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(54) Title: POLYURETHANE RIGID FOAMS

(57) Abstract: The invention is directed to polyurethane rigid foams which can be prepared by reacting a) polyisocyanates with b) compounds having at least two hydrogen atoms which are reactive toward isocyanate groups in the presence of c) blowing agents and d) at least one flame retardant, wherein the compounds having at least two hydrogen atoms which are reactive toward isocyanate groups b) comprise at least one polyether polyol bi) and at least one polyester polyol bii) and the flame retardant d) comprises ex-
pandable graphite di).



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Polyurethane rigid foams

Description

- 5 The invention relates to polyurethane rigid foams with improved flame retardant properties, to a process for producing them by reacting polyisocyanates with compounds having at least two hydrogen atoms which are reactive toward isocyanate groups in the presence of at least one flame retardant, and a polyol component containing the flame retardant.
- 10 Rigid polyurethane foams have been known for a long time and are used predominantly for insulation against heat and cold, e.g. in refrigeration appliances, in hot water storages, in district heating pipes or in building and construction. The insulation of buildings is often carried out by means of spray technology. A summarizing overview of the production and use of rigid polyurethane foams may be found, for example, in the *Kunststoff-Handbuch*, Volume 7, Polyurethane, 1st
- 15 edition 1966, edited by Dr. R. Vieweg and Dr. A. Höchtlen, 2nd edition 1983, edited by Dr. Günter Oertel, and 3rd edition 1993, edited by Dr. Günter Oertel, Carl Hanser Verlag, Munich, Vienna.

Important requirements which rigid polyurethane foams have to meet are a low thermal conductivity, good flowability, satisfactory adhesion of the foam to the covering layers and good mechanical properties.

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A further challenge which is always present in the use of rigid polyurethane foams is improving the flame resistance of the foams. Flame retardants are usually added to the foam for this purpose. The addition of the flame retardants can alter the mechanical properties and the processing properties of the foams. Furthermore, it is desirable to restrict the use of flame retardants, in particular those based on halogens, especially bromine, in the production of rigid polyurethane foams for environmental reasons.

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It is known to use expandable graphite as flame retardant, in polyurethane foams. Expandable graphite is a very effective flame retardant and can be used in flexible foams as well as in rigid foams.

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WO 00/35999 describes a process for preparing polyurethane rigid foams using expandable graphite as a flame retardant. The expandable graphite is used in combination with other flame retardants, preferably phosphorus containing compounds, and in the presence of halogen atoms containing reactive compounds. The polyols used for preparing the polyurethane foams are polyether polyols.

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DE 199 12 988 describes flame retardant polyurethane foams containing filler materials. The filler material is a mixture of inorganic high temperature stable fillers, micro porous high temperature stable fillers and filler which can be thermal activated to expand, as expandable graphite. These fillers can be adhesive bonded by adhesives, preferably by organic phosphates, as ammonia phosphate or melamine phosphate.

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DE 103 10 006 describes halogen free flame retardant polyurethane rigid foams containing expandable graphite and ABC extinguishing powder.

5 The ABC extinguishing powder is described as a mixture of ammonia salts, as ammonia phosphate and ammonia carbonate, further it may contain inorganic fillers, as silica. The expandable graphite is mixed to the isocyanate component, the ABC extinguishing powder is mixed to the polyol component. There is no detailed description of the polyol component, the polyols used in the examples are polyether polyols.

10 It was the object of the present invention to provide polyurethane rigid foams with an improved flame retardation, which can be used for insulation of buildings. It must be possible to apply the foam by spray technology. The components, in particular the polyol component, should be stable. The foams should have a good adherence to the substrates, such as concrete, in particular when applied with the spray foam technology, and good mechanical properties.

15 The object has been achieved via the use of expandable graphite as flame retardant and a mixture of a polyether alcohol and a polyester alcohol as polyol component.

The invention therefore provides a rigid polyurethane foam obtainable by reacting
20 a) polyisocyanates with
b) compounds having at least two hydrogen atoms which are reactive toward isocyanate groups in the presence of
c) blowing agents and
d) at least one flame retardant,

25 wherein the compounds having at least two hydrogen atoms which are reactive toward isocyanate groups b) comprise at least one polyether polyol bi) and at least one polyester polyol bii) and the flame retardant d) comprises expandable graphite di).

30 The invention further provides a process for production of said rigid polyurethane foam. The invention further provides a polyol component for manufacturing said rigid polyurethane foam.

For the purposes of the invention, a rigid foam is preferably a foam to DIN 7726, i.e. the foam exhibits a compressive stress, or compressive strength to DIN 53421/DIN EN ISO 604, greater
35 than or equal to 80 kPa, preferably greater than or equal to 150 kPa, particularly preferably greater than or equal to 180 kPa, for 10% compression. The proportion of closed cells in the rigid foam is moreover greater than 85%, preferably greater than 90%, to DIN ISO 4590.

For the purposes of the invention, flame-retardant foam is a foam whose flame height is not
40 greater than 15 cm to EN ISO 11925-2 GB/T 8626-2007. Polyurethane rigid foams whose average burning leftover is larger than 150mm, whose minimum burning leftover is larger than 0mm, average smoke temperature is lower than 200°C according to DIN 4201 part 1 or GB/T 8625-2005; Polyurethane rigid foam whose smoke density grade is smaller than 75 according to GB/T 8627-2007. Polyurethane rigid foam fulfilled above criteria and be classified as hardly flammable
45 (B1 class) material.

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In a preferred embodiment of the invention the expandable graphite di) is used in an amount of 2 to 25 % by weight preferred 5-20 % by weight, more preferred 8-15 % by weight, based on the weight of component b, c) and d). The particle diameter of the expandable graphite is between
5 0.01 and 0.5 mm, preferably between 0.1 and 0.5 mm. The expansion rate of the expandable graphite when heating up to higher than 400°C is 150-500.

The expandable graphite di) can be used as only flame retardant. In a preferred embodiment the expandable graphite di) is used in combination with other flame retardants dii).

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The flame retardants dii) can be reactive with isocyanates or not reactive with isocyanates. In one embodiment the flame retardants dii) are phosphorus containing compounds.

Examples for these compounds are alkoxyated alkylphosphonic acids. These compounds are
15 reactive with isocyanates.

Another group of phosphorus containing compounds are low-molecular-weight, phosphorus-containing flame retardants which do not react with isocyanates. These compounds preferably have a molar mass below 300 g/mol, specifically below 300 g/mol, preferably below 200 g/mol,
20 and particularly preferably from 150 to 190 g/mol, and preferably have fewer than 4 phosphorus atoms in the molecule, especially fewer than 3, more especially fewer than 2, and especially 1 phosphorus atom. Preference is given to phosphonates and/or phosphates. Particular preference is given to phosphates and phosphonates selected from the group consisting of diethyl ethanephosphonate (DEEP), dimethyl propylphosphonate (DMPP), and triethyl phosphate (TEP), and
25 particular preference is given to those selected from the group consisting of diethyl ethanephosphonate (DEEP) and triethyl phosphate (TEP), diethyl ethanephosphonate (DEEP) particularly being used. The amount preferably used of these flame retardant is from 5 to 80, particularly preferably from 5 to 60, with particular preference from 10 to 50, percent by weight, based on the total weight of the flame retardant d).

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Another group of phosphorus containing compounds which do not react with isocyanates has a higher-molecular-weight, preferably with a molar mass above 300 g/mol. Preferably they have at least 1 phosphorus atom in the molecule. Preference is given to phosphonates and/or phosphates, especially phosphates. Preferred examples for these are diphenyl cresyl phosphate (DPC) and/or
35 triphenyl phosphate, in particular diphenyl cresyl phosphate. The amount preferably used of these compounds is from 0.5 to 80, particularly preferably from 10 to 70, with particular preference from 20 to 60 or from 30 to 50, and in particular from 35 to 45, percent by weight, based on the total weight of the flame retardant d).

Other examples for phosphorus containing compounds are ammonium phosphate and ammonium polyphosphate.

In a preferred embodiment of the invention the phosphorus containing flame retardant dii) is selected from the group, containing diethyl ethylphosphonate, dimethyl propylphosphonate, triethyl
45 phosphate and tris(2-chlorisopropyl)phosphate.

Other possible flame retardants dii) are melamine and reaction products of melamine.

5 In another embodiment of the invention the additional flame retardant are halogen atoms, preferred chlorine and/or bromine, more preferred bromine atoms containing compounds. Examples are chloralkylphosphates, bromine neopentylethane, dibromine neopentylethane, brominephthalic acid esters, dibromine propane.

10 In another embodiment of the invention the flame retardant dii) is a phosphorus and halogen containing compound. Examples are chloroalkyl phosphates, preferred is tris(2-chloroisopropyl) phosphate.

The flame retardants dii) can be used as a single component. In a preferred embodiment of the invention the flame retardant dii) is a mixture of at least two components.

15 In one embodiment the flame retardant dii) is a mixture of at least one phosphorus containing flame retardant and at least one halogen containing flame retardant. In a preferred embodiment the flame retardant dii) is a mixture of at least one phosphorus containing flame retardant and at least one phosphorus halogen containing flame retardant.

20 The flame retardants dii) are preferably used in an amount of 5 to 40 % by weight, in particular from 5 to 25 % by weight, based on the weight of components b), c) and d).

25 The polyurethane rigid foams are produced via reaction of polyisocyanates a) with compounds having at least two hydrogen atoms which are reactive toward isocyanate groups b), in the presence of blowing agents, the flame retardants d), catalysts, and conventional auxiliaries and/or additives. Details of the starting materials used are as follows.

30 Organic polyisocyanates that can be used are any of the known organic di- and polyisocyanates, preferably aromatic polyfunctional isocyanates.

35 Individual examples which may be mentioned are tolylene 2,4 and 2,6-diisocyanate (TDI) and the corresponding isomer mixtures, diphenylmethane 4,4', 2,4' and 2,2' diisocyanate (MDI) and the corresponding isomer mixtures, mixtures composed of diphenylmethane 4,4'- and 2,4'- diisocyanates, polyphenyl polymethylene polyisocyanates, mixtures composed of diphenylmethane 4,4'-, 2,4'- and 2,2'- diisocyanates and of polyphenyl polymethylene polyisocyanates (crude MDI) and mixtures composed of crude MDI and of tolylene diisocyanates. The organic di- and polyisocyanates may be used individually or in the form of mixtures.

40 Use is also often made of what are known as modified polyfunctional isocyanates, i.e. products obtained via chemical reaction of organic di and/or polyisocyanates. By way of example, mention may be made of di- and/or polyisocyanates containing uretdione groups, carbamate groups, isocyanurate groups, carbodiimide groups, allophanate groups and/or urethane groups. The modified polyisocyanates may, if appropriate, be mixed with one another or with unmodified

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organic polyisocyanates, such as diphenylmethane 2,4'- or 4,4'-diisocyanate, crude MDI, or tolylene 2,4- and/or 2,6-diisocyanate.

5 Use may also be made here of reaction products of polyfunctional isocyanates with polyhydric polyols, or else of mixtures of these with other di- and polyisocyanates.

An organic polyisocyanate which has proven particularly successful is crude MDI, in particular with NCO content of from 29 to 33% by weight and a viscosity at 25°C in the range from 150 to 1000 mPas.

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The polyester polyols bii) used are mostly prepared via condensation of polyhydric alcohols with polybasic carboxylic acids having from 2 to 12 carbon atoms.

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In one embodiment, the polyhydric alcohols are diols, having from 2 to 12 carbon atoms, preferably from 2 to 6 carbon atoms, e.g. ethylene glycol, propylene glycol, diethylene glycol, dipropylene glycol, butane diol-1,4 or butane diol-1,3. It is possible to use minor amounts of 3- or more functional alcohols, as glycerol or trimethylol propane.

20

The polybasic carboxylic acids are e.g. succinic acid, glutaric acid, adipic acid, suberic acid, azelaic acid, sebacic acid, decanedicarboxylic acid, maleic acid, fumaric acid, or preferably phthalic acid, isophthalic acid, terephthalic acid, or the isomeric naphthalenedicarboxylic acids. Most preferred are adipic acid, phthalic acid, isophthalic acid, and terephthalic acid.

25

In another embodiment of the invention the polyester polyols bii) can be prepared by reaction of phthalates, preferred polyethylene terephthalates, with alcohols.

The polyester polyols bii) preferably have preferred a hydroxyl number of 160 to 750 mg KOH/g. The polyester alcohols bii) used mostly have a functionality of from 2 to 4.

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In a preferred embodiment of the invention the polyester polyol bii) is based on at least one aromatic compound, mostly of an aromatic carboxylic acid.

In a particularly preferred embodiment the polyester polyol bii) is the esterification product of

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b1) 10 to 70 mol-% of a dicarboxylic acid composition containing

b11) 50 to 100 mol-% of one or more aromatic dicarboxylic acids or derivatives thereof,

b12) 0 to 50 mol-% of one or more aliphatic dicarboxylic acids or derivatives thereof,

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b2) 2 to 30 mol-% of one or more fatty acids or derivatives thereof,

b3) 10 to 70 mol-% of one or more aliphatic or cycloaliphatic diols having 2 to 18 carbon atoms or alkoxylates thereof,

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b4) 2 to 50 mol-% of a polyetherpolyol having a functionality of ≥ 2 , obtainable by the alkoxylation of a polyol.

5 Preferably, component b11) contains at least one compound selected from the group consisting of terephthalic acid, dimethylterephthalate (TMP), polyethyleneterephthalate (PET), phthalic acid, phthalic acid anhydride and isophthalic acid. In particular, component b11) contains at least one compound selected from the group consisting of terephthalic acid, dimethylterephthalate, polyethyleneterephthalate and phthalic acid anhydride. Very particularly preferred, component b11) contains phthalic acid anhydride, terephthalic acid or mixtures thereof.

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In general, the aliphatic dicarboxylic acids or derivatives thereof are present in the dicarboxylic acid composition in an amount of from 0 to 30 mol-%, preferable from 0 to 10 mol-%. In a particularly preferred embodiment, the dicarboxylic acid composition b11) contains no aliphatic dicarboxylic acids or derivatives thereof and consists of 100 mol-% of one or more aromatic dicarboxylic acids or derivatives thereof.

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Preferably, component b2) is present in an amount of from 3 to 20 mol-%, more preferably from 5 to 18 mol-%.

20 Preferably, component b3) is present in an amount of from 20 to 60 mol-%, more preferably from 25 to 55 mol-%, in particular from 30 to 45 mol-%.

Preferably, component b4) is present in an amount of from 2 to 40 mol-%, more preferably from 8 to 35 mol-%, particularly preferred from 15 to 25 mol-%.

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In a preferred embodiment of the invention a fatty acid or a derivative thereof is selected from the group consisting of castor oil, palm oil, polyhydroxy fatty acids, ricinoleic acid, hydroxyl-modified oils, grapeseed oil, black cumin oil, pumpkin kernel oil, borage seed oil, soybean oil, wheat germ oil, rapeseed oil, sunflower oil, peanut oil, apricot kernel oil, pistachio oil, almond oil, olive oil, macadamia nut oil, avocado oil, sea buckthorn oil, sesame oil, hemp oil, hazelnut oil, primula oil, wild rose oil, safflower oil, walnut oil, hydroxyl-modified fatty acids and fatty acid esters based on myristoleic acid, palmitoleic acid, stearic acid, palmitic acid, oleic acid, vaccenic acid, petroselinic acid, gadoleic acid, erucic acid, nervonic acid, linoleic acid, α - and γ -linolenic acid, stearidonic acid, arachidonic acid, timnodonic acid, clupanodonic acid and

30
35 cervonic acid.

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In a particularly preferred embodiment, the fatty acid or derivative thereof b2) is selected from oleic acid, bio-diesel oil, soybean oil, grapeseed oil and beef tallow (suet), in particular oleic acid.

Very particularly preferred, component b2) does not contain any triglyceride. Particularly preferred, components b2) are the fatty acids as such or the alkyl monoesters thereof or mixtures of fatty acids and alkyl monoesters thereof.

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Preferably, the aliphatic or cycloaliphatic diol b3) is selected from the group consisting of ethylene glycol, diethylene glycol, or propylene glycol, propane diol-1,3, butane diol-1,4, pentane diol-1,5, hexane diol-1,6, 2-methyl-propane diol-1,3 and 3-methyl-pentane diol-1,5, and alkoxylates thereof. Particularly preferred are monoethylene glycol and diethylene glycol, in particular diethylene glycol.

Preferably, the polyether polyol b4) is selected from the group consisting of polyethylene glycol (PEG) and the reaction product of glycerine, trimethylol propane (TMP) or pentaerythritol with an alkylene oxide.

In particular a polyether polyol b4) having a functionality of ≥ 2 , obtained by the alkoxylation of a polyol having a functionality of ≥ 3 , is used. Preferably, the functionality of the polyether polyol b4) is ≥ 2.7 , more preferably ≥ 2.9 . In general, the functionality of the polyether polyol is ≤ 6 , more preferably ≤ 5 , particularly preferred ≤ 4 .

In one embodiment, the polyether polyol b4) is obtained by reacting a polyol having a functionality of > 2 with ethylene oxide and/or propylene oxide, in particular ethylene oxide.

In a further preferred embodiment, the polyether polyol b4) is obtained by alkoxylation, preferably ethoxylation, of a polyol selected from the group consisting of sorbitol, trimethylolpropane, glycerine, polyglycerine and mixtures thereof. Particularly preferred polyols are selected from the group consisting of trimethylol propane and glycerine.

The polyether polyols b4) are prepared by known methods, for example by anionic polymerization of propylene oxide or ethylene oxide, preferably ethylene oxide, using alkali metal hydroxides or alkali metal alkoxides or amine catalysts such as dimethylethanol amine and imidazole, in particular imidazole.

In a very preferred embodiment the polyether polyol b4) consists of the reaction product of glycerine with ethylene oxide and/or propylene oxide, particularly ethylene oxide. In a further very preferred embodiment the polyether polyol b4) consists of the reaction product of trimethylolpropane with ethylene oxide and/or propylene oxide, in particular ethylene oxide.

Preferably, the polyether polyol b4) has an OH number of from 150 to 1250 mg KOH/g, more preferably from 300 to 950 mg KOH/g, and particularly preferred from 500 to 800 mg KOH/g.

In a further preferred embodiment at least 200 mmol, preferably at least 400 mmol, more preferably at least 600 mmol, particularly preferred at least 800 mmol, and in particular at least 1000 mmol of component b4) are used per kg of component B.

In a very particularly preferred embodiment of the invention, the polyether polyol b4) is a reaction product of dimethylol propane or glycerine, preferably glycerine, with ethylene oxide, having an OH number of from 500 to 800 mgKOH/g, preferably 500 to 600 mg KOH/g, obtained by alkoxylation using imidazole as catalyst.

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In a further particularly preferred embodiment, the polyether polyol b4) is the reaction product of trimethylol propane or glycerine, preferably glycerine, with ethylene oxide, having an OH number of from 500 to 800 mg KOH/g, preferably 500 to 650 mg KOH/g, obtained by alkoxylation using imidazole as catalyst, the aliphatic or cycloaliphatic diol b3) is diethylene glycol and the fatty acid or derivative thereof b2) is oleic acid.

Polyether polyols bi) particularly used are those prepared by known processes, e.g. via anionic polymerization of alkylene oxides onto H-functional starter substances in the presence of catalysts, preferably alkali metal hydroxides or double-metal-cyanide catalysts (DMC catalysts).

Alkylene oxides used are mostly ethylene oxide or propylene oxide, or else tetrahydrofuran, various butylene oxides, or styrene oxide, and preferably pure propylene 1,2-oxide. The alkylene oxides can be used alone, in alternating succession, or in the form of a mixture.

Starter substances particularly used are compounds having at least 2, preferably from 2 to 8 hydroxy groups or having at least two primary amino groups in the molecule.

Starter substances used and having at least 2, preferably from 2 to 8, hydroxy groups in the molecule are preferably trimethylolpropane, glycerol, pentaerythritol, sugar compounds, such as glucose, sorbitol, mannitol, and sucrose, polyhydric phenols, resols, e.g. oligomeric condensates composed of phenol and formaldehyde, and Mannich condensates composed of phenols, of formaldehyde, and of dialkanolamines, and also melamine.

Starter substances used and having at least two primary amino groups in the molecule are preferably aromatic di and/or polyamines, such as phenylenediamines, 2,3-, 2,4-, 3,4-, and 2,6-tolylenediamine, and 4,4'-, 2,4'-, and 2,2' diaminodiphenylmethane, and also aliphatic di- and polyamines, such as ethylenediamine.

The preferred functionality of the polyether polyols bi) is from 2 to 8 and their preferred hydroxy numbers are from 25 to 800 mg KOH/g, in particular from 150 to 570 mg KOH/g.

In a preferred embodiment of the invention the polyether polyol bi) has a functionality of 2 to 3, most preferred of 2. The hydroxyl numbers of these polyether polyols are in the range of 110 to 570 mgKOH/g.

In a particularly preferred embodiment the polyether polyol bi) is polyethylene glycol.

The polyether polyol bi) is used preferably in an amount of 3 to 20% by weight, based on the weight of components b), c) and d)1

Other compounds having at least two hydrogen atoms reactive toward isocyanate are crosslinking agents and chain extenders which may be used concomitantly, if appropriate. Addition of di-functional chain extenders, trifunctional or higher-functionality crosslinking agents, or else, if appropriate, mixtures of these can prove advantageous for modification of mechanical properties.

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Chain extenders and/or crosslinking agents preferably used are alkanolamines and in particular diols and/or triols with molecular weights below 400, preferably from 60 to 300.

5 In a preferred embodiment of the invention the polyester alcohol bi) is used in an amount of 30 to 60 % by weight, preferably 32 to 48 % by weight, the polyether alcohol bi) is used in an amount of 3 to 20 % by weight, based on the weight of components b), c) and d).

10 Blowing agents which can be used are chemical blowing agents, such as water and/or formic acid, these reacting with isocyanate groups with elimination of carbon dioxide and, respectively, carbon dioxide and carbon monoxide. The compounds known as physical blowing agents can preferably also be used in combination with water or preferably instead of water. These are compounds inert with respect to the starting components, mostly liquid at room temperature, and evaporating under the conditions of the urethane reaction. The boiling point of these compounds is preferably below 50°C. Among the physical blowing agents are also compounds which are gaseous at room tem-
15 perature and which are introduced or dissolved into the starting components under pressure, examples being carbon dioxide, low-boiling alkanes, and fluoroalkanes.

The blowing agents are mostly selected from the group consisting of alkanes, formic acid and and/or cycloalkanes having at least 4 carbon atoms, dialkyl ethers, esters, ketones, acetals,
20 fluoroalkanes having from 1 to 8 carbon atoms, and tetraalkylsilanes having from 1 to 3 carbon atoms in the alkyl chain, in particular tetramethylsilane.

Examples which may be mentioned are propane, n-butane, isobutane, cyclobutane, n pentane, isopentane, cyclopentane, cyclohexane, dimethyl ether, methyl ethyl ether, methyl butyl ether,
25 methyl formate, acetone, and also fluoroalkanes which can be degraded in the troposphere and therefore do not damage the ozone layer, e.g. trifluoromethane, difluoromethane, 1,1,1,3,3-pentafluorobutane, 1,1,1,3,3- pentafluoropropane, 1,1,1,2-tetrafluoroethane, difluoroethane, and heptafluoropropane. The physical blowing agents mentioned may be used alone or in any desired combinations with one another.

30 The usual amount used of the blowing agent component is from 1 to 55% by weight, preferably from 1 to 40% by weight, particularly preferably from 2 to 30% by weight, and in particular from 5 to 25% by weight, based on the total weight of the following components: polyol, blowing agent, catalyst system, and any foam stabilizers, flame retardants, and other additives.

35 The amount of water is preferred in a range of 0.1 to 2.0 % by weight, based on the weight of the components b), c) and d).

40 Catalysts used in particular comprise compounds which markedly accelerate the reaction of the isocyanate groups with the groups reactive with isocyanate groups. Examples of these catalysts are basic amines, e.g. secondary aliphatic amines, imidazoles, amidines, and also alkanolamines, Lewis acids, or organometallic compounds, in particular those based on tin. Catalyst systems composed of a mixture of various catalysts can also be used.

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If isocyanurate groups are to be incorporated in the rigid foam, specific catalysts are needed. Iso-
cyanurate catalysts usually used are metal carboxylates, in particular potassium acetate and its
solutions. The catalysts may be used alone or in any desired mixture with one another, as required.
The system should include catalysts, which make a balance of blowing, gel, and trimerization
5 reaction rates to give the spray chemical system a proper foaming speed thus to improve the foam
final properties.

Auxiliaries and/or additives which may be used are substances known per se for this purpose, e.g.
surfactants, foam stabilizers, cell regulators, fillers, pigments, dyes, antioxidants, hydrolysis sta-
10 bilizers, antistatic agents, fungistatic agents, and bacteriostatic agents.

Further details concerning the starting materials used for carrying out the inventive process,
blowing agents, catalysts, and also auxiliaries and/or additives are found by way of example in
Kunststoffhandbuch [Plastics Handbook], volume 7, "Polyurethane" ["Polyurethanes"] Carl-
15 Hanser-Verlag Munich, 1st edition, 1966, 2nd edition, 1983, and 3rd edition, 1993.

To produce the polyurethane rigid foams the polyisocyanates a) and the compounds having at least
two hydrogen atoms reactive toward isocyanate groups b) are reacted in amounts such that the
isocyanate index for the polyurethane foams is in the range from 100 to 400, preferably from 150 to
20 350.

The rigid polyurethane foams can be produced batchwise or continuously with the aid of known
mixing apparatuses. Known mixing apparatuses can be used to mix the starting components.

25 The inventive rigid isocyanate-based foams a) are usually produced by the two-component proc-
ess. In this process, the compounds having at least two hydrogen atoms reactive toward isocy-
anate groups are mixed with the blowing agents, with the catalysts, and also with the other
auxiliaries and/or additives to give what is known as a polyol component, and this is reacted with
the polyisocyanates or mixtures composed of the polyisocyanates and, if appropriate, blowing
30 agents, also termed the isocyanate component.

The starting components are usually mixed at a temperature of from 5 to 70°C, preferably from 20
to 65°C. The reaction mixture may be mixed using high or low-pressure feed machinery.

35 In a preferred embodiment of the invention the foam is produced via spray foam technology. This
technology is well known and for instance described in the Kunststoffhandbuch [Plastics
Handbook], volume 7, "Polyurethane" ["Polyurethanes"] Carl-Hanser-Verlag Munich, 1st edition,
1966, 2nd edition, 1983, and 3rd edition, 1993, pages 333 to 335. The liquid components a) and b)
are combined in a nozzle and sprayed on the area which shall be covered with the foam. Then the
40 foam hardens on the surface.

The density of the rigid foams produced is preferably from 10 to 400 kg/m³, preferably from 20 to
200 kg/m³, in particular from 30 to 100 kg/m³.

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The foam of the invention, in particular the spray foam have good mechanical properties and satisfied GB/T50404.

5 The flame height of the foams is not preferred greater than 15 cm according to EN ISO 11925-2 or GB/T 8626-2007.

10 The average burning leftover of the polyurethane rigid foam is usually larger than 150 mm, whose minimum burning leftover is larger than 0mm, the average smoke temperature is lower than 200°C according to DIN 4201 part 1 or GB/T 8625-2005.

The smoke density grade of the polyurethane rigid foam is usually smaller than 75 according to GB/T 8627-2007.

Examples 1 to 5 and Comparative Example C1:

15 The following components were used:

Polyetherol 1: polyethylene oxide - adduct of ethylene diamine, OH number 470

20 Polyetherol 2: ethylene oxide/propylene oxide – adduct of vicinal toluylene diamine, OH number 405, having an EO content of 15.3 wt-%;

Polyetherol 3: polyethylene glycol, OH number 190;

25 Polyesterol 1: aromatic polyester polyol based on phthalate and diethylene glycol, OH number 40 ;

Polyesterol 2: aromatic polyester polyol based on phthalate and diethylene glycol, OH number 175;

TEP: triethylphosphate;

30 TCCP: tris(chlorisopropyl)phosphate;

APP: ammoniumpolyphosphate;

35 Surfactant 1: polysiloxane - type surfactant (DC193 from Air Product);

Surfactant 2: non silicone-type surfactant containing N-vinyl-2-pyrrolidone (LK443 from Air Product);

Catalyst 1: tin catalyst (Dabco 120 from Air product);

40 Catalyst 2: amine catalyst (PT303 from Air product);

Catalyst 3: amine catalyst (PT304 from Air product);

45 Catalyst 4: potassium acetate in monoethylene glycol;

Blowing agent: 1,1-dichloro-1-fluoroethane;

Expandable graphite A has an average particle size of 0.18 mm;

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Expandable graphite B has an average particle size of 0.15 mm;

Expandable graphite C has an average particle size of 0.17 mm.

- 10 Expandable graphite is made by immersing natural flake graphite into a bath of chromic acid, then into concentrated sulfuric acid, followed by drying and milling to different sizes.

The compositions (in wt-%) of examples 1-5 and comparative example C1 are summarized in Table 1.

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Table 1

Example	1	2	3	4	5	C1
Expandable Graphite	A	B	B	A	C	
Spray Temperature [°C]	50	60	60	50	50	40
Polyetherol 1			4,90			
Polyesterol 1			34,10			
APP					7,00	
Expanded Graphite	16,38	10,79	13,04	25,48	15,00	
Polyetherol 2			9,80	0,00	0,00	
Polyesterol 2	44,44	46,62		38,52	41,77	50,12
Polyetherol 3	4,27	4,48		3,70	4,02	
TEP	4,27	4,48		5,93	4,02	
TCPP	4,27	4,48	12,25	3,70	4,02	19,76
Surfactant 1	0,43	0,45	0,49	0,37	0,40	0,54
Surfactant 2	0,85	0,90	0,49	0,74	0,80	0,54
Catalyst 1	0,24	0,25	0,24	0,22	0,22	0,27
Catalyst 2	1,28	1,34	1,43	1,11	1,20	1,45
Catalyst 3	2,36	2,47	2,39	2,15	2,27	2,65
Catalyst 4	1,37	1,43		1,19	1,29	1,54
Water	0,34	0,33	0,43	0,30	0,32	0,48
Blowing agent	19,49	21,97	20,43	16,59	17,67	22,65
Total	100	100	100	100	100	100

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The polyol component A according to Table 1 and the isocyanate component B were mixed at the respective temperature indicated in Table 1 and sprayed to a surface. The isocyanate component B was polymeric MDI with a NCO content of 31.2 % by weight. The "mix ratio" is the mass ratio of the isocyanate component to the polyol component. The calculated NCO index is given in Table 2.

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The foam properties are summarized in Table 2. The Oxygen Index is the lowest concentration in the atmosphere, expressed in percent, that will support sustained combustion of the material.

10 Table 2

Example	1	2	3	4	5	C1
mix ratio	85	100	100	89	90	95
calculated NCO index	314,14	357,39	242,76	379,53	353,94	336,23
Compressive strength [Mpa] (DIN EN826)	40.5/ 0.175	0.20/ 43.5	37.9/ 0.203	45.1/ 0.222	46.4/ 0.246	0.127/ 38.1
Adhesion Strength [Mpa] (DIN53292)		0,15	0,24		0,13	0,11
Tensile Strength [Mpa] (DIN53292)	0,42	0,32	0,27	0,34	0,42	0,08
Close cell content [%] (DIN ISO4590)	86,00	88,00	91,00	90,00	90,00	80,00
Thermal conductivity [mW/m*K] (ASTM C518)	21,26	21,26	20,31	21,51	21,67	23,03
Water absorption [%]	2,30	2,20	1,80	2,00	6,00	2,00
Oxygen Index		33,60				28,20
B1 test achieved (DIN4102-1)	yes	yes	no	yes	yes	no
B2-fire test (DIN4102 B2)	4,00	4,50	6,00	4,00	3,00	5,00
Dimensional Stability at 30°C Length [%] (DIN ISO2796)	0,20	0,30	0,00	0,10	0,10	0,10
Width [%] (DIN ISO2796)	0,20	0,30	0,00	0,10	0,40	0,60

Example	1	2	3	4	5	C1
Thickness [%] (DIN ISO2796)	0,40	0,10	1,00	0,50	0,00	0,50
Dimensional Stability at 80°C Length [%] (DIN ISO2796)	2,00	0,20	0,10	0,50	1,50	12,50
Width [%] (DIN ISO2796)	3,30	0,10	0,00	0,60	0,50	13,00
Thickness [%] (DIN ISO2796)	1,00	0,30	1,50	0,60	0,90	1,00

Example 6

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A polyol component and an isocyanate component are mixed at a temperature of 60 °C and sprayed to a surface.

10 The starting materials of the polyol component are listed in Table 3, the foam properties are listed in Table 4. The isocyanate used was polymeric MDI with an NCO content of 31.2 % by weight at a calculated NCO index of 357.4.

Table 3

Component	Parts by weight
Expandable Graphite	20
Polyester Polyol A	30
Polyether Polyol B	8.52
Phosphor containing flame retardant	10
surfactant	1.31
Gel Catalyst	0.24
Blowing catalyst	1.31
Trimerization catalyst	3.79
Water	0.52
HCFC 141b HF	21.35
Total	100.00

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Polyester Polyol A: Aromatic polyester polyol with an OH number of 175 mg KOH/g and a functionality of 2;

20 Polyether Polyol B: Polyether polyol with an OH value 190 mg KOH/g and a functionality of 2, started with ethylene glycol.

Table 4

Parameter	Example 6
Foam Core density [kg/m ³]	37.4
compressive strength [Mpa]	0.167
Tensile Strength [Mpa]	0.4
thermal conductivity [mw/m*k]	20.63
water absorption [%]	2.4
B2-fire test	6
Dimensional Stability at 80°C length [%]	-0.3
Width [%]	0
Thickness [%]	0
Dimensional Stability at 80°C length [%]	-0.1
width [%]	0.2
thickness [%]	-0.9
Adhesion with concrete [Mpa]	0.15
B1 class (hardly flammable)	achieved

Claims

1. Polyurethane rigid foams which can be prepared by reacting
 - a) polyisocyanates with
 - b) compounds having at least two hydrogen atoms which are reactive toward isocyanate groups in the presence of
 - c) blowing agents and
 - d) at least one flame retardant,
- wherein the compounds having at least two hydrogen atoms which are reactive toward isocyanate groups b) comprise at least one polyether polyol bi) and at least one polyester polyol bii) and the flame retardant d) comprises expandable graphite di).
2. Polyurethane rigid foams according to claim 1, wherein the expandable graphite di) is used in an amount of 2 to 25 % by weight, based on the weight of components b), c) and d).
3. Polyurethane rigid foams according to claim 1 or 2, wherein the polyether polyol bi) is used in an amount of 3 to 20 % by weight, based on the weight of components b), c) and d).
4. Polyurethane rigid foams according to any one of claims 1 to 3, wherein the polyester polyol bii) is used in an amount of 30-60 % by weight, based on the weight of components b), c) and d) .
5. Polyurethane rigid foams according to any one of claims 1 to 4, wherein the polyether polyol bi) has a hydroxyl number of 110 to 570 mg KOH/g.
6. Polyurethane rigid foams according to any one of claims 1 to 5, wherein the polyether polyol bi) has a functionality of 2 to 3.
7. Polyurethane rigid foams according to any one of claims 1 to 6, wherein the polyester polyol bii) has a hydroxyl number of 160 to 750 mg KOH/g.
8. Polyurethane rigid foams according to any one of claims 1 to 7, wherein the polyester polyol bii) has a functionality of 2 to 4.
9. Polyurethane rigid foams according to any one of claims 1 to 8, wherein the polyester polyol bii) is the esterification product of
 - b1) 10 to 70 mol-% of a dicarboxylic acid composition containing
 - b11) 50 to 100 mol-% of one or more aromatic dicarboxylic acids or derivatives thereof,
 - b12) 0 to 50 mol-% of one or more aliphatic dicarboxylic acids or derivatives thereof,

- b2) 2 to 30 mol-% of one or more fatty acids or derivatives thereof,
- b3) 10 to 70 mol-% of one or more aliphatic or cycloaliphatic diols having 2 to 18 carbon atoms or alkoxylates thereof,
- b4) 2 to 50 mol-% of a polyether polyol having a functionality of ≥ 2 , obtainable by the alkoxylation of a polyol.
10. Polyurethane rigid foams according to any one of claims 1 to 9, wherein the flame retardant d) comprises an additional component dii).
11. Polyurethane rigid foams according to claim 10, wherein the additional component dii) is a phosphorus containing component.
12. Polyurethane rigid foams according to claim 11, wherein the additional component dii) is selected from the group consisting of diethyl ethylphosphonate, dimethyl propylphosphonate, triethyl phosphate and tris(2-chloroisopropyl)phosphate.
13. Polyurethane rigid foams according to any one of claims 1 to 12 whose flame height is not greater than 15 cm according to EN ISO 11925-2 or GB/T 8626-2007.
14. Polyurethane rigid foams according to any one of claims 1 to 13 whose average burning leftover is larger than 150 mm, whose minimum burning leftover is larger than 0 mm, average smoke temperature is lower than 200 °C according to DIN 4201 part 1 or GB/T 8625-2005.
15. Polyurethane rigid foams according to any one of claims 1 to 14 whose smoke density grade is smaller than 75 according to GB/T 8627-2007.
16. A process for preparing polyurethane rigid foams of any one of claims 1 to 15, wherein the flame retardant d) is mixed to component b).
17. A process according to claim 16, wherein the foam is prepared by means of the spray foam process.
18. A polyol component, comprising
- bi) a polyether polyol,
- bii) a polyester polyol,
- c) a blowing agent,
- d) a flame retardant d),
- wherein the flame retardant d) comprises expandable graphite.

19. A polyol component according to claim 18, wherein the flame retardant d) comprises as an additional component dii) a phosphorous containing component.
- 5 20. A polyol component according to claim 18 or 19, wherein the additional component dii) is selected from the group consisting of diethyl ethylphosphonate, dimethyl propylphosphonate, triethyl phosphate and tris(2-chlorisopropyl)phosphate.
- 10 21. A polyol component according to any one of claims 18 to 20, wherein the polyester polyol bii) is the esterification product of
- b1) 10 to 70 mol-% of a dicarboxylic acid composition containing
- 15 b11) 50 to 100 mol-% of one or more aromatic dicarboxylic acids or derivatives thereof,
- b12) 0 to 50 mol-% of one or more aliphatic dicarboxylic acids or derivatives thereof,
- b2) 2 to 30 mol-% of one or more fatty acids or derivatives thereof,
- 20 b3) 10 to 70 mol-% of one or more aliphatic or cycloaliphatic diols having 2 to 18 carbon atoms or alkoxylates thereof,
- 25 b4) 2 to 50 mol-% of a polyetherpolyol having a functionality of ≥ 2 , obtainable by the alkoxylation of a polyol.
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