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(54) Title: PROCESS FOR MAKING RIGID POLYURETHANE FOAMS HAVING HIGH ADHESION

(57) Abstract: Use, in a water-blown rigid polyurethane or urethane-modified polyisocyanurate foam, of a polyalkyleneoxydiol having an OH value of 100 to 600 mg KOH/g, where the diol represents from 0.1 to 40 % by weight of the foam weight, for improving the adhesion.



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DESCRIPTION

PROCESS FOR MAKING RIGID POLYURETHANE FOAMS HAVING HIGH ADHESION

5 This invention relates to a process for the preparation of rigid polyurethane or urethane-modified polyisocyanurate foams, to foams prepared thereby, and to novel compositions useful in the process. The foams have high adhesion to facing materials.

10 Rigid polyurethane and urethane-modified polyisocyanurate foams are in general prepared by reacting the appropriate polyisocyanate and isocyanate-reactive compound (usually a polyol) in the presence of a blowing agent. One use of such foams is as a thermal insulation medium as for example in the construction of refrigerated storage devices. The thermal insulating properties of rigid foams are dependent upon a number of factors including, for closed cell
15 rigid foams, the cell size and the thermal conductivity of the contents of the cells, the type of fire retardant if any is used, the amount thereof, etc.

Currently, there is a trend towards foams that are free of fire retardants. Most of the fire retardants are halogenated; especially bromine-containing additives are now under
20 environmental pressure. Further, it is known that reduced fire retardant content would also give reduced smoke generation during burning, an issue of increasing importance.

Thus, there is a trend towards foams that would have intrinsic fire retardant properties; these foams are known as polyisocyanurate rigid foams (PIR foams) (as opposed to "traditional"
25 polyurethane rigid foams also known as PUR foams). These PIR foams are obtained at a high NCO index, especially above 150%. In the manufacture of these foams physical blowing agents are currently used. Halogenated blowing agents, although providing good results, are now also under environmental pressure: this is especially true for CFC's (chlorofluorocarbons). Alternative physical blowing agents are HCFC's
30 (hydrochlorofluorocarbons), HFC's (hydrofluorocarbons) and HC's (hydrocarbons). Since these blowing agents, with the exception of HC's, still contain halogen, they still suffer from the same drawbacks; further the HC's are highly flammable substances and hence cause safety problems. The "ideal" blowing agent, especially for use in PIR foams, would then be water.

35 Water-blown PUR and PIR foams (collectively referred to as polyurethane foams) however suffer from major drawbacks. They exhibit poor adhesion, especially to metal (which can also

be seen with other blowing agents such as hydrocarbons in, e.g., PIR foams), poor friability and surface brittleness. These phenomena are even more acute at high NCO index.

Attempts to solve these problems have used a polyol used in the field of flexible polyurethane foams.

US-P-5,070,115 and US-P-5,350,780 discloses a process for preparing rigid foams having improved adhesion comprising reacting a polyisocyanate with (i) a polyester polyol having a functionality of at least 2 and an OH value of at least 150 and/or a polyether polyol having a functionality of at least 2 and an OH value of at least 200 and (ii) a polyoxyalkylenepolyol having a functionality of at least 2 and an OH value below 100. US-P-5,418,258, to the same assignee, discloses a prepolymer of a polyisocyanate with said polyoxyalkylenepolyol having a functionality of at least 2 and an OH value below 100. NCO index actually disclosed is below 150 in all three US patents.

US-P-5,494,942 discloses a process similar to the one of US-P-5,418,258; the prepolymer being obtained starting from polymeric MDI and a polyoxyalkylenepolyol having a functionality of at least 2 and a molecular weight of at least 2000 (which for a functionality of 2 corresponds to an OH value below 56). The NCO index actually disclosed is also below 150 in this US patent.

WO-A-98/33832 discloses a specific polyol mixture, comprising a major part of a polyether and/or polyester polyol (with OH values ranging from 200 to 2000) and a minor part of a polyolefin polyol (with OH values preferably below 100). Adhesion to polyethylene is said to be improved.

These solutions however exhibit also drawbacks. First, the amount of flexible polyol needed to achieve a noticeable effect is quite high. Secondly, these polyols are rather expensive. Last, it may happen that the two types of polyols (rigid and flexible) are subject to phase separation.

There is thus a need for foam compositions that (i) would allow water as a blowing agent, (ii) without resort to a high molecular weight flexible polyol, (iii) while providing good adhesion of the foam to facing material, especially metal, (iv) while at the same time preserving compression strength and also enhancing other features such as friability, and (v) while at the same time providing foams with very good insulating and physical properties.

These objects are met by using in the process of making rigid polyurethane or urethane-modified polyisocyanurate foam, a polyalkyleneoxydiol having an OH value of 100 to 600 mg KOH/g, where the diol represents from 0.1 to 40% by weight of the foam weight.

- 5 The foams of the invention also are preferably of the closed cell type. This means the closed cell content of the foam is at least 60%, preferably at least 80%, most preferably at least 85%. Closed cell content is measured according to standard ASTM D2856.

10 The instant invention is based on the surprising effect that this specific diol provides an improved adhesion of the foam to the facing material, especially in case of PIR foams.

The diol that is used in the invention is a polyalkyleneoxydiol. It is preferably comprised of ethyleneoxy and/or propyleneoxy units. More preferably, the ethyleneoxy mol content is at least 50%, advantageously at least 75%, more preferably 100%, based on the total
15 oxyalkylene units present.

The preferred diol for use in the invention is PEG (polyethyleneglycol) as well as PPG (polypropyleneglycol).

- 20 While the OH value of the diol generally ranges from 100 to 600 mg KOH/g, it is preferably below 500 mg KOH/g and most preferably between 150 and 400 mg KOH/g.

PEG 600, PEG 300 and PEG 400 (PEG having molecular weights of 600, 300 and 400, respectively) are well suited for the invention purposes.

25 The content of the diol is generally from 0.1 to 30 % by weight of the foam, preferably from 1 to 20 %, most preferably from 2 to 10 %. The amounts of diol used are higher in case of high NCO index.

- 30 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 or urethane-modified polyisocyanurate foams, and in particular the aromatic polyisocyanates such as diphenylmethane diisocyanate in the form of its 2,4'-, 2,2'- and 4,4'-isomers and mixtures thereof, the mixtures of diphenylmethane diisocyanates (MDI) and oligomers thereof known
35 in the art as "crude" or polymeric MDI (polymethylene polyphenylene polyisocyanates) having an isocyanate functionality of greater than 2, toluene diisocyanate in the form of its 2,4- and 2,6-isomers and mixtures thereof, 1,5-naphthalene diisocyanate and 1,4-diisocyanatobenzene. Other organic polyisocyanates which may be mentioned include

the aliphatic diisocyanates such as isophorone diisocyanate, 1,6-diisocyanatohexane and 4,4'-diisocyanatodicyclohexylmethane.

Further suitable polyisocyanates for use in the process of the invention are those described in EP-A-0320134.

- 5 Modified polyisocyanates, such as carbodiimide or uretonimine modified polyisocyanates can also be employed.

Still other useful organic polyisocyanates are isocyanate-terminated prepolymers prepared by reacting an excess organic polyisocyanate with a minor amount of an active hydrogen-containing compound.

- 10 Preferred polyisocyanates to be used in the present invention are the polymeric MDI's.

The further isocyanate-reactive compounds that can be used in combination with the specific diol of the invention are those traditionally used in the art (they will be referred to as "major polyol"). They can be generally disclosed as being a polyol having a functionality of at least
15 2 and an OH value above 100 mg KOH/g. Suitable major polyols to be used in the process of the present invention include any of those known in the art for the preparation of rigid polyurethane or urethane-modified polyisocyanurate foams. Of particular importance for the preparation of rigid foams are polyols and polyol mixtures having average hydroxyl numbers above 100, preferably from 300 to 1000, especially from 200 to 700 mg KOH/g, and hydroxyl
20 functionalities of from 2 to 8, especially from 2.5 to 8. 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 diethyleneglycol (DEG), glycerol, trimethylolpropane, triethanolamine, pentaerythritol, sorbitol and sucrose;
25 polyamines, for example diethanolamine (DELA), ethylene diamine (EDA), tolylene diamine (TDA), diaminodiphenylmethane (DADPM) and polymethylene polyphenylene polyamines; and aminoalcohols, for example ethanolamine and diethanolamine; and mixtures of such initiators. Other suitable polymeric polyols include polyesters obtained by the condensation of appropriate proportions of glycols and higher functionality polyols with dicarboxylic or
30 polycarboxylic acids. Still further suitable polymeric polyols include hydroxyl-terminated polythioethers, polyamides, polyesteramides, polycarbonates, polyacetals, polyolefins and polysiloxanes. Polyether polyols, especially amine-initiated, and polyester polyols, especially aromatic polyester polyols, are preferred.

- 35 It has to be understood that mixtures of major polyols are encompassed as well. Specific mixtures encompass polyether polyols mixtures, polyester polyols mixtures and polyether polyols and polyester polyols mixtures.

For example, one major polyol may be:

a mixture of two or more polyether polyols; or

a mixture of at least one polyether polyol and at least one polyester polyol.

One preferred mixture is one in which the polyether polyol is an amine-initiated polyol and/or the polyether polyol is an aromatic polyol.

In these mixtures, the preferred weight ratio of the first polyether polyol to the second polyether polyol can be in the range of 1 to 3, while the preferred weight ratio polyether polyol to polyester polyol can be in the range of 1 to 3.

The functionality of the polyol blend can vary within the broad limits indicated above; preferably the average functionality is from 2 to 4.5.

In addition to the above-mentioned polyols, it is also possible to use any of the known flexible polyols (polyols used for making flexible foams) that are traditionally used to impart adhesion.

The quantities of the polyisocyanate compositions and the polyfunctional isocyanate-reactive compositions (including the diol of the invention) to be reacted will depend upon the nature of the rigid polyurethane or urethane-modified polyisocyanurate foam to be produced and will be readily determined by those skilled in the art. The NCO index as used herein, is the ratio of NCO-groups over isocyanate-reactive hydrogen atoms (including water) present in a formulation, given as a percentage:

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

In general the NCO index is higher than 90 %, preferably higher than 100 %, especially above 130 %, particularly above 150 % and preferably between 150 and 300 %. Higher indexes up to 500 %, and even higher, are also contemplated.

Any type of blowing agent known for the manufacture of rigid PUR or PIR foams can be used in the present invention. As blowing agent, one can use water, hydrocarbons, hydrofluorocarbons, dialkyl ethers, cycloalkylene ethers and ketones, fluorinated ethers, perfluorinated hydrocarbons, and hydrochlorofluorocarbons (e.g. 1-chloro-1,2-difluoroethane, 1-chloro-2,2-difluoroethane, 1-chloro-1,1-difluoroethane, 1,1-dichloro-1-fluoroethane and monochlorodifluoromethane).

Preferably, water is used as the chemical blowing agent. The amount of water used in the foam of the invention is generally between 0.1 and 25 % by weight, preferably between 1 and 10 % by weight, based on the total foam weight.

5 In a preferred embodiment of the invention water is used as the sole blowing agent. The amount of water is then generally between 1 and 10 % by weight, preferably between 1 and 5 % by weight based on the total foam weight.

10 In addition to water, other chemical blowing agents can be used, as well as other physical blowing agents (especially of the hydrocarbon and hydrofluorocarbon series, such as depicted below). These co-blowing agents represent up to 50%, preferably up to 25% of the expansion of the foam, when the foam is mainly water-blown.

Suitable physical blowing agents include hydrocarbons, hydrofluorocarbons, as well as others.

15 Suitable hydrocarbon blowing agents include lower aliphatic or cyclic, linear or branched hydrocarbons such as alkanes, alkenes and cycloalkanes, preferably having from 4 to 8 carbon atoms. Specific examples include n-butane, iso-butane, 2,3-dimethylbutane, cyclobutane, n-pentane, iso-pentane, technical grade pentane mixtures, cyclopentane, methylcyclopentane, 20 neopentane, n-hexane, iso-hexane, n-heptane, iso-heptane, cyclohexane, methylcyclohexane, 1-pentene, 2-methylbutene, 3-methylbutene, 1-hexene and any mixture of the above. Preferred hydrocarbons are n-butane, iso-butane, cyclopentane, n-pentane and isopentane and any mixture thereof.

25 Suitable hydrofluorocarbon blowing agents include lower aliphatic or cyclic, linear or branched hydrocarbons such as alkanes, alkenes and cycloalkanes, preferably having from 2 to 8 carbon atoms, which are substituted with at least one, preferably at least three, fluorine atom(s). Specific examples include 1,1,1,2-tetrafluoroethane (HFC 134a), 1,1,2,2-tetrafluoroethane, trifluoromethane, heptafluoropropane, 1,1,1-trifluoroethane, 1,1,2- 30 trifluoroethane, 1,1,1,2,2-pentafluoropropane, 1,1,1,3-tetrafluoropropane, 1,1,1,3,3-pentafluoropropane, 1,1,3,3,3-pentafluoropropane (HFC 245fa) and 1,1,1,3,3-pentafluoro-n-butane. The preferred hydrofluorocarbons are HFC 134a and HFC 245fa.

35 The total quantity of blowing agent to be used in a reaction system for producing cellular polymeric materials will be readily determined by those skilled in the art, but will typically be from 1 to 25 % by weight based on the foam weight. This quantity of blowing agent is in general such that the resulting foam has the desired bulk density which is generally in the range of 15 to 70 kg/m³, preferably 20 to 50 kg/m³, most preferably 25 to 45 kg/m³.

When a blowing agent has a boiling point at or below ambient it is maintained under pressure until it is mixed with the other components. Alternatively, it can be maintained at subambient temperatures until mixed with the other components.

5

In addition to the polyisocyanate and polyfunctional isocyanate-reactive compositions and the blowing agents, the foam-forming reaction mixture will commonly contain one or more other auxiliaries or additives conventional to formulations for the production of rigid polyurethane and urethane-modified polyisocyanurate foams. Such optional additives include crosslinking agents, for examples low molecular weight polyols such as triethanolamine, foam-stabilizing agents or surfactants, for example siloxane-oxyalkylene copolymers, urethane catalysts, for example tin compounds such as stannous octoate or dibutyltin dilaurate or tertiary amines such as dimethylcyclohexylamine or triethylene diamine, isocyanurate catalysts, fire retardants, for example halogenated alkyl phosphates such as tris chloropropyl phosphate and Non-halogenated fire retardants such as triethylphosphate and diethylethylphosphonate, fillers such as carbon black, cell size regulators such as insoluble fluorinated compounds. The use of such additives is well known to those skilled in the art.

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Examples of suitable commercially available surfactants include: from Crompton OSI : Niax L5100, L5110, L5115, L5320, L5340, L5420, L5421, L5430, L5440, L6164, L6701, L6900, L6906, L6908, L6910, L6912, L6980, L7002, Y5889, Y10325, Y1045, Y10733, Y10745, Y10754, Y1076, Y10764, Y10774, Y10786, Y10788, Y10790, Y10805, Y10806; from Air Products : DABCO 5454, DC190, DC193, DC197, DC198, DC1248, DC1598, DC5000, DC5043, DC5098, DC5103, DC5169, DC5241, DC5244, DC5258, DC5356, DC5357, DC5365, DC5367, DC5374, DC5454, DC5555, DC5557, DC5588, DC5598, DC5604; from Pelron : PELRON 9315, PELRON 9475, PEL SIL 9346, PEL SIL 9475, PEL SIL 9547, PEL SIL 9562, PEL SIL 9567, PEL SIL 9736, PEL SIL 9752, PEL SIL 9758, PEL SIL 9797; from Goldschmidt : TEGOSTAB B1048, B1400A, B1903, B2219, B3136, B4113, B4351, B4380, B4690, B8017, B8036, B84PI, B8404, B8405, B8406, B8407, B8408, B8409, B8416, B8418, B8423, B8425, B8427, B8432, B8433, B8434, B8435, B8441, B8444, B8450, B8453, B8454, B8455, B8457, B8458, B8460, B8461, B8462, B8465, B8466, B8467, B8469, B8471, B8474, B8476, B8680, B8681, B8863T, B8870, B8871, B8906, B8934, BF227, BF2370.

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In operating the process for making rigid foams according to the invention, the known one-shot, prepolymer or semi-prepolymer techniques may be used together with conventional mixing methods and the rigid foam may be produced in the form of slabstock, moldings, cavity fillings, sprayed foam, frothed foam or laminates with other materials such as hardboard, plasterboard, plastics, paper or metal.

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According to one embodiment, the invention is carried out according to the one-shot technique, all polyols being in the isocyanate-reactive composition.

According to a second embodiment, the invention is carried out according to the prepolymer technique, the polyisocyanate being first reacted with a part, preferably all of the diol.

- 5 It is also possible to have the diol of the invention in both the prepolymer and the isocyanate-reactive composition, if needed.

10 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 isocyanate-reactive components. In particular, many reaction systems employ a polyisocyanate-reactive composition, which contains the major additives such as the blowing agent and the catalyst in addition to the isocyanate-reactive component or components.

15 Therefore the present invention also provides an isocyanate-reactive composition comprising the present mixture of the specific polyol(s) and the blowing agent (preferably water). The amount of diol is generally between 1 and 80 %, preferably between 5 and 50 %, most preferably between 10 and 30 % by weight based on the isocyanate-reactive composition. However the diol content can also be as high as 100% of the isocyanate-reactive compounds.

20 The various aspects of this invention are illustrated, but not limited by the following examples.

The following reaction components are referred to in the examples, in which:

Polyol 1: Sucrose initiated polyether polyol, F_n is 2.4, OH value is 160 mg KOH/g.

25 Polyol 2: Sorbitol initiated polyether polyol, F_n is 5.5, OH value is 460 mg KOH/g.

Polyol 3: Sucrose initiated polyether polyol, F_n is 3.96, OH value is 570 mg KOH/g.

Polyol 4: DADPM initiated polyether polyol, F_n is 3.6, OH value is 310 mg KOH/g.

Polyol 5: Sorbitol polyether polyol, F_n is 5.66, OH value is 340 mg KOH/g.

30 Polyol 6: Voranol RA 800, an EDA initiated polyether polyol, commercially available from Dow.

Polyol 7: Isoexter 4531, an aliphatic polyester polyol, commercially available from Coim.

Polyol 8: Stepanpol 2352, an aromatic polyester polyol, commercially available from Stepan.

Polyol 9: TDA initiated polyether polyol, F_n is 4, OH value is 350 mg KOH/g.

PEG600: polyethyleneglycol, F_n is 2, OH value is 187 mg KOH/g.

35 PEG300: polyethyleneglycol, F_n is 2, OH value is 374 mg KOH/g.

Tegostab B 8406: Silicone surfactant from Goldschmidt.

Niax A1: Amine catalyst from Union Carbide.

Polycat 43: trimerisation catalyst from Air Products.

SFC: Dimethylcyclohexylamine catalyst.

SFB: Dimethylbenzylamine catalyst.

Dabco K15: trimerisation catalyst from Air Products.

Isocyanate: Polymeric MDI, F_n is 2.85, NCO value is 30.5%.

5 Ixol B251: Brominated fire retardant from Solvay.

TCPP: Trichloropropylphosphate, fire retardant

TCEP: Trichloroethylphosphate, fire retardant

TEP: Triethylphosphate, fire retardant

DEEP: Diethylethylphosphonate, fire retardant

10 DMMP: Dimethylmethylphosphonate, fire retardant

Example 1: PIR Example

15 After mixing the polyols and non-reactive components, the polyol blend and the polyisocyanate are poured together and the properties evaluated on a handmix foam. Chemicals are mixed at 2000 rpm for 5 seconds. Reactivity and free rise density was checked on a cup foam; for evaluation of other physical properties, free rise blocks of 20x20x30 cm were made.

20 The following table indicates the composition. Amounts are indicated in parts by weight.

Table 1

Formulation	Ref. Ex	Ex. A	Ex. B	Ex. C
Polyol 1	20	20	20	20
Polyol 3	56.8	56.8	56.8	56.8
PEG600	-	11	24	55
B 8406	4	4	4	5
NiAx A1	0.13	0.13	0.13	0.13
SFC	1.2	1.2	1.3	1.4
Dabco K15	3.0	3.0	3.2	3.5
Water	4.7	4.8	5.4	5.6
Isocyanate	326	339	369	405
Index (%)	200	200	200	200

25 The results are summarized in the next table. Tests are performed at room temperature. The various standards for measuring the characteristics are given below:

	Reactivity	ISO 845
	Closed Cell Content	ASTM D 2856
	Compression strength	DIN 53421
	(NMCS stands for Normalized Mean Compression Strength)	
5	Friability	BS 4370 method 12
	DIM VAC	method described by D. Daems, I.D. Rosbotham, Utech 94, The Hague, The Netherlands, Paper 18 (1994).
	B2 test	DIN 4102
10	Adhesion	See below

Adhesion is measured according to the following method. The force required for a given width of 5 cm of paper liner (Al/Kraft/PE coated) is measured on the contact face in an early stage of the foam making and after 24-hrs cure. All experiments are performed at room temperature. An Instron apparatus is used. By using the above liner, an adhesion of more than 100 N/m indicates that the foam will exhibit good adhesion also to metal.

Table 2

	Ref. Ex	Ex. A	Ex. B	Ex. C
Reactivity (sec)				
Cream time	9	9	8	8
Full Cup time	22	20	22	19
String time	32	34	34	32
Tack Free time	60	60	65	60
End Of Rise time	60-65	70	80	65
Density (kg/m ³)	36	37.5	36	37.9
Closed Cell Content (%)	90	89	87	87
Compression strength (kPa)				
NMCS (OD of 36 kg/m ³)	198	180	164	155
Friability (%)	24	13.5	18.7	12.4
Early Adhesion (N/m)				
5 min	10	17	36	18
6 min	20	40	60	104
7 min	46	42	63	207
8 min	20	40	92	353
9 min	12	40	34	395
10 min	12	25	26	416
Final Adhesion (N/m)	50	50	110	350

Example 2: PIR Example

5

The following table indicates the composition (amounts in pbw). The prepolymer is manufactured as follows. The isocyanate is charged and heated to about 60°C. PEG600 is added over a period of 30 min. The weight ratio isocyanate:PEG is 95:5. NCO value of this prepolymer is 28.5%.

10

Table 3

Formulation	Ref. Ex	Ex. D	Ex. E
Polyol 1	20	20	20
Polyol 4	45	45	45
Polyol 8	32.5	32.5	32.5
PEG600	-	15	-
B 8406	4	4	4
Niax A1	0.13	0.13	0.13
SFC	0.73	0.73	0.73
Dabco K15	2.75	2.75	2.75
Water	3.9	4.1	4.1
Isocyanate	247	267	-
Isocyanate/PEG600 Prepolymer*	-	-	273
Index (%)	200	200	200

* equivalent to 15 parts of PEG600 in the resin side

5 The results are summarized in the next table.

Table 4

	Ref. Ex	Ex. D	Ex. E
Reactivity (sec)			
Cream time	8	9	7
Full Cup time	22	23	22
String time	30	35	34
Tack Free time	60	65	60
End Of Rise time	60	60	65
Density (kg/m ³)	37.8	38	37
Closed Cell Content (%)	89	90	89
Compression strength (kPa)			
NMCS (OD of 36 kg/m ³)	195	187	198
Friability (%)	13	10	5
Early Adhesion (N/m)			
5 min	33	9	34
6 min	66	37	68
7 min	94	99	108
8 min	122	150	154
9 min	70	200	160
10 min	50	233	209
Final Adhesion (N/m)	90-100	200	280

Example 3: PIR Example

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The following table indicates the composition (amounts in pbw).

Table 5

Formulation	Ex. F	Ex. G
Polyol 1	20	20
Polyol 4	45	-
Polyol 9	-	45
Polyol 8	32.5	32.5
PEG300	21	21
TEP	21	21
B 8406	6	6
Niax A1	0.1	0.1
SFB	2	2
Dabco K15	1.14	1.14
Water	4.7	4.7
Isocyanate	306.2	316.1
Index (%)	200	200

The results are summarized in the next table.

Table 6

	Ex. F	Ex. G
Reactivity (sec)		
Cream time	15	15
Full Cup time	47	54
String time	60	75
Tack Free time	-	-
End Of Rise time	-	-
Density (kg/m ³)	41.5	42
Closed Cell Content (%)	91	89
Compression strength (kPa)		
NMCS (OD of 36 kg/m ³)	166	194
Early Adhesion (N/m)		
5 min	10	27
6 min	40	150
7 min	90	180
8 min	140	230
9 min	170	280
10 min	236	300
Dim Vac (%)		
length	-7.33	-1.70
width	-8.43	-1.40
thickness	1.19	1.09

From the above tables, it can be seen that adhesion is good. It should be borne in mind that the adhesion test is carried out at room temperature, which is a severe test (in most cases, heat is applied to the foam panel, e.g. 60°C for 10 minutes). In case of applied heat, the foams of the invention also exhibit higher adhesion than the reference foams. The foams of the present invention even exhibit better adhesion at room temperature than the reference foams at elevated temperatures.

Example 4: PIR Example

The following table indicates the composition (amounts in pbw).

Table 7

Formulation	Ref. Ex.	Ex. H	Ex. I	Ex. J	Ex. K	Ex. L
Polyol 1	20	20	20	20	20	20
Polyol 4	45	45	45	45	45	45
Polyol 8	32.5	32.5	32.5	32.5	32.5	32.5
PEG300	21	21	21	21	21	21
TCPP	-	12.6	-	-	-	-
TCEP	-	-	12.6	-	-	-
DEEP	-	-	-	12.6	-	-
TEP	-	-	-	-	12.6	-
DMMP	-	-	-	-	-	12.6
B 8406	6	6	6	6	6	6
Niax A1	0.1	0.1	0.1	0.1	0.1	0.1
SFB	2	2	2	2	2	2
Dabco K15	1.14	1.14	1.14	1.14	1.14	1.14
Water	4.7	4.7	4.7	4.7	4.7	4.7
Isocyanate	306.2	306.2	306.2	306.2	306.2	306.2
Index (%)	200	200	200	200	200	200

The results are summarized in the next table.

5

Table 8

	Ref. Ex.	Ex. H	Ex. I	Ex. J	Ex. K	Ex. L
Compression strength (kPa)						
NMCS (OD of 44 kg/m ³)	222	224	218	200	197	184
B2 (cm)		12	12	13	13	11

Thus, only minimum amounts of fire retardant are needed to meet the requirements of the B2 test (i.e. a spread of flame less than 15 cm).

10

Example 5: PUR Example

The following table indicates the composition (amounts in pbw).

15

Table 9

Formulation	Ref. Ex	Ex. M
Polyol 2	13.36	13.36
Polyol 3	15.06	15.06
Polyol 5	13	13
Polyol 6	2	2
Polyol 7	14.31	14.31
PEG600	-	4.77
TCPP	11.42	11.42
DEEP	5	5
Ixol B251	19.08	19.08
B 8406	2	2
Polycat 43	0.3	0.3
SFC	1.1	1.1
Water	3.4	3.4
Isocyanate	171.9	171.9
Index (%)	130	130

The results are summarized in the next table.

Table 10

	Ref. Ex	Ex. M
Reactivity (sec)		
Cream time	15	15
Full Cup time	32	32
String time	39	39
Tack Free time	-	-
End Of Rise time	75	75
Density (kg/m ³)	37	37
Early Adhesion (N/m)		
4 min	56	113
5 min	144	157
6 min	130	162
7 min	125	104
8 min	109	149
9 min	170	133
10 min	135	187
Final Adhesion (N/m)	300	350

The foams of the invention exhibit a remarkable improvement as far as adhesion is concerned,
 5 while the other properties of the foam are not affected.

CLAIMS

1. A process for making a rigid polyurethane or urethane-modified polyisocyanurate foam comprising reacting, in the presence of a blowing agent, at least one polyisocyanate with an isocyanate-reactive composition comprising:
5 (a) at least one polyol having a functionality of at least 2 and an OH value above 100 mg KOH/g; and
(b) at least one polyalkyleneoxydiol having an OH value of 100 to 600 mg KOH/g, where the diol represents from 0.1 to 40% by weight of the total foam weight.
10
2. The process of claim 1, in which the foam is of the closed cell type.
3. The process of claim 1 or 2, in which the NCO index is higher than 90 %.
- 15 4. The process of claim 3, in which the NCO index is between 150 and 300 %.
5. The process of any one of the preceding claims, in which the diol is a polyetherdiol based on ethyleneoxy and/or propyleneoxy, where the ethyleneoxy mol content is at least 50% based on total oxyalkylene units.
20
6. The process of any one of the preceding claims, in which the diol has an OH value between 150 and 400 mg KOH/g.
7. The process of any one of the preceding claims, in which the diol is
25 polyethyleneglycol.
8. The process of claim 7, in which the diol has a molecular weight of about 600 or 300 or 400.
- 30 9. The process of any one of the preceding claims, in which the blowing agent comprises water.
10. The process of any one of the preceding claims, in which the at least one polyol (a) comprises: at least one polyether polyol and at least one polyester polyol, where the
35 average OH value is at least 200 mg KOH/g.

11. The process of any one of claims 1 to 9, in which the at least one polyol (a) comprises:
at least a first polyether polyol and at least a second polyether polyol, where the
average OH value is at least 200 mg KOH/g.
- 5 12. The process of any one of the preceding claims, which is carried out according to the
one-shot technique.
13. The process of any one of claims 1 to 11, which is a prepolymer process, where said
prepolymer is obtained by reacting part or all of the diol with part of the
10 polyisocyanate.
14. The process of any one of the preceding claims, in which the polyisocyanate is MDI-
based.
- 15 15. The process of any one of the preceding claims, in which the foam is made on a metal
surface to which it adheres.
16. A rigid polyurethane or urethane-modified polyisocyanurate foam obtainable by the
process of any one of the preceding claims.
- 20 17. An isocyanate-reactive composition comprising: (a) at least one polyol having a
functionality of at least 2 and an OH value above 100 mg KOH/g; (b) at least one
polyalkyleneoxydiol having an OH value of 100 to 600 mg KOH/g, where the diol
represents from 1 to 100% by weight of the isocyanate-reactive composition weight;
25 and (c) optionally water.
18. The isocyanate-reactive composition of claim 17, in which the diol represents 1 to 80%
by weight of the isocyanate-reactive composition.
- 30 19. The isocyanate-reactive composition of claim 17 or 18, in which the diol is as defined
in any one of claims 5 to 8.
20. The isocyanate-reactive composition of claim 17 to 19, in which the at least one polyol
(a) is as defined in claim 10 or 11.
- 35 21. Use, in a water-blown rigid polyurethane or urethane-modified polyisocyanurate foam,
of a polyalkyleneoxydiol having an OH value of 100 to 600 mg KOH/g, where the diol
represents from 0.1 to 40% by weight of the foam weight, for improving the adhesion.

22. Use according to claim 21 in polyisocyanurate foams.

INTERNATIONAL SEARCH REPORT

International Application No

PCT/EP 01/06410

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C08G18/40 C08G18/48

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

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)

WPI Data, PAJ, EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	DE 36 27 236 A (BASF AG) 18 February 1988 (1988-02-18) column 9, line 7 - line 9; claim 1 ---	1,5-7,9, 11,12, 14,16-20
A	DE 39 10 100 C (BAYER AG) 4 January 1990 (1990-01-04) claims 1,2,6; table & US 5 350 780 A 27 September 1994 (1994-09-27) cited in the application -----	1-6, 9-12, 14-22



Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

° Special categories of cited documents:

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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

Date of the actual completion of the international search

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/EP 01/06410

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