvement in thermal conductivity with ever increasing proportions of halogenated olefins relative to cyclopentane 95. A minimum of thermal conductivities is achieved when the molar proportion of the halogenated olefins to the molar proportion of cyclopentane 95 is between 20 and 55 mol%. Surprisingly, a further increase in the molar proportion of the halogenated olefins markedly above 70 mol%, preferably 65 mol%, more preferably 60 mol% and in particular 55 mol%, in combination with the inventive polyol components results in an increase in the thermal conductivities of the produced foams. In addition, a higher proportion of both halogenated olefins above 70 mol% causes a deterioration in foam quality at the underside (examples 22, 23 and 25). In combination with pentane S80/20 too, the polyol components having a low proportion of hydrophobic groups in components (b) - (g) exhibit a markedly improved thermal conductivity relative to the noninventive polyol components (example 28 vs. example 29). However, compared to the noninventive reaction mixtures the use of pentane S 80/20 results in significantly poorer thermal conductivities and foam qualities at the underside of the different outer layers (example 28).

Claims

1. A process for producing polyisocyanurate foams, wherein

a) aromatic polyisocyanate,
b) isocyanate-reactive compounds comprising at least one polyetherol (b1) and/or polyesterol (b2), wherein the number-average content of isocyanate-reactive hydrogen atoms of components (b1) and (b2) is at least 1.7,
c) catalyst,
d) blowing agents,
e) flame retardants,
f) optionally auxiliary and additional substances,
g) optionally compounds having aliphatic hydrophobic groups and not falling under the definition of compounds (a) to (f)

are mixed to afford a reaction mixture and allowed to cure to afford a rigid polyisocyanurate foam, wherein

blowing agent (d) comprises at least one aliphatic halogenated hydrocarbon compound (d1) composed of 2 to 5 carbon atoms, at least one hydrogen atom and at least one fluorine and/or chlorine atom and compound (d1) comprises at least one carbon-carbon double bond, and a hydrocarbon compound having 4 to 8 carbon atoms (d2) and the molar proportion of halogenated hydrocarbon compound (d1) is between 20 and 60 mol% and the molar proportion of hydrocarbon compound (d2) is between 40 and 80 mol%, in each case based on the total content of the blowing agents (d1) and (d2),

and components (b) to (f) may comprise compounds having aliphatic hydrophobic groups and the content of aliphatic hydrophobic groups, based on the total weight of components (b) to (g), is 0% to 4.0% by weight and

the mixing to afford the reaction mixture is carried out at an isocyanate index of at least 240.

2. The process according to claim 1, wherein the hydrocarbon compound (d2) comprises at least 60 mol% of cycloaliphatic hydrocarbon compounds based on the total weight of the hydrocarbon compound (d2).

3. The process according to claim 1 or 2, wherein the hydrocarbon compound (d2) is selected from isomers of pentane.

4. The process according to any of claims 1 to 3, wherein the halogenated hydrocarbon compound (d1) is 1-chloro-3,3,3-trifluoropropene.

5. The process according to any of claims 1 to 4, wherein the blowing agent comprises formic acid.

6. The process according to any of claims 1 to 5, wherein the catalyst (c) comprises at least one amine catalyst having a tertiary amine group and at least one ammonium or alkali metal carboxylate catalyst.

7. The process according to claim 6, wherein the at least one amine catalyst having a tertiary amine group is selected from the group consisting of pentamethyldiethylenetriamine and bis(2-dimethylaminoethyl) ether and the at least one alkali metal carboxylate catalyst is selected from the group consisting of potassium formate, potassium acetate and potassium 2-ethylhexanoate.

8. The process according to any of claims 1 to 7, wherein the compounds having at least one isocyanate-reactive hydrogen atom (b) comprise 0% to 30% by weight of polyetherol (b1) and 70% to 100% by weight of polyesterol (b2), in each case based on the total weight of polyetherol (b1) and polyesterol (b2).

9. The process according to any of claims 1 to 8, wherein the polyether polyol (b1) is the reaction product of a starter molecule having a functionality of 2 to 4 with alkylene oxide, comprising ethylene oxide, and has a hydroxyl number of 150 to 300 mg KOH/g.

10. The process according to any of claims 1 to 9, wherein the polyester polyol (b2) was obtained using aromatic dicarboxylic acid or derivatives thereof.

11. The process according to any of claims 1 to 10, wherein the flame retardants (e) employed are exclusively halogen-free flame retardants.

12. The process according to any of claims 1 to 11, wherein the reaction mixture is applied to a continuously moving outer layer.

13. The process according to claim 12, wherein the application of the reaction mixture onto a continuously moving outer layer is carried out on a double belt line for production of sandwich elements.

14. The process according to any of claims 1 to 13, wherein premixtures comprising an isocyanate component (A) comprising aromatic polyisocyanate (a) and a polyol component (B) comprising isocyanate-reactive compounds (b) are employed in the production of the reaction mixture and all or some of the further components (c) to (g) are added to one of the components (A) or (B) in whole or in part.

15. The process according to any of claims 1 to 14, wherein physical blowing agents (d1) and (d2) are added to the reaction mixture in an extra stream.

16. A rigid polyisocyanurate foam obtainable by a process according to any of claims 1 to 15.