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(54) A PROCESS FOR PREPARING A RIGID POLYURETHANE FOAM AND LAMINATE ARTICLES THEREWITH
VERFAHREN ZUR HERSTELLUNG VON POLYURETHANHARTSCHAUM, SOWIE DARAUS HERGESTELLTE VERBUNDARTIKEL
PROCEDE DE PREPARATION D'UNE MOUSSE POLYURETHANNE DURE ET ARTICLES STRATIFIES PRODUITS AVEC CETTE DERNIERE

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(73) Proprietor: THE DOW CHEMICAL COMPANY
Midland, Michigan 48640 (US)

(72) Inventors:
- OTTENS, Andreas
  D-48351 Everswinkel (DE)
- KELLER, Peter
  D-48356 Nordwalde (DE)

(74) Representative:
- MÜLLER, Ulrich
  D-22844 Norderstedt (DE)

- Huber, Bernhard, Dipl.-Chem. et al
  Patentanwälte
  H. Weickmann, Dr. K. Fincke
  F.A. Weickmann, B. Huber
  Dr. H. Liska, Dr. J. Prechtel, Dr. B. Böhm,
  Kopernikusstrasse 9
  81679 München (DE)

(56) References cited:
- EP-A- 0 188 806
- EP-A- 0 547 515

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This invention relates to a process for preparing a rigid polyurethane foam, and a laminate article containing such foam, from a urethane-modified polyisocyanate. Rigid polyurethane foam is extensively used in the appliance and construction industry where its attractive thermal insulation performance is valued. Unfortunately as such rigid polyurethane foam frequently can be friable it is often necessary to protect it from physical damage by use of a protective facing material. The selection of suitable facing material is generally application related and can be for appliance units, a plastic; for rigid insulation boardstock, paper; or for refrigerated containers or roadstock, metal. End products comprising a facing material and rigid polyurethane foam desirably should exhibit an overall attractive structural strength and durability. To help provide for such traits, the foam advantageously should exhibit attractive adhesion properties to the facing material and not be particularly susceptible to internal failure, for example tearing.

The adhesion of foam to a facing material can be enhanced by pretreatment of the facing material using generally known methods including corona treatment. Alternatively, enhanced adhesion properties may be obtained by selection of the materials used to prepare the polyurethane foam. Patent publication EP-A-462,438 discloses the use of certain urethane-modified polyisocyanates when preparing water-blown rigid polyurethane foam exhibiting improved adhesion properties to a solid surface, notably metal. Further improvement of the disclosed adhesion properties would be desirable to better meet the demanding industrial performance requirements. Additionally, it would be desirable to develop a foaming process performance requirements. Additionally, it would be desirable to develop a foaming process wherein an article comprising a facing material and a rigid polyurethane foam can be prepared under more convenient processing conditions including, for example, a lower process temperature without substantial loss of adhesion properties.

In one aspect, this invention relates to a process for preparing a rigid polyurethane foam by contacting under reaction conditions a urethane-modified polyisocyanate with a polyol, being an isocyanate-reactive substance which is an amine-terminated polyoxyalkylene, a polyether polyol or a polyester polyol, in the presence of a blowing agent characterized in that:

a) the urethane-modified polyisocyanate has an isocyanate content of from 10 to 29 weight percent and is the reaction product of a polymethylene polyphenylisocyanate, having an average isocyanate functionality of from 2.5 to 3.5, with a polyoxyalkylene polyol having a molecular weight of at least 2000 and an oxyethylene content of at least 35 weight percent;

b) the blowing agent comprises from 1 to 10 parts of water per 100 parts by weight of polyol and is free of any perhalogenated hydrocarbon, with the exception of perfluoroalkanes,

wherein the urethane-modified polyisocyanate is present in an amount to provide from 0.7 to 2 isocyanate groups per isocyanate-reactive hydrogen atom present from the polyol and water.

In a preferred aspect of the above mentioned process:

a) the urethane-modified polyisocyanate has an isocyanate content of from 22 to 27 weight percent and is the reaction product of a polymethylene polyphenylisocyanate having an average isocyanate functionality of from 2.7 to 3.2, with a polyoxyalkylene polyol that has a molecular weight of from 4000 to 12000 and an oxyethylene content of at least 50 weight percent;

b) the polyol comprises a polyether polyol or a polyester polyol which has a molecular weight of from 200 to 15000;

c) the blowing agent consists of water present in an amount of from 2 to 8 parts per 100 parts by weight of (b), and

d) the urethane-modified polyisocyanate is present in an amount to provide from 0.9 to 1.5 isocyanate groups per isocyanate-reactive hydrogen atom present from the polyol and water.

In yet another aspect, this invention relates to a rigid polyurethane foam obtained according to the above mentioned process.

In yet another aspect, this invention relates to a laminate comprising a facing material having contiguous to it a rigid polyurethane foam obtained by contacting under reaction conditions a urethane-modified polyisocyanate with a polyol, being an isocyanate-reactive substance which is an amine-terminated polyoxyalkylene, a polyether polyol or a polyester polyol, in the presence of a blowing agent to provide a polymerizing mixture which is brought into contact with the facing material and permitted to terminate its polymerization reaction, characterized in that:

a) the urethane-modified polyisocyanate has an isocyanate content of from 10 to 29 weight percent and is the reaction product of a polymethylene polyphenylisocyanate, having an average isocyanate functionality of from 2.5 to 3.5, with a polyoxyalkylene polyol having a molecular weight of at least 2000 and an oxyethylene content of at least 35 weight percent;
b) the blowing agent comprises from 1 to 10 parts of water per 100 parts by weight of polyahi and with the exception of perfluoroalkanes is free of any perhalogenated hydrocarbon,

wherein the urethane-modified polyisocyanate is present in an amount to provide from 0.7 to 2 isocyanate groups per isocyanate-reactive hydrogen atom present from the polyahi and water, and wherein the facing material has a temperature of from 15°C to 60°C.

In yet another aspect, this invention relates to a two component rigid polyurethane foam-forming system, suitable for use in the above mentioned process which, based on total weight of (a) and (b) present, comprises:

a) from 25 to 75 weight percent of a urethane-modified polyisocyanate that has an isocyanate content of from 10 to 29 weight percent and is the reaction product of a polyethylene polyphenylisocyanate having an average isocyanate functionality of from 2.5 to 3.5 with a polyoxyalkylene polyl having a molecular weight of at least 2000 and an oxyethylene content of at least 35 weight percent; and

b) from 75 to 25 weight percent of a polyahi composition containing:

(i) a polyester polyl or a polyester polyl which has a molecular weight of from 200 to 15000; and

(ii) water from 1 to 10 parts per 100 parts by weight of (b)(i).

Polyurethane foam obtained according to this invention exhibits attractive adhesion properties to various facing materials including notably metal, and especially when such foam is prepared in the presence of a blowing agent consisting of water.

The urethane-modified polyisocyanate required in the present invention has an isocyanate content of from 10 to 29, preferably from 20, more preferably from 22, and preferably up to 27, more preferably up to 26 weight percent. The urethane-modified polyisocyanate is the reaction product of a molar excess of polyethylene polyphenylisocyanate with a polyoxyalkylene polyl having a molecular weight of at least 2000 and an oxyethylene content of at least 35 weight percent. The polyethylene polyphenylisocyanate used has an average isocyanate functionality of from 2.5 to 3.5, preferably from 2.7, and preferably up to 3.2. Suitable polyethylene polyphenyl isocyanates include mixtures of polyethylene polyphenylisocyanate with methylene diphenylisocyanate (MDI) including the 4,4'- and 2,4'-MDI isomers. In such mixtures, the polyethylene polyphenylisocyanate typically constitutes from 95 to 51, preferably from 85 to 55 percent; and the MDI isomers from 5 to 49, more preferably from 15 to 45 percent based on total weight of the mixture. The ratio of the 4,4'-MDI to 2,4'-MDI typically is from 100:0 to 50:50, and more usually from 98:2 to 60:40. Exemplary of suitable polyethylene polyphenylisocyanates include those designated by the trademark VORANATE such as VORANATE M550 and especially VORANATE M220, available from The Dow Chemical Company. VORANATE M220 is understood to have an isocyanate functionality of 2.7 and to contain 60 weight percent polyethylene polyphenylisocyanate and 40 weight percent MDI, predominantly 4,4'-MDI.

As mentioned, the polyoxyalkylene polyl used to prepare the urethane-modified polyisocyanate has a molecular weight of at least 2000 and an oxyethylene content of at least 35 weight percent. The molecular weight of the polyoxyalkylene polyl preferably is from at least 3000, more preferably from at least 4000, and up to 15000, more preferably up to 12000, and yet more preferably up to 10000. To provide for a resulting foam with attractive adhesion properties the oxyethylene content of the polyoxyalkylene polyl preferably is from at least 50, and preferably from 55 to 95, and yet more preferably from 55 to 65 weight percent. In a highly preferred embodiment of the invention, the polyl has a molecular weight from 4500 to 12000 and an oxyethylene content of from 55 to 80 weight percent. The balance of the molecular weight of the polyl when not derived from the oxyethylene content is normally attributed to the initiator and other oxyalkylene units as present including oxybutylene, oxtetramethylene, and particularly oxypolypropylene. The polyoxyalkylene polyl advantageously has an average of from at least 2, preferably from at least 3, and preferably up to 8, more preferably up to 7 hydroxyl groups/molecule. In a preferred embodiment, the molecular weight and functionality of the polyl is such to provide a hydroxyl equivalent weight of at least 1000, and preferably from 1000 to 3500, and more preferably from 1500 to 2500. Suitable polyoxyalkylene polyls can be obtained by reacting ethylene oxide, and optionally other alkylenes oxides including propylene oxide, with initiators such as water, glycine, α-methylglucoside, α-(2-hydroxyethyl)glucoside, sorbitol or sucrose. Exemplary of suitable commercially available polyoxyalkylene polyls include those designated by the trademark VORANOL such as VORANOL CP 1421 of The Dow Chemical Company. Equally suitable polyoxyalkylene polyls for preparation of the urethane-modified polyisocyanate include the glycine initiated polyoxyalkylene-oxypolypropylene adducts having an oxyethylene content of from 40 to 68 weight percent and a hydroxyl equivalent weight of from 2200 to 3500, as disclosed in U.S. Patent 5,114,989.

The urethane-modified polyisocyanate may be prepared using conditions that have already been described in the prior art such as, for example, EP-A-320,134, EP-A-344,551 and U.S. Patent 5,114,989.

In the present invention, the above described urethane-modified polyisocyanate is reacted with a polyahi in the
presence of a blowing agent and optionally other additives. The polyah to used in the process of this invention is an isocyanate-reactive substance which is an amine-terminated polyoxyalkylene, a polyether polyl, or a polyester polyl, or mixtures of two or more thereof. Particularly suitable are polyester and especially polyester polyols having a molecular weight of from 200 to 15000. Such polyester and polyether polyols typically will contain an average of at least 2, and up to 8 hydroxyl groups/molecule. The presence of polyether polyols equivalent to the polyoxyalkylene polyol as required for the urethane-modified polyisocyanate is not excluded though preferred are polyether polyols as typically used in the production of rigid polyurethane foam and having a molecular weight of from 200 to 2000, preferably from 250 to 1500. Examples of these isocyanate-reactive materials are described more fully in U.S. Patent 4,394,491, particularly in columns 3-5 thereof. Exemplary of suitable commercially available polyether polyols include those designated by the trademark VORANOL such as VORANOL RN411, VORANOL RN490, VORANOL RA640, VORANOL CP260, VORANOL CP450, VORANOL P1010 and VORANOL CP1055 from The Dow Chemical Company.

Optionally, in addition to the above mentioned polyester and polyether polyols the polyah may also comprise chain extending or cross linking agents of molecular weight less than 200, and typically from 60 to 180. Such agents include for example (d)ethylene glycol, (d)propylene glycol, glycerine, trimethylolpropane and alkanolamines including (d)ethanolamine or (d)propanolamine. When present such agents generally constitute from more than 3, and up to 25, and usually from 4 to 15, weight percent of the total weight of polyahl including such agent present.

The blowing agent comprises from 1 to 10 parts of water per 100 parts by total weight of polyahl and is free of any perhalogenated hydrocarbon with the possible exception of perfluoroalkanes. The water preferably is present in an amount of from 1.5 to 8, and more preferably in from 2 to 8 parts per 100 parts by total weight of polyahl. In a highly preferred embodiment of the invention, the blowing agent consists only of water. In a less preferred embodiment, water may be used in combination with one or more physical blowing agents including aliphatic hydrocarbons such as pentane, cyclopentane, hexane and cyclohexane; hydrogen-containing chlorofluorocarbons such as dichlorotrifluoromethane and dichlorofluoromethane; and polyfluorocarbons such as tetrafluoroethane, decafluoropentane or dodecafluorohexane. In any event, advantageously the blowing agent is present in amount to provide the resulting foam with a free rise density of from 15 to 200, preferably from 20 to 150, more preferably from 20 to 100, and yet more preferably from 25 to 50 kg/m³.

In addition to the foregoing critical components, it is often desirable to employ certain other ingredients when preparing the polyurethane foam. Among these additional ingredients are catalysts, surfactants, preservatives, colorants, antioxidants, reinforcing agents, fillers, and phosphorus-containing compounds which may function as adhesion promoters or flame retardants. In making polyurethane foam, it is generally highly preferred to employ a minor amount of a surfactant to stabilize the foaming reaction mixture until it cures. Such surfactants advantageously comprise a liquid or solid organosilicone surfactant. Other, less preferred surfactants include polyethylene glycol ethers of long chain alcohols, tertiary amine or alkanolamine salts of long chain alkyl acid sulfate esters, alkyl sulfonic esters and alkyl arylsulfonic acids. Such surfactants are employed in amounts sufficient to stabilize the foaming reaction mixture against collapse and the formation of large, uneven cells. Typically, from 0.2 to 5 parts of surfactant per 100 parts by weight polyahl is sufficient for this purpose.

One or more catalysts for the reaction of the polyahl or water with the polyisocyanate are advantageously used. Suitable catalysts include tertiary amine compounds and organometallic compounds. Exemplary tertiary amine compounds include N-methylmorpholine, N-cocomorpholine, N-ethylmorpholine, triethylendiamine, pentaethyldiethylenetriamine, tetramethylendiamine, dimethycyclohexylamine, 1-methyl-4-dimethylaminophenol, 3-methoxy-N-dimethylaminomethylenamine, 3-dimethylaminopropylamine, diethylenetriamine, N,N-dimethyl-N,N'-dimethyl isopropylpropylenediamine, N,N-diethyl-3-dimethylaminopropylamine, and dimethylbenzyamine. Exemplary organometallic catalysts include organomercuric, organolead, organoferrous and organotin catalysts, with organotin catalysts being preferred among these. Suitable tin catalysts include stannous chloride, tin salts of carboxylic acids such as di butyltin di-2-ethyl hexanoate, as well as other organometallic compounds such as are disclosed in U.S. Patent 2,846,408. A catalyst for the trimerization of polyisocyanates, such as an alkali metal alkoxide, carboxylate, including especially acetate, or quaternary amine salts, may also optionally be employed herein. Such catalysts are used in an amount which measurably increases the rate of reaction of the polyisocyanate. Typical amounts are from 0.001 to 3 parts of catalyst per 100 parts by weight of polyahl.

Advantageously phosphorus-containing compounds may be present in an amount sufficient to impart a desired degree of flame retardancy to the foam. Typically such compounds are present in at least 4, preferably from 5 to 20, and more preferably from 7 to 15 parts per 100 parts by total weight of polyahl present. Suitable phosphorus-containing compounds, preferably halogen-free, for the purpose of flame retardancy include tric(trichloroethyl)phosphate (TCEP), tricresylphosphate, tris(chloropropyl)phosphate (TPCP), triethylphosphate (TEP), dimethyl methyl phosphonate (DMMP) and diethyl methyl phosphate (DEEP). Use of halogen-free phosphorus-containing compounds is preferred as this can reduce hazards associated with combustion products.

Certain phosphorus-containing compounds have been observed to promote adhesion and cohesion properties of the foam and advantageously are present. Such compounds include cyclic organophosphorus-containing compounds
including 1-alkyl, or aryl -1-oxophospholene and -1-thiophospholene compounds. Exemplary and preferred of such cyclic organophosphorus compounds include 1-methyl-1-oxophospholene, 1-ethyl-1-oxophospholene, 1-propyl-1-oxophospholene, or mixtures thereof. Advantageously, the cyclic phosphorus-containing compound is present in a quantity up to 5.0, preferably up to 4.0, and more preferably up to 3.0, and advantageously from at least 0.05, preferably from at least 0.1, and more preferably from at least 0.2 weight percent based on total weight of polyol(s). Other known adhesion promoting substances such as cyclic amide compounds including N-methyl pyrrolidinone may also be present. Mixtures of phosphorus-containing compounds for the purpose of promoting flame retardancy and foam adhesion may be present in the foaming process.

To prepare polyurethane foam according to the present invention, the urethane-modified polyisocyanate, polyol, blowing agent, and other optional additives are brought together at a temperature of from 15°C to end up to 60°C, preferably from 20°C to 40°C and more preferably from 20°C to 30°C and permitted to polymerize. The urethane-modified polyisocyanate is present in an amount to provide from 0.7 to 2, preferably from 0.9 to 1.5, and more preferably from 1.1 to 1.4 isocyanate group per isocyanate-reactive hydrogen atom present from the polyol and water. The mixing apparatus and various types of mixing head and spray apparatus as conveniently used may be employed herein. It is often convenient, but not necessary, to preblend certain of the raw materials prior to reacting the polyisocyanate and polyol. For example, it is often useful to blend the polyol(s), blowing agent, surfactants, catalysts and other components except for polyisocyanates, and then contact this mixture with the polyisocyanate composition. Alternatively, all components can be introduced individually to the mixing zone where the polyisocyanate composition and polyol(s) are contacted. Suitable procedures for the preparation of polyurethane foams are discussed in U.S. Patents 24514 and 3,821,130, and G.B. Patent 1,523,528.

As mentioned in one aspect, this invention relates to a process for preparing a laminate article comprising a facing material having contiguous to it a rigid polyurethane foam as described above. In such a process the above described urethane-modified polyisocyanate, polyol, blowing agent and other optional additives are brought together to give a polymerizing mixture which is then subsequently brought into contact with the facing material and permitted to terminate its polymerization reaction. To assist in termination of the polymerization reaction and promote optimum adhesion properties of foam to facing material, it is found advantageous to provide the facing material with a temperature of from 15°C to 60°C, preferably from 20°C, more preferably from 25°C, and preferably up to 45°C, more preferably up to 35°C.

The selection of the facing material is in accordance with suitability for its intended end application and can be a plastic resin, a cellulose-based material, a lignocellulose-based material or a metal sheet or foil. The polyurethane foam obtained as described hereinabove is observed to have attractive adhesion properties to notably metal surfaces and accordingly particularly suited to the manufacture of laminate articles comprising a metal facing material. The metal may be a metal sheet or metal foil of, for example, aluminum but preferably is steel. The average thickness of the metal sheet or foil is dependent on the application but typically will range from 0.001 to 10, usually from 0.1 to 5, and more usually from a butt 0.2 to 1.5 millimeters. Optionally, the surface of the metal which is to be in contact with the foam may be pretreated to enhance the adhesion between the foam and metal.

As mentioned in another aspect, this invention is a two component polyurethane foam-forming system which comprises: (a) a urethane-modified polyisocyanate as described hereinabove; and (b) a polyol composition. The polyol composition comprises a polyol as described hereinabove, and water in from 1 to 10 parts per 100 parts by weight of polyol. Component (a) is present in from 25 to 75, preferably from 35 to 65 percent; and component (b) in from 75 to 25, preferably from 65 to 35 percent, based on total weight of components (a) and (b).

The invention is illustrated by the following examples in which all parts and percentages are by weight, unless otherwise stated. Where reported, properties of foams as obtained are observed according to the following test procedures; tensile strength - DIN 53292.

Examples 1 to 13

A number of urethane-modified polyisocyanate compositions are prepared according to the following general procedure.

An excess of isocyanate A is reacted, at a temperature of 45°C to 60°C, with a given polyol; the resulting crude urethane-modified polyisocyanate is stabilized by addition of a trace amount of benzoyl chloride. Quantities of reacting components and characterizing data of the urethane-modified polyisocyanate so obtained are given in Table 1.

Isocyanate A: -VORANATE M220, a polymethylene polyphenyl-isocyanate mixture with an NCO content of 31.6 wt%, average functionality of 2.7, and containing 40 wt% methane diphenylisocyanate isomers, available from The Dow Chemical Company.

Polyol A: -VORANOL P400, a 400 molecular weight polyoxypropylene diol, available from The Dow Chemical Company.

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Polyl B - VORANOL P1010, a 1000 molecular weight polyoxypropylene diol, available from The Dow Chemical Company.


Polyl D - VORANOL EP-1900, a 3800 molecular weight polyoxypropylene-oxyethylene diol (20 wt% oxyethylene), available from The Dow Chemical Company.

Polyl E - VORANOL E400, a 400 molecular weight polyoxyethylene diol, available from The Dow Chemical Company.

Polyl F - VORANOL CP1000, a 1000 molecular weight polyoxypropylene triol, available from The Dow Chemical Company.

Polyl G - VORANOL CP3001, a 3000 molecular weight polyoxypropylene-oxyethylene triol (10 wt% oxyethylene), available from The Dow Chemical Company.

Polyl H - VORANOL CP4702, a 4800 molecular weight polyoxypropylene-oxyethylene triol (18 wt% oxyethylene), available from The Dow Chemical Company.

Polyl J - VORANOL CP6001, a 6000 molecular weight polyoxypropylene-oxyethylene triol (14 wt% oxyethylene), available from The Dow Chemical Company.

Polyl K - An experimental polyoxyethylene-oxypropylene triol (75 wt% oxyethylene; randomly distributed) with molecular weight of 1000.

Polyl L - VORANOL CP1421, a 5000 molecular weight polyoxypropylene-oxyethylene triol (75 wt% oxyethylene), available from The Dow Chemical Company.

Polyl M - An experimental polyoxyethylene-oxypropylene triol (68 wt% oxyethylene; randomly distributed) with molecular weight of 7800.

Polyl N - An experimental polyoxyethylene-oxypropylene polyol (68 wt% oxyethylene; randomly distributed) with molecular weight of 12000 obtained from an carbohydrate initiator mixture which has an average hydroxyl functionality of 6.9.

The so prepared urethane-modified polysisocyanate composition are used to prepare a laminate comprising a steel facing sheet and contiguous to said sheet a polyurethane foam. The polysisocyanate is intimately mixed with the below given polyal composition in an amount to provide for an isocyanate reaction index of 130 and the resulting reacting mixture poured in to a mold thermostated to 20°C and having dimensions of 200 × 200 × 40 mm, which is then subsequently closed. One face of the mold contains a steel facing of thickness of 1 mm. The amount of reacting mixture poured into the mold is sufficient to provide for a molded foam having an overall molded density of 70 kg/m³. The laminate comprising metal facing and molded polyurethane foam is removed from the mold after 15 minutes.

**Polyal Composition:**

| 32.5 parts | VORANOL RN482, a sorbitol-initiated oxypropylene polyol with a molecular weight of 700, available from The Dow Chemical Company. |
| 62 parts   | VORANOL CP1056, a 1000 molecular weight polyoxypropylene triol, available from The Dow Chemical Company. |
| 1 part     | a 50.50 wt% blend of silicon-based surfactants TEGOSTAB B1048 and B8427 available from Th Goldschmidt AG. |
| 1.05 parts | Catalyst mixture containing CURITHANE 206, a proprietary amine-based trimerization catalyst available from The Dow Chemical Company; NiAX A1 a proprietary amine-based catalyst available from Union Carbide Corp; and N,N-dimethylcyclohexylamine, present in a weight ratio of 12:8:1. |
| 3.5 parts  | water |

Properties, where observed, for the resulting foam are also given in Table 1. With reference to the "Saw test" the percentage value provides an indication of the number of laminate articles which broke at the foam/metal interface when being cut. A low percentage value or zero is indicative of a foam exhibiting strong adhesion to the metal. A foam exhibiting a high tensile strength is indicative of a product having attractive cohesive properties and being less susceptible to internal stress-strain failure.

The reported data indicates demonstrates that use of urethane-modified polysocyanates which are adducts of polyoxyalkylene triols result in better tensile strengths of the resulting foam than when using urethane-modified polysocyanates which are adducts of polyoxyalkylene diols, as does use of polyoxyalkylene diols or triols having a higher molecular weight. When using urethane-modified polysocyanates which are adducts of polyoxyalkylene polyols that
have a significant oxyethylene content, the resulting foams exhibit an unexpectedly superior tensile strength. This is particularly well illustrated by Example 11 in comparison to Example 8 or 9 which relate to urethane-modified polyisocyanates that are adducts of polyoxyalkylene triol having a similar molecular weight but a substantially lower oxyethylene content.

Example 14.

Individual molded polyurethane foam laminates are prepared as described for Example 13, only in this case the mold temperatures are respectively 20°C, 30°C, 35°C, 40°C and 45°C. The maximum observed tensile strengths for the resulting foam are observed to be:

<table>
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<tr>
<th>Temperature</th>
<th>Tensile Strength (kPa)</th>
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<tr>
<td>20°C Foam</td>
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<tr>
<td>30°C Foam</td>
<td>290 kPa</td>
</tr>
<tr>
<td>35°C Foam</td>
<td>470 kPa</td>
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<tr>
<td>40°C Foam</td>
<td>450 kPa</td>
</tr>
<tr>
<td>45°C Foam</td>
<td>430 kPa</td>
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</tbody>
</table>

Optimum tensile strength is observed at a temperature in the range of from 30°C to 35°C.
<table>
<thead>
<tr>
<th></th>
<th>Example 1*</th>
<th>Example 2*</th>
<th>Example 3*</th>
<th>Example 4*</th>
<th>Example 5*</th>
<th>Example 6*</th>
<th>Example 7*</th>
<th>Example 8*</th>
<th>Example 9*</th>
<th>Example 10*</th>
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<td>Foam Tensile Strength (kPa)</td>
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* Not an example of this invention
Claims

1. A process for preparing a rigid polyurethane foam by contacting under reaction conditions a urethane-modified polyisocyanate with a polyol, being an isocyanate-reactive substance which is an amine-terminated polyoxyalkylene, a polyether polyol or a polyester polyol, in the presence of a blowing agent characterized in that:

   a) the urethane-modified polyisocyanate has an isocyanate content of from 10 to 29 weight percent and is the reaction product of a polyethylene polyphenylisocyanate, having an average isocyanate functionality of from 2.5 to 3.5, with a polyoxyalkylene polyl having a molecular weight of at least 2000 and an oxyethylene content of at least 35 weight percent;
   b) the blowing agent comprises from 1 to 10 parts of water per 100 parts by weight of polyol and is free of any perhalogenated hydrocarbon, with the exception of perfluoroalkanes, wherein the urethane-modified polyisocyanate is present in an amount to provide from 0.7 to 2 isocyanate groups per isocyanate-reactive hydrogen atom present from the polyol and water.

2. A process as claimed in Claim 1 wherein the urethane-modified polyisocyanate is the reaction product of a polyoxyalkylene polyl which has at least 3 hydroxyl groups/molecule and a molecular weight of at least 3000.

3. A process as claimed in Claim 2 wherein the polyoxyalkylene polyl has a molecular weight of from 4000 to 12000 and an oxyethylene content of at least 50 weight percent.

4. A process as claimed in Claims 2 or 3 wherein the blowing agent consists of water.

5. A process as claimed in Claim 1 wherein:

   a) the urethane-modified polyisocyanate has an isocyanate content of from 22 to 27 weight percent and is the reaction product of a polyethylene polyphenylisocyanate having an average isocyanate functionality of from 2.7 to 3.2, with a polyoxyalkylene polyl that has a molecular weight of from 4000 to 12000 and an oxyethylene content of at least 50 weight percent;
   b) the polyol comprises a polyether polyl or a polyester polyl which has a molecular weight of from 200 to 15000;
   c) the blowing agent consists of water present in an amount of from 2 to 8 parts per 100 parts by weight of (b), and
   d) the urethane-modified polyisocyanate is present in an amount to provide from 0.9 to 1.5 isocyanate groups per isocyanate-reactive hydrogen atom present from the polyol and water.

6. A process as claimed in Claim 5 in which is present a fire retardant additive comprising tricresylphosphosphate, triethylphosphate (TEP), dimethylmethyl phosphonate (DMP) or diethylmethyl phosphonate (DEMP).

7. A process as claimed in Claims 5 or 6 in which is present a phosphorus-containing foam achesion or cohesion promoter compound comprising an 1-alkyl-1-oxophospholene, 1-aryl-1-oxophospholene or the equivalent thio- phosphorus compounds.

8. A rigid polyurethane foam obtained according to the process of any one of the preceding claims.

9. A laminate comprising a facing material having contiguous to it a rigid polyurethane foam obtained by contacting under reaction conditions a urethane-modified polyisocyanate with a polyol, being an isocyanate-reactive substance which is an amine-terminated polyoxyalkylene, a polyether polyl or a polyester polyl, in the presence of a blowing agent to provide a polymerizing mixture which is brought into contact with the facing material and permitted to terminate its polymerization reaction, characterized in that:

   a) the urethane-modified polyisocyanate has an isocyanate content of from 10 to 29 weight percent and is the reaction product of a polyethylene polyphenylisocyanate, having an average isocyanate functionality of from 2.5 to 3.5, with a polyoxyalkylene polyl having a molecular weight of at least 2000 and an oxyethylene content of at least 35 weight percent;
   b) the blowing agent comprises from 1 to 10 parts of water per 100 parts by weight of polyol and with the exception of perfluoroalkanes is free of any perhalogenated hydrocarbon,
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wherein the urethane-modified polyisocyanate is present in an amount to provide from 0.7 to 2 isocyanate groups per isocyanate-reactive hydrogen atom present from the polyol and water, and wherein the facing material has a temperature of from 15°C to 65°C.

5 10. A laminate as claimed in Claim 9 wherein the blowing agent consists of water and wherein the facing material is a metal foil or sheet.

11. A two component rigid polyurethane foam-forming system which, based on total weight of (a) and (b) present, comprises:

10 a) from 25 to 75 weight percent of a urethane-modified polyisocyanate that has an isocyanate content of from 10 to 29 weight percent and is the reaction product of a polymethylene polyphenylisocyanate having an average isocyanate functionality of from 2.5 to 3.5 with a polyoxyalkylene polyol having a molecular weight of at least 2000 and an oxyethylene content of at least 35 weight percent; and

15 b) from 75 to 25 weight percent of a polyol composition containing:

(ii) a polyether polyol or a polyester polyol which has a molecular weight of from 200 to 15000; and

(ii) water in from 1 to 10 parts per 100 parts by weight of (b)(i).

20 Patentansprüche

1. Verfahren zur Herstellung eines Polyurethanhartschaums durch Inkontaktsprengen eines Urethan-modifizierten Polyisocyanaten mit einem Polyol, welches eine Isocyanat-reactive Substanz ist, welche ein Ammoniaterminiertes Polyoxyalkylein, ein Polyetherpolyl oder ein Polyesterpolyl ist, unter Reaktionsbedingungen in Gegenwart eines Treibmittels, dadurch gekennzeichnet, daß:

30 a) das Urethan-modifizierte Polyisocyanat einen Isocyanatgehalt von 10 bis 29 Gewichtsprozent aufweist und das Reaktionsprodukt eines Polymethylene polyphenylisocyanate mit einer durchschnittlichen Isocyanatfunktionalität von 2.5 bis 3.5 mit einem Polyoxyalkyleinpolyol mit einem Molekulargewicht von mindestens 2000 und einem Oxyethylengehalt von mindestens 35 Gewichtsprozent ist;

35 b) das Treibmittel 1 bis 10 Teile Wasser pro 100 Gewichtsteile Polyol umfaßt und frei von jeglichem perhalogeniertem Kohlenwasserstoff mit der Ausnahme von Perfluoralkanen ist;

worin das Urethan-modifizierte Polyisocyanat in einer Menge vorliegt, um von 0.7 bis 2 Isocyanatgruppen pro Isocyanat-reaktivem Wasserstoffatom bereitzustellen, das von dem Polyol und dem Wasser vorliegt.

2. Verfahren nach Anspruch 1, worin das Urethan-modifizierte Polyisocyanat das Reaktionsprodukt eines Polyoxyalkyleinpolyols ist, das mindestens 3 Hydroxygruppen/Molekül und ein Molekulargewicht von mindestens 3000 aufweist.


5. Verfahren nach Anspruch 1, worin:

40 a) das Urethan-modifizierte Polyisocyanat einen Isocyanatgehalt von 22 bis 27 Gewichtsprozent aufweist und das Reaktionsprodukt eines Polymethylene polyphenylisocyanate mit einer durchschnittlichen Isocyanatfunktionalität von 2.7 bis 3.2 mit einem Polyoxyalkyleinpolyol ist, das ein Molekulargewicht von 4000 bis 12000 und einen Oxyethylengehalt von mindestens 50 Gewichtsprozent aufweist;

50 b) das Polyol ein Polyetherpolyl oder ein Polyesterpolyl umfaßt, das ein Molekulargewicht von 200 bis 15000 aufweist;
c) das Treibmittel aus Wasser besteht, das in einer Menge von 2 bis 8 Teilen pro 100 Gewichtsteilen von (b) vorliegt, und
d) das Urethan-modifizierte Polysicyanat in einer Menge vorliegt, um von 0,9 bis 1,5 Isocyanatgruppen pro Isocyanat-reaktivem Wasserstoffatom bereitzustellen, welches von dem Polyahl und dem Wasser vorliegt.

6. Verfahren nach Anspruch 5, wovon ein Flammverzögerungsadditiv umfassend Triersylphosphat, Triethylphosphat (TEP), Dimethylmethylphosphonat (DMMP) oder Diethylmethylphosphonat (DEEP) vorliegt.

7. Verfahren nach Anspruch 5 oder 6, worin eine Phosphor enthaltende Schaumadhäsion oder -kohäsion fördernde Verbindung vorliegt, umfassend ein 1-Alkyl-1-oxophospholen, 1-Aryl-1-oxophospholen oder die äquivalenten Thiophospholenverbindungen.

8. Polyurethanhartschaum erhalten durch das Verfahren nach einem der vorhergehenden Ansprüche.

9. Verbundstoff, umfassend ein Deckmaterial, das benachbart zu sich einen Polyurethanhartschaum aufweist, erhalten durch Inkontaktbringen eines Urethan-modifizierten Polysicyanats mit einem Polyahl, das eine Isocyanat-reaktive Substanz ist, die ein Amin-terminiertes Polyoxalkylken, ein Polyetherpolyol oder ein Polyesterpolyol ist, unter Reaktionsbedingungen in Gegenwart eines Treibmittels, um ein Polymerisiergernisch zu ergeben, welches mit dem Deckmaterial in Kontakt gebracht wird und dem erlaubt wird, seine Polymerisationsreaktion zu beenden, dadurch gekennzeichnet, daß:


   b) das Treibmittel von 1 bis 10 Teile Wasser pro 100 Gewichtsteile Polyahl umfaßt und mit der Ausnahme von Perfluoralkanen frei von jeglichem perhalogeniertem Kohlenwasserstoff ist,

wodurch das Urethan-modifizierte Polysicyanat in einer Menge vorliegt, um von 0,7 bis 2 Isocyanatgruppen pro Isocyanat-reaktivem Wasserstoffatom bereitzustellen, das von dem Polyahl und dem Wasser vorliegt und worin das Deckmaterial eine Temperatur von 15 °C bis 60 °C aufweist.

10. Verbundstoff nach Anspruch 9, worin das Treibmittel aus Wasser besteht und worin das Deckmaterial eine Metalloidein oder ein Blech ist.

11. Polyurethanhartschaum bildendes Zweikomponenten-System, welches, bezogen auf das vorliegende Gesamtgewicht von (a) und (b) umfaßt:

   a) von 25 bis 75 Gewichtsprozent eines Urethan-modifizierten Polysicyanats, das einen Isocyanatgehalt von 10 bis 29 Gewichtsprozent aufweist und das Reaktionsprodukt eines Polymethylenpolyphenyliocyanats mit einer durchschnittlichen Isocyanatfunktionalität von 2,5 bis 3,5 mit einem Polyoxalkylkenpolyol ist, das ein Molekulargewicht von mindestens 2000 und einen Oxysylengewicht von mindestens 35 Gewichtsprozent aufweist und

   b) von 75 bis 25 Gewichtsprozent einer Polyahlzusammensetzung, enthaltend:

      (i) ein Polyetherpolyol oder ein Polyesterpolyol, das ein Molekulargewicht von 200 bis 15000 aufweist und

      (ii) Wasser von 1 bis 10 Teile pro 100 Gewichtsteile von (b)(i).

Revisions:

1. Procédé de préparation d'une mousse rigide de polyuréthane par mise en contact, dans des conditions de réaction, d'un polyisocyanate à modification uréthane avec un polyahl qui est un produit apte à réagir avec un isocyanate et qui est un polyoxalkylène à terminaison amine, un polyéther-polyol ou un polyester-polyol, en présence d'un
agent d'expansion, caractérisé en ce que :

a) le polyisocyanate à modification uréthane a une teneur en isocyanate de 10 à 29% en poids et est le produit de réaction d’un polyméthylène polyphénylisocyanate ayant une fonctionnalité isocyanate moyenne de 2,5 à 3,5, avec un polyoxyalkylène polyol ayant une masse moléculaire d'eau moins 2000 et une teneur en oxyéthylène d'eau moins 35% en poids,

b) l'agent d'expansion comprend 1 à 10 parties d'eau pour 100 parties en poids de polyahl et est exempt de tout hydrocarbure perhalogéné, à l'exception des perfluoroalcanes,

le polyisocyanate à modification uréthane étant présent en une quantité qui fournit 0,7 à 2 groupes isocyanate par atome d'hydrogène apte à réagir avec un isocyanate, présent dans le polyahl ou l'eau.

2. Procédé selon la revendication 1, dans lequel le polyisocyanate à modification uréthane est le produit de réaction d'un polyoxyalkylène polyol ayant au moins 3 groupes hydroxyle par molécule et une masse moléculaire d'eau moins 3000.

3. Procédé selon la revendication 2, dans lequel le polyoxyalkylène polyol a une masse moléculaire de 4000 à 12000 et une teneur en oxyéthylène d'eau moins 50% en poids.

4. Procédé selon la revendication 2 ou 3, dans lequel l'agent d'expansion est constitué d'eau.

5. Procédé selon la revendication 1, dans lequel :

a) le polyisocyanate à modification uréthane a une teneur en isocyanate de 22 à 27% en poids et est le produit de réaction d’un polyméthylène polyphénylisocyanate ayant une fonctionnalité isocyanate moyenne de 2,7 à 3,2, avec un polyoxyalkylène polyol ayant une masse moléculaire de 4000 à 12000 et une teneur en oxyéthylène d'eau moins 50% en poids,

b) le polyahl comprend un polyéther-polyol ou un polyester-polyol qui a une masse moléculaire de 200 à 15000,

c) l'agent d'expansion est constitué d'eau qui est présente en une quantité de 2 à 8 parties pour 100 parties en poids de (b), et

d) le polyisocyanate à modification uréthane est présent en une quantité qui fournit 0,9 à 1,5 groupe isocyanate par atome d'hydrogène apte à réagir avec un isocyanate, présent dans le polyahl ou l'eau.

6. Procédé selon la revendication 5, dans lequel est présent un additif retardant l'inflammation, comprenant du phosphate de triésyle, du phosphate de triéthyle (TEP), du méthylphosphonate de diméthyle (DMMP) ou de l'éthylphosphonate de diéthyle (DEEP).

7. Procédé selon la revendication 5 ou 6, dans lequel est présent un composé favorisant l'adhérence ou la cohésion de la mousse, contenant du phosphore, qui est un 1-alkyl-1-oxophospholène, un 1-aryl-1-oxophospholène ou le composé thiophospholène équivalent.

8. Mousse rigide de polyuréthane, obtenue par le procédé selon l'une quelconque des revendications précédentes.

9. Stratifié comprenant un matériau de revêtement, auquel est contigué une mousse rigide de polyuréthane que l'on obtient en mettant en contact, dans des conditions de réaction, un polyisocyanate à modification uréthane avec un polyahl qui est un produit apte à réagir avec un isocyanate et qui est un polyoxyalkylène à terminaison amine, un polyéther-polyol ou un polyester-polyol, en présence d'un agent d'expansion, de façon à obtenir un mélange de polymérisation qui est mis en contact avec le matériau de revêtement et dont on laisse la réaction de polymérisation se terminer, caractérisé en ce que :

a) le polyisocyanate à modification uréthane a une teneur en isocyanate de 10 à 29% en poids et est le produit de réaction d’un polyméthylène polyphénylisocyanate ayant une fonctionnalité isocyanate moyenne de 2,5 à 3,5, avec un polyoxyalkylène polyol ayant une masse moléculaire d'eau moins 2000 et une teneur en oxyéthylène d'eau moins 35% en poids,

b) l'agent d'expansion comprend 1 à 10 parties d'eau pour 100 parties en poids de polyahl et est exempt de tout hydrocarbure perhalogéné, à l'exception des perfluoroalcanes,
atome d'hydrogène apte à réagir avec un isocyanate, présent dans le polyøhyl ou l'eau, et le matériau de revêtement ayant une température de 15°C à 60°C.

10. Stratifié selon la revendication 9, pour lequel l'agent d'expansion est constitué d'eau et pour lequel le matériau de revêtement est une feuille métallique.

11. Système à deux constituants pour la formation d'une mousse rigide de polyuréthane, qui renferme, les pourcentages étant rapportés au poids total de (a) et (b) :

a) 25 à 75% en poids d'un polyisocyanate à modification uréthane, qui a une teneur en isocyanate de 10 à 29% en poids et qui est le produit de réaction d'un polyméthylène polyphénylisocyanate ayant une fonctionnalité isocyanate moyenne de 2,5 à 3,5, avec un polyoxyalkylènepolyol ayant une masse moléculaire d'eau moins 2000 et une teneur en oxyéthylène d'eau moins 35% en poids, et

b) 75 à 25% en poids d'une composition à base de polyøhyl, contenant :

(i) un polyéther-polyol ou un polyester-polyol ayant une masse moléculaire de 200 à 15000, et

(ii) de l'eau à raison de 1 à 10 parties pour 100 parties en poids de (b)(i).