(12) (19) (CA) **Demande-Application**

(21) (A1) **2,249,954**
(22) 1998/10/13
(43) 1999/04/15

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(51) Int.Cl.^{6} C08G 18/79, C08G 18/48, C08J 9/08
(30) 1997/10/15 (19745462.3) DE

(54) MOUSSES DE POLYURETHANE SEMI-RIGIDES A BASE DE POLYISOCYANATES MODIFIES PAR DU BIURET, COMPOSITES STRUCTURAUX FABRIQUES A L'AIDE DE CES MOUSSES ET PROCEDE DE FABRICATION

(54) SEMI-RIGID POLYURETHANE FOAMED MATERIALS BASED ON BIURET-MODIFIED POLYISOCYANATES, COMPOSITE STRUCTURAL COMPONENTS USING SAID SEMI-RIGID POLYURETHANE FOAMED MATERIALS, AND A PROCESS FOR THE PRODUCTION THEREOF

(57) Divulgation de mousses de polyuréthane semi-rigides de densité allant de 60.1 à 200 kg/m^3. On obtient ces mousses en faisant réagir a) un polyisocyanate ayant une teneur en NCO de 30-47% et renfermant un diisocyanate de toluène ayant une structure de biuret et une teneur en NCO située dans la gamme allant de 33 à 47 %, en poids, b) un polyol de polyéther ayant un poids moléculaire moyen allant de 1,000 à 12,000 et une fonctionnalité ≥ 2, c) de 0.5 à 8%, d'eau, par rapport au poids total des composants b), c), d), e) et f), d) facultativement, un autre polyol de poids moléculaire moyen allant de 62 à moins de 1,000 et de fonctionnalité ≥ 2, e) facultativement, des adjuvants, des additifs et des composés ignifuges supplémentaires, utilisés pour ce genre d'application, et f) facultativement, des agents d'expansion. L'indice d'isocyanate, mesuré comme étant le rapport entre le nombre de groupements isocyanates présents dans le composant a) et la somme des groupements isocyanates réactifs présents dans les composants b) à f), est maintenu entre 30 et 180. On décrit également un procédé pour produire ces mousses et leur utilisation dans des composites structuraux.

(57) Semi-rigid polyurethane foamed materials are described which have a density of 60.1 to 200 kg/m^3. These foamed materials are obtainable by the reaction (a) a polyisocyanate component which has an NCO content of 30-47%, and which comprises a toluene diisocyanate which has a biuret structure and which has an NCO value within the range from 33 to 47% by weight, (b) a polyether polyol component with an average molecular weight of 1,000 to 12,000 and a functionality ≥ 2, (c) from 0.5 to 8% by weight of water, based on the total weight of components (b), (c), (d), (e) and (f), (d) optionally, a further polyol component with an average molecular weight of 62 to less than 1,000 and a functionality ≥ 2, (e) optionally, with further adjuvant substances, additives and flame retardants known in the art, and (f) optionally blowing agents, while maintaining an isocyanate index of 30 to 180 with respect to the ratio of isocyanate groups present in component (a) to the sum of isocyanate-reactive groups present in components (b) to (f). A process for producing said foamed materials and the use thereof in composite structural components are also described.

LeA 32610 US

SEMI-RIGID POLYURETHANE FOAMED MATERIALS BASED ON BIURET-MODIFIED POLYISOCYANATES, SAID COMPOSITE STRUCTURAL COMPONENTS USING THESE SEMI-RIGID POLYURETHANE FOAMED MATERIALS, AND A PROCESS FOR THE PRODUCTION THEREOF

ABSTRACT OF THE DISCLOSURE

Semi-rigid polyurethane foamed materials are described which have a density of 60.1 to 200 kg/m^3. These foamed materials are obtainable by the reaction

(a) a polyisocyanate component which has an NCO content of 30-47%, and which comprises a toluene diisocyanate which has a biuret structure and which has an NCO value within the range from 33 to 47% by weight,

(b) a polyether polyol component with an average molecular weight of 1,000 to 12,000 and a functionality ≥ 2,

(c) from 0.5 to 8% by weight of water, based on the total weight of components (b), (c), (d), (e) and (f),

(d) optionally, a further polyol component with an average molecular weight of 62 to less than 1,000 and a functionality ≥ 2,

(e) optionally, with further adjuvant substances, additives and flame retardants known in the art, and

(f) optionally blowing agents,

while maintaining an isocyanate index of 30 to 180 with respect to the ratio of isocyanate groups present in component (a) to the sum of isocyanate-reactive groups present in components (b) to (f).

A process for producing said foamed materials and the use thereof in composite structural components are also described.

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SEMI-RIGID POLYURETHANE FOAMED MATERIALS BASED ON BIURET-MODIFIED POLYISOCYANATES, COMPOSITE STRUCTURAL COMPONENTS USING SAID SEMI-RIGID POLYURETHANE FOAMED MATERIALS, AND A PROCESS FOR THE PRODUCTION THEREOF

This invention relates to the production of semi-rigid polyurethane foamed materials by the reaction of biuret-modified polyisocyanates based on toluene diisocyanate (TDI) with polyether polyols using water as a blowing agent.

The production of polyurethane foamed materials is sufficiently well-known (see PUR-Handbuch, G. Oertel 1993, Volume 7, page 236 *et seq.*). Polyurethane foamed materials are used, for example, in the furniture and automobile sectors and are employed, for example, to form backing foams for sheet-like products for use as instrument panels or dashboards in motor vehicles.

In the automobile market, there is increasing emphasis on the requirement for weight-saving while maintaining the physical properties of the foam at the same level as the prior art foams. In order to fulfil this already-existing requirement by reducing the weight or density of the foam, the water content of the polyol component in general has to be increased considerably, and the formulation has to be adapted to this increased amount of water. However, the existing systems which are based on diphenylmethane diisocyanate (MDI) such as, for example, the semi-rigid backing foam Bayfill® supplied by Bayer AG, become increasingly more difficult to process as the water content increases, since existing molds and production options are not matched to the high internal pressures and gas yields. The processing ranges of foam systems such as these are becoming increasingly narrow.

With increasing dwell pressure, there is also a demand for an increase in productivity by reducing the demolding time from the current 4 to 5 minutes to < 2.5 minutes.

At the same time, however, the other properties of the foams, and particularly the properties required in long-term use, should not be impaired.

The object of the present invention was to provide semi-rigid polyurethane molded foamed materials characterized by a high foamed material hardness, a low density, and a demolding time which is as short as possible.

Surprisingly, it has now been found that the use of biuret-modified TDI for the production of semi-rigid polyurethane molded foamed materials results in foamed materials which have a low density which was previously unattainable. At the same time, these foamed materials exhibit good hardness and a short demolding time.

SUMMARY OF THE INVENTION

The present invention relates to semi-rigid polyurethane foamed materials having a density of 60.1 to 200 kg/m^3, and which are prepared by reacting

(a) a polyisocyanate component having an NCO group content of 20 to 47% by weight, and which comprises a toluene diisocyanate having a biuret structure and having an NCO group content of from 33 to 47% by weight,

with

(b) a polyether polyol component having an average molecular weight of 1,000 to 12,000, a functionality of at least 2, and, optionally, a solids content of no more than 50% by weight, based on the total weight of component (b),

(c) from 0.5 to 8% by weight, based on the total weight of components (b), (c), (d), (e) and (f), of water,

(d) optionally, a polyol component having an average molecular weight of 62 to less than 1,000, and a functionality of at least 2,

(e) optionally, additives,

and

(f) optionally, additional blowing agents,

wherein the ratio of isocyanate groups in component (a) to the sum of isocyanate-reactive groups present in components (b) through (e) is such that the isocyanate index ranges from 30 to 180, preferably 60 to 140, most preferably 80 to 120, with the reaction being carried out in an open or a closed molding tool.

The present invention also relates to a process of preparing the semi-rigid polyurethane foamed materials having a density of 60.1 to 200 kg/m^3 as described above.

In addition, the present invention relates to composite moldings comprising

A) a semi-rigid, inner polyurethane foam layer,

B) a supporting outer and/or inner layer made of plastics, metal or derived timber materials, for example, and

C) an outer layer comprising a flexible skin of plastics or of a natural product,

wherein A) said semi-rigid, inner polyurethane foam layer comprises polyurethane foamed materials having a molded density of 60.1 to 200 kg/m^3, and which are prepared by reacting:

(a) a polyisocyanate component having an NCO group content of 20 to 47% by weight, and which comprises a toluene diisocyanate having a biuret structure and an NCO group content of from 33 to 47% by weight,

with

(b) a polyether polyol component having an average molecular weight of 1,000 to 12,000, a functionality of at least 2, and, optionally, a solids content of no more than 50% by weight, based on the total weight of component (b),

(c) from 0.5 to 8% by weight, based on the total weight of components (b), (c), (d), (e) and (f), of water,

(d) optionally, a polyol component having an average molecular weight of 62 to less than 1,000 and a functionality of at least 2,

(e) optionally, additives,

and

(f) optionally, additional blowing agents,

wherein the ratio of isocyanate groups in component (a) to isocyanate-reactive groups in components (b) through (e) is such that the isocyanate index is from 30 to 180, preferably 60 to 140, most preferably 80 to 120, with the reaction being carried out in open or closed molding tools.

The preferred polyurethane foamed materials in accordance with the present invention are those in which the NCO group content of the TDI having a biuret structure of the polyisocyanate component (a) is either within the range of from 33 to 40% by weight, or of from 40 to 47% by weight. The preferred polyurethane foamed materials are also produced from the above process wherein component (e) additives comprises catalysts such as the so-called polymeric catalysts, as are described in, for example, U.S. Patent 5,445,879, the disclosure of which is herein incorporated by reference.

A polyisocyanate component (a) which has been mixed with TDI, MDI and/or polymeric MDI after the formation of biuret from the TDI can preferably be used for the production of the semi-rigid foamed materials according to the invention.

The polyisocyanate component (a) most preferably comprises, for example, one of the following compositions:

- TDI 80 (2,4- and 2,6-TDI in a weight ratio of 80:20 parts by weight) / TDI biuret / polymeric MDI (wherein the composition has an overall NCO group content of 42%);

- TDI biuret / polymeric MDI (wherein the composition has an overall NCO group content of 35%);
- TDI 80 / TDI biuret (wherein the composition has an overall NCO group content of 42%);
- TDI 80 / TDI biuret (wherein the composition has an overall NCO group content of 40%);
- TDI 100 (100% by weight 2,4-TDI) / TDI biuret (wherein the composition has an overall NCO group content of 42%);
  and
- TDI 80 / TDI biuret (wherein the composition has an overall NCO group content of 37%).

The production of TDI having a biuret structure has already been known for a very long time and can be effected in various ways, as is documented in numerous patent specifications. On an industrial scale, 3 procedures are important:

(1) the reaction of TDI with t-butanol (as described in, for example, DD-A-214,847);

(2) the reaction of TDI with water (as described in, for example, DE-A-2,117,575 and in British Patent 1,365,629);

and

(3) the reaction of TDI with an amine (as described in, for example, U.S. Patents 3,903,126 and 4,618,706, the disclosures of which are herein incorporated by reference, and as described in DE-A-2,261,065, DE-A-1,174,749, and DE-A-3,114,638).

A common feature of all three of these processes is the batch-wise reaction of components to form the biuret. In processes (1) and (2) described above, gaseous reaction products (i-butene, CO_2) are produced in this stage, which have to be disposed of or conveyed away. Moreover, NCO groups produced from an amine are converted back to the amine again, which makes little sense economically. It is therefore preferred to use the amine process, i.e., process (3), as set forth above. In order to achieve a constant high conversion in this amine variant, it is necessary to take up the amine for the entire duration of the reaction in a solvent which is subsequently distilled off again.

The TDI with a biuret structure is preferably produced by a continuous process, by the reaction of the pure starting materials (i.e., TDI and amine), as described in, for example, U.S. Patent 4,837,359, the disclosure of which is herein incorporated by reference, and in EP-A-0,277,353, without the necessity of having to effect further work-up or the subsequent disposal of by-products.

The TDI with a biuret structure is most preferably produced in a single-step continuous process, as described in, for example, DE-A 1 9,707,577, by continuously 1) mixing together TDI with organic diamines comprising aromatically bonded amino groups in a molar ratio of at least 8:1 in a mixing chamber, and 2) reacting the mixture at a temperature above 180°C, wherein the maximum dwell time of the reactants or of the reaction mixture in the mixing chamber after combining the reactants is 60 seconds.

A mixture of 80% by weight toluene-2,4-diisocyanate and 20% by weight toluene-2,6-diisocyanate (TDI 80), the mixture TDI 65, or TDI 100 is preferably used for the process of preparing the TDI with a biuret structure.

Other starting materials include organic diamines comprising aromatically bonded amino groups and having molecular weights of less than 300. Preferred organic diamines include 2,4- and/or 2,6-diaminotoluene or diphenylmethane-diamine.

During the formation of biuret, the TDI and the diamine are continuously reacted in quantitative ratios which correspond to an equivalent ratio of isocyanate groups to amino groups of at least 8:1, preferably of 10:1 to 20:1, wherein the amino groups are included in the calculation as monofunctional groups. It is essential that the starting materials are reacted with each other immediately after they have been thoroughly mixed, at a temperature above 180°C, preferably above 200°C. The heating of TDI has to be carried out within a period of time which is as short as possible, preferably within a period of less than 30 seconds, on account of the known temperature-sensitivity of this compound.

After the preheating step described above, continuous streams of the reactants are combined in a mixing chamber for a maximum dwell time of 60 seconds.

After passing through the mixing chamber and, optionally, through a dwell time section disposed downstream of the mixing chamber, the reaction mixture is continuously passed through suitable heat exchangers, and is cooled, continuously or in steps and within 10 minutes at most, to a temperature within the range of from 120 to 200°C. It is subsequently cooled as rapidly as possible, by means of a high-efficiency cooling device, to a temperature of less than 50°C, in order to suppress dimerization, which would otherwise occur as a secondary reaction and which would result in the unwanted formation of solids.

The present invention also relates to a process for the production of semi-rigid polyurethane foamed materials having a molded density of 60.1-200 kg/m^3, and comprising reacting:

(a) a polyisocyanate component having an NCO group content of 30-47% by weight, and which comprises a toluene diisocyanate having a biuret structure and having an NCO group content in the range of from 33 to 47% by weight,

with

(b) a polyether polyol component having an average molecular weight of 1,000 to 12,000, a functionality of at least 2, and, optionally, a solids content of no more than 50% by weight, based on the total weight of component (b),

(c) from 0.5 to 8% by weight, based on the total weight of components (b), (c), (d), (e) and (f), of water,

(d) optionally, a polyol component having an average molecular weight of 62 to less than 1,000 and a functionality of at least 2,

(e) optionally, additives,

and

(f) optionally, additional blowing agents,

wherein the ratio of isocyanate groups in component (a) to the sum of isocyanate-reactive groups present in components (b) through (e) is such that the isocyanate index is in the range of from 30 to 180, preferably 60 to 140 and most preferably 80 to 120, with the reaction being carried out in an open or a closed molding tool.

Compared with, for example, instrument panel systems, etc., which employ prior art MDI polyisocyanates, the systems according to the invention which comprise biuret isocyanates have the following advantages:

- TDI is used for the first time for instrument panels, etc.
- additional, considerable reductions in weight and density are possible,
- higher water contents are now possible,
- the degree of hardness of the semi-rigid foams can be varied over a very wide range via the isocyanate index,

and

- on account of their open-cell character, they have a very low gas-sensitivity, thereby making a wide range of different weights possible, without gas problems.

TDI having a biuret structure is advantageously used as a starting material for semi-rigid foamed materials according to the invention. The foamed materials according to the invention can be obtained as block foamed materials, but are, in general, obtained as molded foamed materials. The production of molded foam can be carried out via what is commonly referred to as the one-shot process. The TDI having a biuret structure as described above is used in this process, optionally in admixture with additional MDI or TDI, and particularly with TDI 80, MDI 80/20, TDI 65 or TDI 100.

Polyether polyols or mixtures thereof, which are produced in the manner known in the art by the alkoxylation of suitable starter molecules or mixtures of suitable starter molecules, are used as polyether polyol component (b), wherein propylene oxide in particular, and, optionally, ethylene oxide in addition are used for alkoxylation. These polyether polyols have an average molecular weight of 1,000 to 12,000, and an average functionality of at least 2. Examples of suitable starter molecules include, for example, water, ethylene glycol, propylene glycol, trimethylolpropane, glycerol, pentaerythritol, sorbitol, and/or cane sugar. The preferred polyether polyols are those which have a primary OH group content of greater than 50%, and most preferably of greater than 70%. Polyether polyols of this type are formed by the grafting on of terminal ethylene oxide units.

Highly reactive polyols are most preferably used. These are trifunctional polyols, which in addition to a high molecular weight, which is usually between about 4,800 and 6,000 g/mole, contain at least 70% of primary hydroxyl groups, such that the OH number thereof is between 35 and 28. These polyols are composed of up to 87% of propylene oxide, but can exclusively contain ethylene oxide terminal groups. Polyester polyols can also optionally be used in conjunction as a portion of component (b).

Styrene-acrylonitrile (SAN), which are known in the art, can be added as a solid, in an amount up to a solids content of 50% by weight, based on the total weight of the polyether polyol component (b). For the production of the foamed materials in accordance with the present invention, however, the additional use of solids in polyether polyol component (b), and also the additional use of crosslinking component (d), can be omitted completely.

If a crosslinking component (d) is to be added, suitable substances of this type which can be used as crosslinking agents include compounds such as, for example, diethanolamine, triethanolamine, glycerol, trimethylolpropane (TMP), addition products of crosslinking compounds such as these with ethylene- and/or propylene oxide with an OH number of less than 1,000, and, also, glycols with a molecular weight less than 1,000, for example.

Triethanolamine, glycerol, TMP, or low molecular weight EO- and/or PO- addition products thereof, are particularly preferred as crosslinking components (d).

Furthermore, adjuvant substances, additives and/or flame retardants known in the art can optionally also be included as further components (e). The term "adjuvant substances" should be understood in particular to mean catalysts and stabilizers which are known in the art.

It is possible to use melamine, for example, as a flame retardant in accordance with the present invention.

Examples of substances which can optionally be used as adjuvant substances and additives include catalysts of the type known in the art. Some suitable examples of catalysts include tertiary amines such as, for example, triethylamine, tributylamine, N-methyl-morpholine, N-ethyl-morpholine, N,N,N',N'-tetramethyl-ethylenediamine, pentamethyldiethylene-triamine and higher homologues (as described in, for example, U.S. Patent 4,143,003, the disclosure of which is herein incorporated by reference, and in DE-A-2,624,527 and 2,624,528), 1,4-di-aza-bicyclo-(2,2,2)-octane-N-methyl-N'-dimethylaminoethyl-piperazine, bis-(dimethylaminoalkyl)-piperazine (as described in, for example, DE-A-2,636,787), N,N-dimethylbenzylamine, N,N-dimethylcyclohexylamine, N,N-diethylbenzyl-amine, bis-(N,N-diethylaminoethyl)-adipate, N,N,N',N'-tetramethyl-1,3-butanediamine, N,N-dimethyl-β-phenylethylamine, 1,2-dimethylimidazole, 2-methylimidazole, monocyclic and bicyclic amidines (as described in, for example, U.S. Patent 3,814,707, the disclosure of which is herein incorporated by reference, and in DE-A-1,720,633), bis-(dialkylamino)-alkyl ethers (as described in, for example, U.S. Patent 3,330,782, the disclosure of which is herein incorporated by reference, and as described in, for example, U.S. Patent 3,694,510, the disclosure of which is herein incorporated by reference, and in DE-A-1,030,558, DE-A-1,804,361 and 2,618,280), as well as tertiary amines comprising amide groups (preferably formamide groups) as described in, for example, U.S. Patents 4,248,930 and 4,348,536, the disclosures of which are herein incorporated by reference, and in DE-A-2,523,633 and 2,732,292. Mannich bases, which are known in the art, comprising secondary amines such as dimethylamine and aldehydes, preferably formaldehyde, or ketones such as acetone, methyl ethyl ketone or cyclohexanone, and phenols such as phenol, nonylphenol or bisphenol, are also suitable as catalysts.

Examples of tertiary amines which contain active hydrogen atoms which are reactive towards isocyanate groups and which can be used as catalysts include compounds such as triethanolamine, triisopropanolamine, N-methyl-diethanolamine, N-ethyl-diethanolamine, N,N-dimethyl-ethanolamine, and the reaction products thereof with alkylene oxides such as, for example, propylene oxide and/or ethylene oxide, and also secondary-tertiary amines as set forth in U.S. Patent 4,248,930, the disclosure of which is herein incorporated by reference, and in DE-A-2,732,292.

Silaamines comprising carbon-silicon bonds, such as those which are described in, for example, DE-A-1,229,290, are also suitable as catalysts. Such compounds include, for example, 2,2,4-trimethyl-2-silamorpholine and 1,3-diethyl-aminomethyl-tetramethyl-disiloxane.

Other suitable catalysts include nitrogen-containing bases such as, for example, tetraalkylammonium hydroxides, and also alkali metal hydroxides such as sodium hydroxide, alkali metal phenolates such as sodium phenolate, or alkali metal alcoholates such as sodium methylate. Hexahydrotriazines can also be used as catalysts (see, for example, DE-A-1,769,043).

The reaction between NCO groups and Zerewitinoff-active hydrogen atoms is also considerably increased by lactams and azalactams, wherein an associative linkage is first formed between the lactam and the compound comprising acidic hydrogen. Associative linkages of this type and the catalytic effect thereof are described in, for example, U.S. Patents 3,758,444 and 3,867,373, the disclosures of which are herein incorporated by reference, and in DE-A-2,062,286, 2,062,289, 2,117,576, 2,129,198, 2,330,175 and 2,330,211.

Organic compounds of metals, and particularly organic compounds of tin, can also be used as catalysts in accordance with the present invention. In addition to sulfur-containing compounds such as, for example, di-n-octyltin mercaptide (as described in, for example, DE-A-1,769,367 and U.S. Patent 3,645,927, the disclosure of which is herein incorporated by reference, the preferred organic compounds of tin include tin(II) salts of carboxylic acids such as, for example, tin(II) acetate, tin(II) octoate, tin(II) ethylhexoate and tin(II) laurate; and tin(IV) compounds such as, for example, dibutyltin oxide, dibutyltin dichloride, dibutyltin diacetate, dibutyltin dilaurate, dibutyltin maleate or dioctyltin diacetate.

All of the aforementioned catalysts can, of course, be used as mixtures. Combinations of organic compounds of metals with amidines, amino-pyridines or hydrazinopyridines (as described in, for example, U.S. Patents 4,006,124, 4,115,320 and 4,150,212, the disclosures of which are herein incorporated by reference, and in DE-A-2,434,185, 2,601,082 and 2,603,834) are of particular interest in this respect.

The so-called polymeric catalysts, such as those described in, for example, U.S. Patent 5,445,879, the disclosure of which is herein incorporated by reference, and in DE-A-4,218,840, are preferably used as the catalysts which are optionally present (i.e. component (e)). These catalysts are the reaction products, which exist in the form of alkali metal salts, of (i) tri-functional alcohols or alcohols of higher functionality, of a molecular weight range of 92 to 1,000, with (ii) intramolar carboxylic acid anhydrides. The reaction products contain (as a statistical mean) at least 2, preferably 2 to 5 hydroxyl groups, and at least 0.5, preferably 1.0 to 4 carboxylate groups, wherein the counterions to the carboxylate groups constitute alkali cations. It can be seen from the content of carboxylate groups that the “reaction products” of starting components (i) and (ii) can also be mixtures of actual reaction products with excess amounts of alcohols (i).

Examples of suitable polyhydric alcohols for the production of these reaction products include glycerol, trimethylolpropane, sorbitol, pentaerythritol, mixtures of polyhydric alcohols of this type, alkoxylation products of the aforementioned molecular weight range of polyhydric alcohols of this type, or mixtures of alcohols of this type, wherein propylene oxide and/or ethylene oxide are used in an arbitrary sequence or in admixture for alkoxylation, but propylene oxide is preferably used exclusively for alkoxylation.

Examples of suitable intramolecular carboxylic acid anhydrides for the production of these reaction products include maleic anhydride, phthalic anhydride, hexahydrophthalic anhydride, succinic anhydride, pyromellitic anhydride or any mixtures of anhydrides of this type. Maleic anhydride is most preferably used.

Other representatives of catalysts which can be used, as well as details on the mode of action of these catalysts, are described in, for example, Kunststoff-Handbuch, Volume VII, edited by Vieweg and Höchtlen, Carl-Hanser-Verlag, Munich 1966, e.g., on pages 96 to 102.

The catalysts are typically used in an amount between about 0.001 and 10% by weight, based on the total weight of the components containing at least two hydrogen atoms which are capable of reacting with isocyanate groups.

Further additives which may optionally be used include surface-active additives such as emulsifiers and foam stabilizers. Example of suitable emulsifiers include the sodium salts of castor oil sulfonates or salts of fatty acids with amines such as diethylamine oleate or diethanolamine stearate. Alkali metal salts or ammonium salts of sulfonic acids such as dodecylbenzene-sulfonic acid or dinaphthylmethanedisulfonic acid or of fatty acids such as ricinoleic acid or of polymeric fatty acids can also be used in conjunction as surface-active additive substances.

Polyether siloxanes, especially water-soluble representatives thereof, are mainly used as foam stabilizers. In general, these compounds are synthesized so that a copolymer of ethylene oxide and propylene oxide is bonded to a polydimethylsiloxane radical. Foam stabilizers of this type are described in, for example, U.S. Patents 2,834,748, 2,917,480 and 3,629,308, the disclosures of which are herein incorporated by reference. Polysiloxane-polyoxyalkylene copolymers which are multiple-branched via allophanate groups as described in, for example, U.S. Patents 4,096,162 and 4,163,830, the disclosures of which are herein incorporated by reference, and in DE-A-2,558,523, are of particular interest.

Other possible additives include reaction retarding agents such as, for example, substances which have an acidic reaction such as hydrochloric acid or organic acid halides, and also cell regulators of the type known in the art such as paraffins or fatty alcohols or dimethylpolysiloxanes, as well as pigments or colorants, and flame retardants of the type known in the art, e.g., trischloroethyl phosphate, tricresyl phosphate or ammonium phosphate and polyphosphate, and also stabilizers against the effects of ageing and weathering, plasticizers and substances with a fungistatic and bacteriostatic effect, as well as fillers such as barium sulfate, silaceous earth, carbon black or whitening.

Other examples of surface-active additives and foam stabilizers and of cell regulators, reaction retarders, stabilizers, flame-retardant substances, plasticizers, colorants and fillers, and of substances having a fungistatic or bacteriostatic effect which are optionally used in accordance with the present invention, as well as details on the mode of use and mode of action of these additives, are described in, for example, the Kunststoff-Handbuch, Volume VII, edited by Vieweg and Höchtlen, Carl-Hanser-Verlag, Munich 1966, e.g., on pages 103 to 113.

It is possible to use all the blowing agents which are known for the production of PU foams as blowing agent component (f) which is optionally used in the present invention. Examples of some suitable organic blowing agents include acetone, ethyl acetate, halogen-substituted alkanes such as, for example, methylene chloride, chloroform, ethylidene chloride, vinylidene chloride, mono-fluorotrichloromethane, chlorodifluoromethane and dichlorodifluoromethane, and also butane, hexane, heptane or diethyl ether. Some examples of suitable inorganic blowing agents include air, CO_2 or N_2O. A blowing effect can also be achieved by the addition of compounds which decompose at temperatures above room temperature with the evolution of gases, of nitrogen for example, e.g. azo compounds such as azodicarbonamide or azoisobutyronitrile. Examples of suitable organic blowing agents include hydrogen-containing fluoroalkanes (i.e., chlorofluoro-hydrocarbons), as well as lower alkanes, such as, for example, butane, pentane, isopentane, cyclopentane, and hexane or iso-hexane, optionally in admixture with each other and/or with the addition of water. Further examples of blowing agents, as well as details on the use of blowing agents, are described in the Kunststoff-Handbuch, Volume VII, edited by Vieweg and Höchtlen, Carl-Hanser-Verlag, Munich 1966, e.g., on pages 108 and 109, 453 to 455 and 507 to 510.

Water (i.e., component (c)) is preferably, however, the sole blowing agent. In another preferred embodiment, water (i.e., component (c)) and CO_2 (i.e., component (F)) are used as blowing agents.

With the polyurethane foamed materials according to the invention, it is surprisingly possible to achieve a good processing band-width (e.g., variation of characteristic properties or temperature) and good physical properties (e.g., crushing hardness, tensile strength) while using a water content in the polyol formulation during production which is considerably higher than that of the prior art. Polyurethane moldings can thus be produced which have a significantly lower density or hardness than was hitherto possible with the isocyanates according to the prior art. Moreover, at an identical solids content, the polyurethane foamed materials according to the present invention exhibit a considerable increase in hardness in relation to comparable prior art foamed materials, simply by altering the mixture ratio of the isocyanate and polyol components. Thus, the use of solids can optionally be dispensed with completely.

According to the invention, by using TDI having a biuret structure for the production of the polyurethane foamed materials according to the invention, a significant shortening of the tack-free time can be achieved using a catalyst content which is otherwise customary for standard mixtures, and a short demolding time after the completion of the foaming process can thus be achieved. Surprisingly, there is thus not only a considerable shortening of the times of reaction, such as that which is otherwise usually observed on increasing the amount of catalyst in order to achieve shorter demolding times.

According to the invention, the reaction components are reacted by the single-step process known in the art, namely by the prepolymer process or the semi-prepolymer process, wherein mechanized devices are often employed, such as, for example, those devices which are described in, for example, U.S. Patent 2,764,565, the disclosure of which is herein incorporated by reference. Details of processing devices which are also suitable according to the invention are described in the Kunststoff-Handbuch, Volume VII, edited by Vieweg and Höchtlen, Carl-Hanser-Verlag, Munich 1966, e.g., on pages 121 to 205.

During the production of the foamed materials, foaming can also be conducted according to the invention in closed molds. The reaction mixture is introduced into a mold in the course of this procedure. Metals, such as, for example, aluminum, or plastics such as, for example, epoxy resin, are suitable as mold materials. The foamable reaction mixture foams in the mold and forms the molded article. Mold foaming can be conducted such that the molded article has a cellular structure at its surface. It can also be conducted so that the molded article has a solid skin at its surface and a cellular core, i.e., such that it forms an integral skin foam or a compact skin foam. In this connection, the procedure according to the invention may be such that an amount of foamable reaction mixture is introduced into the mold which just fills the mold. However, a procedure may also be used in which more foamable reaction mixture is introduced into the mold than is necessary to fill the interior of the mold with foamed material. "Overcharging" is thus employed in the latter case; a procedure of this type is known from and described in, for example, U.S. Patents 3,178,490 and 3,182,104, the disclosures of which are herein incorporated by reference.

"External mold release agents" such as silicone oils, waxes or soaps which are known in the art are often used in conjunction in mold foaming. What are termed "internal mold release agents" can also be used, optionally in admixture with external mold release agents. Examples of internal mold release agents such as these have become known from, for example, U.S. Patents 3,925,527 and 4,201,847, the disclosures of which are herein incorporated by reference, and in DE-A-2,121,670 and 2,307,589.

Cold-curing foamed materials can also be produced in accordance with the present invention as described in, for example, U.S. Patent 3,887,483, the disclosure of which is herein incorporated by reference, and in British Patent 1,162,517 and DE-A-2,153,086.

Foamed materials can also of course be produced by block foaming or by the double conveyor belt process which is known in the art.

The products which can be produced according to the invention may be employed in, for example, the following areas of application: dashboards, arm rests, instrument panel linings, glove compartment covers, door interior linings, and in similarly constructed components in other areas of industry.

Assembled articles of manufacture such as, for example instrument panels comprise not only A) the semi-rigid polyurethane foam according to the present invention as described above, but also comprise B) a supporting outer and/or inner layer made of plastics for example, such as a PC/ABS blend, ABS, ABS-GF, SMA, PP-GMT, metals such as sheet steel or aluminum, or derived timber products such as cellulose fibers bonded with PP or phenolic resins, and C) an outer layer comprising a flexible skin of plastics, such as a PVC, TPO or TPU slush-molded skin, a PVC/ABS skin or a natural product such as leather.

As used herein, the phrase "average molecular weight" refers to the number average molecular weight as determined by end-group analysis.

The following examples further illustrate details for the process of this invention. The invention, which is set forth in the foregoing disclosure, is not to be limited either in spirit or scope by these examples. Those skilled in the art will readily understand that known variations of the conditions of the following procedures can be used. Unless otherwise noted, all temperatures are degrees Celsius and all percentages are percentages by weight.

EXAMPLES

Free foam production (laboratory):

The components, which were conditioned at 25°C, were caused to react by means of stirrers (SPW or Pendraulik stirrers), using the following procedure: the isocyanate component was introduced into the reaction vessel which contained the polyol formulation. The components were subsequently mixed in the reaction vessel by means of stirrers. The rotational speed was 1400 rpm and the time of stirring was 10 seconds.

Determination of the start time:

The start time is the period from the start of mixing (immersion of the stirrer disc) until the clearly identifiable start of reaction. The start of reaction is manifested by an increase in volume of the reacting mixture.

Determination of the rise time:

The rise time is to be understood as the time interval between the start of mixing and the maximum vertical expansion of the foam. In MDI systems, which slump again due to their open-celled character, the transition point from the rise phase to the slump phase is deemed to be the end of the rise phase; in systems which do not slump, the end of the expansion of the foam is deemed to be the end of the rise phase.

Production of moldings:

The raw materials were processed by the reaction injection molding (RIM) technique. This is a filling technique in which the highly active liquid starting components are introduced into the mold within a short time via metering and mixing units.

The raw material components were heated to temperatures of 25 to 30°C. Before the actual production of the molding, the scheduled instrument panel mold was heated to the temperature of about 40°C which was necessary for the foaming process. Thereafter, adhering foam residues from previous tests were removed, the aeration slots or aeration holes were cleaned, and finally the inner walls of the mold were treated with a suitable mold release agent. After the pressure, temperature, mixture ratio (=isocyanate index) and feeding time of the raw material components had been set, the molded article was produced by mechanically mixing the raw materials and discharging the ready-to-foam mixture linearly into the mold. After the input was complete, the mold was closed. After the elapse of the molding time specific to the raw material system, the mold was opened and the molded part was removed.

Raw materials used:

Polyether 1: a trimethylolpropane/propylene oxide/ethylene oxide adduct, having an OH number of 28 mg KOH/g, and a MW of 6,000

Polyether 2: a trimethylolpropane/propylene oxide/ethylene oxide adduct, having an OH number of 35 mg KOH/g, and a MW of 4,800

Polyether 3 : a styrene acrylonitrile (SAN) polymer polyol having an OH number of 28 mg KOH/g, and containing 20% by weight solids

Crosslinking agent 1: glycerol, characterized by an OH number of 1,825 mg KOH/g

Crosslinking agent 2: diethanolamine, characterized by an OH number of 1,600 mg KOH/g

Cell opener 1: a glycerol/propylene oxide/ethylene oxide adduct, having an OH number of 36 mg KOH/g

Crosslinking agent 4: a triethanolamine/propylene oxide adduct, having an OH number of 1,825 mg KOH/g

Catalyst 1: 2,2'-bis(dimethylaminoethyl)ether as a 70% (by weight) solution in dipropylene glycol

Catalyst 2: triethylenediamine as a 33% (by weight) solution in dipropylene diglycol

Catalyst 3: Desmorapid VP.PU 59IF05; commercially available from Bayer AG (as described in, for example, U.S. Patent 5,445,879, the disclosure of which is herein incorporated by reference, and in DE-OS 4,218,840)

Catalyst 4: Desmorapid VP.PU 59IF06; commercially available from Bayer AG (as described in, for example, U.S. Patent 5,445,879, the disclosure of which is herein incorporated by reference, and in DE-A-4,218,840)

Bonding agent 1: an adipic acid/1,6-hexanediol polyester as a 50% (by weight) solution in benzyl butyl phthalate

Dispersing agent 1: a mixture of C_{12}-C_{18} fatty alcohols which were alkoxylated to an OH number of 52 with a 1:1 EO/PO mixture

The following TDI components with a biuret structure were used for the production of the foamed materials according to the invention:

Isocyanate 1: a mixture comprising TDI 80 and TDI biuret, having an overall NCO group content of 37% by weight

The TDI with a biuret structure was produced in the manner known in the art, such as that explained in the description. This substance was correspondingly mixed with TDI 80 to the given NCO value.

The semi-rigid foamed materials which were produced in accordance with the present invention were compared with semi-rigid foams according to the prior art. The following prior art isocyanate component was used for this purpose:

Isocyanate A: Desmodur MDI 44V20; a commercially product of Bayer AG, based on diphenylmethane diisocyanate and having an approximate NCO group content of 31.5

The following examples are presented in the form of a Table. Example 1 is a comparative example and representative of the prior art. The reaction times, tack-free times and demolding times given therein are defined as follows:

reaction times = cream time/gel time/rise time at an isocyanate index of 100

tack-free time = period within which the surface of a free foam no longer tends to stick at an isocyanate index of 100

MR 100: mixing ratio at an index of 100:100 (parts per weight of polyol formulation per x parts per weight of isocyanate)

Comparison of foaming results for a comparable polyol formulation:

Examples 1 to 5:

Example	1	2	3	4	5
Polyether 1	71.18	71.18	71.18	70.24	70.24
Polyether 2	-	-	-	-	-
Polyether 3	17.92	17.92	18.32	17.35	17.35
Crosslinking agent 1	-	-	-	-	-
Crosslinking agent 2	-	-	-	3.00	3.00
Cell opener 1	-	-	-	-	-
Crosslinking agent 4	2.69	2.69	2.69	8.68	8.68
Water	2.62	2.62	2.22	1.56	1.80
Dispersing agent 1	-	-	-	-	-
Catalyst 1	-	-	-	-	-
Catalyst 2	-	-	-	-	-
Catalyst 3	4.00	4.00	4.00	-	-
Catalyst 4	-	-	-	-	1.00
Black paste N	0.95	0.95	0.95	-	-
Bonding agent 1	1.95	1.95	1.95	-	-
Sum of parts by weight	101.31	101.31	101.31	100.83	102.07
MR 100	48.9	41.7	36.7	40.4	43.4

Comparison of foaming results for a comparable polyol formulation:

Examples 1 to 5: (Cont.)

Example	1	2	3	4	5
Desmodur 44V20	Isocyanate A	Isocyanate 1	Isocyanate 1	Isocyanate 1	Isocyanate 1
Isocyanate Index	100	100	100	100	100
Cream time [sec]	9	3	5	7	5
Rise time [sec]	100	100	120	131	80
Tack-free time [sec]	120	>240	>240	>180	-
Free foamed bulk density [kg/m^3]	45	36	67	59	48
Weight [g] of instrument panel mold 1, perforated metal support, open mode of filling	3020	2600	3000	-	-
Weight [g] of instrument panel mold 2, plastics support partially surrounded by foam, closed mode of filling	-	-	-	~1750	1930

Comparison of foaming results for a comparable polyol formulation:

Examples 6-10:

Example	6	7	8	9	10
Polyether 1	70.24	70.24	-	-	90.00
Polyether 2	-	-	75.00	75.00	-
Polyether 3	17.35	17.35	20.00	20.00	-
Crosslinking agent 1	1.00	1.00	0.50	0.50	1.00
Crosslinking agent 2	3.00	3.00	1.00	1.00	0.50
Cell opener 1	-	-	1.50	1.50	-
Crosslinking agent 4	8.68	8.68	-	-	-
Water	2.30	2.80	2.50	3.80	3.80
Dispersing agent 1	-	-	5.00	5.00	5.00
Catalyst 1	-	-	0.50	0.50	0.50
Catalyst 2	-	-	0.67	0.67	0.50
Catalyst 3	-	-	-	-	-
Catalyst 4	-	-	-	-	-
Black paste N	-	-	-	-	-
Bonding agent 1	-	-	-	-	-
Sum of parts by weight	102.57	103.07	106.67	107.97	101.30
MR 100	49.4	55.3	40.9	55	58.2

Comparison of foaming results for a comparable polyol formulation:

Examples 6-10: (Cont.)

Example	6	7	8	9	10
Desmodure 44V20	Isocyanate 1	Isocyanate 1	Isocyanate 1	Isocyanate 1	Isocyanate 1
Characteristic number	100	100	100	100	100
Cream time [sec]	4-5	4-5	4	5	7
Rise time [sec]	77	69	64	66	133
Tack-free time [sec]	120	96	123	144	183
Free foamed bulk density [kg/m^3]	48	41	46	33	26
Weight [g] of instrument panel mold 1, perforated metal support, open mode of filling	-	-	2600	-	-
Weight [g] of instrument panel mold 2, plastics support partially surrounded by foam, closed mode of filling	1700	1690	<1800	1070	1000

Although the invention has been described in detail in the foregoing for the purpose of illustration, it is to be understood that such detail is solely for that purpose and that variations can be made therein by those skilled in the art without departing from the spirit and scope of the invention except as it may be limited by the claims.

The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:-

1. A semi-rigid polyurethane foam having a density of 60.1 to 200 kg/m^3, and being prepared by reacting

(a) a polyisocyanate component having an NCO group content of from 30 to 47% by weight, and comprising a toluene diisocyanate having a biuret structure and an NCO group content of from 33 to 47% by weight,

with

(b) a polyether polyol component having an average molecular weight of from 1,000 to 12,000, a functionality of at least 2, and, optionally, a solids content of no more than 50 parts by weight, based on the total weight of (b),

(c) from 0.5 to 8% by weight based on the total weight of components (b), (c), (d), (e) and (f), of water,

(d) optionally, a polyol component having an average molecular weight of from 62 to less than 1,000 and a functionality of at least 2,

(e) optionally, additives,

and

(f) optionally, blowing agents,

wherein the ratio of isocyanate groups in component (a) to the sum of isocyanate-reactive groups present in components (b) through (e) is such that the isocyanate index ranges from 30 to 180, with the reaction being carried out in an open or a closed mold.

2. The semi-rigid polyurethane foam of Claim 1, wherein the isocyanate index ranges from 60 to 140.

3. The semi-rigid polyurethane foam of Claim 1, wherein the NCO group content of the toluene diisocyanate having a biuret structure is in the range of from 33 to 40% by weight or of from 40 to 47% by weight.

4. The semi-rigid polyurethane foam Claim 1, wherein component (e) comprises catalysts as additives, wherein said catalysts the reaction products, which are present in the form of an alkali metal salt, of (i) alcohols which are at least trihydric with (ii) intramolecular carboxylic acid anhydrides.

5. The semi-rigid polyurethane foam of Claim 1, wherein (a) said polyisocyanate component comprises a mixture of a toluene diisocyanate having a biuret structure, and an isocyanate selected from the group consisting of toluene diisocyanate, diphenylmethane diisocyanate and polymethylene poly(phenylisocyanate).

6. The semi-rigid polyurethane foam of Claim 5, wherein (a) said polyisocyanate component is selected from the group consisting of:

(a)(1) a mixture comprising TDI 80 (2,4- and 2,6-TDI; 80/20 parts by weight), TDI biuret, and polymeric MDI, and having an overall NCO group content of 42% by weight;

(a)(2) a mixture comprising TDI 80 and TDI biuret, and having an overall NCO group content of 42% by weight;

(a)(3) a mixture comprising TDI 80 and TDI biuret, and having an overall NCO group content of 40% by weight;

(a)(4) a mixture comprising TDI 100 and TDI biuret, and having an overall NCO group content of 42% by weight;

and

(a)(5) a mixture comprising TDI 80 and TDI biuret, and having an overall NCO group content of 37% by weight.

7. The semi-rigid polyurethane foam of Claim 1, wherein (a) said polyisocyanate component additionally comprises a mixture of toluene diisocyanate, diphenylmethane diisocyanate and/or polymeric diphenylmethane diisocyanate.

8. A process for the production of a semi-rigid polyurethane foam having a molded density of 60.1 to 200 kg/m^3, comprising reacting

(a) a polyisocyanate component having an NCO group content of 30 to 47% by weight, and comprising a toluene diisocyanate having a biuret structure and an NCO group content of from 33 to 47% by weight; with

(b) a polyether polyol component having an average molecular weight of 1,000 to 12,000, a functionality at least 2, and, optionally, a solids content of no more than 50% by weight, based on the total weight of component (b);

(c) from 0.5 to 8 % by weight, based on the total weight of components (b), (c), (d), (e) and (f), of water;

(d) optionally, a polyol component having an average molecular weight of 62 to less than 1,000 and a functionality of at least 2;

(e) optionally, additives;

and

(f) optionally, additional blowing agents,

wherein the ratio of isocyanate groups in component (a) to the sum of isocyanate-reactive groups present in components (b) through (e) is such that the isocyanate index ranges from 30 to 180, with the reaction being carried out in an open or a closed mold.

9. The process of Claim 8, wherein the isocyanate index ranges from 60 to 140.

10. A composite molding comprising

A) a semi-rigid, inner polyurethane foam layer,

B) a supporting middle and/or outer layer made of plastics, metal or derived timber materials, and

C) an outer layer comprising a flexible skin comprising a plastic or a natural product, wherein A) said semi-rigid, inner polyurethane foam layer has a density of 60.1 to 200 kg/m^3 and is prepared by reacting:

(a) a polyisocyanate component having an NCO group content of from 30 to 47% by weight, and comprising a toluene diisocyanate having a biuret structure and an NCO group content of from 33 to 47% by weight,

with

(b) a polyether polyol component having an average molecular weight of from 1,000 to 12,000, a functionality of at least 2, and, optionally, a solids content of no more than 50 parts by weight, based on the total weight of (b),

(c) from 0.5 to 8% by weight based on the total weight of components (b), (c), (d), (e) and (f), of water,

(d) optionally, a polyol component having an average molecular weight of from 62 to less than 1,000 and a functionality of at least 2,

(e) optionally, additives,

and

(f) optionally, blowing agents,

wherein the ratio of isocyanate groups in component (a) to the sum of isocyanate-reactive groups present in components (b) through (e) is such that the isocyanate index ranges from 30 to 180, with the reaction being carried out in an open or a closed mold.

11. The composite molding of Claim 10, wherein said isocyanate index ranges from 60 to 140.