Title: AQUEOUS SOLUTIONS OF FLUORESCENT WHITENING AGENTS

(57) Abstract: Compositions comprising (A) a total of from 2 to 30% by weight, based on the total composition (A) + (B), of one or more amino alcohols of formula (1) herein R₁, R₂, R₃ and R₄ are each independently of the others hydrogen, C₁-C₄ alkyl, C₅-C₁₀ ary1 or C₅-C₁₀ aralkyl, and R₅ and R₆ are each independently of the other hydrogen or C₁-C₄ alkyl; and (B) from 70 to 98% by weight, based on the total composition (A) + (B), of a fluorescent whitening agent of formula (2) herein X is hydrogen, an alkali metal ion, an ammonium ion or a hydroxyalkyl ammonium radical derived from the amino alcohol of formula (1), and R₇, R₈, R₉ and R₁₀ are each independently of the others -OR₁₁, -NR₁₂R₁₂ or a group of formula (3) wherein R₁₃ and R₁₄ are each independently of the other hydrogen, alkyl, hydroxyalkyl, alkoxyalkyl, carboxyalkyl, dicarboxyalkyl, H₂N-CO-alkyl or alkythio, are distinguished by high solubility in water and by high storage stability of the aqueous solutions.
**Aqueous solutions of fluorescent whitening agents**

The present invention relates to a composition comprising a sulfo-group-containing fluorescent whitening agent and a β-amino alcohol, to aqueous solutions comprising such a composition and also to the use of the aqueous solutions in the whitening of textile fibres or paper.

Liquid commercial forms of fluorescent whitening agents have the advantage over powders or granules that they are dust-free, can be measured out better and result in a substantial increase in the rate of dissolution in water. However, the solubility of most sulfo-group-containing fluorescent whitening agents in water is insufficient to produce adequately concentrated solutions. In addition, when the aqueous solutions are stored, the fluorescent whitening agents have a tendency to crystallise out. An improvement in solubility and in storage stability is therefore desirable.

It is known that the solubility of fluorescent whitening agents can be increased by adding specific auxiliaries such as urea or ε-caprolactam. However, relatively large amounts of such additives have to be added and then removed subsequently in a laborious waste-water treatment procedure.

It has now been found that the aqueous solubility of sulfo-group-containing fluorescent whitening agents and the storage stability of the aqueous solutions can be substantially improved by the addition of a β-amino alcohol in a relatively small amount.

The present invention relates to a composition comprising

\[(A)\] a total of from 2 to 30 % by weight, based on the total composition \((A) + (B)\), of one or more amino alcohols of formula (1)

![Chemical Structure](image)

wherein \(R_1, R_2, R_3\) and \(R_4\) are each independently of the others hydrogen,
C_{1-12}alkyl, C_6-C_{24}aryl or C_6-C_{24}aralkyl, and R_5 and R_3 are each independently of the other hydrogen or C_{1-4}alkyl; and

(B) from 70 to 98 % by weight, based on the total composition (A) + (B), of a fluorescent whitening agent of formula (2)

\[
\begin{align*}
\text{wherein } X & \text{ is hydrogen, an alkali metal ion, an ammonium ion or a hydroxyalkyl-} \\
& \text{ammonium radical derived from an amino alcohol of formula (1), and} \\
R_7, R_5, R_9 \text{ and } R_{10} & \text{ are each independently of the others -OR_{11}, -NR_{11}R_{12} or a group of formula} \\
\end{align*}
\]

\[
\text{wherein } R_{11} \text{ and } R_{12} \text{ are each independently of the other hydrogen, alkyl, hydroxy-} \\
\text{alkyl, alkoxyalkyl, carboxyalkyl, dicarboxyalkyl, H}_2\text{N-CO-alkyl or alkylthio.}
\]

When any radicals in formula (1) or (2) are alkyl, such radicals may be straight-chain or branched radicals. Examples thereof are methyl, ethyl, propyl, isopropyl, n-butyl, isobutyl, sec-butyl, tert-butyl, amyl, tert-amyl (1,1-dimethylpropyl), 1,1,3,3-tetramethylbutyl, hexyl, 2-methylpentyl, neopentyl, cyclopentyl, cyclohexyl and their respective isomers.

Aryl radicals as substituents R_1 to R_4 have preferably from 5 to 24, especially from 6 to 14, carbon atoms and may be substituted, for example by hydroxy, C_1-C_4alkyl, C_1-C_4alkoxy, C_1-C_4hydroxyalkyl, halogen or by the radical -NH-CO-R, wherein R is amino, C_1-C_4alkyl or unsubstituted or hydroxy-, C_1-C_4alkyl-, C_1-C_4alkoxy-, C_1-C_4hydroxyalkyl- or halo-substituted phenyl.

Examples of suitable aryl groups are phenyl, tolyl, mesityl, isityl, 2-hydroxyphenyl, 4-hydroxyphenyl, 2-chlorophenyl, 4-chlorophenyl, 2,6-dichlorophenyl, 2-aminophenyl, 3-aminophenyl, 4-aminophenyl, 4-methoxyphenyl, 4-ethoxyphenyl, 4-acetylaminophenyl, naphthyl and phenanthryl.
Aralkyl groups as substituents R₁ to R₄ have preferably from 6 to 36, especially from 7 to 12, carbon atoms and may be unsubstituted or substituted by one or more C₁-C₄ alkyl groups, C₁-C₆ alkoxy groups, halogen atoms or radicals -NH-CO-R, wherein R is amino, C₁-C₄ alkyl or unsubstituted or C₁-C₄ alkyl-, C₁-C₆ alkoxy- or halo-substituted phenyl.

Examples of suitable aralkyl groups are benzyl, 2-phenylethyl, tolylmethyl, mesitylmethyl and 4-chlorophenylmethyl.

X may be, for example, hydrogen, Na⁺, K⁺, NH₄⁺, N(CH₃)₄⁺, a di- or tri-alkanolammonium radical, e.g. di- or tri-ethanolammonium, or a hydroxyalkylammonium radical derived from the amino alcohol of formula (1).

X is preferably hydrogen, Na⁺ or K⁺.

Hydroxyalkyl groups suitable as R₁₁ or R₁₂ are, for example, 4-hydroxy-n-butyl, 3-hydroxy-n-propyl, 2-hydroxy-n-propyl and, especially, 2-hydroxyethyl.

Examples of alkoxyalkyl groups are 2-methoxyethyl and 2-ethoxyethyl.

Carboxyalkyl groups are, for example, 4-carboxy-n-butyl, 3-carboxy-n-propyl, 2-carboxy-n-propyl and, especially, 2-carboxyethyl.

Suitable alkylthio groups are, for example, methylthio, ethylthio and n-propylthio.

Preferred compositions according to the invention comprise, as component (A), 2-amino-2-methyl-1-propanol, 1-amino-2-propanol or a mixture of 2-amino-2-methyl-1-propanol and 2-(N-methylamino)-2-methyl-1-propanol.

As component (B), preference is given to a compound of formula (2) wherein R₇ and R₈ are each a group of formula \( \text{NH} \quad \text{or} \quad \text{NHR}_{11} \) wherein \( R_{11} \) is as defined in claim 1.

Preference is furthermore given to compositions according to the invention comprising, as component (B), a compound of formula (2) wherein \( R_{9} \) and \( R_{10} \) are each -NR₁₁R₁₂ wherein
R_{11} and R_{12} are each independently of the other hydrogen, 2-hydroxyethyl, 2-carboxyethyl, -CH_{2}CH_{2}-CONH_{2} or -CH(COOH)-CH_{2}COOH.

As component (B), special preference is given to compounds of formulae (2a) - (2f)

(2a),

(2b),

(2c),

(2d),
Compounds of formula (2) wherein the cation X is derived from an amino alcohol of formula (1) are novel advantageous fluorescent whitening agents in the form of the corresponding hydroxyalkylammonium salts.

The invention accordingly relates also to a compound of formula

wherein X' is a hydroxyalkylammonium radical derived from an amino alcohol of formula (1) as described hereinbefore and R_7, R_6, R_9 and R_{10} are as defined hereinbefore.

Special preference is given to compounds of formula (3) wherein the hydroxyalkylammonium radical is derived from 2-amino-2-methyl-1-propanol, 1-amino-2-propanol or a mixture of 2-amino-2-methyl-1-propanol and 2-(N-methylamino)-2-methyl-1-propanol.
Such hydroxyalkylammonium salts are prepared by methods known per se, for example by ion exchange of an alkali metal salt or by treating the free acid with the corresponding amino alcohol (1).

As mentioned hereinbefore, an objective of the invention is to produce aqueous solutions having fluorescent whitening agent concentrations that are as high as possible.

The invention accordingly relates also to an aqueous solution containing

(A) from 0.5 to 10 % by weight of an amino alcohol of formula (1) according to claim 1 or mixtures thereof,

(B) from 5 to 40 % by weight of a fluorescent whitening agent of formula (2) according to claim 1 or mixtures thereof,

(C) from 50 to 90 % by weight water, and

(D) from 0 to 40 % by weight of additives,

the sum of components (A) + (B) + (C) + (D) being 100 % by weight.

The solutions according to the invention may comprise, as optional component (D), various auxiliaries such as, for example, inorganic or organic acids, inorganic salts, urea, non-ionic surfactants, preservatives or water-miscible organic solvents.

Such additives may, depending on the fluorescent whitening agent used, further improve the properties of the solutions; for example, they may increase the maximum fluorescent whitening agent concentration or further reduce the viscosity.

Preferred solutions according to the invention comprise, as component (D), a preservative.

Water-miscible organic solvents such as alcohols, ether alcohols, glycols or carboxylic acid amides may act as solubility promoters.

Examples of such solvents are propanol, isopropanol, ethylene glycol, propylene glycol, glycerol, di- or tri-ethylene glycol, dipropylene glycol, ethylene glycol monomethyl ether, ethylene glycol monoethyl ether, diethylene glycol monooethyl ether, formamide, dimethylformamide, dimethylacetamide, ethanolamine, diethanolamine, triethanolamine, N-methylpyrrolidone, polyethylene glycols and polyvinylpyrrolidones.
The solutions according to the invention are generally obtained by dissolving the appropriate fluorescent whitening agent or dye in water or a mixture of water and a water-miscible organic solvent with addition of the amino alcohol of formula (1), where appropriate with heating and stirring.

The solutions according to the invention may, depending on the nature of the dissolved fluorescent whitening agent, be used for the whitening of a very wide variety of high molecular weight organic materials. Suitable substrates for whitening are, for example, synthetic, semi-synthetic or natural textile fibres, paper or washing compositions.

The whitening of paper, and also of textiles, may be carried out in the course of surface finishing. For that purpose, the solutions according to the invention are added to the coating compositions required therefor, the latter being understood to be preparations for the coating of paper and other textile and non-textile, natural or synthetic, organic materials, such as, for example, paper coating compositions. Whitening may be accomplished by incorporating solutions according to the invention in the coating compositions to be applied, which are then applied to the substrates in a manner known per se.

Because the solutions according to the invention can be diluted very readily and rapidly with water, they are also excellently suitable for the whitening of textile substrates using conventional fluorescent whitener agent application methods (e.g. the exhaust method or pad thermo method). For that purpose, the concentrated solutions are so diluted with water that the resulting application solutions, to which conventional auxiliaries may also be added, have the desired fluorescent whitening agent concentrations.

Textile fibres suitable for whitening are those of synthetic materials, e.g. polyamide, of semi-synthetic materials, e.g. regenerated cellulose, and also of natural materials, e.g. wool or cotton, as well as fibre blends, e.g. polyester/cotton, it being possible for the natural fibres also to be provided with a finish in a manner customary in the textile industry.

The textile materials to be whitened may be in a variety of processing states (raw materials, semi-finished products or finished products). Fibre materials may be, for example, in the form of staple fibres, flocks, hanks, textile threads, yarns, twisted yarns, non-woven fibre materials, felts, batts, flocked articles, textile composites or knitted articles but are preferably in the form of woven textiles.
Treatment thereof is carried out using the dilute solutions according to the invention, optionally after adding dispersants, stabilisers, wetting agents and further auxiliaries. Depending on the fluorescent whitening agent dissolved, it may be found to be advantageous to carry out the procedure in an acid, alkaline or, preferably, neutral bath. Treatment is usually carried out at temperatures of about from 20 to 140°C, for example at the boiling point of the bath or thereabout (about 90°C).

The following auxiliaries may also be added to the bath:

dyes (shading), pigments (coloured or, especially, white pigments), carriers, wetting agents, softening agents, swelling agents, antioxidants, light stabilisers, heat stabilisers, chemical bleaching agents, crosslinking agents, finishing agents and also agents used in various textile finishing methods, especially agents for synthetic resin finishes, and also flame retardant, soft handle, dirt release or antistatic finishes or antimicrobial finishes.

Diluting the concentrated fluorescent whitening agent solutions according to the invention to form the corresponding application baths is carried out in such a manner that, when the substrate in question is impregnated, it takes up the fluorescent whitening agent in an amount of at least 0.0001 % by weight, but at most 2 % by weight, preferably from 0.0005 to 0.5 % by weight. The required concentration is derived by simple means from those values depending on the liquor ratio to be used, the nature of the substrate and the fluorescent whitening agent dissolved.

The solutions according to the invention may also be added to washing baths or to washing compositions. To washing baths there is simply added an amount of solution that contains the desired amount of fluorescent whitening agent. The solutions according to the invention may be added to washing compositions in any phase of the production process, for example to the slurry before atomisation of the washing powder or during preparation of liquid washing agent combinations.

The Examples that follow illustrate the invention:

The solutions described in Examples 1, 2 and 3 are produced by mixing the individual components and are subjected to a storage stability and temperature stability test.
The results are compiled in Table 1.

Example 1:
- 22 % by weight compound of formula (2b) wherein X is H
- 5 % by weight 1-amino-2-propanol
- 73 % by weight deionised water

Example 2:
- 22 % by weight compound of formula (2b) wherein X is H
- 5 % by weight 2-amino-2-methyl-1-propanol
- 73 % by weight deionised water

Example 3:
- 19.9 % by weight compound of formula (2b) wherein X is H
- 2.5 % by weight 2-amino-2-methyl-1-propanol
- 2.0 % by weight KOH (50 %)
- 75.6 % by weight deionised water
Table 1:  Storage stability test at different temperatures

<table>
<thead>
<tr>
<th>Ex.</th>
<th>Temp.</th>
<th>1 day</th>
<th>1 week</th>
<th>2 weeks</th>
<th>1 month</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>-5°C</td>
<td>sample frozen</td>
<td>O.K.</td>
<td>O.K.</td>
<td>O.K.</td>
</tr>
<tr>
<td></td>
<td>0°C</td>
<td>O.K.</td>
<td>O.K.</td>
<td>O.K.</td>
<td>O.K.</td>
</tr>
<tr>
<td></td>
<td>RT</td>
<td>O.K.</td>
<td>O.K.</td>
<td>O.K.</td>
<td>O.K.</td>
</tr>
<tr>
<td></td>
<td>40°C</td>
<td>O.K.</td>
<td>O.K.</td>
<td>O.K.</td>
<td>O.K.</td>
</tr>
<tr>
<td></td>
<td>60°C</td>
<td>O.K.</td>
<td>O.K.</td>
<td>O.K.</td>
<td>O.K.</td>
</tr>
<tr>
<td>2</td>
<td>-5°C</td>
<td>sample frozen</td>
<td>O.K.</td>
<td>O.K.</td>
<td>O.K.</td>
</tr>
<tr>
<td></td>
<td>0°C</td>
<td>O.K.</td>
<td>O.K.</td>
<td>O.K.</td>
<td>O.K.</td>
</tr>
<tr>
<td></td>
<td>RT</td>
<td>O.K.</td>
<td>O.K.</td>
<td>O.K.</td>
<td>O.K.</td>
</tr>
<tr>
<td></td>
<td>40°C</td>
<td>O.K.</td>
<td>O.K.</td>
<td>O.K.</td>
<td>O.K.</td>
</tr>
<tr>
<td></td>
<td>60°C</td>
<td>O.K.</td>
<td>O.K.</td>
<td>O.K.</td>
<td>O.K.</td>
</tr>
<tr>
<td>3</td>
<td>-5°C</td>
<td>O.K.</td>
<td>sample frozen</td>
<td>trace of crystal formation on boiling chips</td>
<td>sample frozen</td>
</tr>
<tr>
<td></td>
<td>0°C</td>
<td>O.K.</td>
<td>O.K.</td>
<td>O.K.</td>
<td>O.K.</td>
</tr>
<tr>
<td></td>
<td>RT</td>
<td>O.K.</td>
<td>O.K.</td>
<td>O.K.</td>
<td>O.K.</td>
</tr>
<tr>
<td></td>
<td>40°C</td>
<td>O.K.</td>
<td>O.K.</td>
<td>O.K.</td>
<td>O.K.</td>
</tr>
<tr>
<td></td>
<td>60°C</td>
<td>O.K.</td>
<td>O.K.</td>
<td>O.K.</td>
<td>O.K.</td>
</tr>
</tbody>
</table>

RT = room temperature

Table 2:  Temperature ramp

<table>
<thead>
<tr>
<th>Ex.</th>
<th>0°C</th>
<th>-2°C</th>
<th>-4°C</th>
<th>-6°C</th>
<th>-8°C</th>
<th>-10°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>O.K.</td>
<td>O.K.</td>
<td>O.K.</td>
<td>O.K.</td>
<td>O.K.</td>
<td>frozen</td>
</tr>
<tr>
<td>2</td>
<td>O.K.</td>
<td>O.K.</td>
<td>O.K.</td>
<td>O.K.</td>
<td>frozen</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>O.K.</td>
<td>O.K.</td>
<td>O.K.</td>
<td>O.K.</td>
<td>reversibly frozen</td>
<td></td>
</tr>
</tbody>
</table>

Table 3:  5 freeze/thaw cycles

<table>
<thead>
<tr>
<th>Example</th>
<th>1</th>
<th>2</th>
<th>3</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>O.K.</td>
<td>O.K.</td>
<td>O.K.</td>
</tr>
</tbody>
</table>
What is claimed is:

1. A composition comprising

   (A) a total of from 2 to 30 % by weight, based on the total composition (A) + (B), of one or
   more amino alcohols of formula (1)

   
   \[
   \begin{array}{c}
   \text{R}_3 \\
   \text{R}_1 \\
   \text{C} \\
   \text{R}_2 \\
   \text{C} \\
   \text{OH} \\
   \end{array}
   \]

   \[
   \text{(1)}
   \]

   wherein \( \text{R}_1, \text{R}_2, \text{R}_3 \) and \( \text{R}_4 \) are each independently of the others hydrogen, \( \text{C}_1-\text{C}_{12} \)alkyl,
   \( \text{C}_6-\text{C}_{24} \)aryalkyl or \( \text{C}_6-\text{C}_{25} \)aralkyl, and \( \text{R}_5 \) and \( \text{R}_6 \) are each independently of the other hydrogen
   or \( \text{C}_1-\text{C}_{4} \)alkyl; and

   (B) from 70 to 98 % by weight, based on the total composition (A) + (B), of a
   fluorescent whitening agent of formula (2)

   
   \[
   \begin{array}{c}
   \text{R}_9 \\
   \text{SO}_3\text{X} \\
   \text{N} \\
   \text{R}_{10} \\
   \text{N} \\
   \text{R}_7 \\
   \text{SO}_3\text{X} \\
   \text{N} \\
   \text{R}_8 \\
   \text{N} \\
   \text{R}_6 \\
   \text{N} \\
   \text{R}_5 \\
   \text{N} \\
   \text{R}_4 \\
   \text{H} \\
   \text{C} \\
   \text{N} \\
   \text{R}_3 \\
   \text{H} \\
   \end{array}
   \]

   \[
   \text{(2)}
   \]

   wherein \( \text{X} \) is hydrogen, an alkali metal ion, an ammonium ion or a hydroxyalkyl-
   ammonium radical derived from an amino alcohol of formula (1), and
   \( \text{R}_7, \text{R}_8, \text{R}_9 \) and \( \text{R}_{10} \) are each independently of the others \(-\text{OR}_{11}, -\text{NR}_{11}\text{R}_{12} \) or a group of
   formula

   \[
   \begin{array}{c}
   \text{N} \\
   \text{R}_{11} \\
   \text{H} \\
   \text{N} \\
   \text{R}_{12} \\
   \text{H} \\
   \end{array}
   \]

   wherein \( \text{R}_{11} \) and \( \text{R}_{12} \) are each independently of the other hydrogen, alkyl, hydroxyalkyl,
   alkoxyalkyl, carboxyalkyl, dicarboxyalkyl, \( \text{H}_2\text{N}-\text{CO} \)-alkyl or alkylthio.

2. A composition according to claim 1, comprising, as component (A), 2-amino-2-methyl-1-
propanol, 1-amino-2-propanol or a mixture of 2-amino-2-methyl-1-propanol and

25 2-(N-methylamino)-2-methyl-1-propanol.
3. A composition according to either claim 1 or claim 2, comprising, as component (B), a compound of formula (2) wherein \( R_7 \) and \( R_9 \) are each a group of formula

\[
\text{\begin{figure}
\includegraphics{formula}
\end{figure}}
\]

or

\[
\text{\begin{figure}
\includegraphics{formula}
\end{figure}}
\]

wherein \( R_{11} \) is as defined in claim 1.

4. A composition according to any one of the preceding claims, comprising, as component (B), a compound of formula (2) wherein \( R_8 \) and \( R_{10} \) are each \(-\text{NR}_{11}\text{R}_{12}\) wherein \( R_{11} \) and \( R_{12} \) are each independently of the other hydrogen, 2-hydroxyethyl, 2-carboxyethyl, -\( \text{CH}_2\text{CH}_2\text{-CONH}_2 \) or -\( \text{CH(CHOH)}\text{-CH}_2\text{COOH} \).

5. A composition according to either claim 1 or claim 2, comprising, as component (B), a compound of formula (2a) - (2f)

\[
\text{\begin{figure}
\includegraphics{formula}
\end{figure}}
\]

(2a),

\[
\text{\begin{figure}
\includegraphics{formula}
\end{figure}}
\]

(2b),

15
wherein X is as defined in claim 1.
6. A compound of formula

\[
\begin{align*}
\text{\textit{R}\text{\textsubscript{7}}} & \quad \text{\textit{R}\text{\textsubscript{9}}} \\
\text{\textit{N}} & \quad \text{\textit{N}} \\
\text{\textit{N}} & \quad \text{\textit{N}} \\
\text{\textit{H}} & \quad \text{\textit{SO}}\text{\textsubscript{3}X'} \\
\text{\textit{R}\text{\textsubscript{10}}} & \quad \text{\textit{X'O}}\text{\textsubscript{3}S} \\
\text{\textit{N}} & \quad \text{\textit{N}} \\
\text{\textit{R}\text{\textsubscript{8}}} & \quad \text{\textit{R}\text{\textsubscript{8}}} \\
\end{align*}
\]

wherein \(X'\) is a hydroxyalkylammonium radical derived from an amino alcohol of formula (1) according to claim 1 and \(R_7, R_8, R_9\) and \(R_{10}\) are as defined in claim 1.

7. A compound of formula (3) according to claim 6, wherein the hydroxyalkylammonium radical is derived from 2-amino-2-methyl-1-propanol, 1-amino-2-propanol or a mixture of 2-amino-2-methyl-1-propanol and 2-(N-methylamino)-2-methyl-1-propanol.

8. An aqueous solution containing

(A) from 0.5 to 10 % by weight of an amino alcohol of formula (1) according to claim 1 or mixtures thereof,

(B) from 5 to 40 % by weight of a fluorescent whitening agent of formula (2) according to claim 1 or mixtures thereof,

(C) from 50 to 90 % by weight water, and

(D) from 0 to 40 % by weight additives,

the sum of components (A) + (B) + (C) + (D) being 100 % by weight.

9. An aqueous solution according to claim 8, comprising, as component (D), a preservative.

10. Use of the aqueous solution according to claim 8 in the whitening of natural, semi-synthetic or synthetic textile fibres.

11. Use of the aqueous solution according to claim 8 in the whitening of paper.
**INTERNATIONAL SEARCH REPORT**

**International Application No:**
PCT/EP2004/052119

**A. CLASSIFICATION OF SUBJECT MATTER**

- IPC 7 D21H21/30 D06L3/12 C11D3/42

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 D21H D06L C11D

- 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 database and, where practical, search terms used)
  - EPO-Internal

**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>X</td>
<td>US 3 012 971 A (CRAWFORD SAYLER RALPH ET AL) 12 December 1961 (1961-12-12) the whole document</td>
<td>1-5, 8, 11</td>
</tr>
<tr>
<td>X</td>
<td>GB 1 256 660 A (FARBENFABRIKEN BAYER AG) 15 December 1971 (1971-12-15) the whole document</td>
<td>1, 2, 8, 10</td>
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<tr>
<td>X</td>
<td>GB 1 394 349 A (IMPERIAL CHEMICAL INDUSTRIES LIMITED) 24 January 1973 (1973-01-24) page 2, line 44 - line 53; claims 1-13</td>
<td>1, 3-5, 8</td>
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<tr>
<td>X</td>
<td>US 3 239 513 A (HEINRICH HAUSERMANN) 8 March 1966 (1966-03-08) column 4, line 55 - column 5, line 11; example 4</td>
<td>1, 3-5, 8, 11</td>
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</table>

Further documents are listed in the continuation of box C.

**Date of the actual completion of the international search**

10 December 2004

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

15.02.2005

**Name and mailing address of the ISA**

European Patent Office, P.B. 5818 Patentlaan 2
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Form PCT/ISA/210 (second sheet) (January 2004)
<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>
</table>
| X        | US 4 364 845 A (FRINGEL WERNER)  
21 December 1982 (1982-12-21)  
column 2, line 20 - line 44; claims 1,3 | 1-5,8-11             |
### INTERNATIONAL SEARCH REPORT

**Box II** Observations where certain claims were found unsearchable (Continuation of Item 2 of first sheet)

This International Search Report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
   because they relate to subject matter not required to be searched by this Authority, namely:

2. ☐ Claims Nos.:
   because they relate to parts of the International Application that do not comply with the prescribed requirements to such an extent that no meaningful International Search can be carried out, specifically:

3. ☐ Claims Nos.:
   because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

**Box III** Observations where unity of invention is lacking (Continuation of Item 3 of first sheet)

This International Searching Authority found multiple inventions in this International application, as follows:

- see additional sheet

1. ☐ As all required additional search fees were timely paid by the applicant, this International Search Report covers all searchable claims.

2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.

3. ☐ As only some of the required additional search fees were timely paid by the applicant, this International Search Report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☑ No required additional search fees were timely paid by the applicant. Consequently, this International Search Report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:
   - 1-5, 8-11

**Remark on Protest**

☐ The additional search fees were accompanied by the applicant's protest.

☐ No protest accompanied the payment of additional search fees.
This International Searching Authority found multiple (groups of) inventions in this international application, as follows:

1. claims: 1-5, 8-11
   A composition; an aqueous solution; use of the aqueous solution

2. claims: 6, 7
   A compound
<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>
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<tbody>
<tr>
<td>US 3012971 A</td>
<td>12-12-1961</td>
<td>GB 890420 A, DE 1119646 B</td>
<td>28-02-1962, 14-12-1961</td>
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