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(54) Title: FORMULATION FOR REDUCTION OF FORMALDEHYDE EMISSION IN PU FOAM

(57) Abstract: A composition comprising an isocyanate reactive compound, a polyisocyanate and a aldehyde reducing compound of the general formula R^1-CH_2-R^2, wherein R^1 is *- SO_2–R^3, a pyridyl derivative, or *–CH=CHR^3; R^2 is *- SO_2–R^3, a pyridyl derivative, *–CH=CHR^2, *–C(O)R^4 or *–CN, R^4 is NH, NH-R^5, NR^6/R^7, OR^8 or R^9 and wherein R^3, R^5, R^6, R^7, R^8, or R^9 are independently of one another selected from the group consisting of an aliphatic hydrocarbon, araliphatic hydrocarbon, and an aromatic hydrocarbon, which are optionally substituted, wherein the * represents the place of R^1 or R^2 that is bound to the CH_2 of the R^1-CH_2-R^2 formula.

Formulation for reduction of formaldehyde emission in PU foam

Present invention is related to a composition for the reduction of formaldehyde emission in PU foam. The invention is also related to a method for reducing the reduction of formaldehyde emission in PU foam.

Polyurethane and polyurea materials are well known in the art. Polyurethane and polyurea foams, in particular so-called flexible polyurethane and polyurea foams, are used in a multitude of applications. More and more, the emission of components, such as in particular aldehyde components and dimethylformamide, is seen as a disadvantage. Various attempts have been made to integrate so-called scavengers in the polyurethane foam. As an example DE10003157A1 discloses polymeric polyethylene imines being dissolved in a solvent, after which the solution is sucked into the foam structure. After drying or evaporation of the solvent, the polymeric molecules remain in the foam structure and act as aldehyde scavengers. This process is cost and labor intensive, a significant amount of scavenging polymer is needed and the polymers are not necessarily all bonded to the chemical polyurethane or polyurea structure. The standards and regulations for emissions from polyurethane foam have become more stringent, especially within the automotive industry. The requirements within the automotive industry only allow very low emissions or almost no emissions of aldehydes, such as formaldehyde, and dimethylformamide from these polyurethane foams. A test method has been developed, namely the VDA 276 test method. Some automotive OEM's specify stringent formaldehyde emissions lower than 30 $\mu g/m^3$ for 1 kg foam measured according to the VDA 276 test method measured at 65°C. Patent application WO2014/026802 describes a foam where the emission of formaldehyde is decreased, when using the VDA 276 test and where the foam was made using a composition comprising an amine component. Also WO2016/005479 describes compositions that can be used for making polyurethanes which are able to reduce formaldehyde and acetaldehyde emissions. Patent application US2016/0304686 describes compounds that are able to reduce the emission of formaldehyde.

Some of these above described compounds are not easy to handle, and often require extra steps like heating, or premixing before the compounds are solved in the composition. Therefore, it is an object to find other compounds that are able to reduce the emission of organic compounds, more in particular, to reduce the formaldehyde emission in polyurethane foam, and that are easy

to handle. It is an object of the invention to provide a composition which does not impair the production of polyurethanes. Furthermore, it is an object to find compounds that are able to reduce the formaldehyde emission. These objects, amongst others, are at least partially met by using a composition according to claim 1.

In a first aspect, the invention is related to a composition comprising an isocyanate reactive compound, a polyisocyanate and an aldehyde reducing compound of the general formula R^1 - CH_2 -R^2, wherein R^1 is *- SO_2 – R^3, a pyridyl derivative, or *–CH=CHR^3; R^2 is *- SO_2 – R^3, a pyridyl derivative, *–CH=CHR^2, *–C(O)R^4 or *–CN, R^4 is NH, NH-R^5, NR^6/R^7, OR^8 or R^9 and wherein R^3, R^5, R^6, R^7, R^8, or R^9 are independently of one another selected from the group consisting of an aliphatic hydrocarbon, araliphatic hydrocarbon, and an aromatic hydrocarbon, which are optionally substituted, wherein the * represents the place of R^1 or R^2 that is bound to the CH_2 of the R^1 - CH_2 -R^2 formula. The pyridyl derivative according to the invention is bound on the 2, 3, 4 or 5 position to the CH_2 of the R^1 - CH_2 -R^2 formula. Preferably, it is bound on the 3 position. The pyridyl derivative may be substituted e.g. with aliphatic hydrocarbon, araliphatic hydrocarbon or aromatic hydrocarbon, which can also be substituted. The inventors surprisingly found that this composition is able to reduce the emission of aldehyde, such as the formaldehyde in polyurethane to a level of less than 30 µg/m³ for 1 kg foam when tested with the VDA 276 test method. Further, the inventors found that some of these compounds may be easily soluble in the polyisocyanate and or the isocyanate reactive compound.

For the purposes of the invention an isocyanate reactive compound is suitable to react with the isocyanate groups of e.g. polyisocyanate compounds. This reaction results in the formation of polyurea or polyurethane materials, and also modified polyurethanes which can comprise isocyanurate structures, allophanate structures, urea structures, carbodiimide structures, uretonimine structures, biuret structures, and other isocyanate adducts. The polyurethane materials comprise polyisocyanate polyaddition products, for example thermosets, and foams based on polyisocyanate polyaddition products, for example flexible foams, semi rigid foams, rigid foams, and integral foams and also polyurethane coatings and binders.

The polyurethane of the invention is preferably used in the interior of means of transport, such as ships, aircraft, trucks, cars or buses.

The polyisocyanate components in the composition of the invention comprise any of the polyisocyanates known for the production of polyurethanes. These comprise the aliphatic,

cycloaliphatic, and aromatic difunctional or polyfunctional isocyanates known from the prior art, and also any desired mixtures thereof. Examples are diphenylmethane 2,2'-, 2,4'-, and 4,4'-diisocyanate, the mixtures of monomeric diphenylmethane diisocyanates with diphenylmethane diisocyanate homologs having a larger number of rings (polymer MDI), isophorone diisocyanate (IPDI) and its oligomers, tolylene 2,4- and 2,6-diisocyanate (TDI), and mixtures of these, tetramethylene diisocyanate and its oligomers, hexamethylene diisocyanate (HDI) and its oligomers, naphthylene diisocyanate (NDI), and mixtures thereof. It is preferably to use tolylene 2,4- and/or 2,6-diisocynate (TDI) or a mixture thereof, monomeric diphenylmethane diisocyanates, and/or diphenylmethane diisocyanate homologs having a larger number of rings (polymer MDI), and mixtures of these. The polyisocyanate component used can also take the form of a polyisocyanate prepolymer. The isocyanate component, according to this invention, is preferably a polyisocyanate and may comprise any number of polyisocyanates, including but not limited to, toluene diisocyanates (TDI), diphenylmethane diisocyanate (MDI) – type isocyanates, and prepolymers of these isocyanates.

Semi-prepolymers and prepolymers which may be obtained by reacting polyisocyanates with compounds containing isocyanate-reactive hydrogen atoms are also isocyanate components. Examples of compounds containing isocyanate-reactive hydrogen atoms include alcohols, glycols or even relatively high molecular weight polyether polyols and polyester polyols, mercaptans, carboxylic acids, amines, urea and amides. Examples of suitable prepolymers are reaction products of polyisocyanates with monohydric or polyhydric alcohols.

The prepolymers are prepared by conventional methods, e.g. by reacting polyhydroxyl compounds which have a molecular weight of from 400 to 5000, in particular mono- or polyhydroxyl polyethers, optionally mixed with polyhydric alcohols which have a molecular weight below 400, with excess quantities of polyisocyanates, for example aliphatic, cycloaliphatic, araliphatic, aromatic or heterocyclic polyisocyanates.

The composition according to the invention further comprises a polyisocyanate reactive compound. Preferably, the polyisocyanate reactive compound is selected from the group consisting of polyether polyol, polyester polyol, polyether polyamine and a polyester polyamine.

Given as examples of the polyether polyols are polyethylene glycol, polypropylene glycol, polypropylene glycol-ethylene glycol copolymer, polytetramethylene glycol, polyhexamethylene

glycol, polyheptamethylene glycol, polydecamethylene glycol, and polyether polyols obtained by ring-opening copolymerisation of alkylene oxides, such as ethylene oxide and/or propylene oxide, with isocyanate-reactive initiators of functionality 2 to 8. Preferably the polyether polyols are based on propylene oxide and/or ethylene oxide.

Polyester diols obtained by reacting a polyhydric alcohol and a polybasic acid are given as examples of the polyester polyols. As examples of the polyhydric alcohol, ethylene glycol, polyethylene glycol, tetramethylene glycol, polytetramethylene glycol, 1,6-hexanediol, 3-methyl-1,5-pentanediol, 1,9-nonanediol, 2-methyl-1,8-octanediol, and the like can be given. As examples of the polybasic acid, phthalic acid, dimer acid, isophthalic acid, terephthalic acid, maleic acid, fumaric acid, adipic acid, sebacic acid, and the like can be given.

The term "isocyanate reactive component" or “polyisocyanate reactive component” as used herein includes any component with a “isocyanate reactive group(s)” or “isocyanate reactive moiety or moieties”. The term “isocyanate reactive group” as use herein includes any group or moiety containing an active hydrogen group or moiety. For the purposes of this disclosure, an active hydrogen containing group refers to a group containing a hydrogen atom which, because of its position in the molecule, displays significant activity according to the Zerewitnoff test described by Wohler in the Journal of the American Chemical Society, Vol. 49, page 3181 (1927). Illustrative of such active hydrogen groups are -OH, $-NH_2$, and -NH.

The aldehyde reducing compound according to the invention has the general formula R^1 - CH_2 - R^2, wherein R^1 is *- SO_2 – R^3, a pyridyl derivative, or *–CH=CHR^3; R^2 is *- SO_2 – R^3, a pyridyl derivative, *–CH=CHR^2, *–C(O)R^4 or *–CN, R^4 is NH, NH-R^5, NR^6/R^7, OR^8 or R^9 and wherein R^3, R^5, R^6, R^7, R^8, or R^9 are independently of one another selected from the group consisting of an aliphatic hydrocarbon, araliphatic hydrocarbon, and an aromatic hydrocarbon, which are optionally substituted, wherein the * represents the place of R^1 or R^2 that is bound to the CH_2 of the R^1 - CH_2 -R^2 formula. According to this invention, “aldehyde reducing compounds” means that the compound is capable of reducing the emission of aldehyde in polyurea or polyurethane materials, and modified polyurethanes compared to polyurea or polyurethane materials, and modified polyurethanes made of a composition not comprising the aldehyde reducing compound.

Especially preferred examples of aldehyde reducing compounds are 1-(4-pyridyl) acetone, methanesulfonylacetone, methylphenylsulfonylacetate, dimethylglutaconate, bis(phenylsulfonyl) methane, 1-(p-tolylsulfonyl)-2-propanone.

In one embodiment, the molecular weight of the compound is below 250.
In one embodiment, the amount of the aldehyde reducing compound is from 0.01 pbw to 2 pbw, preferably from 0.05 pbw to 1.0 pbw, even more preferably between 0.05 pbw and 0.7 pbw calculated on the total weight of the composition. The amount can vary depending on the type of polyurethane that is made and the isocyanate component and the isocyanate reactive component that is used. Preferably the amount of the aldehyde reducing compound is an effective amount that is able to reduce the emission of formaldehyde and/or acetaldehyde.

In one embodiment, the moieties R^3, R^5, R^6, R^7, R^8, or R^9 are independently of one another selected from the group consisting of aliphatic hydrocarbons, which are optionally substituted. Preferably the aliphatic hydrocarbons have 1 to 15, preferably 2 to 10, carbon atoms, which may have substitution. Substituents in that case are preferably one or more isocyanate-reactive groups, which advantageously comprise isocyanate-reactive hydrogen atoms. Groups of this kind that are isocyanate-reactive may be, for example, —OH, —NH— or —NH_2 groups, with carboxylic acid groups or carboxylic amide groups preferably not being considered to be isocyanate-reactive groups. Particularly preferred as isocyanate-reactive groups are one or more OH groups, more particularly an OH group.
The aldehyde reducing compound can first be blend with the polyisocyanate or can first be blend with the isocyanate reactive compound, before it is mixed with the other compounds and then used to make polyurethane foam.

In another embodiment, the composition further comprises at least a catalyst selected from blowing and/or gelling catalysts, and optionally fire retardants, antioxidants, surfactants, physical or chemical blowing agents, fillers, pigments, or any other typical additives used in polyurethane materials. These compounds are very well known in the art and can be used at any known and practically used concentration.

In a second aspect, the invention is related to a method for reducing the emission of formaldehyde and/or acetaldehyde from a polyurethane or polyurea foam, the method comprising mixing the composition as described above.

The invention is now illustrated with below reference to the examples.
The above and other characteristics, features and advantages of the present invention will become apparent from the following detailed description which illustrates, by way of example, the principles of the invention. This description is given for the sake of example only, without limiting the scope of the invention.

It is to be noticed that the term "comprising", used in the claims, should not be interpreted as being restricted to the means listed thereafter; it does not exclude other elements or steps. It is thus to be interpreted as specifying the presence of the stated features, steps or components as referred to, but does not preclude the presence or addition of one or more other features, steps or components, or groups thereof. Thus, the scope of the expression "a device comprising means A and B" should not be limited to devices consisting only of components A and B. It means that with respect to the present invention, the only relevant components of the device are A and B.

Throughout this specification, reference to "one embodiment" or "an embodiment" are made. Such references indicate that a particular feature, described in relation to the embodiment is included in at least one embodiment of the present invention. Thus, appearances of the phrases "in one embodiment" or "in an embodiment" in various places throughout this specification are not necessarily all referring to the same embodiment, though they could. Furthermore, the particular features or characteristics may be combined in any suitable manner in one or more embodiments, as would be apparent to one of ordinary skill in the art.

In the context of the present invention the following term has the following meaning:
The VDA 276 test method (also called VOC chamber test) is an emission measurement method to measure the emissions from a foam sample done in a $1m^3$ chamber where the foam is exposed to 65°C and 5%RH (relative humidity) for several hours. VDA 276 (Verband Der

Automobil industrie) is a specific automotive emission method used by a host of automotive OEM's (original equipment manufacturers) to specify the permissible emission levels coming from automotive interior parts.

Examples 1

The following tables show the PU formulations used and results of the VDA-276 test. Table 1 shows the formulation and results of the foam whereto 1-(4-pyridyl)acetone, methanesulfonylacetone, dimethylglutaconate, bis(phenylsulfonyl) methane, and methylphenylsulfonylacetate were added. Table 2 shows the formulation and results of the foam whereto 1-(p-tolylsulfonyl)-2-propanone was added. For each formulation about 1 kg foam was made via hand mix foam procedure for the VDA -276 emission test (air sampling after 4 h, at 65°C/5% Rel humidity and an air exchange of 0.4 /hour).

	REF1	EXP1	EXP2	EXP3	REF2	EXP4	REF3	EXP5
Daltocel F428, g	100	100	100	100	100	100	100	100
Water, g	4	4	4	4	4	4	4	4
Jeffcat ZF10, g	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
Jeffcat DPA, g	1	1	1	1	1	1	1	1
Diethanolamine, g	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3
Tegostab B8734LF2, g	0.9	0.9	0.9	0.9	0.9	0.9	0.9	0.9
1-(4-pyridyl)acetone(2), g	-	0.3	-	-	-	-	-	-
Methanesulfonylacetone (2), g	-		0.3	-	-	-	-	-
Methylphenylsulfonylacetate (1),g	-	-	-	0.3	-	-	-	-
Dimethylglutaconate (1),g	-	-	-	-	-	0.3	-	-
Bis(phenylsulfonyl) methane (1),g							-	0.3
Suprasec 2185, g	12.8	12.8	12.8	12.8	12.8	12.8		
Suprasec 3056, g	51.2	51.2	51.2	51.2	51.2	51.2		
Suprasec S2447, g	-	-	-	-	-	-	60	60
VDA 276 formaldehyde emissions, µg/m3.kg foam	148	57	16	48	229	98	141	67

Table 1: Polyol formulation and result of the formaldehyde emission. All the components are available from Huntsman International LLC, except for Tegostab B8734 LF-2 which is available from Evonik. (1) Added to the isocyanate; (2) Added to the water/amine blend.

	REF	EXP6
KONIX FA-703, g	91.4	91.4
Daltocel F526,g	3	3
Water, g	3.5	3.5
Jeffcat ZF10, g	0.2	0.2
Jeffcat DPA, g	0.5	0.5
DMEA, g	0.4	0.4
Tegostab B8734LF2, g	0.5	0.5
Suprasec 7007, g	67.3	67.3
1-(p-tolylsulfonyl)-2-propanone (1)	-	0.3
VDA 276 formaldehyde emissions, **µg/m3.kg foam**	166	45

Table 2: Polyol formulation and result of the formaldehyde emission. All the components are available from Huntsman International LLC, except for Konix FA-703 and Tegostab B8734 LF-2 which are available from Evonik. (1) Added to the isocyanate;

Claims

1. A composition comprising an isocyanate reactive compound, a polyisocyanate and a aldehyde reducing compound of the general formula R^1 - CH_2 -R^2, wherein R^1 is *- SO_2 – R^3, a pyridyl derivative, or *–CH=CHR^3; R^2 is *- SO_2 – R^3, a pyridyl derivative, *–CH=CHR^2, *–C(O)R^4 or *–CN, R^4 is NH, NH-R^5, NR^6/R^7, OR^8 or R^9 and wherein R^3, R^5, R^6, R^7, R^8, or R^9 are independently of one another selected from the group consisting of an aliphatic hydrocarbon, araliphatic hydrocarbon, and an aromatic hydrocarbon, which are optionally substituted, wherein the * represents the place of R^1 or R^2 that is bound to the CH_2 of the R^1 - CH_2 -R^2 formula.

2. The composition according to claim 1, wherein the amount of the aldehyde reducing compound is between 0.01 to 2.0 pbw calculated on the total weight of the composition.

3. The composition according to any one of the claims 1 to 2, wherein R^4 or R^5 are independently of one another aliphatic hydrocarbons, which are optionally substituted.

4. The composition according to any one of the claims 1 to 3, wherein the isocyanate reactive compound is selected from the group consisting of a polyether polyol, a polyester polyol, a polyether polyamine and a polyester polyamine.

5. The composition according to any one of the claims 1 to 4, wherein the composition further comprises a catalyst, selected from blowing and/or gelling catalysts, fire retardants, antioxidants, surfactants, physical or chemical blowing agents, filler pigments and, or any other typical additive used in polyurethane materials.

6. A method for reducing the emission of formaldehyde and/or acetaldehyde from a polyurethane or polyurea foam, the method comprising mixing the composition according to any one of the claims 1 to 5.

INTERNATIONAL SEARCH REPORT

International application No
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A. CLASSIFICATION OF SUBJECT MATTER
INV. C08K5/00 C08G18/48 C08G18/66 C08G18/76 C08G18/32
ADD.

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)
C08K 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 practicable, search terms used)
EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2016/304686 A1 (OTERO MARTINEZ IRAN [DE] ET AL) 20 October 2016 (2016-10-20) cited in the application claims 1,2	1-6
X	EP 2 138 520 A2 (BAYER MATERIALSCIENCE AG [DE]) 30 December 2009 (2009-12-30) claim 7	1-6

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

☒ See patent family annex.

* Special categories of cited documents :

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

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

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"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

"&" 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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