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(54) Title: PROCESS FOR MAKING RIGID AND FLEXIBLE POLYURETHANE FOAMS

(57) Abstract: Process for preparing rigid and flexible polyurethane foams by reacting a polyisocyanate, polyols and water in the presence of a catalyst, where the polyisocyanate comprises a prepolymer which is the reaction product of a polyisocyanate and a polyalkyleneglycol monoalkylether.

PROCESS FOR MAKING RIGID AND FLEXIBLE POLYURETHANE FOAMS

The present invention is concerned with the use of a polyisocyanate prepolymer based on a polyalkyleneglycol monoalkylether in preparing rigid foams and flexible foams and with the foams thus obtained.

EP-A-0339848 discloses a process for making open-celled polyurethane foam, comprising reacting a MDI composition with a polyol component comprising:

- 1) an oxyalkylation product of ethylene diamine having an hydroxyl number of from 600 to 850;
- 2) a polyoxyalkylene triol having a hydroxyl number of from 28 to 56; and
- 3) a polyethyleneglycol monoalkyl ether having a MW of from 300 to 1000;

and a blowing agent comprising water, the weight of polyethylene glycol monoalkyl ether being at least four times the weight of water, and the isocyanate index being in the range from 25 to 90. A prepolymer with part only of said polyethylene glycol monoalkyl ether is foreseen in this document.

Conventional flexible polyurethane foams are widely known. Such foams show a relatively high resilience (ball rebound), a relatively low modulus, a relatively high sag factor and a relatively low hysteresis loss. Such foams further show a major glass-rubber transition below ambient temperature, generally in the temperature range of -100°C to -10°C . The commonly applied relatively high molecular weight polyether and polyester polyols in such foams are responsible for the sub-ambient glass transition temperature (T_g^S). These polyether and polyester polyols are often referred to as soft segments. Above T_g^S the foam displays its typical flexible properties until softening and/or melting of the isocyanate-

derived urethane/urea clusters ("hard domains") takes place. This softening and/or melting temperature (T_g^h and/or T_m^h) often coincides with the onset of thermal degradation of polymer segments. The T_g^h and/or T_m^h for flexible polyurethane foams is generally higher than 100°C , often even exceeding 200°C . At the T_g^s a sharp decrease of the modulus of the flexible foam is observed. Between T_g^s and T_g^h/T_m^h the modulus remains fairly constant with increasing temperature and at T_g^h/T_m^h again a substantial decrease of the modulus may take place. A way of expressing the presence of T_g^s is to determine the ratio of the Young's storage modulus E' at -100°C and $+25^\circ\text{C}$ as per Dynamic Mechanical Thermal Analysis (DMTA measured according to ISO/DIS 6721-5). For conventional flexible polyurethane foams the

$E'_{-100^\circ\text{C}}$

ratio is at least 25.

$E'_{+25^\circ\text{C}}$

Another feature of T_g^s by DMTA (ISO/DIS 6721-5) is that for conventional flexible polyurethane foams the maximum value of the

Young's loss modulus E''

ratio of $\frac{E''}{E'}$ (tan δ_{max} .) over the

Young's storage modulus E'

$-100^\circ\text{C}/+25^\circ\text{C}$ temperature range varies from 0.20 - 0.80 in general. The Young's loss modulus E'' is measured by DMTA (ISO/DIS 6721-5) as well.

In patent application PCT/EP9601594 a completely new class of flexible polyurethane foams is described such foams having no major glass-rubber transition between -100°C and $+25^\circ\text{C}$. In more quantitative terms these foams show a ratio $E'_{-100^\circ\text{C}}/E'_{+25^\circ\text{C}}$ of 1.3 to 15.0, preferably of 1.5 to 10 and most preferably of 1.5 to 7.5. The tan δ_{max} over the -100°C

to +25°C temperature range is below 0.2.

The apparent core density of such foams may range from 4-30 kg/m³ and preferably ranges from 4-20 kg/m³ (measured according to ISO/DIS845). Such foams are made by crushing a rigid foam.

In the making of these foams, rather high amounts of water and isocyanate are used. This gives rise to two problems:

Firstly, water and isocyanate are poorly miscible. It has been previously recognized that the overall miscibility of the reaction components is a process parameter that has an influence on the final foam such as the cell structure and mechanical properties. Especially under conditions where the mechanical mixing is relatively poor and, as a result of that, the system components are not mixed sufficiently, the polymerization is affected. This results in poor polymer network build-up and, consequently, the mechanical properties of the formed polymer are relatively poor.

Secondly, because of the high water levels, the exotherm is generally measured to be high, which in some cases may lead to scorch.

There is thus a need for a formulation that would improve overall miscibility of the foam reactants and reduce the reaction exotherm.

The present invention provides such a formulation and process. Without wishing to be bound to any theory, it is believed that when the polyol blend (which in itself is an emulsion), is brought into contact with the isocyanate, the water-rich phase is emulsified into the isocyanate. The isocyanate of the invention facilitates the formation, and once formed, stabilizes the formed emulsion, providing an intimate contact between water and isocyanate. Other

advantages are also obtained, which are significant increase of the robustness of the foaming system and an improved crushability of the rigid foams.

- 5 The isocyanates of the invention have a reduced NCO value, which results in lower reaction exotherms. The risk of scorch is thus reduced.

10 In the context of the present application hereinafter a flexible polyurethane foam is a crushed foam having a ball rebound (measured according to ISO 8307) of at least 40%, preferably at least 50% and most preferably 55-85% in at least one of the three dimensional directions and a sag factor (CLD 65/25) of at least 2.0 (measured according to ISO
15 3386/1). Preferably such flexible foams have a Young's storage modulus at 25°C of at most 500 kPa, more preferably at most 350 kPa and most preferably between 10 and 200 kPa (Young's storage modulus measured by DMTA according to ISO/DIS 6721-5). Further, such flexible foams preferably
20 have a sag factor (CLD 65/25) of at least 3.5 and most preferably 4.5-10 (measured according to ISO 3386/1). Still further such flexible foams preferably have a CLD hysteresis loss (ISO 3386/1) of below 55%, more preferably below 50% and most preferably below 45%.

25

In the context of the present patent application hereinafter a rigid polyurethane foam is an uncrushed foam having a ball rebound measured in the direction of foam rise of less than 40% (ISO 8307 with the proviso that no preflex conditioning
30 is applied, that only one rebound value per sample is measured and that test pieces are conditioned at 23°C ± 2°C and 50 ± 5% relative humidity) and/or having a CLD 65/25 sag factor measured in the direction of foam rise of less than 2.0 (ISO 3386/1 with the proviso that the sag factor is
35 determined after the first load - unload cycle); these

properties both being measured at a core density of the foam of 3-27 kg/m³ (ISO 845). Preferably the ratio $E'_{-100^{\circ}\text{C}}/E'_{+25^{\circ}\text{C}}$ of such a rigid foam is 1.3-15. If in the present application ISO 8307 and ISO 3386/1 are mentioned in relation to rigid foams they refer to the tests as described above including the provisos.

In the context of the present invention the following terms have the following meaning:

1) isocyanate index or NCO index or index:
the ratio of NCO-groups over isocyanate-reactive hydrogen atoms present in a formulation, given as a percentage:

$$\frac{[\text{NCO}] \times 100}{[\text{active hydrogen}]} \quad (\%).$$

In other words the NCO-index expresses the percentage of isocyanate actually used in a formulation with respect to the amount of isocyanate theoretically required for reacting with the amount of isocyanate-reactive hydrogen used in a formulation.

It should be observed that the isocyanate index as used herein is considered from the point of view of the actual foaming process involving the isocyanate ingredient and the isocyanate-reactive ingredients. Any isocyanate groups consumed in a preliminary step to produce modified polyisocyanates (including such isocyanate-derivatives referred to in the art as quasi or semi-prepolymers and prepolymers) or any active hydrogens consumed in a preliminary step (e.g. reacted with isocyanate to produce modified polyols or polyamines) are not taken into account in the calculation of the isocyanate index. Only the free isocyanate groups and the free isocyanate-reactive hydrogens (including those of the water) present at the actual foaming

stage are taken into account.

2) The expression "isocyanate-reactive hydrogen atoms" as used herein for the purpose of calculating the isocyanate index refers to the total of active hydrogen atoms in hydroxyl and amine groups present in the reactive compositions; this means that for the purpose of calculating the isocyanate index at the actual foaming process one hydroxyl group is considered to comprise one reactive hydrogen, one primary amine group is considered to comprise one reactive hydrogen and one water molecule is considered to comprise two active hydrogens.

3) Reaction system: a combination of components wherein the polyisocyanates are kept in one or more containers separate from the isocyanate-reactive components.

4) The expression "polyurethane foam" as used herein refers to cellular products as obtained by reacting polyisocyanates with isocyanate-reactive hydrogen containing compounds, using foaming agents, and in particular includes cellular products obtained with water as reactive foaming agent (involving a reaction of water with isocyanate groups yielding urea linkages and carbon dioxide and producing polyurea-urethane foams) and with polyols, aminoalcohols and/or polyamines as isocyanate-reactive compounds.

5) The term "average nominal hydroxyl functionality" is used herein to indicate the number average functionality (number of hydroxyl groups per molecule) of the polyol or polyol composition on the assumption that this is the number average functionality (number of active hydrogen atoms per molecule) of the initiator(s) used in their preparation although in practice it will often be somewhat less because of some terminal unsaturation.

35

6) The word "average" refers to number average unless indicated otherwise.

The foams according to the present invention are prepared by
5 reacting a polyisocyanate (1), an isocyanate-reactive
compound (2), said compound (2) having an average equivalent
weight of at most 374 and an average number of isocyanate-
reactive hydrogen atoms of from 2 to 8, an isocyanate-
reactive compound (3), said compound (3) having an average
10 equivalent weight of more than 374 and an average number of
isocyanate-reactive hydrogen atoms of from 2 to 6 and water
in the presence of a catalyst to prepare a rigid polyurethane
foam and by crushing this rigid polyurethane foam to prepare
a flexible polyurethane foam, where the polyisocyanate
15 comprises a prepolymer which is the reaction product of
polyisocyanate and a polyalkyleneglycol monoalkylether.

The term "reaction product" covers notably those embodiments
where the molar ratio NCO:OH is from 99:1 to 75:25.

20 This term "reaction product" covers notably the embodiment
where the amount of polyalkyleneglycol monoalkylether
represents from 5 to 20% by weight of the weight of the final
prepolymer.

25 Said polyalkyleneglycol monoalkylether is of the formula R-A-
OH, where R is an alkyl group containing 1 to 20, preferably
1 to 6 carbon atoms and A is a polyalkyleneoxy chain having a
total chain length of 2 to 40 units. Preferred
30 polyalkyleneglycol monoalkylethers are mono(C₁-C₄alkyl)ethers
of polyethyleneglycol. The polyalkyleneoxy chain preferably
consists of ethyleneoxy and/or propyleneoxy units, most
preferably of ethyleneoxy units. The molecular weight of the
polyalkyleneglycol monoalkylether is preferably between 100
35 and 1000.

According to one embodiment, said polyalkylene glycol monoalkyl ether is completely reacted in the prepolymer. According to this embodiment, the polyol(s) composition reacting with the isocyanate (the prepolymer thereof) is free
5 of said polyalkylene glycol monoalkyl ether.

According to another embodiment, the amount of polyalkylene glycol monoalkyl ether is less than four times the amount of water used in the process of the invention.

10 The isocyanate used in making the prepolymer is preferably polymeric MDI (or variants thereof as defined below), the polymeric MDI having an average functionality 2.3 to 2.9, and preferably 2.5 to 2.7.

15 The (polymeric) MDI prepolymer has an NCO value preferably between 15 and 29%, most preferably between 20 and 29%.

The polyisocyanate used in the invention comprises the polyalkyleneglycol monoalkylether containing prepolymer in
20 varying amounts. While it can be comprised of solely the prepolymer, it may also comprise limited amounts of polyalkyleneglycol monoalkylether containing prepolymer. For example, the polyisocyanate can comprise from 100 to 20% by weight of the polyalkyleneglycol monoalkylether containing
25 prepolymer.

Suitable organic polyisocyanates for use in the process of the present invention include any of those known in the art for the preparation of rigid polyurethane foams, like
30 aliphatic, cycloaliphatic, araliphatic and, preferably, aromatic polyisocyanates, such as toluene diisocyanate in the form of its 2,4 and 2,6-isomers and mixtures thereof and diphenylmethane diisocyanate in the form of its 2,4'-, 2,2'- and 4,4'-isomers and mixtures thereof, the mixtures of
35 diphenylmethane diisocyanates (MDI) and oligomers thereof

having an isocyanate functionality greater than 2 known in the art as "crude" or polymeric MDI (polymethylene polyphenylene polyisocyanates), the known variants of MDI comprising urethane, allophanate, urea, biuret, carbodiimide, uretonimine and/or isocyanurate groups.

Mixtures of toluene diisocyanate and diphenylmethane diisocyanate and/or polymethylene polyphenylene polyisocyanates may be used. Most preferably polyisocyanates are used which have an average isocyanate functionality of 2.1-3.0 and preferably of 2.2-2.8.

Preferably MDI, crude or polymeric MDI and/or liquid variants thereof are used said variants being obtained by introducing uretonimine and/or carbodiimide groups into said polyisocyanates, such a carbodiimide and/or uretonimine modified polyisocyanate having an NCO value of at least 20% by weight, and/or by reacting such a polyisocyanate with one or more polyols having a hydroxyl functionality of 2-6 and a molecular weight of 62-500 so as to obtain a modified polyisocyanate having an NCO value of at least 20% by weight.

The isocyanate blended with the prepolymer is preferably polymeric MDI, a mixture of 2,4' and 4,4' MDI or a prepolymer of a mixture of 2,4' and 4,4' MDI. When blending with a mixture of 2,4' and 4,4' MDI or a prepolymer of a mixture of 2,4' and 4,4' MDI, the ratio of 2,4' and 4,4' MDI amounts preferably from 0/100 to 70/30. The isocyanate or isocyanate prepolymer used in the blending may contain uretonimine and/or carbodiimide groups. The polyol used in the manufacturing of the prepolymer based on the mixture of 2,4' and 4,4' MDI has a functionality 2 to 8, preferably 2 to 3, and a molecular weight from 62 to 8000. An example of such a prepolymer is an isocyanate reacted with diols with molecular weight between 62 and 250. Such prepolymers have an NCO value

between 20 and 30%. Another example is a prepolymer reacted with a diol or a triol, or a mixture of a diol and a triol, with hydroxyl values between 21 and 100 mgKOH/g. Such prepolymers typically have an NCO value between 6 and 25%.

5 The NCO value of the isocyanate used in blending with the polyalkyleneglycol monoalkylether containing prepolymer amounts typically to 20 to 33.6%.

10 The NCO value of the polyisocyanate containing the polyalkyleneglycol monoalkylether prepolymer to produce the rigid foam is typically from 16 to 32%, more preferably between 20 and 30% and most preferably between 25 and 30%.

15 Increased levels of 2,4'MDI in the isocyanate used in blending with the polyalkyleneglycol monoalkylether prepolymer are preferred (it is believed this improves system miscibility). This level is preferably above 20%, especially above 30%.

20 Prepolymerisation of the isocyanate used in blending is also preferred according to one embodiment (it is believed this also improves system miscibility).

25 More in particular the foams according to the present invention are prepared by reacting the above polyisocyanate (1), a polyol (2) having a hydroxyl number of at least 150 mg KOH/g and an average nominal hydroxyl functionality of from 2 to 8, a polyol (3) having a hydroxyl number of from 10 to less than 150mg KOH/g and an average nominal hydroxyl functionality of from 2 to 6 and water in the presence of a catalyst to prepare a rigid polyurethane foam and by crushing
30 this rigid polyurethane foam to prepare a flexible polyurethane foam.

35 Isocyanate-reactive compounds (2) include any of those known in the art for that purpose like polyamines, aminoalcohols

and polyols. Of particular importance for the preparation of the rigid foams are polyols and polyol mixtures having hydroxyl numbers of at least 150 mg KOH/g and an average nominal hydroxyl functionality of from 2 to 6. Suitable polyols have been fully described in the prior art and include reaction products of alkylene oxides, for example ethylene oxide and/or propylene oxide, with initiators containing from 2 to 8 active hydrogen atoms per molecule. Suitable initiators include : polyols, for example ethylene glycol, diethylene glycol, propylene glycol, dipropylene glycol, butane diol, glycerol, trimethylolpropane, triethanolamine, pentaerythritol, sorbitol and sucrose; polyamines, for example ethylene diamine, tolylene diamine, diaminodiphenylmethane and polymethylene polyphenylene polyamines; and aminoalcohols, for example ethanolamine and diethanolamine; and mixtures of such initiators. Other suitable polyols include polyesters obtained by the condensation of appropriate proportions of glycols and higher functionality polyols with polycarboxylic acids. Still further suitable polyols include hydroxyl terminated polythioethers, polyamides, polyesteramides, polycarbonates, polyacetals, polyolefins and polysiloxanes. Still further suitable isocyanate-reactive compounds include ethylene glycol, diethylene glycol, propylene glycol, dipropylene glycol, butane diol, glycerol, trimethylolpropane, ethylene diamine, ethanolamine, diethanolamine, triethanolamine and the other initiators mentioned before. Mixtures of such isocyanate-reactive compounds may be used as well. Most preferably polyols are used which do not comprise primary, secondary or tertiary nitrogen atoms.

Isocyanate-reactive compounds (3) include any of those known in the art for that purpose, like polyamines, aminoalcohols and polyols.

Of particular importance for the preparation of the rigid

foams are polyols and polyol mixtures having a hydroxyl value of 10 to less than 150 and preferably of 15-60 mg KOH/g and an average nominal hydroxyl functionality of from 2 to 6 and preferably of from 2 to 4. These high molecular weight polyols are generally known in the art and include reaction products of alkylene oxides, for example ethylene oxide and/or propylene oxide, with initiators containing from 2 to 6 active hydrogen atoms per molecule. Suitable initiators include : polyols, for example ethylene glycol, diethylene glycol, propylene glycol, dipropylene glycol, butane diol, glycerol, trimethylolpropane, triethanolamine, pentaerythritol and sorbitol; polyamines, for example ethylene diamine, tolylene diamine, diaminodiphenylmethane and polymethylene polyphenylene polyamines; and aminoalcohols, for example ethanolamine and diethanolamine; and mixtures of such initiators. Other suitable polyols include polyesters obtained by the condensation of appropriate proportions of glycols and higher functionality polyols with polycarboxylic acids. Still further suitable polyols include hydroxyl terminated polythioethers, polyamides, polyesteramides, polycarbonates, polyacetals, polyolefins and polysiloxanes. Preferred polyols are the polyether polyols comprising ethylene oxide and/or propylene oxide units and most preferably polyoxyethylene polyoxypropylene polyols having an oxyethylene content of at least 10% and preferably 10-85% by weight. Other polyols which may be used comprise dispersions or solutions of addition or condensation polymers in polyols of the types described above. Such modified polyols, often referred to as "polymer" polyols have been fully described in the prior art and include products obtained by the in situ polymerisation of one or more vinyl monomers, for example styrene and acrylonitrile, in polymeric polyols, for example polyether polyols, or by the in situ reaction between a polyisocyanate and an amino- or hydroxy-functional compound,

such as triethanolamine, in a polymeric polyol.

The polymer modified polyols which are particularly interesting in accordance with the invention are products
5 obtained by in situ polymerisation of styrene and/or acrylonitrile in polyoxyethylene polyoxypropylene polyols and products obtained by in situ reaction between a polyisocyanate and an amino or hydroxy-functional compound (such as triethanolamine) in a polyoxyethylene
10 polyoxypropylene polyol. Polyoxyalkylene polyols containing from 5 to 50% of dispersed polymer are particularly useful. Particle sizes of the dispersed polymer of less than 50 microns are preferred. Mixtures of such isocyanate-reactive compounds may be used as well. Most preferably polyols are
15 used which do not comprise primary, secondary or tertiary nitrogen atoms.

The relative amount of isocyanate-reactive compound (2) and (3) or polyol (2) and (3) may vary widely and preferably
20 ranges from 0.1:1 to 4:1 (w:w).

The relative quantities of the polyisocyanate and the isocyanate-reactive compounds to be reacted may vary within a wide range. In general an isocyanate index will be applied
25 of from 25 to 300, preferably of from 30 to 200, preferably 91 to 200 and most preferably of from 102 to 150.

In order to prepare a foam water is used as a blowing agent. However if the amount of water is not sufficient to obtain
30 the desired density of the foam any other known way to prepare polyurethane foams may be employed additionally, like the use of reduced or variable pressure, the use of a gas like air, N₂ and CO₂, the use of more conventional blowing agents like chlorofluorocarbons, hydrofluorocarbons,
35 hydrocarbons and fluorocarbons, the use of other reactive

blowing agents, i.e. agents which react with any of the ingredients in the reacting mixture and due to this reaction liberate a gas which causes the mixture to foam and the use of catalysts which enhance a reaction which leads to gas formation like the use of carbodiimide-formation-enhancing catalysts such as phospholene oxides. Combinations of these ways to make foams may be used as well. The amount of blowing agent may vary widely and primarily depends on the desired density. Water may be used as liquid at below-ambient, ambient or elevated temperature and as steam.

One combination of blowing agent is water and CO₂ wherein the CO₂ is added to the ingredients for making the foam in the mixing head of a device for making the foam, to one of the isocyanate-reactive ingredients and preferably to the polyisocyanate before the polyisocyanate is brought into contact with the isocyanate-reactive ingredients.

Per 100 parts by weight of polyisocyanate (1), isocyanate-reactive compound (2) and compound (3) or polyol (2) and polyol (3) and water, preferably the amount of compound (2) or polyol (2) ranges from 2-20 parts by weight, the amount of compound (3) or polyol (3) ranges from 5-35 parts by weight and the amount of water ranges from 1 to 17 parts by weight, the remainder being polyisocyanate. Most preferably these amounts are 55-80, 3-20, 10-30 and 2-6 parts by weight for the polyisocyanate, polyol (2), polyol (3) and water respectively. This encompasses another aspect of the invention : if a cyclic polyisocyanate and more in particular an aromatic polyisocyanate and most in particular an MDI or polymethylenepolyphenylene polyisocyanate is used the content of cyclic and more in particular of aromatic residues in the flexible foam is relatively high as compared to conventional flexible polyurethane foams. The foams according to the invention preferably have a content of benzene rings, derived

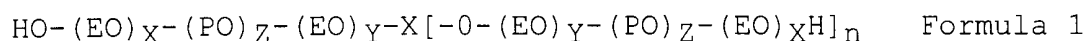
from aromatic polyisocyanates, which is 30 to 56 and most preferably 35 to 50% by weight based on the weight of the foam. Since polyols, polymer polyols, fire retardants, chain extenders and/or fillers which contain benzene rings may be used, the overall benzene ring content of the flexible foam may be higher and preferably ranges from 30 to 70 and most preferably from 35 to 65% weight as measured by calibrated Fourier Transform Infra Red Analysis.

10 The present invention is more in particular concerned with a process for preparing rigid polyurethane foams by reacting the above polyisocyanate (1), a polyether polyol (2) having a hydroxyl number of at least 150 mg KOH/g and an average nominal hydroxyl functionality of from 2 to 8, a polyether
15 polyol (3) having a hydroxyl number of from 10 to less than 150 mg KOH/g and an average nominal hydroxyl functionality of from 2 to 6 and water, wherein the amount of polyisocyanate (1), polyol (2), polyol (3) and water is 55-80, 3-20, 10-30 and 2-6 parts by weight respectively per 100 parts by weight
20 of polyisocyanate (1), polyol (2), polyol (3) and water, in the presence of a catalyst and wherein the reaction is conducted at an isocyanate index of 70-200 and wherein the polyisocyanate is reacted with one or more isocyanate-reactive compositions comprising one or more of the
25 aforementioned polyol (2), polyol (3) and water.

This preferred process gives foams with reduced thermal degradation, especially when such foams are made as large buns e.g. on a moving conveyor belt (slab-stock foam), the
30 foams have improved stability and a low amount of extractables.

An even further preferred process is a process for preparing a rigid foam by reacting a polyisocyanate (1), a polyether
35 polyol (2) having an average equivalent weight of 70-300 and

preferably of 70-200, having an average nominal hydroxyl functionality of from 2 to 6 and preferably from 2 to 3 and an oxyethylene content of at least 75% by weight, a polyether polyol (3) having an average equivalent weight of 1000-3000,
 5 having an average nominal hydroxyl functionality of 2 to 3 and preferably of 2 and having the structure



- 10 wherein EO is an ethylene oxide radical, PO is a propylene oxide radical, $x=1-15$ and preferably 3-10, $y=0-6$ and preferably 1-4, z is such so as to arrive at the above equivalent weight, $n = 1-2$ and X is a hydrocarbon radical having 2-10 and preferably 2-6 carbon atoms or a radical
 15 having the formula $-\text{CH}_2-\text{CH}_2-(\text{OCH}_2-\text{CH}_2)_{1-2}-$, and water in the presence of a catalyst wherein the amount of polyisocyanate (1), polyol (2), polyol (3) and water is 55-80, 3-20, 10-30 and 2-6 parts by weight respectively per 100 parts by weight of polyisocyanate (1), polyol (2), polyol (3) and water and
 20 wherein the reaction is conducted at an isocyanate index of 70-200, preferably 102-200, most preferably 102-150 and wherein the polyisocyanate is reacted with one or more isocyanate-reactive compositions comprising one or more of the aforementioned polyol (2), polyol (3) and water.
 25 Preferably the amount of water is 3-5 parts by weight calculated on the same basis as above. Preferably the weight ratio of water and polyol (3) is 0.1 to 0.4:1 and the weight ratio of polyol (3) and of polyol (2) + water is 0.9-2.5:1
- 30 Most preferred polyether polyols (3) are those according to formula 1, described hereinbefore. Those having a nominal hydroxyl functionality of 3 may be prepared by ethoxylation of an initiator, followed by propoxylation and again ethoxylation, wherein the initiator is a triol like glycerol
 35 and/or trimethylol propane. Those having a nominal

hydroxyl functionality of 2 may be prepared by ethoxylation of ethylene glycol, diethylene glycol and/or triethylene glycol, followed by propoxylation and again ethoxylation; or by propoxylation of ethylene glycol, diethylene glycol and/or triethylene glycol followed by ethoxylation; or by propoxylation of a polyoxyethylene polyol having 4-15 oxyethylene groups followed by ethoxylation. Mixtures of such most preferred polyols may be used as well. Although not necessary other polyols may be used together with these most preferred polyols according to formula 1, provided the amount does not exceed 30% by weight based on the weight of these polyols according to formula 1. Such polyols according to formula 1 are commercially available (e.g. Daltocel F430 from HUNTSMAN).

As catalyst those may be used which enhance the formation of urethane and urea bonds like amines, such as triethylene diamine, tin compounds, such as dibutyltin dilaurate and stannous octoate, and/or phosphates like NaH_2PO_4 and Na_2HPO_4 . Amine catalysts may be used; according to one embodiment they are not used, with the exception of ethylenediaminetetraacetic acid (EDTA), ethylenebis-(oxyethylene-nitrilo)tetraacetic acid (EGTA), N-(2-hydroxyethyl)-ethylenediaminetriacetic acid (HEDTA), 1,3-diamino-2-hydroxypropane-N,N,N',N'-tetraacetic acid (DHPTA).

Preferably the following combination of catalysts is used: a tin salt of a carboxylic acid having 2-18 carbon atoms (hereinafter called "catalyst 1"), together with a lithium, sodium, potassium, rubidium, cesium, magnesium, calcium, strontium and/or barium salt of a protic acid, the acid having at least 2 acidic hydrogen atoms and having a pK_a in water of 2-10 (hereinafter called "catalyst 2"), in a ratio of catalyst 1: catalyst 2 of 30:70 to 95:5 and in an amount of catalyst 1 and catalyst 2 of each 0.1-5% by weight (calculated on the weight of all ingredients used to prepare

the foam).

One can use the catalyst system as disclosed in PCT/EP9705507, incorporated herein by reference.

5

The amount of catalyst preferably varies from 0.2 to 3% by weight calculated on the weight of all ingredients used to prepare the polyurethane foam.

10 Catalysts (e.g. the catalysts of PCT/EP9705507) are preferably mixed with the isocyanate-reactive compounds before the foaming reaction takes place. More preferably catalyst 1 is mixed with a part of the isocyanate-reactive compounds and catalyst 2 is mixed with another part of the
15 isocyanate-reactive compounds; subsequently these mixtures are fed to a mixing head of a foaming device where they are mixed with the polyisocyanate.

In addition to the polyisocyanate, the isocyanate-reactive
20 compounds and the blowing agent, one or more auxiliaries or additives known per se for the production of polyurethane foams may be used. Such optional auxiliaries or additives include foam-stabilizing agents or surfactants, for example siloxane-oxyalkylene copolymers and polyoxyethylene
25 polyoxypropylene block copolymers, anti-oxidants, anti-static agents, UV stabilisers, anti-microbial and anti-fungal compounds and fillers like latex, TPU, silicates, barium and calcium sulphates, chalk, glass fibers or beads and polyurethane waste material. Preferably additives and
30 auxiliaries are used which do not comprise primary, secondary or tertiary nitrogen atoms.

In operating the process for making rigid foams according to the invention, the known one-shot, prepolymer or semi-
35 prepolymer techniques may be used together with conventional

mixing methods and the rigid foam may be produced in the form of slabstock, mouldings including foam in fabric and pour-in-place applications, sprayed foam, frothed foam or laminates with other materials such as hardboard, plasterboard,
5 plastics, paper or metal or with other foam layers.

It is convenient in many applications to provide the components for polyurethane production in pre-blended formulations based on each of the primary polyisocyanate and
10 isocyanate-reactive components. In particular, an isocyanate-reactive composition may be used which contains the catalysts and the auxiliaries, additives and the blowing agent in addition to the isocyanate-reactive compounds (2) and (3) in the form of a solution, an emulsion or dispersion.

15 The isocyanate-reactive components may also be supplied independently to the polyisocyanate as two or more compositions containing the catalysts and the additives and auxiliaries.

20 The rigid foam is prepared by allowing the aforementioned ingredients to react and foam until the foam does not rise any more.

After rise curing of the foam may be continued as long as
25 desirable. In general a curing period of 1 minute to 24 hours and preferably of 5 minutes to 12 hours will be sufficient. If desired curing may be conducted at elevated temperature. Subsequently the foam may be crushed. It is however preferred to allow the rigid foam obtained to cool
30 down to below 80°C, preferably below 50°C and most preferably to ambient temperature prior to crushing. The rigid foam (i.e. before crushing) preferably has a core density of 3-35 and more preferably of 8-25 kg/m³ (ISO 845).

35 The rigid foam (i.e. before crushing) prepared has a

substantial amount of open cells. Preferably the cells of the rigid foam are predominantly open.

The crushing may be conducted in any known manner and by any known means. The crushing may for instance be conducted by
5 applying mechanical force onto the foam by means of a flat or pre-shaped surface or by applying variations of external pressure.

In most cases a mechanical force sufficient to decrease the
10 dimension of the foam in the direction of the crushing by 1-90%, preferably by 50-90% will be appropriate. If desired crushing may be repeated and/or carried out in different directions of the foam. Due to the crushing the ball rebound increases considerably in the direction of the crushing. Due
15 to the crushing the density of the foam may increase. In most cases this increase will not exceed 30% of the density before crushing.

The foam may be crushed in the direction of foam rise. A
20 special foam is obtained when the crushing is conducted in a direction perpendicular to the direction of foam rise : then a foam is obtained with a highly anisotropic cell structure.

Although it is difficult to give more precise directions for
25 the crushing since it will inter alia depend on the density of the foam, the rigidity of the foam, the type of crushing device used, we believe those skilled in the art are sufficiently aware of the phenomenon of crushing of polyurethane foams that they will be able to determine the
30 appropriate crushing manner and means with the above guidance, certainly in the light of the following examples.

By crushing the ball rebound is increased at least in the direction of crushing. The increase is at least 10%. The
35 core density of the flexible foam is 3-30 and preferably 3-20

kg/m³.

After the crushing the foam may be subjected to a heat treatment in order to reduce the density increase caused by the crushing. This heat treatment is conducted at 70-200°C and preferably at 90-180°C for 0.5 minute to 8 hours and preferably for 1 minute to 4 hours.

After the crushing and optionally the heating a novel flexible foam is obtained which has exceptional properties.

Despite the fact that the foam is flexible, it does not show a significant change of the Young's storage modulus E' over a temperature range from -100°C to +25°C, as described before. The oxygen index of the foam prepared from aromatic polyisocyanates preferably is above 20 (ASTM 2863). Further it shows a Young's storage modulus at 25°C of at most 500 kPa, preferably at most 350 kPa, most preferably between 10-200 kPa and a sag factor (CLD 65/25, ISO 3386/1) of at least 2.0, preferably at least 3.5 and most preferably of 4.5-10. CLD hysteresis loss values for the foams are below 55% and preferably below 50% (which is calculated by the formula

$$\frac{(A - B)}{A} \times 100\%,$$

wherein A and B stand for the area under the stress/strain curve of the loading (A) and unloading (B) as measured according to ISO 3386/1). Still further these foams can be manufactured with a very low or even negative Poisson's ratio as determined by lateral extension studies under compression of the foams. Finally compression set values of the foams are generally low, preferably below 40% (ISO 1856 Method A, normal procedure).

If the T_g^h is not too high the foam might be used in thermoforming processes to prepare shaped articles. Preferably the T_g^h of the foam is between 80 and 180°C, most

preferably between 80°C and 160°C for such thermoforming applications. Further it was found that foams, which have been made by using a relatively low amount of the polyols having a low molecular weight, show a small or non-visible T_g^h by DMTA (the modulus change at T_g^h is small or the modulus changes gradually until the foam thermally decomposes); such foams may be used for thermoforming activities as well.

10 The foams of the present invention may be used as cushioning material in furniture and automotive and aircraft seating and in mattresses, as carpet backing, as hydrophilic foam in
15 diapers, as packaging foam, as foams for sound insulation in automotive applications and for vibration isolation in general. The foam according to the present invention further may be used together with other, conventional flexible foams to form composites, like e.g. in mouldings; such composites may also be made by allowing the ingredients for making the conventional flexible foam to form said foam in a mould in
20 the presence of the foam according to the present invention or alternatively by allowing the ingredients for making the rigid foam according to the present invention to form said rigid foam in a mould in the presence of the conventional flexible foam followed by crushing the moulding so obtained.
25 Further the foams according to the present invention may be used as textile cover, as cover for other type of sheets, as carpet underlay or felt-replacement; the so-called flame lamination technique may be applied to adhere the foam to the textile, the carpet or the other sheet. In this respect it is
30 important to note that the foam according to the present invention is suitable to be cut in sheets of limited thickness, e.g. of about 1 cm and less. Still further the foam according to the present invention may be used as insulation material around pipes and containers.

35

The instant foam may contain those flame retardants disclosed in patent application WO9931173, the content of which is incorporated herein by reference. This application discloses certain flame retardants comprising polybrominated
5 diphenylethers and/or dialkyl esters of polybrominated phthalic acid and/or phosphorous compounds.

The instant foam may also contain flame retardants known in the art, such as melamine and/or guanidine carbonate, as well
10 as others such as a mixture of expandable graphite and phosphorous compounds of the formula $P(O)XYZ$, wherein X, Y and Z are independently selected from the groups -R and -OR' wherein R is an alkyl, aryl or aralkyl group having 1-12 and preferably 1-10 carbon atoms, and R' is an aryl or aralkyl
15 group having 6-12 and preferably 6-10 carbon atoms.

The expandable graphite is already known in the art.

The phosphorous-containing compounds include
20 triphenylphosphine oxide, triphenylphosphate, triphenylphosphonate and compounds having one or more, and preferably one, alkyl group(s) having 1-6 carbon atoms, attached to one or more of the aromatic rings of these triphenylphosphate, - phosphonate and - phosphine oxide, such
25 as the commercially available Reofos 50 and Kronitex CDP both obtainable from FMC Corporation, which have on average one isopropyl and one methyl group per triphenyl phosphate molecule respectively.

30 Preferably, the relative amount of the compounds in such mixtures is such that the weight ratio of phosphorous-containing compound to expandable graphite is from about 1/9 to about 4/1.

35 The amount of fire retardants used to prepare the foam is

preferably such that the combined weight of phosphorous-containing compound and expandable graphite is 5-30%, most preferably 6-20%, by weight calculated on the total formulation (polyisocyanate, polyols, water, catalyst, additives, auxiliaries and fire retardants).

The fire retardants may be fed to the mixing head of the device to make the foam separately or after having been mixed.

10

Also, the foams of the invention show improved physical properties of the foams; in particular tensile strength and tear strength are improved.

15 The invention is illustrated by the following examples.

Examples.

Unless otherwise indicated, all parts are given by weight.

Glossary

20 (all functionalities are nominal functionalities, and equivalent weights are nominal equivalent weights)

Polyol A PO/EO polyol, DEG-initiated, functionality is 2, EO content is 20.2%, all tip. OH value is 30.

Polyol B PEG200

Isocyanate A Polymeric MDI. Functionality is 2.7. NCO value is 30.7%.

Isocyanate B Modified MDI comprising 83.1% of MDI (19.2% of which is 2,4'- and 2,2') and 16.9% uretonimine-modified MDI. Functionality is 2.07. NCO value is 30.9%.

Isocyanate C MDI comprising 30% of 2,4'- and 2,2'. Functionality is 2. NCO value is 33.6%.

Isocyanate D Prepolymer obtained by reacting 9 parts by

weight of Isocyanate A with 1 part of a polyethyleneglycol monomethylether having a MW of 500. Final NCO value is 26.8%

Dabco T9	stannous octoate catalyst from Air Product
Irganox 1135	anti-oxidant from Ciba-Geigy
Irgafos TNPP	anti-oxidant from Ciba-Geigy
EDTA3Na	Ethylenediaminetetraacetic acid trisodium salt hydrate (95%) obtained from Aldrich

Isocyanate D is obtained in the following manner. Isocyanate 900g of isocyanate A and 100g of the polyethyleneglycol monomethylether are mixed in a jar for 2
5 minutes. The jar is closed and put in an oven at 70°C for 6 hours, and allowed to cool to room temperature.

Foams are produced according to the following scheme.

Blend A comprises 200 parts by weight polyol A, 3.6 pbw DabcoT9, 5.6 pbw Irganox1135 and 0.22 pbw Irgafos TNPP. Blend B comprises 40 pbw water and 2.0 pbw EDTA3Na. Blend C is comprised of polyol B. Blend D is comprised of the isocyanate(s). These blends are mixed for 13 seconds at room temperature and poured in a 50cmx50cmx50cm wooden mould, the inner walls of which being covered with paper. One hour after the foam had stopped rising, the foam was taken out from the mould and allowed to cool to ambient temperature. A rigid foam is obtained. The core is crushed by one compression (70%CLD) at 100mm/min in the rise direction followed by another compression (70%CLD of the height after the first compression) at 500mm/min in the rise direction, using an Instron.

The properties of the foam are determined according to the following methods and standards :

Compression hardness

25 CLD 25, 40 and 65% (kPa) ISO 3386-1

Hysteresis Loss (%)

SAG factor (CLD 65/25)

Compression set (thickness)	ISO 1856
Dry 75 % (%)	
Ball rebound (%)	ISO 8307
Ball rebound (%)	ISO 8307

5 The results are summarized in the following table.

Example	1	2	3	4
Blend A (g)	333.8	359.4	341.1	309.6
Blend B (g)	66.9	65.7	62.4	66.8
Blend C (g)	157.8	169.9	161.3	146.4
Blend D (g)	1241.5	1204.9	1234.8	1277.2
Blend D composition (pbw)	53.6 Iso A/ 46.4 Iso B	55 Iso A/ 45 Iso C	57.6 Iso D/ 42.4 Iso C	57.6 Iso D/ 42.4 Iso C
Isocyanate Index	104	104	104	104
Tmax (°C)	215	214	205	209
Uncrushed density (kg/m ³)	13.7	13.2	15.7	13.8
Crushed density (kg/m ³)	17.5	17.8	18.1	14
Density increase (%)	28	36	15	1
Ball rebound (%)	55	51	54	52
CLD40 (kPa)	7.1	7.7	6.9	6.8
Sag factor	5.8	6.3	4.6	4.4
Hysteresis		53.3	46.6	47.9

Claims

1. Process for preparing a rigid foam by reacting a polyisocyanate (1), an isocyanate-reactive compound (2), said compound (2) having an average equivalent weight of at most 374 and an average number of isocyanate-reactive hydrogen atoms of from 2 to 8, an isocyanate-reactive compound (3), said compound (3) having an average equivalent weight of more than 374 and an average number of isocyanate-reactive hydrogen atoms of from 2 to 6 and water in the presence of a catalyst, wherein the polyisocyanate (1) comprises a prepolymer which is the reaction product of a polyisocyanate and a polyalkyleneglycol monoalkylether.
2. The process of claim 1, in which in the prepolymer, the polyalkyleneglycol monoalkylether is a mono(C₁-C₄alkyl)ether of polyethyleneglycol.
3. The process of claim 1 or 2, in which in the prepolymer, the polyalkyleneglycol monoalkylether has a molecular weight between 100 and 1000.
4. The process of claims 1-3, in which in the prepolymer the polyisocyanate is polymeric MDI with a functionality from 2.3 to 2.9.
5. The process of claims 1-4, in which the prepolymer has an NCO value between 15 and 29%, most preferably between 20 and 29%.
6. The process of claims 1-5, in which the polyisocyanate comprises from 100% to 20% by weight of prepolymer.
7. The process of claims 1-6, in which the polyisocyanate blended with the prepolymer is a mixture of 2,4' and 4,4' MDI

or a prepolymer thereof.

8. The process of claims 1-7, comprising reacting the polyisocyanate (1), a polyether polyol (2) having a hydroxyl
5 number of at least 150 mg KOH/g and an average nominal hydroxyl functionality of from 2 to 8, a polyether polyol (3) having a hydroxyl number of from 10 to less than 150 mg KOH/g and an average nominal hydroxyl functionality of from 2 to 6 and water, wherein the amount of polyisocyanate (1), polyol
10 (2), polyol (3) and water is 55-80, 3-20, 10-30 and 2-6 parts by weight respectively per 100 parts by weight of polyisocyanate (1), polyol (2), polyol (3) and water, in the presence of a catalyst and wherein the reaction is conducted at an isocyanate index of 70-200 and wherein the
15 polyisocyanate is reacted with one or more isocyanate-reactive compositions comprising one or more of the aforementioned polyol (2), polyol (3) and water.

9. Process for preparing a flexible foam by crushing the
20 rigid foam prepared according to the process according to any one of claims 1-8.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/EP 00/09730

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C08G18/28 C08G18/48 C08G18/70 C08J9/38 B29C44/56

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C08G C08J B29C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 5 424 386 A (GEBAUER HERBERT ET AL) 13 June 1995 (1995-06-13) column 2, line 9 -column 4, line 30 column 10, line 2 -column 11, line 26; examples 1-3; table 1 ---	1,3-6,9
A	EP 0 339 848 A (ICI PLC) 2 November 1989 (1989-11-02) cited in the application page 2, line 1 -page 3, line 38 ---	1-4,6-8
A	US 5 900 442 A (LEENSLAG JAN WILLEM ET AL) 4 May 1999 (1999-05-04) cited in the application column 3, line 20 -column 7, line 44 example 1 -----	1,8,9

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents :

A document defining the general state of the art which is not considered to be of particular relevance

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O document referring to an oral disclosure, use, exhibition or other means

P document published prior to the international filing date but later than the priority date claimed

T later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

X document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

Y document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

G document member of the same patent family

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

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