Bridged Monoazo Dyes

Compounds of the general formula (I) a process for their preparation and their use for dyeing and/or printing organic substrates.

**Title:** BRIDGED MONOAZO DYES

**Abstract:** Compounds of the general formula (I) a process for their preparation and their use for dyeing and/or printing organic substrates.
Bridged monoazo dyes

The invention relates to novel acid dyes, to a process for their preparation and to their use for dyeing organic substrates.

Bridged dyes based on benzothiazole are known. Yet there continues to be a demand for bridged benzothiazole dyes having improved properties.

The invention provides compounds of the general formula (I)

![Chemical Structure](image)

where

- $R_1, R'_1, R_2$ and $R'_2$ are independently hydrogen, unbranched C$_{1-6}$alkyl or branched C$_{3-6}$alkyl, unbranched C$_{1-6}$alkoxy or branched C$_{3-6}$alkoxy, halogen or -NHCO-(C$_{1-6}$alkyl) with an unbranched C$_{1-6}$alkyl group or -NHCO-(C$_{3-6}$alkyl) with a branched C$_{3-6}$alkyl group,
- $R_3$ and $R'_3$ are independently unbranched C$_{1-6}$alkyl or branched C$_{3-6}$alkyl,
- $R_4$ and $R'_4$ are independently unbranched C$_{1-6}$alkylene or branched C$_{3-6}$alkylene or arylene or -CH$_2$-arylene which is optionally substituted by unbranched C$_{1-6}$alkyl or branched C$_{3-6}$alkyl, -OH, -CN or by further -SO$_2$H groups, and
- $X$ is any bridge or a direct bond.

In preferred compounds of the formula (I) $X$ is a direct bond or a bridge of the formula -(CH$_2$)$_y$- where $y$ is 1, 2, 3, 4, 5 or 6, or branched C$_{3-6}$alkylene which can be further substituted by -OH or -CN or the bridge X is -CH=CH-, C$_{3-6}$alkylene, phenylene, naphthylene or a five-membered or six-membered ring which can also contain one or two heteroatoms, or $X$ is a bridge of N, S or O, or -NH-(C$_{1-6}$)-alkylene-NH-, -NH-arylene-
NH-, -NH-C(O)-, -NH-C(O)-NH-, -NH-C(O)-A-C(O)-NH-, CO, SO₂, NH or a heteroatom, or or X is a bridge C wherein this carbon atom C is a member of a five or six-membered aliphatic ring which is further unsubstituted or is substituted by unbranched C₁₆alkyl or branched C₃₆alkyl, unbranched C₁₆alkoxy or branched C₃₆alkoxy, -OH or -CN.

A in -NH-C(O)-A-C(O)-NH- is a group of the formula -(CH₂)ₓ where y is 1, 2, 3, 4, 5, or 6, or branched C₃₆alkylene which can be substituted by -OH or -CN or is -CH=CH-, phenylene, naphthylene or a five-membered or six-membered ring which can also contain one or two heteroatoms especially N, S or O.

In further preferred compounds, the bridge X is a bridge of the formula -(CH₂)ₓ where y′ is 1, 2, 3 or 4, especially -CH₂- or -CH₂CH₂-, or branched C₃₆alkyl, especially -C(CH₃)₂-, CO, SO₂, NH or -NH-C(O)-NH-. In further preferred compounds the bridge X is a heteroatom selected from the group of S or O. In particularly preferred compounds the bridge X is -CH₂- or -CH₂CH₂-.

In further preferred compounds, the bridge X is a bridge of the formula

```
  X
 / \
X    X
  |
  (CH)₂
```

wherein z is independently 5 or 6, wherein the asterix defines the point of attachment to the benzthiazole part of the dyestuff. By preference X is the bridging cyclohexyl moiety

```
  X
 / \
X    X
  |
  /\n /  /
/   /
```

wherein the asterix defines the point of attachment to the benzthiazole part of the dyestuff.

In preferred compounds of the formula (I)

R₁, R₁', R₂ and R₂' are independently hydrogen, unbranched C₁₆alkyl or branched C₃₆alkyl, unbranched C₁₆alkoxy or branched C₃₆alkoxy, halogen
or -NHCO-(C_{1,4}alkyl) with an unbranched C_{1,4}alkyl group or -NHCO-(C_{3,4}alkyl) with a branched C_{3,4}alkyl group,

R_3 and R'_3 are independently unbranched C_{1,4}alkyl or branched C_{3,4}alkyl,
R_4 and R'_4 are independently arylene or -CH_2-arylene which is optionally substituted by unbranched C_{1,6}alkyl or branched C_{3,6}alkyl, -OH, -CN or by further -SO_3H groups, and
X is any bridge or a direct bond.

In more preferred compounds of the formula (I)

R_1, R'_1, R_2 and R'_2 are independently hydrogen, methyl, ethyl, methoxy, ethoxy, halogen or acylamino,
R_3 and R'_3 are independently methyl or ethyl,
R_4 and R'_4 are independently arylene or -CH_2-arylene which is optionally substituted by unbranched C_{1,6}alkyl or branched C_{3,6}alkyl, -OH, -CN or by further -SO_3H groups, and
X is any bridge or a direct bond.

Very particular preference is given to compounds of the formula (I) where

R_1, R'_1, R_2 and R'_2 are independently hydrogen, methyl, ethyl, methoxy, ethoxy, halogen or acylamino,
R_3 and R'_3 are each ethyl,
R_4 and R'_4 are independently benzylene which is optionally substituted by unbranched C_{1,6}alkyl or branched C_{3,6}alkyl, -OH, -CN or by further -SO_3H groups, and
X is any bridge or a direct bond.

Very particular preference is further given to compounds of the formula (I) where R_4 and R'_4 is a -CH_2-phenylene group which is not further substituted. It is very particularly preferred for the groups -R_4-SO_3H and -R'_4-SO_3H to be

\[ \text{CH}_2-\text{SO}_3H \]
The branched C₃₋₆-alkyl groups or unbranched C₁₋₆-alkyl groups can be further substituted with hydroxyl groups or cyano groups. Preferably, the alkyl groups are not further substituted.

The invention also provides a process for preparing compounds of the formula (I). The invention's compounds of the formula (I) can be prepared in conventional processes under conventional conditions.

In the process of the invention, compounds of the formula (II)

\[
\begin{align*}
\text{H}_2\text{N} & \quad \text{N} \quad \text{S} \quad \text{N} \\
\text{X} & \quad \text{S} \quad \text{N} & \quad \text{NH}_2
\end{align*}
\]

(II)

which are known from the literature or synthesized as per Bull. Soc. Chim. France 1974, 641-648, are conventionally diazotized and coupled onto two equivalents of a compound of the formula (III)

\[
\begin{align*}
\text{R}_1 & \quad \text{N} \quad \text{R}_3 \\
\text{R}_2 & \quad \text{R}_4 \quad \text{SO}_3\text{H}
\end{align*}
\]

(III)

where the substituents are each as defined above. The diamine is cooled down to 0 – 10°C or preferably to 0 – 5°C and diazotized by addition of nitrosylsulphuric acid. Thereafter, the diazotized amine is allowed to react with the compound (III), preferably in aqueous solution.

The dyes of the formula (I) can be isolated from the reaction medium as per known processes, for example by salting out with an alkali metal salt, filtration and drying, if appropriate under reduced pressure at elevated temperature.

Depending on the reaction and/or isolation conditions, the dyes of the formula (I) can be obtained as free acid, as salt or as mixed salt which contains for example one or more cations selected from alkali metal ions, for example the sodium ion, or an ammonium ion.
or alkylammonium cation, for example mono-, di- or trimethyl- or -ethylammonium
cations. The dye can be converted by conventional techniques from the free acid into a
salt or into a mixed salt or vice versa or from one salt form into another. If desired, the
dyes can be further purified by diafiltration, in which case unwanted salts and synthesis
by-products are separated from the crude anionic dye. In diafiltration, the crude dye is
forced through a semipermeable membrane under an applied pressure to remove salts
and synthesis by-products and partly remove water.

The dyes of the formula (I) and their salts are particularly suitable for dyeing or printing
fibrous material consisting of natural or synthetic polyamides in red to violet shades. The
dyes of the formula (I) and their salts are suitable for producing Inkjet printing inks and
for using these Inkjet printing inks to print fibrous material which consists of natural or
synthetic polyamides or cellulose (paper for example).

The invention accordingly provides from another aspect for the use of the dyes of the
formula (I), their salts and mixtures for dyeing and/or printing fibrous materials
consisting of natural or synthetic polyamides. A further aspect is the production of Inkjet
printing inks and their use for printing fibrous materials consisting of natural or synthetic
polyamides.

Dyeing is carried out as per known processes, see for example the dyeing processes
22, pages 658-673 or in the book by M. Peter and H.K. Rouette, Grundlagen der
dyeing in the exhaust process at a temperature of 30 to 140°C, more preferably 80 to
120°C and most preferably at a temperature of 80 to 100°C, and at a liquor ratio in the
range from 3:1 to 40:1.

The substrate to be dyed can be present in the form of yarn, woven fabric, loop-
formingly knitted fabric or carpet for example. Fully fashioned dyeings are even
permanently possible on delicate substrates, examples being lambswool, cashmere, alpaca
and mohair. The dyes of the invention are particularly useful for dyeing fine-denier fibres (microfibres).

The dyes according to the present invention and their salts are highly compatible with known acid dyes. Accordingly, the dyes of the formula (I), their salts or mixtures can be used alone in a dyeing or printing process or else as a component in a combination shade dyeing or printing composition together with other acid dyes of the same class, i.e. with acid dyes possessing comparable dyeing properties, such as for example fastness properties and exhaustion rates from the dyebath onto the substrate. The dyes of the present invention can be used in particular together with certain other dyes having suitable chromophores. The ratio in which the dyes are present in a combination shade dyeing or printing composition is dictated by the hue to be obtained.

The novel dyes of the formula (I), as stated above, are very useful for dyeing natural and synthetic polyamides, i.e. wool, silk and all nylon types, on each of which dyeings having a high fastness level, especially good light fastness and good wet fastnesses (washing, alkaline perspiration) are obtained. The dyes of the formula (I) and their salts have a high rate of exhaustion. The ability of the dyes of the formula (I) and their salt to build up is likewise very good. On-tone dyeings on the identified substrates are of outstanding quality. All dyeings moreover have a constant hue under artificial light. Furthermore, the fastness to decating and boiling is good.

One decisive advantage of the novel dyes is that they are metal free and provide very level dyeings.

The compounds according to the invention can be used as an individual dye or else, owing to their good compatibility, as a combination element with other dyes of the same class having comparable dyeing properties, for example with regard to general fastnesses, exhaustion value, etc. The combination shade dyeings obtained have similar fastnesses to dyeings with the individual dye.
The invention's dyes of the formula (I) can also be used as red components in trichromatic dyeing or printing. Trichromatic dyeing or printing can utilize all customary and known dyeing and printing processes, such as for example the continuous process, exhaustion process, foam dyeing process and Ink-Jet process.

The composition of the individual dye components in the trichromatic dye mixture used in the process of the invention depends on the desired hue. A brown hue for example preferably utilizes 55 - 65% by weight of a yellow component, 20 - 30% by weight of the invention's red component and 10 - 20% by weight of a blue component.

The yellow component, as described above, can consist of a single component or of a mixture of different red individual components conforming to the formula (I). Preference is given to double and triple combinations. When a red individual component consisting of just one red component of the formula (III) is to be used, it should not account for more than 50% by weight of the trichromatic dye mixture.

Particularly preferred blue and/or yellow components are described in WO2002/46318.

In the examples which follow, parts and percentages are by weight and temperatures are reported in degrees Celsius.

**Preparation Example 1**

31.2 parts of the diamine of the structure

\[
\begin{align*}
\text{H}_2\text{N} & \text{S} \text{N} \text{S} \text{N} \text{NH}_2 \\
\text{HN} & \text{S} \text{N} \text{S} \text{N} \text{NH}_2
\end{align*}
\]

are suspended at 50°C in 500 parts of 85% phosphoric acid and 200 parts of acetic acid. The suspension is cooled down to 0 – 5°C and diazotized by addition of 67 parts of 40% nitrosylsulphuric acid. Excess nitrite is destroyed with urea after one hour.
61.2 parts of N-ethyl-N-benzylaminobenzene-3'-sulphonic acid are dissolved in 500 parts of water and 30% caustic soda at pH 9. 300 parts of ice are added to cool down to 0°C before the diazo compound is metered in at not more than 5°C over an hour. The dye suspension obtained is heated to 70°C and filtered off.

The residue is dissolved at 70°C in 1500 parts of water with caustic soda at pH 10. The dye is reprecipitated by addition of 50 parts of sodium chloride and 2000 parts of alcohol and filtered. It conforms to the structure

and dyes polyamides and wool in a red hue with a high build-up capacity. The dyeings have excellent wet fastnesses and good light fastness.

$$\lambda_{\text{max}} \text{ (dimethylformamide: water 1:1 (weight/weight) + 0.2 weight-% ammonium acetate): 536 nm}$$

The following dyes can be prepared similarly to Preparation Example 1 (The $$\lambda_{\text{max}}$$ were measured in a dimethylformamide with water in 1:1 ratio (weight/weight) + 0.2 weight-% ammonium acetate (dimethylformamide: water 1:1 w/w + 0.2 wt.-% ammonium acetate):

<table>
<thead>
<tr>
<th>Ex.</th>
<th>X</th>
<th>R₁</th>
<th>R₂</th>
<th>R₃</th>
<th>R₄</th>
<th>$$\lambda_{\text{max}}$$ [nm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>CH₂CH₂</td>
<td>H</td>
<td>H</td>
<td>C₂H₅</td>
<td><img src="image" alt="" /></td>
<td>530</td>
</tr>
<tr>
<td>Ex.</td>
<td>X</td>
<td>R&lt;sub&gt;1&lt;/sub&gt;</td>
<td>R&lt;sub&gt;2&lt;/sub&gt;</td>
<td>R&lt;sub&gt;3&lt;/sub&gt;</td>
<td>R&lt;sub&gt;4&lt;/sub&gt;</td>
<td>λ&lt;sub&gt;max&lt;/sub&gt; [nm]</td>
</tr>
<tr>
<td>-----</td>
<td>------</td>
<td>--------------</td>
<td>--------------</td>
<td>--------------</td>
<td>--------------</td>
<td>-----------------</td>
</tr>
<tr>
<td>3</td>
<td>CH&lt;sub&gt;2&lt;/sub&gt;</td>
<td>H</td>
<td>CH&lt;sub&gt;3&lt;/sub&gt;</td>
<td>C&lt;sub&gt;2&lt;/sub&gt;H&lt;sub&gt;5&lt;/sub&gt;</td>
<td>-CH&lt;sub&gt;2&lt;/sub&gt;</td>
<td>544</td>
</tr>
<tr>
<td>4</td>
<td>O</td>
<td>H</td>
<td>H</td>
<td>C&lt;sub&gt;2&lt;/sub&gt;H&lt;sub&gt;5&lt;/sub&gt;</td>
<td>-CH&lt;sub&gt;2&lt;/sub&gt;</td>
<td>544</td>
</tr>
<tr>
<td>5</td>
<td>O</td>
<td>H</td>
<td>CH&lt;sub&gt;3&lt;/sub&gt;</td>
<td>C&lt;sub&gt;2&lt;/sub&gt;H&lt;sub&gt;5&lt;/sub&gt;</td>
<td>-CH&lt;sub&gt;2&lt;/sub&gt;</td>
<td>550</td>
</tr>
<tr>
<td>6</td>
<td>O</td>
<td>H</td>
<td>H</td>
<td>C&lt;sub&gt;2&lt;/sub&gt;H&lt;sub&gt;5&lt;/sub&gt;</td>
<td>CH&lt;sub&gt;2&lt;/sub&gt;CH&lt;sub&gt;2&lt;/sub&gt;SO&lt;sub&gt;3&lt;/sub&gt;H</td>
<td>540</td>
</tr>
<tr>
<td>7</td>
<td>O</td>
<td>H</td>
<td>NHCOCH&lt;sub&gt;3&lt;/sub&gt;</td>
<td>C&lt;sub&gt;2&lt;/sub&gt;H&lt;sub&gt;5&lt;/sub&gt;</td>
<td>-CH&lt;sub&gt;2&lt;/sub&gt;</td>
<td>581</td>
</tr>
<tr>
<td>8</td>
<td>C(CH&lt;sub&gt;3&lt;/sub&gt;)&lt;sub&gt;2&lt;/sub&gt;</td>
<td>H</td>
<td>H</td>
<td>C&lt;sub&gt;2&lt;/sub&gt;H&lt;sub&gt;5&lt;/sub&gt;</td>
<td>-CH&lt;sub&gt;2&lt;/sub&gt;</td>
<td>535</td>
</tr>
<tr>
<td>9</td>
<td>SO&lt;sub&gt;2&lt;/sub&gt;</td>
<td>H</td>
<td>H</td>
<td>C&lt;sub&gt;2&lt;/sub&gt;H&lt;sub&gt;5&lt;/sub&gt;</td>
<td>-CH&lt;sub&gt;2&lt;/sub&gt;</td>
<td>554</td>
</tr>
<tr>
<td>10</td>
<td>SO&lt;sub&gt;2&lt;/sub&gt;</td>
<td>H</td>
<td>CH&lt;sub&gt;3&lt;/sub&gt;</td>
<td>C&lt;sub&gt;2&lt;/sub&gt;H&lt;sub&gt;5&lt;/sub&gt;</td>
<td>-CH&lt;sub&gt;2&lt;/sub&gt;</td>
<td>562</td>
</tr>
<tr>
<td>11</td>
<td>SO&lt;sub&gt;2&lt;/sub&gt;</td>
<td>H</td>
<td>NHCOCH&lt;sub&gt;3&lt;/sub&gt;</td>
<td>C&lt;sub&gt;2&lt;/sub&gt;H&lt;sub&gt;5&lt;/sub&gt;</td>
<td>-CH&lt;sub&gt;2&lt;/sub&gt;</td>
<td>584</td>
</tr>
<tr>
<td>12</td>
<td>CH&lt;sub&gt;2&lt;/sub&gt;</td>
<td>H</td>
<td>H</td>
<td>C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;9&lt;/sub&gt;</td>
<td>-CH&lt;sub&gt;2&lt;/sub&gt;</td>
<td>537</td>
</tr>
<tr>
<td>13</td>
<td>CH&lt;sub&gt;2&lt;/sub&gt;</td>
<td>H</td>
<td>CH&lt;sub&gt;3&lt;/sub&gt;</td>
<td>C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;9&lt;/sub&gt;</td>
<td>-CH&lt;sub&gt;2&lt;/sub&gt;</td>
<td>546</td>
</tr>
<tr>
<td>14</td>
<td>C(CH&lt;sub&gt;3&lt;/sub&gt;)&lt;sub&gt;2&lt;/sub&gt;</td>
<td>H</td>
<td>CH&lt;sub&gt;3&lt;/sub&gt;</td>
<td>C&lt;sub&gt;2&lt;/sub&gt;H&lt;sub&gt;5&lt;/sub&gt;</td>
<td>-CH&lt;sub&gt;2&lt;/sub&gt;</td>
<td>543</td>
</tr>
<tr>
<td>15</td>
<td>CO</td>
<td>H</td>
<td>H</td>
<td>C&lt;sub&gt;2&lt;/sub&gt;H&lt;sub&gt;5&lt;/sub&gt;</td>
<td>-CH&lt;sub&gt;2&lt;/sub&gt;</td>
<td>546</td>
</tr>
<tr>
<td>16</td>
<td>CH&lt;sub&gt;2&lt;/sub&gt;</td>
<td>H</td>
<td>H</td>
<td>CH&lt;sub&gt;3&lt;/sub&gt;</td>
<td>-CH&lt;sub&gt;2&lt;/sub&gt;</td>
<td>535</td>
</tr>
<tr>
<td>Ex.</td>
<td>X</td>
<td>R₁</td>
<td>R₂</td>
<td>R₃</td>
<td>R₄</td>
<td>$\lambda_{\text{max}}$ [nm]</td>
</tr>
<tr>
<td>-----</td>
<td>---------</td>
<td>----</td>
<td>----</td>
<td>------</td>
<td>------------</td>
<td>-----------------------------</td>
</tr>
<tr>
<td>17</td>
<td>CH₂CH₂</td>
<td>H</td>
<td>H</td>
<td>CH₃</td>
<td></td>
<td>529</td>
</tr>
<tr>
<td>18</td>
<td>CH₂CH₂</td>
<td>H</td>
<td>CH₃</td>
<td>CH₃</td>
<td></td>
<td>537</td>
</tr>
<tr>
<td>19</td>
<td>C(CH₂)₅</td>
<td>H</td>
<td>H</td>
<td>C₂H₅</td>
<td></td>
<td>533</td>
</tr>
<tr>
<td>20</td>
<td>C(CH₂)₅</td>
<td>H</td>
<td>NHCOCH₃</td>
<td>C₂H₅</td>
<td></td>
<td>574</td>
</tr>
<tr>
<td>21</td>
<td>CO</td>
<td>H</td>
<td>CH₃</td>
<td>C₂H₅</td>
<td></td>
<td>555</td>
</tr>
<tr>
<td>22</td>
<td>CO</td>
<td>H</td>
<td>NHCOCH₃</td>
<td>C₂H₅</td>
<td></td>
<td>587</td>
</tr>
<tr>
<td>23</td>
<td>CH₂CH₂</td>
<td>H</td>
<td>CH₃</td>
<td>C₂H₅</td>
<td></td>
<td>537</td>
</tr>
<tr>
<td>24</td>
<td>CH₂CH₂</td>
<td>H</td>
<td>H</td>
<td>C₄H₉</td>
<td></td>
<td>532</td>
</tr>
<tr>
<td>25</td>
<td>CH₂CH₂</td>
<td>H</td>
<td>CH₃</td>
<td>C₄H₉</td>
<td></td>
<td>538</td>
</tr>
<tr>
<td>26</td>
<td>C(CH₃)₂</td>
<td>H</td>
<td>NHCOCH₃</td>
<td>C₂H₅</td>
<td></td>
<td>571</td>
</tr>
<tr>
<td>27</td>
<td>CH₂</td>
<td>H</td>
<td>NHCOCH₃</td>
<td>C₂H₅</td>
<td></td>
<td>573</td>
</tr>
<tr>
<td>28</td>
<td>CH₂</td>
<td>H</td>
<td>CH₃</td>
<td>CH₃</td>
<td></td>
<td>543</td>
</tr>
<tr>
<td>29</td>
<td>C(CH₂)₅</td>
<td>H</td>
<td>H</td>
<td>C₄H₉</td>
<td></td>
<td>535</td>
</tr>
<tr>
<td>Ex.</td>
<td>X</td>
<td>R&lt;sub&gt;1&lt;/sub&gt;</td>
<td>R&lt;sub&gt;2&lt;/sub&gt;</td>
<td>R&lt;sub&gt;3&lt;/sub&gt;</td>
<td>R&lt;sub&gt;4&lt;/sub&gt;</td>
<td>λ&lt;sub&gt;max&lt;/sub&gt; [nm]</td>
</tr>
<tr>
<td>-----</td>
<td>---------</td>
<td>-------------</td>
<td>-------------</td>
<td>-------------</td>
<td>-------------</td>
<td>-------------------</td>
</tr>
<tr>
<td>30</td>
<td>C(CH2)₅</td>
<td>OCH₃</td>
<td>CH₃</td>
<td>C₂H₅</td>
<td>-CHO₂</td>
<td>555</td>
</tr>
<tr>
<td>31</td>
<td>C(CH2)₅</td>
<td>H</td>
<td>H</td>
<td>CH₃</td>
<td>-CHO₂</td>
<td>534</td>
</tr>
<tr>
<td>32</td>
<td>CH₂CH₂</td>
<td>H</td>
<td>NHCOCH₃</td>
<td>C₂H₅</td>
<td>-CHO₂</td>
<td>566</td>
</tr>
<tr>
<td>33</td>
<td>O</td>
<td>H</td>
<td>CH₃</td>
<td>C₄H₉</td>
<td>-CHO₂</td>
<td>552</td>
</tr>
<tr>
<td>34</td>
<td>O</td>
<td>H</td>
<td>H</td>
<td>C₄H₉</td>
<td>-CHO₂</td>
<td>546</td>
</tr>
<tr>
<td>35</td>
<td>C(CH2)₅</td>
<td>H</td>
<td>CH₃</td>
<td>CH₃</td>
<td>-CHO₂</td>
<td>542</td>
</tr>
<tr>
<td>36</td>
<td>O</td>
<td>H</td>
<td>CH₃</td>
<td>CH₃</td>
<td>-CHO₂</td>
<td>551</td>
</tr>
<tr>
<td>37</td>
<td>CH₂</td>
<td>OCH₃</td>
<td>CH₃</td>
<td>C₂H₅</td>
<td>-CHO₂</td>
<td>557</td>
</tr>
<tr>
<td>38</td>
<td>O</td>
<td>H</td>
<td>H</td>
<td>CH₃</td>
<td>-CHO₂</td>
<td>544</td>
</tr>
<tr>
<td>39</td>
<td>C(CH2)₅</td>
<td>H</td>
<td>CH₃</td>
<td>C₄H₉</td>
<td>-CHO₂</td>
<td>544</td>
</tr>
<tr>
<td>40</td>
<td>CH₂CH₂</td>
<td>H</td>
<td>H</td>
<td>C₂H₅</td>
<td>CH₂CH₂SO₃H</td>
<td>525</td>
</tr>
<tr>
<td>41</td>
<td>CH₂CH₂</td>
<td>OCH₃</td>
<td>CH₃</td>
<td>C₂H₅</td>
<td>-CHO₂</td>
<td>554</td>
</tr>
<tr>
<td>42</td>
<td>CH₂</td>
<td>H</td>
<td>H</td>
<td>C₂H₅</td>
<td>CH₂CH₂SO₃H</td>
<td>530</td>
</tr>
<tr>
<td>43</td>
<td>C(CH2)₅</td>
<td>H</td>
<td>CH₃</td>
<td>C₂H₅</td>
<td>-CHO₂</td>
<td>542</td>
</tr>
</tbody>
</table>
C(CH₂)₆ signifies the bridging cyclohexyl moiety

*\[
\begin{array}{c}
  * \\
  \text{Cyclohexyl} \\
  * 
\end{array}
\]

wherein the asterisk define the point of attachment to the benzthiazole part of the dyestuff.

5

**USE EXAMPLE A**

A dyebath at 40°C, consisting of 2000 parts of water, 1 part of a weakly cation-active levelling agent which is based on an ethoxylated aminopropyl fatty acid amide and which has affinity for dye, 0.25 parts of the dye of Preparation Example 1 and adjusted to pH 5 with 1-2 parts of 40% acetic acid is entered with 100 parts of nylon-6 fabric. After 10 minutes at 40°C, the dyebath is heated to 98°C at a rate of 1°C per minute and then left at the boil for 45-60 minutes. Thereafter it is cooled down to 70°C over 15 minutes. The dyeing is removed from the bath, rinsed with hot and then with cold water and dried. The result obtained is a red polyamide dyeing possessing good light and wet fastnesses.

15

**USE EXAMPLE B**

A dyebath at 40°C, consisting of 2000 parts of water, 1 part of a weakly cation-active levelling agent which is based on an ethoxylated aminopropyl fatty acid amide and which has affinity for dye, 0.3 parts of the dye of Preparation Example 1 and adjusted to pH 5.5 with 1-2 parts of 40% acetic acid is entered with 100 parts of nylon-6,6 fabric. After 10 minutes at 40°C, the dyebath is heated to 120°C at a rate of 1.5°C per minute and then left at this temperature for 15-25 minutes. Thereafter it is cooled down to 70°C over 25 minutes. The dyeing is removed from the dyebath, rinsed with hot and then with cold water and dried. The result obtained is a red polyamide dyeing with good levelness and having good light and wet fastnesses.
USE EXAMPLE C

A dyebath at 40°C, consisting of 4000 parts of water, 1 part of a weakly amphoteric levelling agent which is based on a sulfated, ethoxylated fatty acid amide and which has affinity for dye, 0.4 parts of the dye of Preparation Example 1 and adjusted to pH 5 with 1-2 parts of 40% acetic acid is entered with 100 parts of wool fabric. After 10 minutes at 40°C, the dyebath is heated to boiling at a rate of 1°C per minute and then left at the boil for 40-60 minutes. Thereafter it is cooled down to 70°C over 20 minutes. The dyeing is removed from the bath, rinsed with hot and then with cold water and dried. The result obtained is a red wool dyeing possessing good light and wet fastnesses.

USE EXAMPLE D

100 parts of a woven nylon-6 material are padded with a 50°C liquor consisting of

<table>
<thead>
<tr>
<th>Parts</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>40</td>
<td>parts of the dye of Preparation Example 1,</td>
</tr>
<tr>
<td>100</td>
<td>parts of urea,</td>
</tr>
<tr>
<td>20</td>
<td>parts of a nonionic solubilizer based on butyldiglycol,</td>
</tr>
<tr>
<td>15-20</td>
<td>parts of acetic acid (to adjust the pH to 4),</td>
</tr>
<tr>
<td>10</td>
<td>parts of a weakly cation-active levelling agent which is based on an ethoxylated aminopropyl fatty acid amide and has affinity for dye, and</td>
</tr>
<tr>
<td>810-815</td>
<td>parts of water (to make up to 1000 parts of padding liquor).</td>
</tr>
</tbody>
</table>

The material thus impregnated is rolled up and left to dwell in a steaming chamber under saturated steam conditions at 85-98°C for 3-6 hours for fixation. The dyeing is then rinsed with hot and cold water and dried. The result obtained is a red nylon dyeing having good levelness in the piece and good light and wet fastnesses.

USE EXAMPLE E

A textile cut pile sheet material composed of nylon-6 and having a synthetic base fabric is padded with a liquor containing per 1000 parts
1 part of dye of Preparation Example 1
4 parts of a commercially available thickener based on carob flour ether
2 parts of a nonionic ethylene oxide adduct of a higher alkylphenol
5 1 part of 60% acetic acid.

This is followed by printing with a paste which per 1000 parts contains the following components:

10 20 parts of commercially available alkoxylated fatty alkylamine (displace product)
20 parts of a commercially available thickener based on carob flour ether.

The print is fixed for 6 minutes in saturated steam at 100°C, rinsed and dried. The result obtained is a level-coloured cover material having a red and white pattern.

**USE EXAMPLE F**

A dyebath at 40°C consisting of 2000 parts of water, 1 part of a weakly cation-active levelling agent which is based on an ethoxylated aminopropyl fatty acid amide and has affinity for dye, 0.2 part of the dye of Preparation Example 1, 1.5 parts of a commercially available preparation of C.I. Acid Yellow 236 (Nylosan Yellow F-L) and 0.5 part of the blue dye of Example 46 of the patent application WO99/51681 or of EP1066340 B1:

Example 46 of the patent application WO99/51681 or of EP 1066340 B1

adjusted to pH 5 with 1-2 parts of 40% acetic acid is entered with 100 parts of woven nylon-6,6 fabric. After 10 minutes at 40°C, the dyebath is heated to 98°C at a rate of 1°C
per minute and then left at the boil for 45 to 60 minutes. This is followed by cooling
down to 70°C over 15 minutes. The dyeing is removed from the bath, rinsed with hot
and then with cold water and dried. The result obtained is a level grey polyamide dyeing
having good light and wet fastnesses.

USE EXAMPLE G

100 parts of a chrome-tanned and synthetically retanned shave-moist grain leather are
dyed for 30 minutes in a bath of 300 parts of water and 2 parts of the dye of Preparation
Example 1 at 55°C. After addition of 4 parts of a 60% emulsion of a sulphited fish oil,
the leather is fatliquored for 45 minutes. It is then acidified with 8.5% formic acid and
milled for 10 minutes (final pH in the bath 3.5-4.0). The leather is then rinsed, allowed to
drip dry and finished as usual. The result obtained is a leather dyed in a level clear red
hue with good fastnesses.

Use Examples A to G can also be carried out with dyes 2 to 43 with similar results.

USE EXAMPLE H

3 parts of the dye of Preparation Example 3 are dissolved in 82 parts of demineralized
water and 15 parts of diethylene glycol at 60°C. Cooling down to room temperature
gives a red printing ink which is very highly suitable for ink jet printing on paper or
polyamide and wool textiles.

Use Example H can also be carried out with dyes 1 or 2 and 4 to 43 with similar results.
CLAIMS

1. Compounds of the general formula (I)

\[
\text{HO}_2\text{S} \quad \text{(I)}
\]

where

- \( R_1, R'_1, R_2 \) and \( R'_2 \) are independently hydrogen, unbranched \( C_{1-6}\text{-alkyl} \) or branched \( C_{3-6}\text{-alkyl} \), unbranched \( C_{1-6}\text{-alkoxy} \) or branched \( C_{3-6}\text{-alkoxy} \),
- halogen or \(-\text{NHCO-}(C_{1-6}\text{-alkyl})\) with an unbranched \( C_{1-6}\text{-alkyl} \) group or \(-\text{NHCO-}(C_{3-6}\text{-alkyl})\) with a branched \( C_{3-6}\text{-alkyl} \) group,
- \( R_3 \) and \( R'_3 \) are independently unbranched \( C_{1-6}\text{-alkyl} \) or branched \( C_{3-6}\text{-alkyl} \),
- \( R_4 \) and \( R'_4 \) are independently unbranched \( C_{1-6}\text{-alkylene} \) or branched \( C_{3-6}\text{-alkylene} \) or arylene or \(-\text{CH}_2\text{-arylene} \) which is optionally substituted by unbranched \( C_{1-6}\text{-alkyl} \) or branched \( C_{3-6}\text{-alkyl} \), \(-\text{OH}, -\text{CN} \) or by further \(-\text{SO}_3\text{H} \) groups, and
- \( X \) is any bridge or a direct bond.
2. Compounds according to Claim 1 characterized in that

- $R_1$, $R'_1$, $R_2$ and $R'_2$ are independently hydrogen, unbranched C$_3$alkyl or branched C$_3$alkyl, unbranched C$_4$alkoxy or branched C$_3$alkoxy, halogen or -NHC(O)-(C$_4$alkyl) with an unbranched C$_4$alkyl group or -NHC(O)-(C$_3$alkyl) with a branched C$_3$alkyl group,

- $R_3$ and $R'_3$ are independently unbranched C$_4$alkyl or branched C$_3$alkyl,

- $R_4$ and $R'_4$ are independently arylene or -CH$_2$arylene which is optionally substituted by unbranched C$_1$alkyl or branched C$_3$alkyl, -OH, -CN or by further -SO$_3$H groups, and

- $X$ is any bridge or a direct bond.

3. Compounds according to Claim 2 characterized in that

- $R_1$, $R'_1$, $R_2$ and $R'_2$ are independently hydrogen, methyl, ethyl, methoxy, ethoxy, halogen or acylamino,

- $R_3$ and $R'_3$ are independently methyl or ethyl,

- $R_4$ and $R'_4$ are independently arylene or -CH$_2$arylene which is optionally substituted by unbranched C$_1$alkyl or branched C$_3$alkyl, -OH, -CN or by further -SO$_3$H groups, and

- $X$ is any bridge or a direct bond.

4. Compounds according to Claim 1, 2 or 3 characterized in that $X$ is a direct bond or a bridge of the formula -(CH$_2$)$_y$ where $y$ is 1, 2, 3, 4, 5 or 6, or branched C$_3$alkylene which can be further substituted by -OH or -CN or is -CH=CH$_2$, C$_3$alkylene, phenylene, naphthylene or a five-membered or six-membered ring which can also contain one or two heteroatoms, especially N, S or O, or -NH-(C$_1$alkyl)-alkylene-NH$_2$, -NH-arylene-NH$_2$, -NH-C(O)$_2$NH$_2$, -NH-C(O)-NH$_2$, -NH-C(O)-A-C(O), CO, SO$_2$, NH or a heteroatom and A is a group of the formula -(CH$_2$)$_y$ where $y$ is 1, 2, 3, 4, 5 or 6, or branched C$_3$alkyl which can be substituted by -OH or -CN or is -CH=CH$_2$, C$_3$alkylene, phenylene, naphthylene or a five-
membered or six-membered ring which can also contain one or two heteroatoms especially N, S or O.

5. Process for preparing compounds of the formula (I) according to Claim 1, characterized in that a of the formula (II)

\[
\begin{align*}
\text{H}_2\text{N} & \xrightarrow{\text{N}} \text{S} \\
\text{N} & \xrightarrow{\text{X}} \text{N} \xrightarrow{\text{S}} \text{NH}_2
\end{align*}
\]

is diazotized and coupled onto two equivalents of a compound of the formula (III)

\[
\begin{align*}
\text{R}_1 & \xrightarrow{\text{N}} \text{R}_3 \\
\text{R}_2 & \xrightarrow{\text{N}} \text{R}_4 \xrightarrow{\text{SO}_3\text{H}}
\end{align*}
\]

where the substituents are each as defined above.

6. Use of the compounds of the formula (I) according to Claim 1 for dyeing and/or printing organic substrates.

7. Use of compounds of the formula (I) according to Claim 1 for dyeing and/or printing wool, silk and synthetic polyamides.

8. Use of compounds of the formula (I) according to Claim 1 for producing printing inks for the InkJet process.
**INTERNATIONAL SEARCH REPORT**

### A. CLASSIFICATION OF SUBJECT MATTER

| IPC 7 | C09B35/34 | C09B35/025 | C09D11/00 |

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 | C09B | C09D |

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, PAJ, CHEM ABS Data, WPI Data

### C. DOCUMENTS CONSIDERED TO BE RELEVANT

<table>
<thead>
<tr>
<th>Category</th>
<th>Citation of document, with indication, where appropriate, of the relevant passages</th>
<th>Relevant to claim No.</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>US 4 517 358 A (RAMANATHAN VISVANATHAN) 14 May 1985 (1985-05-14) column 5, line 47 - line 48; claims 1,8</td>
<td>1-8</td>
</tr>
<tr>
<td>A</td>
<td>US 4 581 445 A (RAMANATHAN VISVANATHAN) 8 April 1986 (1986-04-08) column 4, line 12 - line 28; example 1</td>
<td>1-8</td>
</tr>
<tr>
<td>A</td>
<td>US 4 041 024 A (WOLFRUM ET AL) 9 August 1977 (1977-08-09) example 1</td>
<td>1-8</td>
</tr>
</tbody>
</table>

| Further documents are listed in the continuation of box C. | Patient 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** 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 September 2005

**Date of mailing of the international search report**

05/10/2005

**Name and mailing address of the ISA**

European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 H.V. Ilpiewijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl
Fax (+31-70) 340-3016

**Authorized officer**

Ginoux, C
<table>
<thead>
<tr>
<th>Patent document cited in search report</th>
<th>Publication date</th>
<th>Patent family member(s)</th>
<th>Publication date</th>
</tr>
</thead>
<tbody>
<tr>
<td>US 4517358 A</td>
<td>14-05-1985</td>
<td>CH 648337 A5</td>
<td>15-03-1985</td>
</tr>
<tr>
<td></td>
<td></td>
<td>DE 3234785 A1</td>
<td>31-03-1983</td>
</tr>
<tr>
<td></td>
<td></td>
<td>GB 2109805 A</td>
<td>08-06-1983</td>
</tr>
<tr>
<td>US 4581445 A</td>
<td>08-04-1986</td>
<td>CH 653358 A5</td>
<td>31-12-1985</td>
</tr>
<tr>
<td></td>
<td></td>
<td>DE 3333943 A1</td>
<td>29-03-1984</td>
</tr>
<tr>
<td></td>
<td></td>
<td>GB 2129008 A</td>
<td>10-05-1984</td>
</tr>
<tr>
<td>US 4041024 A</td>
<td>09-08-1977</td>
<td>NONE</td>
<td></td>
</tr>
</tbody>
</table>