



Europäisches Patentamt  
European Patent Office  
Office européen des brevets



(11) **EP 1 357 221 A1**

(12) **EUROPEAN PATENT APPLICATION**

(43) Date of publication:  
**29.10.2003 Bulletin 2003/44**

(51) Int Cl.7: **D06P 5/06**, D06P 5/08,  
D06P 3/60

(21) Application number: **02009409.0**

(22) Date of filing: **25.04.2002**

(84) Designated Contracting States:  
**AT BE CH CY DE DK ES FI FR GB GR IE IT LI LU  
MC NL PT SE TR**  
Designated Extension States:  
**AL LT LV MK RO SI**

- **Gökgöl, Mehmet**  
**Istanbul (TR)**
- **Bakkaloglu, Ali**  
**Ückuyular (TR)**
- **Alper, Ali Oguz**  
**Bostanli (TR)**

(71) Applicant: **Cognis Kimya Sanayi ve Ticaret A.S.**  
**81120 Icerenköy-Istanbul (TR)**

(74) Representative: **Reinhardt, Jürgen, Dr.**  
**Cognis Deutschland GmbH & Co. KG**  
**Postfach 13 01 64**  
**40551 Düsseldorf (DE)**

(72) Inventors:  
• **Deren, Ali**  
**41199 Mönchengladbach (DE)**

(54) **Method for printing or dyeing cellulosic textiles**

(57) The present invention concerns an improved process for printing and dyeing cellulosic textiles, especially cotton, whereby a compounds prepared by first, reacting a dicarboxylic acid with 5 to 22 C-atoms with diethylene triamine in a molar ratio of 1:1 at temperatures of 160 to 220°C, whereby during the reaction the formed water is distilled of, to form a condensation prod-

uct accordingly, secondly, react the product of step i) at temperatures between 20 and 40°C with epichlorhydrin in a molar ration of 1:1 to form a cationic quaternized product, finally, add sulfuric acid and water to the product of the second step, is used.

**EP 1 357 221 A1**

## Description

**[0001]** The present invention relates to a method for printing or dyeing textiles, especially cotton. The invention includes the use of a specific cationic compound to enhance such printing and dyeing methods.

**[0002]** There are currently two common methods of textile printing, viz. direct and transfer paper printing. Of these two methods of printing, direct printing is by far the more prevalent form of printing because transfer paper printing is limited to certain synthetic fibres and their mixtures with cellulosic fibres and the effect of transfer paper printing is different from the character of conventional printing.

Direct colouring may take the form of pigment or soluble dyestuff colouring. As is well known, direct colouring with pigments as opposed to soluble dyestuffs, involves physically binding the pigments to the fibre surface using a binder, e.g. acrylic dispersion.

Nowadays, pigment printing is preferred because of its ease of application e.g. the pigment preparations are incorporated in a printing emulsion containing water, thickener, emulsifier and various fixing agents, handle modifiers and, optionally, solvents such as white spirit, the resultant emulsion being printed onto the textiles, dried and heat cured. The disadvantages of pigment colouring are the handle and the limited fastness to rubbing. Furthermore, the pigment colouring process when used in dyeing as opposed to printing has the further disadvantage of being limited to pale shades only, because of limitations in build-up and unsatisfactory rub-fastness properties, in depth generally above 2% by weight fabric pigment preparation on the fibre e.g. 20 g/l with 100% liquor pick up by weight of fabric.

**[0003]** It was the principal objective of the present invention, to provide an process for colouring of textile fibres with pigments which avoids the aforementioned disadvantages. It was found, that the application of a specific cationic compound solves the problem accordingly.

**[0004]** A first embodiment of the present invention concerns to a process for the continuous dyeing and printing of cellulosic fibre material comprising the steps of

(A) applying to said cellulosic material an aqueous dyeing and printing composition, containing at least

- i) a basic material
- ii) a thickener
- iii) a binder
- iv) dyestuff

(B) dry the cellulosic material

(C) apply onto the material an aqueous composition, containing as active material a compound, prepared by

i) first, reacting a dicarboxylic acid with 5 to 22 C-atoms with Diethylene triamine in a molar ratio of 1 : 1 at temperatures of 160 to 200 °C, whereby during the reaction the formed water is distilled off, to form a condensation product accordingly,

ii) secondly, react the product of step i) at temperatures between 20 and 40 °C with epichlorhydrin in a molar ratio of 1 : 1 to form a cationic quaternized product,

iii) finally, add sulfuric acid and water to the product of step ii)

(D) subject the cellulosic material to temperatures between 120 to 180 °C for 5 seconds to 10 minutes for fixing

**[0005]** The process of the invention is in general conventional, but it is characterised by applying after the first dyeing step a selected cationic material onto the fibres. This compound is a quaternized condensation product of a dicarboxylic acid with polyalkyl polyamines, and it is known in the art, but the use of this compound in textile printing was not described prior. It is preferred to select as dicarboxylic acids of the carbon atom range C5 to C22, more preferably to select dicarboxylic acids from the range C7 to C10. Most preferred is the use of adipic acid as starting material for the preparation of the compound according to the present invention. The dicarboxylic acid is reacted in a condensation reaction with a polyamine which is diethylene triamine.

During the reaction, which takes place at temperature from 160 to 200 °C the water, which is the reaction product of the condensation is distilled off. In a preferred embodiment, this condensation reaction is carried out in the temperature range from 160 to 180 °C. the molar ratio between carboxylic acid and amine is approximately 1 : 1. It is preferred to use a slight excess of amine to come to a better yield of the reaction. The condensation reaction is terminated, when no water can be distilled. Subsequently, the reaction product of step one is diluted by hot water and adjusted active content as 35-45% and then is cooled to a temperature between 20 and 40 °C and epichlorhydrin is added. The molar ratio is again approximately 1 : 1 between the product of step one and the epichlorhydrin.

The quaternization reaction is preferably carried out at approximately 35 °C. Reaction is followed and controlled preferably by measuring the viscosity and whenever the viscosity is reached the value of 1000-2000 centipoise (Brookfield viscosimeter, at 25° C), sulfuric acid (aqueous solution) and water is added to terminate the reaction.

The final product is present then in the form of an aqueous solution. It contains preferably an active content of between 10 to 40 % by weight. the rest up to 100 % is water. This aqueous solution is applied onto the fibres by standard means, known to the skilled persons in tex-

tile technology. E.g. by means of a Foulard. Prior to the application of the quaternized compound the fabric has to be dried. This happens by standard methods, e.g. at temperatures of 120 to 140 °C.

The quaternized compound is applied in amounts of 1 to 25 g/l (active ingredient) of the textile bath. After the application of the quaternized compound the fabric is subjected to heat for a time in the range from 5 seconds to 10 minutes, to dry and fix the applied materials. The particular time necessary for this heat application depends on the kind of fabric and can be easily determined by the skilled man in practise.

The process of the present invention is useful in dying or printing cellulosic material, preferred cotton. Despite pure cotton, the process is also applicable onto blends from cotton with other regenerated cellulosic fibres, e.g. viscose and rayon.

**[0006]** The dying and printing composition of step (A) is conventional. It contains as one ingredient a thickener which can be selected from standard thickeners, known in the art. Pigment print pastes are customarily thickened with sodium alginates or their mixtures with carboxymethylated polysaccharides or synthetic polymers based on polyacrylates. These thickeners (except synthetic polymers) provide good rheological properties at comparatively low solids contents and the softest hand among natural and biodegradable thickeners. Polysaccharide is the collective term for macromolecular carbohydrates whose molecules consist of a large number (at least >10, but usually appreciably more) glycosidically linked monosaccharide molecules (glycose). Polysaccharides include in particular the important storage biopolymers starch and glycogen and also the structural polysaccharide cellulose, which like dextran and tunicin may all be considered as a polycondensation product of D-glucose (polyglucosans, glucans), inulin as a polycondensate of D-fructose (polyfructosan, fructan), chitin, alginic acid and others. Whereas the polysaccharides mentioned each contain only one kind of building block, albeit possibly in varying glycosidic linkage, the heteropolysaccharides or heteroglycans, which occur in gums, mucilages and connective tissue in particular, consist of various kinds of monomer units. Preferred polysaccharides useful as thickeners in the subject print pastes are selected from the group of the alginates and of the unsubstituted and/or substituted galactomannans, preferably from the group of the guar derivatives and very particularly preferably are mixtures of the alkoxylated and carboxymethylated species with alginates. Alginates, as will be known, are the salts of alginic acid. Alginic acid is extracted from algae using sodium carbonate solution. The resultant sodium alginate solution is purified and can then be further used. Guar and its derivatives are likewise known compounds. They are derivatives of guar flour. Guaran, the main constituent of guar flour, is a polysaccharide which can be derivatized in various ways, for example by partial esterification or etherification of its hydroxyl groups.

**[0007]** As second compound the composition of step (A) contains in a preferred embodiment ammonia to adjust the pH of the composition. The pH range is adjusted to a level of preferably 9 to 10. Other known compounds for adjusting the pH in such pastes can be used instead of ammonia.

**[0008]** Furthermore, a binder is part of this composition. the binder has the effect to bind the dye particles onto the surface of the fibre. It is preferred to use acrylic acid based binders in accordance with the present invention. The process according to the invention, can be applied using dyestuffs or pigments, however, pigments and vat dyes ( indigo and indantrene dyestuffs).

**[0009]** At least water is part of the composition of step (A). this compositions are present in a thick stage and are always known as print pastes. Furthermore, agents may be added to the paste to improve the printing properties thereof e.g. diethylene glycol. Optionally, emulsifiers (e.g. Emulgator 1030, Cognis) and solvents with low or no aromatic content may also be added. Advantageously, silicone oils and vegetable oils, optionally in the presence of urea, may also be added to the print paste to enhance further the rub fastness and soft handle.

**[0010]** The aqueous solution of step (A) contains ammonia in amounts from 0.1 to 15 % by weight according to the aqueous composition, and a thickener preferably in amounts from 0.1 to 30 % by weight, a binder in amounts from 0.1 to 30 % by weight and the dyestuff in amounts from 0.1 to 20 % by weight according to the aqueous composition.

**[0011]** During the step (C) of the process according to the invention it is preferred to add a wetting agent, preferably selected from non-ionic surfactants. Additives B) according to the invention include the alkoxylated derivatives of fatty alcohols, fatty amines and fatty acids, preferably those having a degree of alkoxylation between 1 and 20 and very particularly preferably those having 3 to 8 ethylene oxide units per molecule.

**[0012]** Particular preference is given to ethoxylated fatty alcohols. Fatty alcohols are primary aliphatic alcohols of the formula  $R^1-OH$ , where  $R^1$  is an aliphatic, linear or branched hydrocarbyl radical having 6 to 22 carbon atoms and 0 and/or 1, 2 or 3 double bonds. Typical examples are hexyl alcohol, caprylic alcohol, 2-ethylhexyl alcohol, decyl alcohol, lauryl alcohol, isotridecyl alcohol, myristyl alcohol, cetyl alcohol, palmoleyl alcohol, stearyl alcohol, isostearyl alcohol, oleyl alcohol, elaidyl alcohol, petroselinyl alcohol, linolyl alcohol, linolenyl alcohol, elaeostearyl alcohol, arachyl alcohol, gadoleyl alcohol, behenyl alcohol, erucyl alcohol and brassidyl alcohol and also their technical grade mixtures which are obtained for example in the high pressure hydrogenation of technical grade methyl esters based on fats and oils or aldehydes from Roelen's oxo process and also as monomer fractions in the dimerization of unsaturated fatty alcohols. Preference is given to technical grade fatty alcohols of 12 to 18 carbon atoms, for example coco-

nut, palm, palm-kernel or tallow fat alcohol. These are converted by conventional methods under pressure and in the presence of gaseous alkoxides, preferably ethylene oxide, and acidic or alkaline catalysts into the desired alkoxyates. Alkoxyated fatty acids or amides are likewise known compounds. For the purposes of the present technical teaching, preference is given to using ethoxylated fatty alcohols whose alkyl chain contains 8 to 12 carbon atoms, and the derivatives containing between 3 and 8 ethylene oxide units in the molecule are particularly advantageous.

**[0013]** It is also possible to use alkylpolyglycosides for this purpose. Preference is further given to the use of additives of type B2), alkyl(oligo)glycosides. Alkyl- and alkenyloligoglycosides are known nonionic surfactants conforming to the formula (I)



where R is a saturated or unsaturated, branched or unbranched alkyl or alkenyl radical of 4 to 22 carbon atoms, G is a sugar radical of 5 or 6 carbon atoms and p is from 1 to 10. They are obtainable by the pertinent processes of preparative organic chemistry. Alkyl- and/or alkenyloligoglycosides are derivable from respectively aldoses and ketoses of 5 or 6 carbon atoms, preferably glucose. The preferred alkyl- and/or alkenyloligoglycosides are thus alkyl and/or alkenyloligoglucosides. The index p in the general formula (I) indicates the degree of oligomerization (DP), i.e. the distribution of mono- and oligoglycosides, and represents a number between 1 and 10. While p always has to be an integer in a given compound and here may take in particular the values  $p = 1$  to 6, the value p for a certain alkyloligoglycoside is an analytically determined arithmetic variable which usually constitutes a fractional number. Preference is given to using alkyl- and/or alkenyloligoglycosides having an average degree of oligomerization p of 1.1 to 3.0. From a performance perspective, preference is given to those alkyl- and/or alkenyloligoglycosides whose degree of oligomerization is less than 1.7 and especially between 1.2 and 1.4. The alkyl or alkenyl radical R1 can be derived from primary alcohols of 4 to 11, preferably 8 to 10, carbon atoms. Typical examples are butanol, hexyl alcohol, caprylic alcohol, decyl alcohol and undecyl alcohol and also their technical grade mixtures as obtained for example in the hydrogenation of technical grade fatty acid methyl esters or in the course of the hydrogenation of aldehydes from Roelen's oxo process. Preference is given to alkyloligoglucosides of chain length C8-C10 (DP = 1 to 3), which are obtained as first cut in the distillative separation of technical grade C8-C18 coconut fat alcohol and can be contaminated with a fraction of less than 6% by weight of C12 alcohol, and also alkyloligoglucosides based on technical grade C9/11 oxo alcohols (DP = 1 to 3). The alkyl or alkenyl radical R1 can further be derived from primary alcohols

of 12 to 22, preferably 12 to 14, carbon atoms. Typical examples are lauryl alcohol, myristyl alcohol, cetyl alcohol, palmoleyl alcohol, stearyl alcohol, isostearyl alcohol, oleyl alcohol, elaidyl alcohol, petroselinyl alcohol, arachyl alcohol, gadoleyl alcohol, behenyl alcohol, erucyl alcohol, brassidyl alcohol and also their technical grade mixtures which may be obtained as described above. Preference is given to alkyloligo-glucosides based on hydrogenated C12/14 coconut alcohol having a DP of 1 to 3. As well as the alkyl(oligo)-glycosides described above, their derivatives, for example derivatives with succinic acid, can be used as well.

**[0014]** A further embodiment of the present invention concerns the use of compounds prepared by first, reacting a dicarboxylic acid with 5 to 22 C-atoms with diethylene triamine in a molar ration of 1 : 1 at temperatures of 160 to 200 °C, whereby during the reaction the formed water is distilled off, to form a condensation product accordingly, secondly, react the product of step at temperatures between 20 and 40 °C with epichlorhydrin in a molar ratio of 1 : 1 to form a cationic quaternized product, iii) finally, add sulfuric acid and water to the product of the second step in a method for the printing or dyeing of cellulosic materials.

## Examples

### Example 1

**[0015]** A printing paste was prepared, containing water, thickener, ammonia, binder and dyestuff. This aqueous paste was applied onto a fabric from 98 % by weight cotton and 2 % by weight lycra. Subsequently, the fabric was dried. As next step according to the present invention a composition, containing the compound of step (C) was applied on a Foulard together with a wetting agent onto the fabric. afterwards, the fabric was dried at 120 °C for x minutes and then the fabric was subjected to a temperature of 140 °C for 2 minutes for fixing.

### Comparative example 1

**[0016]** A printing paste was prepared and applied as in example 1. This paste contains the binder in an amount of 2.5 times than in example 1. But, in contrast to the example of the invention, after the first drying step the fabric was subjected to a temperature of 150 °C for 6 minutes,

**[0017]** The printed fabrics of example 1 and comparative example 1 were tested in a wet rubbing fastness test. The result was, that the fabric according to the invention has a better result ( two marks) in this test than the fabric which was prepared in conventional manner, although the amount of binder was reduced and the drying time was decreased.

**[0018]** The fabrics of example 1 and comparative example 1 were additionally subjected to a washing test. The fabric was washed three times each at 60 °C for 75

minutes. The fabrics of the invention showed a better colourfastness than the fabrics according to the standard process.

#### Example 2

**[0019]** In a second sets of examples a printing paste, containing water, thickener, ammonia, binder and a black dyestuff were printed onto a single jersey fabric. Subsequently, the fabric was dried and by Foulard-application an aqueous composition according to the invention was applied. As last step the fabric was dried at 170 °C.

#### Comparative example 2

**[0020]** The process of example 2 was repeated, but without the application of the composition according to the invention. Again, the results of the washing tests showed a better result of the fabrics according to the present invention in comparison to the fabric, printed in a standard manner.

#### Claims

1. A process for the continuous dyeing and printing of cellulosic fibre material comprising the steps of

(A) applying to said cellulosic material an aqueous dyeing and printing composition, containing at least

- i) a basic material
- ii) a thickener
- iii) a binder
- iv) dyestuff

(B) dry the cellulosic material

(C) apply onto the material an aqueous composition, containing as active material a compound, prepared by

- i) first, reacting a dicarboxylic acid with 5 to 22 C-atoms with diethylene triamine in a molar ratio of 1 : 1 at temperatures of 160 to 200 °C, whereby during the reaction the formed water is distilled off, to form a condensation product accordingly,
- ii) secondly, react the product of step i) at temperatures between 20 and 40 °C with epichlorhydrin in a molar ratio of 1:1 to form a cationic quaternized product,
- iii) finally, add sulfuric acid and water to the product of step ii)

(D) subject the cellulosic material to tempera-

tures between 120 to 180 °C for a time period of between 5 seconds to 10 minutes for fixing

2. A process according to claim 1, characterised that ammonia is used as basic material.

3. A process according to claims 1 and 2, **characterised in that** the fibre material is cotton.

4. A process according to claims 1 to 3, **characterised in that** the fibre material is a blend of cotton with regenerated cellulosic fibre materials such as viscose and rayon.

5. A process according to claims 1 to 4, **characterised in that** the dicarboxylic acid in step (C) i) is adipic acid.

6. A process according to claims 1 to 5, **characterised in that** the temperature in step (C) i) is adjusted in the range of 160 to 180 °C.

7. A process according to claims 1 to 6, **characterised in that** the binder is an acrylic acid polymer based binder.

8. A process according to claims 1 to 7, **characterised in that** the thickener is based on polysaccharides, preferably carboxymethylated polysaccharides and / or synthetic polymer such as polyacrylates.

9. A process according to claims 1 to 8, **characterised in that** the wetting agent is selected from the groups of non-ionic surfactants, preferably selected from ethoxylated fatty alcohols, fatty amines and fatty acids, having a degree of ethoxylation of 1 to 20.

10. A process according to claims 1 to 9, **characterised in that** the wetting agent is selected from alkyl(oligo)glycosides of the formula  $R-O[G]_p$  where R is a saturated or unsaturated alkyl radical of 1 to 6 carbon atoms, G is a glycoside radical and p is 1 to 10.

11. A process according to claims 1 to 10, **characterised in that** the compound of step (C) is used in combination with a wetting agent.

12. A process according to claims 1 to 11, characterised applying the compound as defined in step (C) in amounts of 1 to 25 g/l (active ingredient) of the aqueous composition.

13. Process according to claims 1 to 12, **characterised in that** the aqueous solution of step (A) contains ammonia in amounts from 0.1 to 15 % by weight according to the aqueous composition.

14. Process according to claims 1 to 13, **characterised**

**in that** the aqueous solution of step (A) contains a thickener in amounts from 0.1 to 30 % by weight according to the aqueous composition.

**15.** Process according to claims 1 to 14, **characterised in that** the aqueous solution of step (A) contains a binder in amounts from 0.1 to 30 % by weight according to the aqueous composition. 5

**16.** Process according to claims 1 to 15, **characterised in that** the aqueous solution of step (A) contains the dyestuff (pigment ) in amounts from 0.1 to 20 % by weight according to the aqueous composition. 10

**17.** Use of a compound, prepared by 15

i) first, reacting a dicarboxylic acid with 5 to 22 C-atoms with diethylene triamine in a molar ratio of 1 : 1 at temperatures of 160 to 200 °C, whereby during the reaction the formed water is distilled off, to form a condensation product accordingly, 20

ii) secondly, react the product of step i) at temperatures between 20 and 40 °C with epichlorhydrin in a molar ratio of 1 : 1 to form a cationic quaternized product, 25

iii) finally, add sulfuric acid and water to the product of step ii)

in processes for the printing or dyeing of cellulosic materials. 30

35

40

45

50

55



European Patent  
Office

# EUROPEAN SEARCH REPORT

Application Number  
EP 02 00 9409

| DOCUMENTS CONSIDERED TO BE RELEVANT                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                    |                                                                                                                                                 |                                                              |                                              |
|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-------------------------------------------------------------------------------------------------------------------------------------------------|--------------------------------------------------------------|----------------------------------------------|
| Category                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                               | Citation of document with indication, where appropriate, of relevant passages                                                                   | Relevant to claim                                            | CLASSIFICATION OF THE APPLICATION (Int.Cl.7) |
| X                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                      | US 4 531 946 A (CHRISTIE NICK J ET AL)<br>30 July 1985 (1985-07-30)                                                                             | 17                                                           | D06P5/06                                     |
| Y                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                      | * column 1, line 40 - column 2, line 52 *<br>* column 7, line 1 - line 28 *<br>* column 9, line 17 - line 21 *<br>* examples I-III *<br>---     | 1-16                                                         | D06P5/08<br>D06P3/60                         |
| Y                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                      | WO 88 02043 A (BASF AUSTRALIA ;DONENFIELD HENRY (AU)) 24 March 1988 (1988-03-24)<br>* example 12 *<br>---                                       | 1-13,15,16                                                   |                                              |
| Y                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                      | US 6 007 586 A (AESCHLIMANN PETER ET AL)<br>28 December 1999 (1999-12-28)<br>* example 6 *<br>---                                               | 14                                                           |                                              |
| A                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                      | US 3 311 594 A (EARLE JR RALPH H)<br>28 March 1967 (1967-03-28)<br>* example 4 *<br>---                                                         | 1-17                                                         |                                              |
| A                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                      | WO 00 22227 A (HENKEL KGAA ;COPETE VIDAL TERESE (ES); PI SUBIRANA RAFAEL (ES))<br>20 April 2000 (2000-04-20)<br>* the whole document *<br>----- | 1-17                                                         |                                              |
|                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                        |                                                                                                                                                 |                                                              | TECHNICAL FIELDS SEARCHED (Int.Cl.7)         |
|                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                        |                                                                                                                                                 |                                                              | D06P                                         |
| The present search report has been drawn up for all claims                                                                                                                                                                                                                                                                                                                                                                                                                                                                             |                                                                                                                                                 |                                                              |                                              |
| Place of search<br><b>THE HAGUE</b>                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                    |                                                                                                                                                 | Date of completion of the search<br><b>25 September 2002</b> | Examiner<br><b>Fiocco, M</b>                 |
| CATEGORY OF CITED DOCUMENTS<br>X : particularly relevant if taken alone<br>Y : particularly relevant if combined with another document of the same category<br>A : technological background<br>O : non-written disclosure<br>P : intermediate document<br>T : theory or principle underlying the invention<br>E : earlier patent document, but published on, or after the filing date<br>D : document cited in the application<br>L : document cited for other reasons<br>& : member of the same patent family, corresponding document |                                                                                                                                                 |                                                              |                                              |

EPO FORM 1503 03.92 (P04C01)

**ANNEX TO THE EUROPEAN SEARCH REPORT  
ON EUROPEAN PATENT APPLICATION NO.**

EP 02 00 9409

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report. The members are as contained in the European Patent Office EDP file on  
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

25-09-2002

| Patent document<br>cited in search report |   | Publication<br>date | Patent family<br>member(s) | Publication<br>date |
|-------------------------------------------|---|---------------------|----------------------------|---------------------|
| US 4531946                                | A | 30-07-1985          | US 4605418 A               | 12-08-1986          |
| WO 8802043                                | A | 24-03-1988          | AU 608775 B2               | 18-04-1991          |
|                                           |   |                     | WO 8802043 A1              | 24-03-1988          |
|                                           |   |                     | BR 8707460 A               | 01-11-1988          |
|                                           |   |                     | CA 1295438 A1              | 11-02-1992          |
|                                           |   |                     | EP 0264308 A2              | 20-04-1988          |
|                                           |   |                     | JP 63120182 A              | 24-05-1988          |
|                                           |   |                     | NZ 221708 A                | 26-07-1990          |
|                                           |   |                     | US 4863483 A               | 05-09-1989          |
| US 6007586                                | A | 28-12-1999          | BR 9802332 A               | 20-07-1999          |
|                                           |   |                     | EP 0889159 A2              | 07-01-1999          |
|                                           |   |                     | JP 11071531 A              | 16-03-1999          |
|                                           |   |                     | TW 406149 B                | 21-09-2000          |
| US 3311594                                | A | 28-03-1967          | AU 431460 B                | 04-01-1973          |
|                                           |   |                     | AU 1902367 A               | 19-09-1968          |
|                                           |   |                     | BE 696106 A                | 25-09-1967          |
|                                           |   |                     | CH 484221 A                | 15-01-1970          |
|                                           |   |                     | DE 1720905 A1              | 16-06-1971          |
|                                           |   |                     | FR 1522583 A               | 05-08-1968          |
|                                           |   |                     | GB 1129065 A               | 02-10-1968          |
|                                           |   |                     | GB 1206958 A               | 30-09-1970          |
|                                           |   |                     | NL 6704330 A               | 24-09-1968          |
| WO 0022227                                | A | 20-04-2000          | DE 19846531 A1             | 20-04-2000          |
|                                           |   |                     | WO 0022227 A1              | 20-04-2000          |
|                                           |   |                     | EP 1123436 A1              | 16-08-2001          |