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(54) Title: ISOCYANIC COMPOSITIONS AND USE THEREOF IN THE PREPARATION OF EXPANDED POLYURETHANES WITH IMPROVED FIRE BEHAVIOUR

\[
\Phi \quad \text{CH}_2 \quad \Phi \\
\text{NCO} \quad \text{NCO} \quad \text{NCO} \quad \text{NCO}
\]

(57) Abstract: An isocyanic composition having an isocyanic functionality of between (15)% and (40)% and containing (5) to (75)% by weight of toluene diisocyanate optionally modified with a polyester polyol, (0) to (30)% by weight of diphenylmethane diisocyanate with a (4),(4)' to isomer content of greater than (40)% by weight, (10) to (70)% by weight of 2,4-toluene diisocyanate, (10) to (30)% by weight of MDI polymer of general formula (I): in which \( \Phi \) represents a phenyl group and \( n \) is an integer greater than or equal to (1); and (5) to (30)% by weight of a phosphorus-based flame-retardant additive.
Isocyanic compositions and use thereof in the preparation of expanded polyurethanes with improved fire behaviour

This invention relates to an isocyanic composition and to use of an isocyanic composition in the preparation of a polyurethane, in particular a flexible expanded polyurethane with improved fire behaviour.

The expression “flexible expanded polyurethane with improved fire behaviour” as used in the present description and in the claims means block, (hot- and cold-) moulded expanded polyurethane or polyurethane foam, optionally with an integral skin, capable of giving fire resistance performance qualities which exceed, for example, the test CSE RF4, even up to the category I.IM, or test BS 5852/2 crib 5 without the use of flame-retardant additives of halogenated or phosphohalogenated type or of melamine or derivatives thereof.

In the furnishings and the motor vehicle industry, it is desirable that flexible polyurethane foams exhibit a high level of fire-resistance performance.

Such high performance levels are achieved using flame-retardant additives predispersed in the polyurethane reagents. For example, patent GB-A-2 163 762 describes a process for preparing flexible polyurethane foams in which an isocyanic component is reacted with a polyol component in the presence of an expander and a flame-retardant additive.

According to GB-A-2 163 762, fire-resistant polyurethane foams may be obtained by using melamine as flame-retardant additive and a modified polyol, for example a polyol containing a polymer selected from the products of polyaddition between an alkanolamine and an isocyanate, as polyol component.

Russian patent SU 729 207 describes a process for preparing fire-resistant polyurethane foams which involves the use of a flame-retardant additive selected from bis(chloromethyl) phosphonates, predispersed in one of the two polyurethane reagents.

The presence of flame-retardant agents or additives in the final polyurethane foam, although allowing very satisfactory fire-resistance results to be achieved, may be the cause of other drawbacks, for example, poorer physico-mechanical properties of the foam itself or the release of toxic fumes in the event of combustion.

In EP-A-884 340, the problem of the presence of flame-retardant agents or additives was addressed by using an isocyanic component selected so as to give the final polyurethane foam fire-resistance characteristics without the need to use specific additives. This isocyanic component consists of a mixture comprising:
- 20 to 30% by weight of toluene diisocyanate (TDI);
- 30 to 50% by weight of TDI oligomers with an isocyanic functionality of between 3 and 4;
- 30 to 40% by weight of diphenylmethane diisocyanate (MDI) with a content of 2,4'-isomers of greater than 40% by weight.

To overcome the drawbacks of the prior art associated with the use of flame-retardant agents of halogenated type the Applicant has found that expanded polyurethanes or polyurethane foams with high fire resistance can be prepared, without it being necessary to use specific flame-retardant agents or additives of the halogenated type, but rather using a novel isocyanic composition containing a simple organophosphorus additive in combination with the polyol component.

Thus, one aspect of the present invention provides an isocyanic composition with an isocyanic functionality of between 15% and 40%, comprising:

a) 5 to 75% by weight and preferably 30 to 60% of toluene diisocyanate (TDI) of biuret type, optionally modified with at least one polyether polyol with a functionality of between 2 and 8 and an equivalent weight of between 200 and 2000;

b) 0 to 30% by weight and preferably 10 to 20% of diphenylmethane diisocyanate (MDI) with a 4,4' isomer content of greater than 40% by weight;

c) 10 to 70% by weight and preferably 20 to 50% of 2,4-toluene diisocyanate, either alone or mixed with the 2,6-toluene diisocyanate isomer;

d) 10 to 30% by weight of MDI polymer of general formula (I):
\[
\phi \rightarrow \text{CH}_2 \left[ \begin{array}{c} \phi \rightarrow \text{CH}_2 \\ \text{NCO} \end{array} \right]_n \text{NCO}
\]

in which \(\phi\) represents a phenyl group and \(n\) is an integer greater than or equal to 1; and

e) 5 to 30\% by weight and preferably 10 to 20\% of a phosphorus-based flame-retardant additive.

Preferably the sum of the components (a) to (e) is 100, that is, the composition consists of components a) to e).

According to the present invention, the term "MDI polymer" means polymethylenepolyphenyl polyisocyanates, suitably having an average functionality of between 2.6 and 2.8; such products are commercially available under various names, for instance "Tedimon 31" (Enichem S.p.A.), "Suprasec DNR" (ICI) or Desmodur 44 V20 (Bayer), while "biuret-modified TDI" means a branching product obtained from toluene diisocyanate treated with water under experimentally controlled conditions, for example, as described in European patent 177 059.

The phosphorus-based flame-retardant additive used in the isocyanic composition which is the subject of the present invention preferably comprises an organophosphorus derivatives of general formula (II):

\[
O
\]
\[
R_1O \xrightarrow{\parallel} P \xrightarrow{\parallel} OR_2
\]

or of general formula (III):

\[
O
\]
\[
R_1O \xrightarrow{\parallel} P \xrightarrow{\parallel} OR_2
\]

in which \(R_1, R_2\) and \(R_3\), which may be identical or different, represent a \(C_1\) to \(C_3\) (iso)alkyl radical, optionally substituted with a \(C_4\) to \(C_{10}\) oligomeric adduct \(R_1, R_2\) and \(R_3\) are \(-C_2H_5\), the product of general formula (II) is commercially available under the trade name Fyroil TEP from the company Akzo Nobel Chemicals. Other examples of oligomeric phosphates or phosphonates are Fyroil PNX from the company Akzo Nobel Chemicals,
Antiblaze V490 from the company Albright & Wilson and Exolit OP 550 from the company Clariant.

Preferably the phosphorus-based flame-retardant additive is free of halogens. Suitably, the additive does not comprise a flame-retardant additive of the halogenated or phosphohalogenated type or of melamine or derivatives thereof.

A further aspect of the present invention provides a process for preparing a flexible expanded polyurethane with improved fire behaviour, which comprises reacting:

i) an isocyanic component having an isocyanic functionality of between 15% and 40%, comprising:

a) 5 to 75% by weight and preferably 30 to 60% of toluene diisocyanate (TDI) of biuret type, optionally modified with at least one polyether polyl with a functionality of between 2 and 8 and an equivalent weight of between 200 and 2000;

b) 0 to 30% by weight and preferably 10 to 20% of diphenylmethane diisocyanate (MDI) with a 4,4'- isomer content of greater than 40% by weight;

c) 10 to 70% by weight and preferably 20 to 50% of 2,4-toluene diisocyanate, either alone or mixed with the 2,6-toluene diisocyanate isomer;

d) 10 to 20% by weight of MDI polymer of general formula (I):

\[
\Phi \quad \text{CH}_2 \quad \Phi \quad \text{CH}_2 \quad \Phi
\]

\[
\text{NCO} \quad \text{NCO} \quad \text{NCO} \quad \text{NCO}
\]

in which \( \Phi \) represents a phenyl group and \( n \) is an integer greater than or equal to 1;

e) 5 to 30% by weight and preferably 10 to 20% of a phosphorus-based flame-retardant additive; and

ii) a polyl component comprising at least one polyl, with a functionality of between 2 and 8 and an equivalent weight of between about 200 and 2000, and water.

Preferably, the sum of the components (a) to (e) of the isocyanic component is 100, that is, the isocyanic component consists of components a) to e).
The polyol used in the preparation of the flexible expanded products according to the process is suitably selected from polyether polyols, polyether polyols containing ester groups, polyether polyols containing amine groups, polyester polyols, and the like. Preferred polyols include polyether polyols obtained by condensing C₂ to C₅ olefinic oxides with compounds (starters) containing at least two active hydrogen atoms. Preferred olefinic oxides are ethylene oxide, propylene oxide or mixtures thereof.

The condensation suitably takes place with starters such as glycols, triols, tetrols, amines, alkanolamines and polyamines, or mixtures thereof.

Representative examples of polyether polyols which suitably are used according to the present invention include those based on ethylene oxide and/or propylene oxide and in which the starter is a glycol such as dipropylene glycol; a triol such as glycerol or trimethylolpropane; a tetrol such as pentaerythritol; a diamine such as ethylenediamine, an aromatic amine such as ortho-toluenediamine, an alkanolamine such as triethanolamine, or a polyfunctional hydroxyalkane such as xylitol, arabitol, sorbitol, mannitol, etc.

These polyols may be used in unmodified form or may contain, in dispersion or partially grafted to the polyol chains, solid particles, preferably solid polymer particles, which are smaller than 20 micrometres. Polymers that are suitable for this purpose are: polyacrylonitrile, polystyrene, polyvinyl chloride, etc., or mixtures or copolymers thereof, or urea-based polymers. The said solid particles may be prepared by in situ polymerization in the polyol or may be prepared separately and added to the polyol in a second stage.

The polyol composition also generally comprises further additives known for use in preparing expanded polyurethanes, such as amine catalysts, for instance triethylendiamine, and/or metallic catalysts, for instance stannous octoate, cell regulators, thermal-oxidation stabilizers, pigments, etc. Details regarding the polymerization of polyurethanes are described in, for example, the text "Saunders & Frisch - Polyurethanes, Chemistry and Technology" Interscience, New York, 1964.
In preparing the expanded polyurethanes according to the process which is the subject of the present invention, the expander preferably comprises water, which may be used alone or in combination with secondary expanders in which latter case water preferably comprises the main component of the expander. In the preparation of an expanded polyurethane, the expander suitably brings about the formation of ureic bonds associated with the production of carbon dioxide, which brings about the process of expansion/swelling of the polyurethane resin, with the production of flexible expanded products. An amount of expander of between 1 and 10 parts, especially 3 and 6 parts by weight relative to 100 parts of polyol component is preferred.

Thus, according to a preferred embodiment of the invention in which the expander comprises water, the carbon dioxide produced in situ by the chemical reaction between water and the NCO groups of the polyisocyanate is preferably used as the primary agent for expanding the polyurethane resin. The method for introducing the primary expander into the polymerization mass should not, however, be understood as a limitation, since other gases and other techniques may be used, such as, for example, sparging air, liquid CO₂, nitrogen or another inert gas into the reaction mass by injection from the outside, which are all within the scope of the present invention.

In the preparation of an expanded polyurethane of low density, for example having a density of less than or equal to 25 kg/m³, the expanding function of water alone may not be sufficient to achieve such density values without incurring drawbacks ("scorching") due to the exothermicity of the reaction between water and the isocyanic groups. For this reason, the expanding action of water may be supported by co-expanders including those selected from hydrofluoroalkanes, liquid CO₂, hydrocarbons, for instance n-pentane, i-pentane, cyclopentane, and the like, dimethyl carbonate, or mixtures thereof.

The flexible expanded polyurethane obtained according to the present process preferably has a density of between 20 and 200 kg/m³ and more preferably between 30 and 120 kg/m³. Suitably the expanded polyurethane has a lift (according to ISO standard 2439) of greater than 40 N and preferably between 80 and 400 N, are desirably is free of thermal-oxidative degradation phenomena, such as scorching, and has
excellent mechanical properties such as elongation at break, permanent set, compression strength, permeability to air, and the like.

By virtue of these characteristics, the foams of the present invention may find suitable uses in the industrial sectors of furniture and/or soft furnishings and transportation and/or motor vehicles which typically employ materials with the above-mentioned properties. When subjected to the fire resistance test, products according to the present invention suitably pass the test CSE RF4 up to category l.IM and test BS 5852/2 crib 5.

The invention is illustrated by the following, non-limiting examples.

In the examples, the amount of the various components in the compositions are expressed as parts by weight, except where otherwise indicated.

**EXAMPLE 1**

An isocyanic composition obtained from:

33.0 parts by weight of Tedimon 173; 10.0 parts by weight of Tedimon 31, 44.0 parts by weight of Tedimon 80 and 13.0 parts by weight of Fyrol TEP. The resulting product has a free %NCO of 38.05.

**EXAMPLE 2**

An isocyanic composition obtained by reacting:

57.8 parts by weight of Tedimon 173; 12.2 parts by weight of Tercarol 844; 1.3 parts by weight of Tercarol 241 at 70°C for about 2 hours. At the end of the reaction, 14.5 parts by weight of Fyrol TEP and 14.2 parts by weight of Tedimon 31 are added until a free %NCO of 28.5 is obtained.

**Application Examples**

The compositions of Examples 1 and 2 were used to prepare flexible expanded polyurethanes in combination with the polyol components given in the table below. This table gives the physicomechanical characteristics of the foams and the results of the fire reaction tests.
<table>
<thead>
<tr>
<th>TABLE</th>
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<tr>
<td></td>
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<tr>
<td>Tercarol 427</td>
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<tr>
<td>Tris(monochloroisopropyl) phosphate</td>
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<tr>
<td>Melamine</td>
</tr>
<tr>
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<td>DABCO 33LV, pp</td>
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<td>DABCO T9</td>
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<td>ISOCYANATE of Example 1 (index)</td>
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<td>ISOCYANATE of Example 2 (index)</td>
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<tr>
<td>Density, kg/m³</td>
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<td>50% permanent set, %</td>
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<td>40% compression strength, kPa</td>
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<tr>
<td>Test CSE RF4, category</td>
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<td>Test BS 5852/2 crib 5</td>
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</tbody>
</table>

TEDIMON® 173 - biuret-modified TDI  
TEDIMON® 80 - TDI 80/20  
TEDIMON® 31 - MDI polymer of functionality = 2.7  
TERCAROL® 241 - polyether polyl MW 4000 of functionality = 3  
TERCAROL® 84 - polyether polyl MW 4800 of functionality = 3  
TERCAROL® 427 - polyether polyl MW 6000 of functionality = 3  
DABCO 33LV - triethylenediamine-based catalyst from Air Products  
DABCO T9 - tin octoate from Air Products  
TEGOSTAB B 8716LF - silicone surfactant from Goldschmidt
CLAIMS

1. An isocyanic composition with an isocyanic functionality of between 15% and 40%, comprising:

   a) 5 to 75% by weight of toluene diisocyanate (TDI) of biuret type, optionally modified with at least one polyether polyol with a functionality of between 2 and 8 and an equivalent weight of between 200 and 2000;

   b) 0 to 30% by weight of diphenylmethane diisocyanate (MDI) with a 4,4' isomer content of greater than 40% by weight;

   c) 10 to 70% by weight of 2,4-toluene diisocyanate, either alone or mixed with the 2,6-toluene diisocyanate isomer;

   d) 10 to 30% by weight of MDI polymer of general formula (I):

   \[
   \Phi - \text{CH}_2 \left[ \Phi - \text{CH}_2 \right]_{n-1} \Phi
   \]

   in which \( \Phi \) represents a phenyl group and \( n \) is an integer greater than or equal to 1; and

   e) 5 to 30% by weight of a phosphorus-based flame-retardant additive.

2. An isocyanic composition according to Claim 1, comprising 30 to 60% of component a), 10 to 20% of component b) and 20 to 50% of component c).

3. An isocyanic composition according to any preceding claim, in which the phosphorus-based flame-retardant additive comprises an organophosphorus derivatives of general formula (II):

   \[
   \text{OR}_1 \quad \text{OR}_2
   \]

   or of general formula (III):

   \[
   \text{OR}_1 \quad \text{OR}_2
   \]
in which \( R_1, R_2 \) and \( R_3 \), which may be identical or different, represent a \( C_1 \) to \( C_3 \) (iso)alkyl radical, optionally substituted with a \( C_4 \) to \( C_{10} \) oligomeric adduct.

4. An isocyanic composition according to any preceding claim, in which the phosphorus-based flame-retardant additive is present at a level of 10 to 20%.

5. A process for preparing a flexible expanded polyurethane, which comprises reacting:
   i) an isocyanic component with an isocyanic functionality of between 15% and 40%, comprising:
   a) 5 to 75% by weight of toluene diisocyanate (TDI) of biuret type, optionally modified with at least one polyether polyl with a functionality of between 2 and 8 and an equivalent weight of between 200 and 2000;
   b) 0 to 30% by weight of diphenylmethane diisocyanate (MDI) with a 2,4'-isomer content of greater than 40% by weight;
   c) 10 to 70% by weight of 2,4-toluene diisocyanate, either alone or mixed with at least 20% by weight of 2,6-toluene diisocyanate isomer;
   d) 10 to 20% by weight of MDI polymer of general formula (I):

   \[
   \Phi \biggarrow \text{CH}_2 \biggarrow \Phi \biggarrow \text{CH}_2 \biggarrow \Phi \\
   \text{NCO} \biggarrow \text{NCO} \biggarrow \text{NCO}
   \]

   in which \( \Phi \) represents a phenyl group and \( n \) is an integer greater than or equal to 1;

   e) 5 to 30% by weight of a phosphorus-based flame-retardant additive; and

   ii) a polyl component comprising at least one polyl, with a functionality of between 2 and 8 and an equivalent weight of between about 200 and 2000, and water.

6. A process according to Claim 5, in which the polyl is selected from polyether polyols, polyether polyols containing ester groups, polyether polyols containing amine groups, and polyester polyols.
7. A process according to Claim 6, in which the polyol comprises a polyether polyol obtained by condensing a C₂ to C₆ olefinic oxide with a compound (starter) containing at least two active hydrogen atoms.

8. A process according to any one of claims 5 to 7, in which the expansion of the foam takes place by sparging air, liquid CO₂, nitrogen or other inert gas into the reaction mass by injection from the outside.

9. Use of a composition according to any one of claims 1 to 4, to prepare an expanded polyurethane with improved fire behaviour, having a density of between 20 and 200 kg/m³.
**INTERNATIONAL SEARCH REPORT**

**A. CLASSIFICATION OF SUBJECT MATTER**

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<th>C08K5/5333</th>
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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)

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

Electronic database 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**

<table>
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**X** Further documents are listed in the continuation of box C.

**X** 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
- "E" earlier document 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)
- "O" document referring to an omi 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.
- "&" document member of the same patent family

Date of the actual completion of the international search: 26 April 2002

Date of mailing of the international search report: 13/05/2002

Name and mailing address of the ISA

European Patent Office, P.B. 5018 Patentlaan 2 NL - 2280 HV Rijswijk
Tel: (+31-70) 940-2040, Tx. 31 651 epo nl, Fax: (+31-70) 940-2016

Authorized officer: Scheuer, S
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| Y        | US 4 530 777 A (KENNEDY RICHARD B)  
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column 3, line 10 - line 17  
column 3, line 59 - line 66; example 27 | 1-9                  |
| Y        | GB 1 094 717 A (HOOKER CHEMICAL CORP)  
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page 3, line 60 - line 98  
page 4, line 65; table 2 | 1-9                  |
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