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Published: with international search report (Art. 21(3))
**New formaldehyde scavengers**

The invention relates to new formaldehyde scavengers, a process for reducing the amount of formaldehyde by adding these scavengers and their use.

Formaldehyde is one of the most important starting materials in the chemical industry. It is used for example in the synthesis of urea formaldehyde resins, melamine resins, phenol formaldehyde resins, polyoxymethylene plastics and methylene diphenyl diisocyanates.

Formaldehyde is also a precursor to polyfunctional alcohols such as pentaerythritol, which is used to make paints and explosives. Other formaldehyde derivatives include methylene diphenyl diisocyanate, which is an important component in polyurethane paints and foams, and hexamine, which is used in phenol-formaldehyde resins.

In the textile industry use is made of formaldehyde-based resins as finishers to make fabrics crease-resistant.

Formaldehyde is also used in the production of adhesives, textile aids, bonding agents, moulding sand binders, ion exchanger, moulded and extruded articles, casting resins and hardeners.

Formaldehyde containing material can degas, which is problematic, as is has the major disadvantage that it is classified as a probable human carcinogen by the U.S. Environmental Protection Agency.

Because of the aforementioned risks for human health there was a strong need for effective scavengers for formaldehyde.

In the prior art mainly dithioxamides are known as scavengers, e.g., U.S. Patent No. 3,255,150. Those substances have the disadvantage in polymers that they decompose to sulphur, which accelerate cross-linking activities. Moreover their effectiveness depends on the presence of additional additives or stabilisers, such as phenolic compounds.

There was a strong need for highly effective formaldehyde scavengers, which will also be usable in various applications.

An object of the present invention therefore was to provide an effective formaldehyde scavenger.
Surprisingly, it has now been found that carbodiimides achieve this objective.

The present invention therefore provides new and effective formaldehyde scavengers.

Within the meaning of the present invention, suitable carbodiimides are in particular monomeric, oligomeric and/or polymeric carbodiimides.

As carbodiimides the following compounds according to formula (I)

\[ R'-(N-C=N-R)\text{=N}-R'' \]  

(1) are preferred,

in which

- \( R \) represents an aromatic, aliphatic, cycloaliphatic or aralkylene radical which, in the case of an aromatic or an aralkylene residue, carry preferably no substituents or which is also preferred carry in at least one ortho-position, more preferred in both ortho-positions to the aromatic carbon atom which carries the carbodiimide group, aliphatic and/or cycloaliphatic substituents with at least 2 C-atoms, preferably branched or cyclic aliphatic radicals with at least 3 C-atoms, which can also contain heteroatoms, such as N, S and/or O, i.e. imidazoyl,

- \( R' \) represents aryl, aralkyl or R-NCO, R-NHCONHR\(^1\), R-NHCONR\(^1\)R\(^2\) and R-NHCOOR\(^3\), -NHCOC- R\(^1\), -COO R\(^1\), -O R\(^1\), -N (R\(^1\))\(_2\), -SR\(^1\), -OH, -NH\(_2\), NHRI, epoxy,

- R\(^''\) represents -N=C=N-aryl, -N=C=N-alkyl, -N=C=N-cycloalkyl, -N=C=N-aralkyl, -NCO, -NHCONHR\(^1\), -NHCONR\(^1\)R\(^2\) or -NHCOOR\(^3\), -NHCO- R\(^1\), -COO R\(^1\), -O R\(^1\), -N (R\(^1\))\(_2\), -SR\(^1\), -OH, -NH\(_2\), NH R\(^1\) wherein, in R\(^'\) and in R\(^''\), independently of one another, R\(^1\) and R\(^2\) are the same or different and represent an alkyl, cycloalkyl or aralkyl radical, and R\(^3\) has one of the meanings of R\(^1\) or represents a polyester or a polyamide radical, and

- \( n \) represents an integer from 1 to 5,000, preferably from 2 to 500.
In a first preferred embodiment of this mode, R represents an aromatic or an aralkylene radical, which, in the case of an aromatic or an aralkylene residue, in at least one ortho-position, preferably in both ortho-positions to the aromatic carbon atom which carries the carbodiimide group, carries aliphatic and/or cycloaliphatic substituents with at least 2 C-atoms, preferably branched or cyclic aliphatic radicals with at least 3 C-atoms, more preferably isopropyl residues. This also includes isocyanurate, urethdion and/or urethonimine-based carbodiimides.

In another preferred embodiment of the invention the aromatic or an aralkylene residue carries no substituents.

In a further preferred embodiment of the polymeric carbodiimides, R represents an aromatic residue, which is bonded by a \( C_7 \) to \( C_8 \)-alkyl moiety, preferably a \( C_1 \) to \( C_4 \)-moiety, with the carbodiimide group.

In this mode of the present invention the carbodiimide is preferably represented by the general formula (II)

\[
\begin{align*}
\text{II} & \\
\begin{array}{c}
\text{R}^1 \\
\text{N} \\
\text{N} \\
\text{R}^4 \\
\text{R}^1 \\
\text{R}^2
\end{array}
\end{align*}
\]

in which the residues \( R^1 \) and \( R^4 \) represent independently from each other a linear branched \( C_2 \) to \( C_{20} \)-cycloalkyl residue, a \( C_7 \) to \( C_{15} \)-aryl residue or a \( C_6 \) to \( C_{15} \)-aralkyl residue, which can also contain heteroatoms, such as N, S or O.

It is preferred that the residues \( R^1 \) to \( R^4 \) are \( C_3 \) to \( C_{20} \)-alkyl or \( C_2 \) to \( C_{20} \)-cycloalkyl residues.

It is further preferred that the residues \( R^1 \) to \( R^4 \) are \( C_2 \) to \( C_{20} \)-alkyl residues.

In the present invention, \( C_3 \) to \( C_{20} \)-alkyl and \( C_2 \) to \( C_{20} \)-cycloalkyl stands preferably for ethyl, propyl, isopropyl, sec.-butyl, tert.-butyl, cyclohexyl and/or dodecyl, whereby the residue isopropyl is in particular preferred.
In the present invention, C₆- to C₁₅-aryl and C₆- to C₁₄-aryl stand preferably for phenyl, tolyl, benzyl, naphthyl, pyridyl or thiazolidine, oxazoline and/or oxazolidine.

The definitions of aromatic, aliphatic, cycloaliphatic or aralkylene mentioned before will also apply to formula (I) as a preferred embodiment.

In particular those carbodiimides of the general formula (I) or (II) are preferred in which the ortho-positions to the aromatic carbon atom which carries the carbodiimide group are substituted by isopropyl and in which the para-positions to the aromatic carbon atom which carries the carbodiimide group are also substituted by isopropyl.

Especially preferred is the use of one monomeric carbodiimide according to formula (III)

\[
\begin{align*}
\text{(III).}
\end{align*}
\]

Also especially preferred are carbodiimides according to formula (IV), in which \( n = 1 \) to 5000.

\[
\begin{align*}
\text{(IV)}
\end{align*}
\]

The polycarbodiimides used are commercially available products, for example from Rhein Chemie Rheinau GmbH under the tradenames STABAXOL® P, STABAXOL® P100, STABAXOL® P200 STABAXOL® I, I LF and STABAXOL® P400.

Alternatively they can be prepared according to methods well known by persons skilled in the art.
The compounds can be obtained, for example, by conducting a decarboxylation condensation reaction of various polyisocyanates using an organophosphorus compound or an organometallic compound as a catalyst at a temperature not lower than about 70 °C, without using any solvent or using an inert solvent, such as e.g. toluene, xylol etc..

To prepare the carbodiimides and/or polycarbodiimides of the general formulas (I) - (III), its mono- or diisocyanates can be condensed as starting compounds at elevated temperatures, for example at 40 to 200 °C, in the presence of catalysts with the release of carbon dioxide. Suitable methods are described in DE-A-11 30 594 and in FR 1 180 370.

Examples of a monomeric carbodiimide compounds are carbodiimides based on 1,5-naphthalenediisocyanate, 4,4'-diphenylmethane-diisocyanate, 4,4'-diphenyldimethylmethanediisocyanate, 1,3-phenylenediisocyanate, 1,4-phenylenediisocyanate, 2,4-tolylenediisocyanate, 2,6-tolylenediisocyanate, xylene-diisocyanate, isophoron-diisocyanate, dicyclohexyl-methane-4,4'-diisocyanate, methylecyclohexane-diisocyanate, tertamethylyxylene-diisocyanate as well dicyclohexylcarbodiimide, diisopropylcarbodiimide, dimethylcarbodiimide, disobutylecarbodiimide, dioctylcarbodiimide, hexamethylene-diisocyanate, tert.-butyl-isopropylcarbodiimide, 2,6-diisopropylphenylencarbodiimide, diphenylcarbodiimide, di-tert.-butylecarbodiimide and/or di-β-naphthylcarbodiimide. Among them dicyclohexylcarbodiimide or diisopropylcarbodiimide are particularly preferable in view of availability on an industrial scale.

In another embodiment of the present invention polycarbodiimides are used. These polycarbodiimides are commercially available or can be produced by conventional production methods for polycarbodiimides [for example, the methods disclosed in US 2,941,956; JP-B-47-33279, J. Org. Chem. 28,2069-2075 (1963) and Chemical Review, 1981, Vol. 81, No.4, pages 619 to 621].

The carbodiimide compound includes in particular 4,4'-dicyclohexylmethane-carbodiimide (degree of polymerization = 2 to 20), tetramethylyxylene-carbodiimide (degree of polymerization = 2 to 20), N,N-dimethylphenylcarbodiimide (degree of polymerization = 2 to 20) and N,N'-di-2,6-diisopropylphenylencarbodiimide (degree of polymerization = 2 to 20) and the like, and is not specifically limited as long as the compound has at least one carbodiimide group in a molecule. Furthermore, polymeric aliphatic carbodiimides can be used, for example on the basis of isophorone diamine.
Those compounds are commercially available.

In one preferred embodiment of the present invention the carbodiimides are used as a mixture of at least two different carbodiimides.

In case a mixture of different carbodiimides is used, those used carbodiimides may be selected from the group consisting of monomeric, oligomeric and polymeric carbodiimides. In respect of the monomeric, oligomeric and polymeric carbodiimides, it is referred to the explanations/definitions mentioned above.

In another preferred embodiment of the invention at least one sterically hindered carbodiimide is used, such as Bis-(2,6-diisopropylphenyl)-carbodiimide, polymeric and/or oligomeric carbodiimide based on 1,3,5-triisopropyl-2,4-diisocyanate-phenolate.

Furthermore, it is preferred that the used carbodiimides have a reduced content of free isocyanates. Preferred carbodiimides have a reduced content of free isocyanates lower than 1 wt.-%.

In a preferred embodiment of the present invention the carbodiimide is used in an amount of from 0.001 to 100 wt.-%, preferably from 0.01 to 100 wt.-%.

In those cases, in which the amount of carbodiimide is less than 100% formaldehyde scavenger is used in form of a masterbatch, formulations or dilution, which means, that the carbodiimide is mixed with those formaldehyde containing polymers of the intended use. These intended uses can be e.g. those which are described as application examples later on.

Those polymers can be, but they are not limited to:

- aminoplastics, such as urea formaldehyde resins, melamine resins and/or phenol formaldehyde resins in melted systems or in solvents or water based systems and/or

- thermoplastics, such as polyacetalts like polyoxymethylene in melted systems or in solvents or water based systems as well as their copolymers thereof such as e.g. polyurethane-based compounds and/or

- binders/polymeric compounds/copolymeric compounds which are able to cleave/eliminate formaldehyde e.g. copolymers on acrylate basis such as copolymeric compounds containing
monomeric methacrylic acid, glycidylmethacrylate or C₂-C₁₀-hydroxy-alkylmethacrylate, and/or vinyl-based compounds, such as styrene and/or olefin compounds, such as ethylene, propylene etc..

Most preferred are polyoxymethylene (POM), aminoplastics and/or acrylate copolymers.

Those polymers are commercially available.

Masterbatches, formulations or dilutions can also obtain further additives such as i.e. anti-oxidants, light-stabilizers, flame-retarders, heat-stabilizers, lubricants, nucleating agents, surface active agents, etc..

The present invention also provides a new process for reducing the amount of formaldehyde, in which at least 0.001% carbodiimide is added to the formaldehyde containing polymer, and or the binders/polymeric compounds/copolymeric compounds, which are able to cleave/eliminate formaldehyde, e.g. copolymers on acrylate basis.

The polymers are those mentioned above.

The process parameters depend on the characteristics of the polymer:

In case of a solvent or a water dispersed polymer the following process is preferred:

The carbodiimide and/or mixture of carbodiimides will be added to a solution/ dispersion of a polymer like a solution/ dispersion of aminoplastics and/or thermoplastics, like i.e. polyacetal, by stirring preferably at temperatures above room temperature (elevated temperatures).

In case of a melted polymer the carbodiimide and/or mixture of carbodiimides will be added to the melted polymer, by stirring preferably at temperatures above the melting temperature of the polymer.

In all cases usual mixing equipments, like dissolver or stirrers can be used. Those mixing equipment is commercially available.

In another preferred embodiment of the present invention further additives will be added to the carbodiimide before the mixing procedure. It is also possible to partly add the additives to the polymer and the carbodiimide alternatively.
In case of a melted polymer it is also possible to add the carbodiimide

- during extrusion, to ensure it mixture during extrusion.

- by injection the polymer and/or the carbodiimide together or separately in the injection moulding
  procedure or

- by stirring the carbodiimide and polymer before or during the casting process.

The present invention also provides the use of carbodiimides as defined above for the following applications:

- adhesives, especially adhesives for timber or wooden materials, i.e. as wood composites and
  plywood, textile applications (as the textile industry uses formaldehyde-based resins as finishers to
  make fabrics crease-resistant), in constructions, kitchen and cabinet and furniture making, especially
  for aminoplastics

- plastics articles produced by extrusion, injection moulding or casting, they can also be used in
  adhesives or coatings especially for thermoplastics.

- in bonding agents, binders, especially moulding sand binders, local foams used as insulators, tuners
  or all other applications, including textile, floor mats, carpets, furniture.

The present invention is described in more detail by reference to the following examples, without
being limited to them.

Examples:

The following compounds have been used.

POM (Polyoxyethylene) = Edgetek™ ATC-000/000 Natural UV from PolyOne Corporation, a
polyacetal (POM) homopolymer compound, which was dried 3 h at 90°C before being added to the
extruder.

Stabaxol® P = Aromatic Polymeric Carbodiimide from Rhein Chemie Rheinau GmbH.
In the examples 1 - 4 different amounts of STABAXOL® P have been used as described in table 1. STABAXOL® P was incorporated to a double screw extruder ZSK 25 from Coperion W & P filled with POM at a temperature range from 180 to 220°C. The extruded granulates have been analyzed by photometric detection with pararosaniline after a water steam distillation.

Table 1: Compositions of the examples and test results

<table>
<thead>
<tr>
<th>Example No.</th>
<th>Amount of STABAXOL® P in POM [%]</th>
<th>Amount of formaldehyde [mg/kg]</th>
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<tr>
<td>1</td>
<td>0,00</td>
<td>1670</td>
</tr>
<tr>
<td>2</td>
<td>0,01</td>
<td>7,9</td>
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<tr>
<td>3</td>
<td>0,02</td>
<td>3,7</td>
</tr>
<tr>
<td>4</td>
<td>0,1</td>
<td>&lt; 0,1</td>
</tr>
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</table>

It can clearly be seen, that the amount of formaldehyde can be dramatically reduced by the addition of even small amount of carbodiimides, which clearly demonstrate our invention.
Claims

What is claimed is

1. Formaldehyde scavenger, characterized in that it contains at least one carbodiimide.

2. Formaldehyde scavengers, according to claim 1, characterized in that the carbodiimides are selected from the group of monomeric, oligomeric and/or polymeric carbodiimides.

3. Formaldehyde scavenger, according to claim 1 to 2, characterized in that it contains at least one carbodiimide according to formula (1)

\[ R^1 \rightarrow (N=C=N-R)_a \rightarrow R^\prime \quad (1), \]

in which

- \( \text{R} \) represents an aromatic, aliphatic, cycloaliphatic or aralkylene radical which, in the case of an aromatic or an aralkylene residue, carry preferably no substituents or which is also preferred carry in at least one ortho-position, more preferred in both ortho-positions to the aromatic carbon atom which carries the carbodiimide group, aliphatic and/or cycloaliphatic substituents with at least 2 C-atoms, preferably branched or cyclic aliphatic radicals with at least 3 C-atoms, which can also contain heteroatoms,

- \( \text{R}^1 \) represents aryl, aralkyl or R-NCO, R-NCONHR\(^1\), R-NHCONR\(^1\)R\(^2\) and R-NHCOOR\(^1\), -NH-C=O R\(^1\), -COO R\(^1\), -O R\(^1\), -N (R\(^1\))\(_2\), -SR\(^1\), -OH, -NH\(_2\), NHR\(^1\), epoxy,

- \( \text{R}^\prime \) represents -N=C=O-aryl, -N=C=N-alkyl, -N=C=N-cycloalkyl,
  -N=C=N-aralkyl, -NCO, -NHCONHR\(^1\), -NHCONR\(^1\)R\(^2\) or -NHCOOR\(^1\), -NH-C=O R\(^1\),
  -COO R\(^1\), -O R\(^1\), -N (R\(^1\))\(_2\), -SR\(^1\), -OH, -NH\(_2\), NH R\(^1\) wherein, in R\(^1\) and in R\(^\prime\), independently of one another, R\(^1\) and R\(^2\) are the same or different and represent an alkyl, cycloalkyl or aralkyl radical, and R\(^3\) has one of the meanings of R\(^1\) or represents a polyester or a polyamide radical, and

- \( n \) represents an integer from 1 to 5,000.
4. Formaldehyde scavenger, according to claim 1 to 3, characterized in that it contains at least one carbodiimide according formula (II)

\[ \text{Diagram II} \]

where \( R^1 \) to \( R^4 \) are \( \text{C}_3 \) to \( \text{C}_{20} \)-alkyl or \( \text{C}_2 \) to \( \text{C}_{20} \)-cycloalkyl residues or in which the residues \( R^1 \) and \( R^4 \) represent independently from each other a linear branched \( \text{C}_3 \) to \( \text{C}_{20} \)-cycloalkyl residue, a \( \text{C}_6 \) to \( \text{C}_{15} \)-aryl residue or a \( \text{C}_6 \) to \( \text{C}_{15} \)-alkyl residue, which can also contain heteroatoms.

5. Formaldehyde scavenger, according to claim 1 to 4, characterized in that it contains at least one carbodiimide according formula (III)

\[ \text{Diagram III} \]

6. Formaldehyde scavenger, according to claim 1 to 3, characterized in that it contains at least one carbodiimide according formula (IV)

\[ \text{Diagram IV} \]

in which \( n = 1 \) to 5000.
7. Formaldehyde scavenger, according to claim 1 to 6, characterized in that it also contains aminoplastics, thermoplastics, and/or binders/polymeric compounds/ copolymeric compounds which are able to cleave/eliminate formaldehyde.

8. Formaldehyde scavenger, according to claim 1 to 7, characterized in that it contains the carbodiimide in an amount of from 0.001 to 100 wt.- %.

9. Process for reducing the amount of formaldehyde, in which at least 0.001% formaldehyde scavenger according to claim 1 to 8 is added to the formaldehyde containing polymer and/or binders/polymeric compounds/copolymeric compounds which are able to cleave/eliminate formaldehyde.

10. Use of the formaldehyde scavenger according to one of the claims 1 to 8 for the following applications:

- Adhesives, adhesive for timber or wooden materials, textile applications to make fabrics crease-resistant, in constructions, kitchen and cabinet and furniture making,

- for plastics articles produced by extrusion, injection moulding or casting and/or

- in bonding agents, binders, moulding sand binders, local foams used as insulators, tuners or all other applications including textile, floor mats, carpets, furniture.
INTERNATIONAL SEARCH REPORT

A. CLASSIFICATION OF SUBJECT MATTER
INV. C08K5/29  C08L59/02  C08L59/04
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  C08L

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

C. DOCUMENTS CONSIDERED TO BE RELEVANT

<table>
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<tr>
<th>Category*</th>
<th>Citation of document, with indication, where appropriate, of the relevant passages</th>
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<td>X</td>
<td>WO 2007/090735 A1 (BASF AG [DE]; HAEBERLE KARL [DE]; SIEMENSMEYER KARL [DE]; NOERENBERG R) 16 August 2007 (2007-08-16) page 1, line 5 - page 3, line 14 page 5, line 20 - page 7, line 11 page 10, lines 22-24 page 21, line 19 - page 22, line 8 page 34, line 9 - page 47, line 20; claims</td>
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<td>X</td>
<td>GB 993 600 A (FARBENFARBRIKEN BAYER AG) 26 May 1965 (1965-05-26) page 1, line 6 - page 5, line 15; claims; examples</td>
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<td>A</td>
<td>DE 11 93 240 B (BAYER AG) 20 May 1965 (1965-05-20) column 1, line 10 - column 5, line 23; claims; examples</td>
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Further documents are listed in the continuation of Box C.

* 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 oral disclosure, use, exhibition or other means

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

*"I"* 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.

*"S"* document member of the same patent family

Date of the actual completion of the international search
17 June 2010

Date of mailing of the international search report
25/06/2010

Name and mailing address of the ISA/
European Patent Office, P.B. 5818 Patentlaan 2
NL-2280 HV Rijswijk
Tel. (+31-70) 340-2040,
Fax (+31-70) 340-3016

Authorized officer

Otegui Rebollo, Juan
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<td>US 4 293 469 A (EDELMAN ROBERT) 6 October 1981 (1981-10-06) column 1, lines 13-19 column 2, line 66 - page 9, line 58; claims; examples</td>
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<td>EP 0 117 748 A2 (DU PONT [US]) 5 September 1984 (1984-09-05) page 5, line 6 - page 8, line 2 page 14, line 26 - page 17, line 9; claims; examples</td>
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