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ABSTRACT

The present invention relates to a process for producing an open-cell rigid polyurethane foam. Said foams can contain, besides urethane groups (PUR), also isocyanurate groups (PIR).

POLYURETHANE FOAM AND PROCESS FOR PRODUCING SAME

[0001] The present invention relates to a process for producing a rigid open-celled polyurethane foam. In addition to urethane groups (PUR) the foams may also contain isocyanurate groups (PIR). In the present application unless otherwise stated the description rigid PUR/PIR foam is to be understood as meaning not only rigid foams comprising substantially urethane groups but also rigid foams containing both urethane groups and isocyanurate groups.

[0002] Rigid PUR/PIR foams have long been known. Thermal insulation is a substantial area of application. The use of vacuum insulation panels (VIP) containing rigid PUR/PIR foams for insulation is increasing in importance. Foam quality has a decisive influence on the insulation properties of foams used for vacuum insulation: on the one hand a very small cell size and very homogeneous cell sizes are advantageous and on the other hand a high proportion of open cells is advantageous to allow the foam to be readily evacuated.

[0003] The production of open-celled rigid PUR/PIR foams is likewise known in principle. Certain cell-opening substances are generally added to the reaction mixture to bring about an opening of the cells during the foaming process.

[0004] Thus U.S. Pat. No. 5,350,777 describes the use of alkaline earth metal salts of long-chain fatty acids as cell openers.

[0005] EP-A 498 628 A discloses the production of rigid open-celled foams by way of a thermally activated blowing agent. This process has the disadvantage that the foam cells are opened merely where a minimum temperature is exceeded in the course of the foam process and the obtained foams therefore do not exhibit a uniformly high open-cell content over the entire foam-filled volume.

[0006] DE-A 43 03 809 describes a process for producing rigid foams having an elevated open-cell content where the cell-opening effect of a liquid polyolefin addition is utilized. This process has the disadvantage of a narrow scope of application and also that inexact metering of the polyolefin addition rapidly leads to cell coarsening.

[0007] U.S. Pat. Nos. 5,250,579 and 5,312,846 disclose the cell-opening effect of substances having a surface tension of less than 23 mJ/m². However, these substances have the disadvantage that they contain organically bonded halogen.

[0008] U.S. Pat. No. 5,889,067 discloses a process for producing an open-celled rigid polyurethane foam which comprises the production of the rigid polyurethane foam from polyol with a liquid blowing agent selected from the group consisting of hydrocarbons, hydrofluoroalkanes, perfluoroalkanes, mixtures of these blowing agents with one another or with water by addition of a monohydric fatty alcohol which has a good solubility in the hydrocarbons and serves as a cell-opener and of a foam stabilizer which forms a very small cell in the presence of an isocyanate trimer catalyst and an organic isocyanate. The resulting open-celled rigid polyurethane foam has a cell size of less than about 95 µm and is suitable for example for use as a core material in a vacuum insulation panel.

[0009] EP 905 159 A and EP 905 158 A disclose processes for producing open-celled rigid polyurethane foams which preferably employ water in combination with hydrocarbons or hydrofluorocarbons as a blowing agent. The polyol for-

mulations are said to contain 0.1-80% by weight of polyester alcohols which are preferably reaction products of ricinoleic acid and/or castor oil and/or tall oil fatty acid with polyfunctional alcohols. These components are said to act as emulsifiers for non-halogenated blowing agents. In the examples the claimed polyols are used to produce both open-celled and closed-celled foams, wherein the open-cell content is dependent on the presence of additives known as cell openers. While the cells of the obtained foams are described as fine-celled, according to the legend "very fine-celled" is to be understood as meaning a cell size range of 180-250 µm. In addition, nothing is said about the homogeneity of the cell size distribution.

[0010] EP 2 072 548 A describes a process for producing open-celled rigid PUR/PIR foams having an isocyanate index in the range between 150-400 by reaction of polyisocyanates with polyols having a functionality in the range from 2.5 to 5.5 and a hydroxyl number in the range of 200-400 mg KOH/g in the presence of a blowing agent mixture of water and at least one physical blowing agent is. However, the open-cell content of the foams in the examples is obtained primarily with high proportions of cell-opening substances.

[0011] In the production of rigid PUR/PIR foams a polyol component also containing a blowing agent is reacted with an isocyanate. The reaction of isocyanate with water forms carbon dioxide, which also acts as a blowing agent. It is also known to add CO₂ to the polyol component or to the reaction mixture as a blowing agent.

[0012] An effect on fine-cell content and open-cell content was also found for the use of supercritical CO₂ in combination with certain process steps and components:

[0013] The abrupt decompression of CO₂-containing reaction mixtures is described in WO 2001/98389 A1. This patent application relates to a process for producing slabstock polyurethane foam, wherein a carbon dioxide-containing polyurethane reactive mixture is suddenly decompressed from a pressure above the equilibrium solution pressure of the carbon dioxide to standard pressure. The liquid polyurethane reactive mixture is foamed by the liberation of dissolved carbon dioxide and the foamed mixture is applied to a substrate and subsequently cured to afford slabstock foam. The carbon dioxide is initially fully dissolved in the reactive mixture or at least one of the components polyol and isocyanate at a pressure substantially above the equilibrium solution pressure. Subsequently the pressure is reduced to a pressure close to the equilibrium solution pressure, wherein the pressure is temporarily reduced below the equilibrium solution pressure to liberate small amounts of the carbon dioxide by forming a bubble microdispersion, the components are optionally mixed and the sudden pressure reduction to standard pressure is performed before the liberated carbon dioxide fully redissolves. However, no information about nanocellular foams or supercritical conditions for the blowing agent may be found here.

[0014] WO 2011/054868 A and WO 2011/054873 A disclose production processes for fine-celled urethane-containing foams using CO₂ as a supercritical blowing agent. The production of a microemulsion from the polyol phase and supercritical CO₂ is decisive for the success of the process in both cases. Said microemulsion is to be established through the use of suitable surfactant components. However, there is no indication of how this process is used to produce foams having predominantly open cells.

[0015] WO 2015/109488 A likewise describes a production process for urethane-containing foams using CO₂ as a supercritical blowing agent. The production process is a multistage process, wherein the polyol component must initially be saturated with CO₂ under supercritical conditions before the reaction mixture is subsequently subjected to pressures of at least 100 bar. The produced foams are said to have small cell sizes and a high porosity. However, foams having a high open-cell content are found only when using propylene oxide-based polyethers and when using two very specific cell-opening surfactants in a particular ratio. The process provides foams having densities $\gg 100 \text{ kg/m}^3$. The total duration for the multistage process (saturation, reaction, curing) in the reactor is $\gg 1 \text{ h}$ during which time supercritical conditions must be maintained.

[0016] Proceeding from the present prior art the present invention has for its object to provide a polyol formulation for a reaction mixture with which a very fine-celled, open-celled urethane-containing rigid foam (rigid PUR/PIR foam) may be produced in a simple process. A process for producing very fine-celled, urethane-containing rigid foams having a high open-cell content which overcomes the disadvantages of the prior art shall also be provided. A very high open-cell content combined with a small cell size is of interest for certain applications where this foam property makes it possible to reduce the thermal conductivity of the foam by application of negative pressure.

[0017] To be provided in particular are a polyol formulation and a process with which it is possible to produce rigid polyurethane foams having an apparent density of $25\text{-}300 \text{ kg/m}^3$ and an open-cell content of $>70\%$ and where the cells have an average diameter of $<180 \mu\text{m}$.

[0018] The present invention provides a polyol formulation P) suitable for producing open-celled rigid PUR/PIR foams having an apparent density of $25\text{-}300 \text{ kg/m}^3$, preferably $30\text{-}200 \text{ kg/m}^3$, particularly preferably $40\text{-}130 \text{ kg/m}^3$, an open-cell content of $>70\%$, in particular $>90\%$, very particularly preferably $\geq 94\%$, and having an average cell diameter of $<180 \mu\text{m}$, in particular $<160 \mu\text{m}$ and very particularly preferably $<100 \mu\text{m}$ containing

[0019] an isocyanate-reactive component A) comprising

[0020] at least one polyol component A1) having a functionality f of >2.5 which is selected from the group consisting of polyether polyols, polyester polyols, polycarbonate polyols, polyether polycarbonate polyols and polyether ester polyols,

[0021] a catalyst component D) at least containing a catalytically active compound D1) having Zerewitinoff-active hydrogens,

[0022] assistant and additive substances E) comprising no cell-opening compound,

and

[0023] a blowing agent component C), characterized in that the proportion of all primary OH functions present in the isocyanate-reactive component A) based on the total number of terminal OH functions in the component A) is at least 30% and in that the blowing agent component C) contains formic acid.

[0024] The present invention also provides the foam-forming reaction mixture R) produced with the polyol formulation P) according to the invention and further comprising at least one polyisocyanate component B).

[0025] The invention further provides a process for producing rigid PUR/PIR foams having an apparent density of $25\text{-}300 \text{ kg/m}^3$, preferably $30\text{-}200 \text{ kg/m}^3$, particularly preferably $40\text{-}130 \text{ kg/m}^3$, an open-cell content of $>70\%$, in particular $>90\%$, very particularly preferably $\geq 94\%$, and having an average cell diameter of $180 \mu\text{m}$, in particular $<160 \mu\text{m}$ and very particularly preferably $<100 \mu\text{m}$ comprising the steps of

[0026] i) producing the inventive foam-forming reaction mixture R) containing the polyol formulation P) and at least one polyisocyanate component B),

[0027] ii) introducing the foam-forming reaction mixture R) into a mold,

[0028] iii) foaming the reaction mixture R) and

[0029] iv) demolding the rigid PUR/PIR foam.

[0030] Terms used in the present application are defined as follows:

[0031] The isocyanate index (also known as the index) is to be understood as meaning the quotient of the actually employed amount of substance [mol] of isocyanate groups and the actually employed amount of substance [mol] of isocyanate-reactive groups, multiplied by 100:

$$\text{Index} = (\text{mols of isocyanate groups} / \text{mols of isocyanate-reactive groups}) * 100.$$

[0032] In the context of the present application the “functionality” or “ f ” of a component mixture is to be understood as meaning the respective number-average functionality of the mixture to which the indication refers. Thus for example the functionality of the polyol component A1) is to be understood as meaning the number-average functionality of the mixture of the polyols present in the component A1 based on all isocyanate-reactive functions present.

[0033] In the context of the present application “molar weight” or “molar mass” or “ M_n ” is in each case to be understood as meaning the number-weighted average molar mass.

[0034] In the case of a single added polyol the OH number (also known as hydroxyl number) specifies the OH number of said polyol. Reported OH numbers for mixtures relate to the number-average OH number of the mixture calculated from the OH numbers of the individual components in their respective molar proportions. The OH number specifies the amount of potassium hydroxide in milligrams which is equivalent in an acetylation to the acetic acid quantity bound by one gram of substance. In the context of the present invention said number is determined according to the standard DIN 53240-2 (as at November 2007).

[0035] The isocyanate-reactive component A) contains at least one polyol component A1) selected from the group consisting of polyether polyols, polyester polyols, polyether ester polyols, polycarbonate polyols and polyether polycarbonate polyols.

[0036] The proportion of primary OH functions based on the total number of terminal OH functions of all polyols employed in the component A) is at least 30%, preferably at least 35%, especially preferably at least 38%.

[0037] The polyol component A1) has the further feature that it has a functionality f of >2.5 , preferably $\geq 2.6\text{-}\leq 6.5$ and particularly preferably $\geq 2.8\text{-}\leq 6.1$. Polyol formulations in which the polyol component A1) has a functionality in these ranges provide an optimal viscosity increase until decompression of the counterpressure during injection and allow faster demolding of the foams.

[0038] The polyol component A1) preferably has a hydroxyl number of 280-600 mg KOH/g, particularly preferably of 300-580 mg KOH/g and especially preferably of 350-540 mg KOH/g. This has a particularly advantageous effect on the mechanical properties of the foams.

[0039] In the context of the present application "a polyether polyol" may also be a mixture of different polyether polyols, this also applying analogously to the other polyols recited here.

[0040] The polyether polyols employable according to the invention are the polyether polyols employable in polyurethane synthesis and known to those skilled in the art.

[0041] Employable polyether polyols are for example polytetramethylene glycol polyethers such as are obtainable by polymerization of tetrahydrofuran by cationic ring opening.

[0042] Likewise suitable polyether polyols are addition products of styrene oxide, ethylene oxide, propylene oxide, butylene oxide and/or epichlorohydrin onto di- or polyfunctional starter molecules. The addition of ethylene oxide and propylene oxide is especially preferred. Suitable starter molecules are for example water, ethylene glycol, diethylene glycol, butyl diglycol, glycerol, diethylene glycol, trimethylolpropane, propylene glycol, pentaerythritol, sorbitol, sucrose, ethylenediamine, toluenediamine, triethanolamine, bisphenols, in particular 4,4'-methylenebisphenol, 4,4'-(1-methylethylidene)bisphenol, 1,4-butanediol, 1,6-hexanediol and low molecular weight hydroxyl-containing esters of such polyols with dicarboxylic acids and oligoethers of such polyols.

[0043] It is preferable when based on its total weight the isocyanate-reactive component A) contains at least 50% by weight, preferably at least 60% by weight, especially preferably at least 70% by weight, of polyether polyol. In a preferred embodiment the component A1) consists of polyether polyol to an extent of 100% by weight. These preferred embodiments feature particularly good hydrolysis stability.

[0044] Employable polyether ester polyols are compounds containing ether groups, ester groups and OH groups. Organic dicarboxylic acids having up to 12 carbon atoms are suitable for producing the polyether ester polyols, preferably aliphatic dicarboxylic acids having ≥ 4 to ≤ 6 carbon atoms or aromatic dicarboxylic acids used singly or in admixture. Examples include suberic acid, azelaic acid, decanedicarboxylic acid, maleic acid, malonic acid, phthalic acid, pimelic acid and sebacic acid and in particular glutaric acid, fumaric acid, succinic acid, adipic acid, phthalic acid, terephthalic acid and isophthalic acid. Also employable in addition to organic dicarboxylic acids are derivatives of these acids, for example their anhydrides and also their esters and monoesters with low molecular weight monofunctional alcohols having ≥ 1 to ≤ 4 carbon atoms. The use of proportions of the abovementioned bio-based starting materials, in particular of fatty acids/fatty acid derivatives (oleic acid, soybean oil etc.), is likewise possible and can have advantages, for example in respect of storage stability of the polyol formulation, dimensional stability, fire characteristics and compressive strength of the foams.

[0045] Polyether polyols obtained by alkoxylation of starter molecules such as polyhydric alcohols are a further component used for producing polyether ester polyols. The starter molecules are at least difunctional, but may option-

ally also contain proportions of higher-functional, in particular trifunctional, starter molecules.

[0046] Starter molecules include for example diols having number-average molecular weights M_n of preferably ≥ 18 g/mol to ≤ 400 g/mol, preferably of ≥ 62 g/mol to ≤ 200 g/mol, such as 1,2-ethanediol, 1,3-propanediol, 1,2-propanediol, 1,4-butanediol, 1,5-pentanediol, 1,5-pentanediol, neopentyl glycol, 1,6-hexanediol, 1,7-heptanediol, 1,8-octanediol, 1,10-decanediol, 2-methyl-1,3-propanediol, 2,2-dimethyl-1,3-propanediol, 3-methyl-1,5-pentanediol, 2-butyl-2-ethyl-1,3-propanediol, 2-butene-1,4-diol and 2-butyne-1,4-diol, ether diols such as diethylene glycol, triethylene glycol, tetraethylene glycol, dibutylene glycol, tributylene glycol, tetrabutylene glycol, dihexylene glycol, trihexylene glycol, tetrahexylene glycol and oligomeric mixtures of alkylene glycols, such as diethylene glycol. Starter molecules having functionalities distinct from OH may also be employed alone or in admixture.

[0047] In addition to the diols compounds having >2 Zerewitinoff-active hydrogens, in particular having number-average functionalities of >2 to ≤ 8 , in particular of ≥ 3 to ≤ 6 , may also be co-used as starter molecules for producing the polyethers, for example 1,1,1-trimethylolpropane, triethanolamine, glycerol, sorbitan and pentaerythritol and also triol- or tetraol-started polyethylene oxide polyols having average molar masses M_n of preferably ≥ 62 g/mol to ≤ 400 g/mol, in particular of ≥ 92 g/mol to ≤ 200 g/mol.

[0048] Polyether ester polyols may also be produced by alkoxylation, in particular by ethoxylation and/or propoxylation, of reaction products obtained by the reaction of organic dicarboxylic acids and their derivatives and components with Zerewitinoff-active hydrogens, in particular diols and polyols. Derivatives of these acids that may be used include, for example, their anhydrides, for example phthalic anhydride.

[0049] Suitable polyester polyols are inter alia polycondensates of di- and also tri- and tetraols and di- and also tri- and tetracarboxylic acids or hydroxycarboxylic acids or lactones. Also employable instead of the free polycarboxylic acids are the corresponding polycarboxylic anhydrides or corresponding polycarboxylic esters of lower alcohols to prepare the polyesters.

[0050] Examples of suitable diols are ethylene glycol, butylene glycol, diethylene glycol, triethylene glycol, polyalkylene glycols such as polyethylene glycols and also 1,2-propanediol, 1,3-propanediol, 1,3-butanediol, 1,4-butanediol, 1,6-hexanediol and isomers, neopentyl glycol or neopentyl glycol hydroxypivalate. Also employable in addition are polyols such as trimethylolpropane, glycerol, erythritol, pentaerythritol, trimethylolbenzene or trishydroxyethyl isocyanurate.

[0051] Additional co-use of monohydric alkanols is also possible.

[0052] Examples of polycarboxylic acids that may be used include phthalic acid, isophthalic acid, terephthalic acid, tetrahydrophthalic acid, hexahydrophthalic acid, cyclohexanedicarboxylic acid, adipic acid, azelaic acid, sebacic acid, glutaric acid, tetrachlorophthalic acid, maleic acid, fumaric acid, itaconic acid, malonic acid, suberic acid, succinic acid, 2-methylsuccinic acid, 3,3-diethylglutaric acid, 2,2-dimethylsuccinic acid, dodecanedioic acid, endomethylenetetrahydrophthalic acid, dimer fatty acid, trimer fatty acid, citric acid, or trimellitic acid. It is also possible to use the corresponding anhydrides as an acid source.

[0053] Additional co-use of monocarboxylic acids such as benzoic acid and alkanecarboxylic acids is also possible.

[0054] Hydroxycarboxylic acids that may be co-used as co-reactants in the production of a polyester polyol having terminal hydroxyl groups include for example hydroxycaproic acid, hydroxybutyric acid, hydroxydecanoic acid, hydroxystearic acid and the like. Suitable lactones include caprolactone, butyrolactone and homologs.

[0055] Suitable compounds for producing the polyester polyols also include in particular bio-based starting materials and/or derivatives thereof, for example castor 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 kernel 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, fatty acids, hydroxyl-modified fatty acids and epoxidized fatty acids and fatty acid esters, for example based on myristoleic acid, palmitoleic acid, oleic acid, vaccenic acid, petroselinic acid, gadoleic acid, erucic acid, nervonic acid, linoleic acid, alpha- and gamma-linolenic acid, stearidonic acid, arachidonic acid, timonodonic acid, clupanodonic acid and cervonic acid. Especially preferred are esters of ricinoleic acid with polyfunctional alcohols, for example glycerol. Also preferred is the use of mixtures of such bio-based acids with other carboxylic acids, for example phthalic acids.

[0056] Polycarbonate polyols that may be used are hydroxyl-containing polycarbonates, for example polycarbonate diols. These are obtainable by reaction of carbonic acid derivatives, such as diphenyl carbonate, dimethyl carbonate or phosgene, with polyols, preferably diols, or by copolymerization of alkylene oxides, for example propylene oxide, with CO₂.

[0057] Examples of such diols include ethylene glycol, 1,2- and 1,3-propanediol, 1,3- and 1,4-butanediol, 1,6-hexanediol, 1,8-octanediol, neopentyl glycol, 1,4-bis(hydroxymethyl)cyclohexane, 2-methyl-1,3-propanediol, 2,2,4-trimethylpentane-1,3-diol, dipropylene glycol, polypropylene glycols, dibutylene glycol, polybutylene glycols, bisphenol A, and lactone-modified diols of the above-mentioned type.

[0058] Also employable instead of or in addition to pure polycarbonate diols are polyether-polycarbonate diols obtainable for example by copolymerization of alkylene oxides, such as for example propylene oxide, with CO₂.

[0059] Production processes of the polyols are described for example by Ionescu in "Chemistry and Technology of Polyols for Polyurethanes", Rapra Technology Limited, Shawbury 2005, p. 55 et seq. (chapt. 4: Oligo-polyols for Elastic Polyurethanes), p. 263 et seq. (chapt. 8: Polyester Polyols for Elastic Polyurethanes) and in particular to p. 321 et seq. (chapt. 13: Polyether Polyols for Rigid Polyurethane Foams) and p. 419 et seq. (chapt. 16: Polyester Polyols for Rigid Polyurethane Foams). It is also possible to obtain polyester and polyether polyols by glycolysis of suitable polymer recyclates. Suitable polyether-polycarbonate polyols and the production thereof are described for example in EP 2910585 A, [0024]-[0041]. Examples of polycarbonate polyols and production thereof may be found inter alia in EP 1359177 A. Production of suitable polyether ester polyols is described inter alia in WO 2010/043624 A and in EP 1 923 417 A.

[0060] Polyether polyols, polyethercarbonate polyols and polyether ester polyols having a high proportion of primary OH functions are obtained when the alkylene oxides used for alkoxylation comprise a high proportion of ethylene oxide. The molar proportion of ethylene oxide structures based on the entirety of the alkylene oxide structures present in the polyols of the component A1 is at least 50 mol %. The use of 100 mol % of ethylene oxide is likewise a preferred embodiment.

[0061] The isocyanate-reactive component A) may further contain low molecular weight isocyanate-reactive compounds A2), in particular di- or trifunctional amines and alcohols, particularly preferably diols and/or triols having molar masses M_n of less than 400 g/mol, preferably of 60 to 300 g/mol, for example triethanolamine, diethylene glycol, ethylene glycol, glycerol, may be employed. Provided such low molecular weight isocyanate-reactive compounds are used for producing the rigid polyurethane foams, for example as chain extenders and/or crosslinking agents, and these do not also fall under the definition of component A1), they are advantageously employed in an amount of up to 5% by weight based on the total weight of the component A).

[0062] In addition to the above-described polyols and isocyanate-reactive compounds the component A) may contain further isocyanate-reactive compounds A3), for example graft polyols, polyamines, polyamino alcohols and polythiols. It will be appreciated that the described isocyanate-reactive components also comprise compounds having mixed functionalities.

[0063] A preferred isocyanate-reactive component A) consists to an extent of at least 65% by weight, in particular at least 80% by weight and very particularly preferably to an extent of at least 90% by weight of the polyol component A1) which has a hydroxyl number between 280 to 600 mg KOH/g and a functionality of ≥ 2.8 to ≤ 6.0 , and the proportion of primary OH functions in the component A) is at least 35% (based on all terminal OH functions in the component A).

[0064] The polyol formulation P) optionally contains assistant and additive substances E). The assistant and additive substances contain no cell-opening compounds.

[0065] Cell-opening compounds are described for example in *Kunststoff-Handbuch*, volume 7, Polyurethane, Carl Hanser Verlag, Munich/Vienna, 3rd edition, 1993, pages 104-127.

[0066] The reaction mixture contains no cell-opening compounds, in particular no cell-opening compounds based on polybutadiene.

[0067] Further assistant and additive substances E) that may be employed in the process according to the invention are the customary assistant and additive substances known from the prior art and to the person skilled in the art. These include for example surface-active substances, stabilizers, in particular foam stabilizers, cell regulators, fillers, dyes, pigments, flame retardants, antistats, antihydrolysis agents and/or fungistatic and bacteriostatic substances.

[0068] Employable stabilizers are saturated and unsaturated hydrocarbons such as paraffins, fatty alcohols and esters, for example esters of carboxylic acids.

[0069] The component A) preferably contains in total not more than 3% by weight of stabilizers.

[0070] Also employable as stabilizers are surfactants, for example alkoxyated alkanols such as ethers of linear or branched alkanols having ≥ 6 to ≤ 30 carbon atoms with

polyalkylene glycols having >5 to ≤ 100 alkylene oxide units, alkoxyated alkylphenols, alkoxyated fatty acids, carboxylic esters of an alkoxyated sorbitan (especially Polysorbate 80), fatty acid esters, polyalkyleneamines, alkyl sulfates, phosphatidylinositols, fluorinated surfactants, surfactants comprising polysiloxane groups and/or bis(2-ethyl-1-hexyl) sulfosuccinate. Fluorinated surfactants may be per-fluorinated or partially fluorinated. Examples thereof are partially fluorinated ethoxylated alkanols or carboxylic acids.

[0071] The component A) preferably contains a total of not more than 5% by weight of surfactants, especially preferably not more than 3% by weight, more preferably less than 2% by weight and especially preferably not more than 1.6% by weight of surfactants based on the total weight of the component A).

[0072] Catalysts D) are employed for the production of the rigid PUR/PIR foam. Typically employed as catalysts D) are compounds which accelerate the reaction of hydroxyl group-containing/isocyanate-reactive group-containing compounds of the components with the isocyanate groups of the component B).

[0073] The catalysts D) contain D1) at least one catalytically active amine compound having functional groups which comprise Zerewitinoff-active hydrogens and can therefore react with isocyanate (so-called "incorporable catalysts"). Examples of employable incorporable catalysts are bis(dimethylaminopropyl)urea, bis(N,N-dimethylaminoethoxyethyl)carbamate, dimethylaminopropylurea, N,N,N-trimethyl-N-hydroxyethylbis(aminopropyl ether), N,N,N-trimethyl-N-hydroxyethylbis(aminoethyl ether), diethylethanamine, bis(N,N-dimethyl-3-aminopropyl)amine, dimethylaminopropylamine, 3-dimethylaminopropyl-N,N-dimethylpropane-1,3-diamine, dimethyl-2-(2-aminoethoxyethanol) and (1,3-bis(dimethylamino)propan-2-ol), N,N-bis(3-dimethylaminopropyl)-N-isopropanolamine, bis(dimethylaminopropyl)-2-hydroxyethylamine, N,N,N-trimethyl-N-3-aminopropylbis(aminoethyl ether), 3-dimethylaminoisopropyl-diisopropanolamine or mixtures thereof.

[0074] In a preferred embodiment the catalysts D1) are employed in an amount of $\geq 0.01\%$ to $<2\%$ by weight based on the total weight of the component A).

[0075] Also employable are one or more further catalyst compounds D2), especially the catalytically active compounds known for PUR/PIR chemistry, including not only further amine compounds but also salts such as for example tin (II) acetate, tin (II) octoate, tin (II) ethylhexoate, tin (II) laurate, dibutyltin diacetate, dibutyltin dilaurate, dibutyltin maleate, dioctyltin diacetate, tris(N,N-dimethylaminopropyl)-s-hexahydrotriazine, tetramethylammonium hydroxide, sodium acetate, sodium octoate, potassium acetate, potassium octoate, sodium hydroxide.

[0076] The catalysts D) are generally employed in an amount from 0.001 to 5% by weight, in particular from 0.05 to 2.5% by weight, based on the weight of the component A). It is particularly preferable when the catalysts D) contain both incorporable catalysts D1) and non-incorporable catalysts D2). It is especially preferable when incorporable amine compounds and catalytically active salts are employed in combination.

[0077] The catalysts D1) and D2) are preferably employed in a molar ratio D1/D2 of 0.1 to 16.3, particularly preferably

of 0.3 to 10 and very particularly preferably of 0.8 to 6.0. It is preferable when the catalyst component D) contains as the catalytically active compound D1) an amine compound incorporable into the polyurethane and also the non-catalytically active compound D2) which is a catalytically active salt not incorporable into the polyurethane and the molar ratio of D1/D2 is 0.1 to 16.3, particularly preferably from 0.3 to 10 and very particularly preferably from 0.8 to 6.0. In a particularly preferred embodiment 3-(dimethylamino)propylurea and potassium acetate are employed in a molar ratio D1/D2 of 0.1 to 6.0, particularly preferably of 0.3 to 10 and very particularly preferably of 0.8 to 6.0. The preferred catalyst ratios/catalysts particularly advantageously bring about a defined viscosity increase.

[0078] Production of the rigid PUR/PIR foam employs a blowing agent component C). Blowing agents may be distinguished into chemical and physical blowing agents.

[0079] At least formic acid which belongs to the group of chemical blowing agents is employed as blowing agent C). It is preferable when the formic acid is employed in an amount of 0.5-6% by weight, particularly preferably of 0.5% to 4% by weight, based on the total amount of compounds having isocyanate-reactive hydrogen atoms in the foam-forming reaction mixture R). Formic acid is often employed in common in a mixture with water. If a formic acid/water mixture is employed a ratio of formic acid:water ≥ 0.5 is particularly preferred. In addition to formic acid and optionally water, other chemical blowing agents can also be added.

[0080] In addition, the blowing agent component C) may further comprise physical blowing agents. In the context of the present invention "physical blowing agents" are to be understood as meaning compounds which on account of their physical properties are volatile and unreactive toward the isocyanate component.

[0081] It is preferable when the physical blowing agents are selected from hydrocarbons (for example n-pentane, isopentane, cyclopentane, butane, isobutane, propane), ethers (for example methylal), halogenated ethers, perfluorinated and partially fluorinated hydrocarbons having 1 to 8 carbon atoms, for example perfluorohexane, HFC 245fa (1,1,1,3,3-pentafluoropropane), HFC 365mfc (1,1,1,3,3-pentafluorobutane), HFC 134a or mixtures thereof are used, and also (hydro)fluorinated olefins, for example HFO 1233zd(E) (trans-1-chloro-3,3,3-trifluoro-1-propene) or HFO 1336mzz(Z) (cis-1,1,1,4,4,4-hexafluoro-2-butene) or additives such as FA 188 from 3M (1,1,1,2,3,4,5,5,5-non-afluoro-4-(trifluoromethyl)pent-2-ene), and also mixtures thereof with one another.

[0082] A preferred embodiment employs as blowing agent component C) formic acid and a pentane isomer or a mixture of different pentane isomers, in particular a mixture of cyclopentane and isopentane, as blowing agent component C).

[0083] In a preferred embodiment the formic acid or the formic acid/water mixture is mixed with the further components (A, D, E) of the polyol formulation P) before the optional addition of physical blowing agents and the reaction with the isocyanate component. It is preferable to establish a concentration of 0.5-6 parts of formic acid in 100 parts of polyol formulation P).

[0084] The blowing agent component C) is altogether employed in an amount sufficient to achieve a dimensionally stable foam matrix and the desired apparent density. This is

generally 0.5-30 parts by weight of blowing agent based on 100 parts by weight of the component A.

[0085] The proportion of formic acid in the total blowing agent component C) preferably contains 20-100% by weight, particularly preferably 60-100% by weight and very particularly preferably 80-95% by weight based on the total weight of the blowing agent component C).

[0086] A further preferred embodiment employs not only the formic acid and optionally water but also as a further blowing agent component a physical blowing agent which is in the supercritical or near critical state.

[0087] This physical blowing agent may be selected from the group comprising linear, branched or cyclic C1- to C6-hydrocarbons, linear, branched or cyclic C1- to C6-hydrofluorocarbons, N₂, O₂, argon and/or CO₂. CO₂ in the supercritical or near critical state is especially preferred. Conditions are near-critical in the context of the present invention when the following condition is satisfied: $(T_c - T)/T \leq 0.4$ and/or $(p_c - p)/p \leq 0.4$. Here, T is the temperature prevailing in the process, T_c is the critical temperature of the blowing agent or blowing agent mixture, p is the pressure prevailing in the process and p_c is the critical pressure for the blowing agent or blowing agent mixture.

[0088] Conditions are preferably near-critical when: $(T_c - T)/T \leq 0.3$ and/or $(p_c - p)/p \leq 0.3$ and particularly preferably $(T_c - T)/T \leq 0.2$ and/or $(p_c - p)/p \leq 0.2$.

[0089] Particularly suitable conditions for performing the process according to the invention when using CO₂ are pressures and temperatures above the critical point of CO₂, i.e. ≥ 73.7 bar and $\geq 30.9^\circ$ C., preferably between 74 bar and 350 bar and between 31° C. and 100° C., particularly preferably between 75 bar and 200 bar and between 32° C. and 60° C. When supercritical CO₂ is employed the content of blowing agent component C) is for example $\geq 2\%$ by weight to $\leq 20\%$ by weight based on the total weight of the mixture. Preferred proportions are $\geq 5\%$ by weight to $\leq 15\%$ by weight and particularly preferred proportions are $\geq 6\%$ by weight to $\leq 11\%$ by weight.

[0090] It is also possible to employ a mixture of supercritical CO₂ and other physical blowing agents, in particular selected from the blowing agents specified as preferred hereinabove. When further physical blowing agents are added these preferably contain more than 60% by weight of carbon dioxide, particularly preferably more than 75% by weight, in one embodiment.

[0091] The proportion of blowing agent component C) at least containing formic acid in the mixture of the components A), C), D) and E) is generally $\geq 1\%$ by weight to $\leq 30\%$ by weight, preferably $\geq 10\%$ by weight to $\geq 20\%$ by weight; the proportion of the blowing agent in the foam-forming reaction mixture R) is 0.5% by weight to 15% by weight, preferably 5% by weight to 10% by weight.

[0092] The component B) is a polyisocyanate, i.e. an isocyanate having an NCO functionality of ≥ 2 . Examples of such suitable polyisocyanates include 1,4-butylene diisocyanate, 1,5-pentane diisocyanate, 1,6-hexamethylene diisocyanate (HDI), isophorone diisocyanate (IPDI), 2,2,4- and/or 2,4,4-trimethylhexamethylene diisocyanate, the isomeric bis (4,4'-isocyanatocyclohexyl)methanes or their mixtures of any desired isomer content, 1,4-cyclohexylene diisocyanate, 1,4-phenylene diisocyanate, 2,4- and/or 2,6-tolylene diisocyanate (TDI), 1,5-naphthylene diisocyanate, 2,2'-and/or 2,4'- and/or 4,4'-diphenylmethane diisocyanate (MDI) and/or higher homologs, 1,3- and/or 1,4-bis(2-isocyanatoprop-

2-yl)benzene (TMXDI), 1,3-bis(isocyanatomethyl)benzene (XDI) and also alkyl 2,6-diisocyanatohexanoates (lysine diisocyanates) having C1 to C6-alkyl groups.

[0093] Preferably employed as the isocyanate component B) are mixtures of the isomers of diphenylmethane diisocyanate ("monomeric MDI", "mMDI" for short) and oligomers thereof ("oligomeric MDI"). Mixtures of monomeric MDI and oligomeric MDI are generally described as "polymeric MDI" (pMDI). The oligomers of MDI are higher-nuclear polyphenylpolymethylene polyisocyanates, i.e. mixtures of the higher-nuclear homologs of diphenylmethylene diisocyanate which have an NCO functionality $f > 2$ and have the following structural formula: $C_{15}H_{10}N_2O_2 [C_8H_5NO]_n$, wherein $n = \text{integer} > 0$, preferably $n = 1, 2, 3$ and 4. Higher-nuclear homologs $C_{15}H_{10}N_2O_2 [C_8H_5NO]_m$, $m = \text{integer} \geq 4$ may likewise be present in the mixture of organic polyisocyanates a). Likewise preferred as the isocyanate component B) are mixtures of mMDI and/or pMDI comprising at most up to 20% by weight, more preferably at most 10% by weight, of further aliphatic, cycloaliphatic and especially aromatic polyisocyanates known for the production of polyurethanes, very particularly TDI.

[0094] In addition to the abovementioned polyisocyanates it is also possible to co-use proportions of modified diisocyanates having a uretdione, isocyanurate, urethane, carbodiimide, uretonimine, allophanate, biuret, amide, iminooxadiazinedione and/or oxadiazinetriene structure and also unmodified polyisocyanate having more than 2 NCO groups per molecule, for example 4-isocyanatomethyl-1,8-octane diisocyanate (nonane triisocyanate) or triphenylmethane 4,4',4"-triisocyanate.

[0095] Also employable instead of or in addition to the abovementioned polyisocyanates as the organic isocyanate component B) are suitable NCO prepolymers. The prepolymers are producible by reaction of one or more polyisocyanates with one or more polyols corresponding to the polyols described under the components A1) and A2).

[0096] The isocyanate may be a prepolymer obtainable by reacting an isocyanate having an NCO functionality of ≥ 2 and polyols having a molecular weight of ≥ 62 g/mol to ≤ 8000 g/mol and OH functionalities of ≥ 1.5 to ≤ 6 .

[0097] The NCO content is preferably from $\geq 29.0\%$ by weight to $\leq 32.0\%$ by weight and preferably has a viscosity at 25° C. of ≥ 80 mPas to ≤ 2000 mPas, particularly preferably of ≥ 100 mPas to ≤ 800 mPas (dynamic viscosity determined according to DIN 53019 at 25° C.).

[0098] The number of NCO groups in the polyisocyanate component B) and the number of isocyanate-reactive groups in the component A) may be in a numerical ratio to one another of $\geq 50:100$ to $\leq 500:100$ for example. The rigid polyurethane foams are produced generally by reacting the components A) and B) in amounts such that the isocyanate index in the formulation is 80-150, preferably 90-130, particularly preferably 95-110. In this range urethane groups are preferably formed. In another preferred embodiment the isocyanate index is 150-400. In this range the foams comprise a high proportion of isocyanurate functions which bring about for example an inherent flame retardancy of the foams.

[0099] The invention further provides a process for producing rigid PUR/PIR foams having an apparent density of 25-300 kg/m³, preferably 30-200 kg/m³, particularly preferably 40-130 kg/m³, an open-cell content of $> 70\%$, in particular $> 90\%$, very particularly preferably $\geq 94\%$, and

having an average cell diameter of 180 μm , in particular <160 μm and very particularly preferably <100 μm comprising the steps of

[0100] i) producing the inventive foam-forming reaction mixture R),

[0101] ii) introducing the reaction mixture R) into a mold,

[0102] iii) foaming the reaction mixture R) and

[0103] iv) demolding the rigid PUR/PIR foam.

[0104] In step i) of the process according to the invention the foam-forming reaction mixture R) is produced from the components A)-E).

[0105] To this end the mixture comprising the components A), D), E) may be initially charged for example in a vessel together with the formic acid or the formic acid/water mixture, then optionally mixed with the further blowing agent components C) and admixed with the polyisocyanate B). The mixing of the components may also be effected in a mixing head.

[0106] The mixing, in particular with optionally present physical blowing agent components C) and with B) may be effected under pressure. In a preferred embodiment the components A), D), E) and C) are mixed with the component B) in a high-pressure mixing head.

[0107] When in addition to the formic acid or the formic acid/water mixture CO_2 in the supercritical state is employed as a further blowing agent component the reaction of the components is preferably carried out under conditions supercritical for CO_2 . In this case suitable pressures in the mixing head and/or in the discharge conduit/the discharge conduits for producing the polyurethane foam are for example in the range from ≥ 73.7 bar to ≤ 350 bar and preferably in the range from ≥ 75 bar to ≤ 200 bar. Suitable temperatures are for example $\leq 30.9^\circ\text{C}$. to $\leq 100^\circ\text{C}$. and preferably $\leq 32^\circ\text{C}$. to $\leq 60^\circ\text{C}$. At such pressures supercritical conditions for the employed blowing agent may be maintained.

[0108] In a further embodiment the residence time of the mixture in the mixing head under supercritical conditions for the blowing agent is ≥ 0 seconds to ≤ 20 seconds, preferably from ≥ 0.1 seconds to ≤ 10 seconds and particularly preferably from ≤ 0.5 seconds to ≤ 5 seconds. This has the result that the mixture can polymerize under supercritical conditions. The residence time may be determined by the volume of the reaction chamber (=mixing chamber and/or conduits) in which supercritical conditions prevail divided by the volume of the mixture conveyed in a particular unit time.

[0109] In step ii) of the process according to the invention the inventive foam-forming reaction mixture R) composed of the components A)-E) is introduced into a mold.

[0110] In a preferred embodiment the mold is a closed mold, wherein the counterpressure in the mold during injection is 2-90 bar, preferably 2-80 bar, particularly preferably 5 - 40 bar.

[0111] Possible embodiments therefor are as follows: The counterpressure is achieved by pressurizing the mold with gas (compressed air or nitrogen) either directly and/or via a floating seal, which divides the pressurized space into a gas space and a reaction space, and is established, held and finally decompressed via a proportional valve.

[0112] In step iii) of the process the reaction mixture is foamed.

[0113] In the case where the reaction mixture was injected into a mold under counterpressure a preferred embodiment of step iii) is as follows:

[0114] After termination of step ii) the pressure in the mold is kept constant for a period 1 which is preferably 1-40 seconds, particularly preferably 5-20 seconds and very particularly preferably 8-17 seconds, wherein the viscosity of the reaction mixture initially increases without foaming. It has been found that holding the pressure for the preferred period results in particularly advantageous viscosity ranges of the mixture for this reaction section. Once the period 1 has elapsed the mold is decompressed. The releasing of the pressure from the mold is carried out over a period 2 at a pressure release rate of 1-90 bar/s, preferably 1-80 bar/s, particularly preferably 2-70 bar/s. The releasing may be effected in particular via a proportional valve. The reaction mixture is foamed over period 2. An excessively fast releasing has a negative effect on cell stability and excessively slow releasing has a negative effect on the foaming reaction.

[0115] In step iv) of the process the rigid PUR/PIR foam is demolded.

[0116] One particularly preferred embodiment of the process according to the invention comprises the steps of:

[0117] i) producing a foaming reaction mixture R) from

[0118] an isocyanate-reactive component A) containing at least one polyol component Al) selected from the group consisting of polyether polyols, polyester polyols, polycarbonate polyols, polyether polycarbonate polyols and polyether ester polyols which has an OH functionality F of >2.5 ,

[0119] at least one polyisocyanate component B),

[0120] a blowing agent component C),

[0121] a catalyst component D) at least containing a catalytically active compound D1) having Zerewitinoff-active hydrogens,

[0122] assistant and additive substances E) comprising no cell-opening compound or at least one cell-opening compound,

[0123] wherein the proportion of all primary OH functions present in the isocyanate-reactive component A) based on the total number of terminal OH functions in the component A) is at least 30% and the blowing agent component C) contains formic acid,

[0124] ii) introducing the foaming reaction mixture R) into a closed mold, wherein the counterpressure in the mold during injection is 2-90 bar,

[0125] iii) holding the pressure in the mold for a period 1 of 1-40 s after termination of step ii) and subsequently releasing the pressure from the mold over a period 2 at a pressure release rate of 1-90 bar/s,

[0126] iv) demolding the rigid PUR/PIR foam.

[0127] The present invention further provides a rigid PUR/PIR foam obtainable or obtained by the process according to the invention.

[0128] The process according to the invention makes it possible to obtain rigid PUR/PIR foams having an apparent density of 25-300 kg/m^3 , preferably 30-200 kg/m^3 , particularly preferably 40-130 kg/m^3 , which simultaneously have many open and particularly small cells. It is thus possible to produce rigid foams having an open-cell content of $>70\%$, in particular $>90\%$, very particularly preferably $\geq 94\%$, where the cells exhibit an average diameter of 180 μm , in particular <160 μm and very particularly preferably <100 μm . In a particularly preferred embodiment the cells have an average cell size <90 μm and an open-cell content of $>94\%$. The foams have good mechanical properties, for example good compressive strengths.

[0129] The PUR/PIR foams according to the invention make it possible in preferable fashion to produce foamed moldings and composite systems containing these moldings. The composite systems are often delimited both on the top surface and on the bottom surface by decorative layers. Suitable decorative layers include inter alia metals, plastics, wood and paper. Suitable fields of application of such discontinuously produced PUR/PIR composite systems include in particular industrial insulation of appliances such as refrigerators, chest freezers, fridge-freezers and boilers, cool containers and coolboxes and also of pipes.

[0130] The use of PUR/PIR foams in these fields is known per se to those skilled in the art and has already been described on many occasions. The PUR/PIR foams according to the invention are exceptionally suitable for these purposes since on account of their fine-cell content they feature low coefficients of thermal conductivity which can be still further enhanced by application of a vacuum.

[0131] The invention further relates to a refrigerator, a freezer or a fridge-freezer comprising a rigid PUR/PIR foam obtainable according to the invention, wherein the provided mold is in particular a housing part of the refrigerator, the freezer or the fridge-freezer. The invention shall be more particularly elucidated with reference to the examples and comparative examples which follow.

EXAMPLES

[0132] The comparative examples and examples which follow are intended to more particularly elucidate the invention without limiting it.

Employed Standards/Analytical Instruments

[0133] Determination of apparent density: Foams composed of rubber and plastics—determination of apparent density (ISO 845:2006); German version EN ISO 845:2009

[0134] Determination of open-cell content: Determination of the volume fraction of open and closed cells (ISO 4590:2002); German version EN ISO 4590:2003

[0135] Determination of compressive strength: Rigid foams—determination of pressure properties (ISO 844:2014); German version EN ISO 844:2014

[0136] Determination of OH number: Determination of hydroxyl number—part 2: Method with catalyst according to DIN 53240-2, as at November 2007

[0137] Determination of cell size: Optical microscopy evaluation via VHX 5000 optical microscope; the test specimen to be measured is analyzed at 3 different points in each case over a circular region having a diameter of 5 mm. The resolution is chosen such that the selected region captures around 100 cells. 100 cells are then measured and the smallest and largest cell diameter as well as the average cell diameter are calculated.

[0138] The specified proportion of primary OH functions in [%] in table 1 relates to the proportion of primary OH functions based on the total number of OH functions in the mixture of the polyols present in the formulation.

[0139] Production of the foams according to examples 1 (inventive) and examples 2-4 (comparative) employed the following substances:

[0140] Polyol 1: Polyether polyol based on trimethylolpropane and propylene oxide having a hydroxyl number of 800 mg KOH/g, a functionality of 3 and a viscosity of 6100 mPas at 25° C.

[0141] Polyol 2: Polyether polyol based on trimethylolpropane and ethylene oxide having a hydroxyl number of 550 mg KOH/g, a functionality of 3 and a viscosity of 505 mPas at 25° C.

[0142] Polyol 3: Polyether polyol based on trimethylolpropane and propylene oxide having a hydroxyl number of 550 mg KOH/g, a functionality of 3 and a viscosity of 1800 mPas at 25° C.

[0143] Polyol 4: Polyether polyol based on 1,2-propanediol and propylene oxide having a hydroxyl number of 56 mg KOH/g, a functionality of 2 and a viscosity of 310 mPas at 25° C.

[0144] Polyol 5: Polyether polyol based on 1,2-propanediol and propylene oxide having a hydroxyl number of 112 mg KOH/g, a functionality of 2 and a viscosity of 140 mPas at 25° C.

[0145] Polyol 6: Polyether polyol based on glycerol and propylene oxide having a hydroxyl number of 231 mg KOH/g, a functionality of 3 and a viscosity of 350 mPas at 20° C.

[0146] Polyol 7: Polyether polyol based on glycerol and saccharose and propylene oxide having a hydroxyl number of 470 mg KOH/g and a functionality of 4.9

[0147] Polyol 8: Polyether polyol based on propylene glycol and propylene oxide having a hydroxyl number of 260 mg KOH/g and a functionality of 2

[0148] B 8443: Foam stabilizer (Evonik)

[0149] B 8870: Foam stabilizer (Evonik)

[0150] Ortegol 500: Cell opener (Evonik)

[0151] Ortegol 501: Cell opener (Evonik)

[0152] Potassium acetate/DEG: Catalyst, 25% potassium acetate in diethylene glycol (Covestro)

[0153] Dabco NE1070: Catalyst, about 60% 3-(dimethylamino)propylurea in diethylene glycol (Air Products)

[0154] Polycat 58: Catalyst (Air Products)

[0155] Potassium acetate/EG: Catalyst, 25% potassium acetate in ethylene glycol c-/i-Pentane mixture: Mixture of cyclopentane and isopentane in a 70:30 weight ratio, physical blowing agent

[0156] Water: Blowing agent

[0157] Formic acid: Blowing agent, 95% formic acid

[0158] Isocyanate 1: Mixture of monomeric and polymeric MDI having a viscosity of about 290 m Pa*s at 20° C. (Desmodur 44V20L, Covestro)

[0159] Isocyanate 2: Mixture of monomeric and polymeric MDI having a viscosity of about 1070 m Pa*s at 20° C. (Desmodur 44V70L, Covestro)

Production of Free-Rise Polyurethane Foams

[0160] To produce free-rise polyurethane foams in the laboratory 200 g of the respective polyol formulation composed of the isocyanate-reactive compounds, stabilizers, catalysts, formic acid or physical blowing agents, listed in table 1 below, were weighed in and homogenized using a stirrer. The thus-obtained isocyanate-reactive composition was mixed with the appropriate amount of isocyanate using a Pendraulik stirrer for 10 seconds at 23° C. and poured into an open-top mold (20 cm×20 cm×18 cm). The precise formulations including the results of appropriate physical tests are summarized in table 1.

TABLE 1

		Example			
		1	2*	3*	4*
Formulation					
Polyol 1		13.00	—	13.00	13.00
Polyol 2		32.50	—	32.50	—
Polyol 3		—	—	—	32.50
Polyol 4		13.50	44.1	13.50	13.50
Polyol 5		9.50	—	9.50	9.50
Polyol 6		27.00	—	27.00	27.00
Polyol 7		—	44.1	—	—
Polyol 8		—	9.15	—	—
Water		—	0.55	—	—
B 8443		1.50	—	1.50	1.50
B 8870		—	0.9	—	—
Ortegol 500		—	—	0.50	0.50
Ortegol 501		—	1.8	0.50	—
Potassium acetate/DEG		—	—	1.00	1.00
Dabco NE1070		0.65	—	0.65	0.65
Potassium acetate/EG		—	0.7	—	—
Polycat 58		—	0.5	—	—
Formic acid		2.5	—	—	—
Polyol functionality		2.9	3.87	—	—
Proportion of primary OH	[%]	46.0	0.0	46.0	0.0
Isocyanate 1		107.2	—	92.60	92.60
Isocyanate 2		—	197	—	—
n-Pentane		—	—	6.70	6.70
c-/i-Pentane mixture		—	244	—	—
Index	NCO/OH	100	244	100	100
Free-rise foam reaction times					
Cream time	[s]	15	120	34	50
Fiber time	[s]	60	270	45	87
Rise time	[s]	80	360	55	90
Tack-free time	[s]	95	420	55	95

*Comparison

[0161] The obtained free-rise foams were subsequently characterized with the abovementioned methods of measurement. Their properties are summarized in table 2.

TABLE 2

		Example			
		1	2*	3*	4*
Apparent density	kg/m ³	70	63	63	63
Compressive strength at 10% compression (parallel)	MPa	0.42	0.41	0.41	0.41
Compressive strength at 10% compression (transverse)	MPa	0.37	0.36	0.29	0.36
Open-cell content	%	96	93	95.6	25.6
Average cell size	μm	67	137	150	126
Cell size of smallest cell	μm	25	21	43	73
Cell size of largest cell	μm	129	299	217	174

[0162] Example 1 shows that the specified formulation makes it possible to produce very fine-celled rigid foams having a high proportion of open cells.

[0163] The average cell sizes of the inventive example are markedly smaller than in the comparative examples where no formic acid was used. A comparison of example 1 and comparative example 2, the latter corresponding to example 1 from EP 2 072 548, shows that the cell size of example 1 is about 51% smaller with an average cell size of 67 μm.

This is a distinct advantage in respect of the use of the foams as a core material for vacuum insulation applications since this makes it possible to achieve a lower lambda value at identical pressure.

[0164] Example 1 further shows that even with a polyol formulation without cell-opening substances (Ortegol) foams having a higher open-cell content and a finer cell structure are obtainable when formic acid is employed as a blowing agent.

1. A polyol formulation P) suitable for producing open-celled rigid PUR/PIR foams comprising

an isocyanate-reactive component A) comprising

at least one polyol component A1) having a functionality of >2.5 comprising at least one of polyether polyols, polyester polyols, polycarbonate polyols, polyether polycarbonate polyols and polyether ester polyols,

a catalyst component D) comprising a catalytically active compound D1) having Zerewitinoff-active hydrogens,

an assistant or additive substance E) excluding a cell-opening compound,

and

a blowing agent component C),

wherein the proportion of all primary OH functions present in the isocyanate-reactive component A) based on the total number of terminal OH functions in the component A) is at least 30% and

wherein the blowing agent component C) comprises formic acid.

2. The polyol formulation as claimed in claim 1, wherein the polyol component A1) has a hydroxyl number of 280-600 mg KOH/g as determined by DIN 53240-2 (2007).

3. The polyol formulation P) as claimed in claim 1, wherein the isocyanate-reactive component A) comprises at least 65% by weight of the polyol component A1) which has a hydroxyl number between 280 to 600 mg KOH/g and a functionality of ≥ 2.8 to ≤ 6.0 and the proportion of primary OH functions in the component A) is at least 35% based on all terminal OH functions in the component A).

4. The polyol formulation P) as claimed in claim 1, wherein the isocyanate-reactive component A) comprises polyether polyol in an amount of at least 60% by weight.

5. The polyol formulation P) as claimed in claim 1, wherein the polyol formulation comprises the catalytically active compound D1) in an amount of $\geq 0.01\%$ to $< 2\%$ by weight based on the total weight of the component A).

6. A foam-forming reaction mixture R), comprising

an isocyanate-reactive component A) comprising at least one polyol component A1) comprising at least one of polyether polyols, polyester polyols, polycarbonate polyols, polyether polycarbonate polyols and polyether ester polyols which has an OH functionality of >2.5,

at least one polyisocyanate component B),

a blowing agent component C),

a catalyst component D) comprising a catalytically active compound D1) having Zerewitinoff-active hydrogens, an assistant or additive substance E) excluding a cell-opening compound,

wherein the proportion of all primary OH functions present in the isocyanate-reactive component A) based on the total number of terminal OH functions in the component A) is at least 30% and

wherein the blowing agent component C) comprises formic acid.

7. The foam-forming reaction mixture R) as claimed in claim 8, wherein the content of formic acid is 0.5-6% by weight based on the total amount of compounds having isocyanate-reactive hydrogen atoms in the foam-forming reaction mixture R).

8. A process for producing rigid PUR/PIR foams having an apparent density of 25-300 kg/m³, an open-cell content of >70%, and having an average cell diameter of ≤180 μm, comprising the steps of

- i) producing a foam-forming reaction mixture R) as claimed in claim 6,
- ii) introducing the foam-forming reaction mixture R) into a mold,
- iii) foaming the foam-forming reaction mixture R) and
- iv) demolding a rigid PUR/PIR foam formed from the foam-forming reaction mixture R).

9. The process as claimed in claim 8, wherein step i) is performed in a mixing head or high-pressure mixing head.

10. The process as claimed in claim 8, wherein in step ii) the foam-forming reaction mixture R) is introduced into a closed mold, wherein a counterpressure in the mold during injection is 2-90 bar.

11. The process as claimed in claim 10, wherein

in step iii) the counterpressure in the mold is held for a period 1 of 1-40 s after termination of step ii) and subsequently the counterpressure from the mold is released over a period 2 at a pressure release rate of 1-90 bar/s.

12. An open-celled rigid PUR/PIR foam obtainable by the process as claimed in claim 8.

13. A refrigerator, freezer or a fridge-freezer comprising a rigid PUR/PIR foam as claimed in claim 12.

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