

# PATENT SPECIFICATION

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## (54) 1,4-DIAMINO ANTHRAQUINONE DYESTUFFS

(71) We, SANDOZ LTD., of 35 Lichtstrasse, 4002 Basle, Switzerland, a Swiss Body Corporate, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The invention relates to amino anthraquinones.

The invention provides cationic 1,4-diaminoanthraquinone dyestuffs, free from sulpho groups and in which the 4-amino group is substituted by a xylyl group and the 1-amino group is substituted by a propylene group carrying in the  $\gamma$ -position a radical of formula (a) or (b).



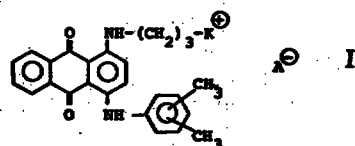
wherein

$R_1$  and  $R_2$ , independently, signify a  $C_{1-4}$  alkyl radical, and

$R_3$  is hydrogen,  $C_{1-4}$  alkyl, 2-hydroxypropyl, 2-hydroxy-ethyl, allyl, benzyl or 2-aminocarbonyl-ethyl.

The anthraquinone nucleus may be further substituted by substituents not deleteriously affecting the dyeing properties of the dyestuffs. Suitable substituents are those conventional in cationic anthraquinone dyestuff chemistry. The anthraquinone nucleus, however, is preferably further unsubstituted.

The preferred compounds provided by the invention are of formula I,



in which  $K^+$  is a radical of formula (a) or (b) above, and  $A^-$  is an anion.

The methyl groups in the xylydino radical

are preferably located on the 2- and 5-, or 2- and 4-positions, particularly the latter.

$R_1$  and  $R_2$ , independently, preferably signify methyl or ethyl, more preferably both being methyl.  $R_3$  is preferably  $C_{1-4}$  alkyl or benzyl, more preferably methyl, ethyl or benzyl, and most preferably methyl.

The exact nature of the anion  $A^-$  is not critical provided, of course, it does not deleteriously affect the dyeing properties of the compounds. It is preferably non-chromophoric and is suitably an anion conventional in the cationic dyestuff art. As examples may be given the halide, e.g. chloride or bromide, anions, the sulphate, methylsulphate, ethylsulphate, aminosulphonate, perchlorate, benzenesulphonate, toluenesulphonate, oxalate, maleinate, acetate, propionate, tartrate, malate, methanesulphonate and benzoate anions as well as anions of zinc chloride double salts and of boric, citric, glycolic, diglycolic and adipic acids.

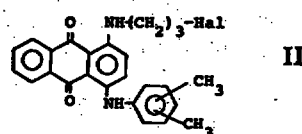
The compounds provided by the invention may be obtained by

a). reacting a 1 - halopropylamino - 4-xylydino - anthraquinone with a secondary or tertiary amine or with pyridine,

b). quaternising or protonising a 1 - amino - propylamino - 4 - xylydinoanthraquinone, or

c). reacting an anthraquinone, substituted in the 4-position by a halogen and in the 1-position by an n-propylamino group carrying in the  $\gamma$  position a radical of formula (a) or (b), with an xylydine.

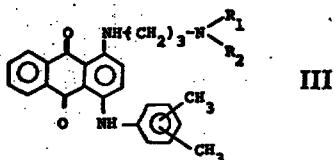
In particular, the invention provides a process for the production of compounds of formula I, stated above, by a). reacting a compound of formula II,



in which Hal signifies a halogen atom with pyridine or an amine of formula

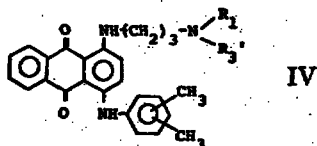


in which  $R_1$ ,  $R_2$  and  $R_3$  are as defined above,  
 bi). obtaining a compound of formula I  
 in which  $K^\oplus$  is a radical of formula (b),  
 above, by reacting a compound of formula III,

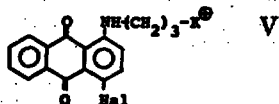


with an agent capable of generating  $R_3^\oplus$  and  
 $A^\ominus$  ions,

bii). obtaining a compound of formula I,  
 in which  $K^\oplus$  is a radical of formula (b),  
 above, in which  $R_3$  is other than hydrogen, by  
 reacting a compound of formula IV



in which  $R_3'$  has a significance of  $R_3$ , above,  
 other than hydrogen, with a compound  $R_2A$   
 in which  $A$  is a radical convertible into  
 $A^\ominus$ , or ci). reacting a compound of formula  
 V,



with a xylidine.

The above processes may be carried out in  
 conventional manner.

Thus, processes a). and ai). are suitably  
 carried out in water, in an inert organic sol-  
 vent or in a mixture of water and such a  
 solvent. A suitable reaction temperature is  
 from  $-50^\circ$  to  $+250^\circ\text{C}$ , preferably from  
 $-10^\circ$  to  $+120^\circ\text{C}$ .

Processes b), bi) and bii) are suitably  
 carried out under conventional quaternisation  
 or protonisation reaction conditions, quater-  
 nisation suitably being carried out in an inert  
 solvent, in an aqueous suspension or in an  
 excess of the quaternisation agent, optionally  
 at elevated temperatures and in buffered  
 medium. In process bi), where it is desired  
 to introduce as  $R_3$  a 2-hydroxypropyl- or 2-  
 hydroxy-ethyl group, the  $R_3^\oplus$  and  $A^\ominus$  gener-  
 ating agent is suitably propylene or ethylene  
 oxide in the presence of an acid HA; where  
 a 2-aminocarbonyl ethyl group is desired to be  
 introduced a suitable generating agent is acryl-  
 amide in the presence of an acid HA. For  
 alkyl, allyl and benzyl significances of  $R_3$ , sui-  
 table agents are compounds  $R_3A$ , especially

alkyl halides such as methyl or ethyl chloride,  
 bromide or iodide, dialkyl sulphates such as  
 dimethyl or diethyl sulphate, and allyl and  
 benzyl chlorides, the above alkyl halides and  
 dialkyl sulphate being particularly suitable  
 $R_2A$  compounds for use in process bii),  
 dimethyl sulphate being particularly preferred.  
 For the protonisation reactions such as pro-  
 cess bi) where  $R_3^\oplus$  is  $H^\oplus$ , such are suitably  
 carried out at from room temperature to  $60^\circ\text{C}$   
 in weak or strongly acid media. Suitable acids  
 as  $R_3^\oplus A^\ominus$  generating agents are acetic acid,  
 sulphuric acid and hydrochloric acid.

Processes c) and ci) are suitably carried  
 out in an inert organic solvent, e.g. an alcoholic  
 solvent such as butanol, or in a mixture of  
 water and such a solvent. Suitable reaction  
 temperatures are from  $80^\circ$  to  $150^\circ\text{C}$ , prefer-  
 ably from  $90^\circ$  to  $110^\circ\text{C}$ . The reaction is  
 advantageously carried out in the presence of  
 an acetate, such as potassium, sodium or  
 ammonium acetate and/or a copper salt.

As will be appreciated, where a compound  
 of the invention is obtained having a particu-  
 lar anion  $A^\ominus$  and it is desired to exchange  
 such for a different anion, interconversion may  
 be carried out in conventional manner, e.g.  
 using ion exchange techniques.

The resulting compounds of the invention  
 may be isolated and purified in conventional  
 manner.

The starting materials employed in the  
 above processes for the production of the com-  
 pounds of the invention are either known or  
 may be obtained from available starting  
 materials in conventional manner.

The compounds of the invention are useful  
 for the dyeing and printing of substrates dye-  
 able with basic dyes, such as comprising homo-  
 or mixed polymers of acrylonitrile or of assym-  
 metrical dicyanoethylene, of synthetic poly-  
 amides or polyesters modified by the intro-  
 duction of acid groups, as well as paper and  
 leather substrates. The above polymeric sub-  
 strates are suitable in fibre, filament or fabric  
 form. The dyeing or printing may be carried  
 out in conventional manner, e.g. textile sub-  
 strates may be dyed, for example, from an  
 aqueous neutral or acidic medium at tempera-  
 tures from  $60^\circ$  to the boil or at higher tem-  
 peratures under superatmospheric pressures.  
 Leather and paper may, for example, be dyed  
 as described in German published specifica-  
 tions 2,306,768 and 1,794,173.

The dyeings obtained on polyacrylonitrile  
 and on acid modified polyamide and polyester  
 substrates show notable fastness to washing,  
 perspiration, sublimation, ironing, dry clean-  
 ing cross-dyeing and solvents. The dyestuffs  
 themselves show good water solubility, produce  
 even dyeings, and are little affected by iron  
 and salt.

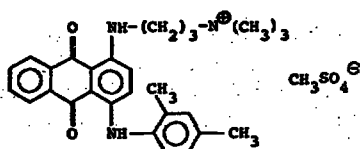
The dyestuffs are conveniently employed in  
 the form of dyeing preparations, e.g. liquid or

solid preparations which may be formed in conventional manner, e.g. grinding or granulating or by dissolution in solvents, optionally with stabilisers or solvent aids, e.g. urea. Such preparations may, for example, be produced as described in French Patent 1,572,030 and 1,381,900.

The following Examples, in which all parts and percentages are by weight and all temperatures in degrees Centigrade, illustrate the invention.

#### Example 1.

42.7 Parts of 1 - (3' - dimethylamino-propyl) - amino - 4 - (2'',4'' - dimethyl-phenyl) - amino - anthraquinone are dissolved in 400 parts of chlorobenzene at 60° and 14 parts of dimethyl sulphate are added over the course of 2 hours. The resultant dyestuff of formula



precipitates and is filtered off at 60° and dried at 80° in a vacuum after washing with chlorobenzene. The highly hydrosoluble dyestuff dyes polyacrylonitrile fibres in greenish blue shades. As well as good overall wet fastness properties the dyestuff has notable insensitivity to iron.

#### Application Example A.

20 Parts of the dyestuff described in Example 1 and 80 parts of dextrin are ground for 4 hours in a powder mill. [The same dyestuff mixture may be obtained by making a paste with 100 parts of water and subsequent spray drying]. 1 Part of the preparation thus obtained is made into a paste with 1 part of 40% acetic acid and the paste is covered with 200 parts of demineralised water and boiled for a short time. It is diluted with 7000 parts of demineralised water, 2 parts of glacial acetic acid are added and it is entered into a dye bath at 60° with 100 parts of polyacrylonitrile fabric. The material, if desired, may already have been pre-treated for 10—15 minutes at 60° in a bath consisting of 8000 parts of water and 2 parts of glacial acetic acid.

The bath is heated to 98—100° over the course of 30 minutes, held at the boil for 1.5 hours and the fabric removed and rinsed. A greenish blue dyeing is obtained, which has good light and wet fastness.

In an alternative procedure 10 parts of the dyestuff of Example 1 are dissolved in 60 parts of glacial acetic acid and 30 parts of water. The solution of the dyestuff obtained, which has a dyestuff content of about 10% may be used for dyeing polyacrylonitrile in similar manner to as described above.

#### Application Example B.

20 Parts of the dyestuff of Example 1 are mixed with 80 parts of dextrin in a ball mill for 48 hours; 1 part of the preparation thus obtained is made into a paste with 1 part of 40% acetic acid, the paste is covered with 200 parts of demineralised water and boiled for a short time. Dyeing takes place as follows using this stock solution:

a) The stock solution is diluted with 7000 parts of demineralised water, 21 parts of calcinated sodium sulphate are added, as well as 14 parts of ammonium sulphate, 14 parts of formic acid and 15 parts of a carrier based on reaction products of ethylene oxide with dichlorophenols, and the resulting dye liquor is entered into a dye bath at 60° with 100 parts of acid modified polyester fabric. The material, if desired, may already have been pre-treated for 10—15 minutes at 60° in a bath consisting of 8000 parts of water and 2 parts of glacial acetic acid. The bath is heated over the course of 30 minutes to 98—100°, held at the boil for one hour and the fabric removed and rinsed. An even greenish-blue dyeing is obtained with good wet fastness properties.

b) The stock solution is diluted with 3000 parts of demineralised water, 18 parts of calcinated sodium sulphate are added, 6 parts of ammonium sulphate and 6 parts of formic acid, and the resulting dye liquor is entered into a dye bath at 60° with 100 parts of acid modified polyester fabric. The bath is a closed vessel which is heated over the course of 45 minutes to 110°, kept at this temperature with shaking for 1 hour, then cooled over the course of 25 minutes to 60° and the dyed substrate removed and rinsed. An even greenish-blue dyeing is obtained which has good wet fastness properties.

c) The procedure is the same as for b), but the closed vessel is heated for 1 hour to 120°.

#### Application Example C.

A stock solution is prepared as in Application Example B above. The solution is diluted with 7000 parts of demineralised water, 21 parts of calcinated sodium sulphate are added, as well as 14 parts of ammonium sulphate, 14 parts of formic acid and 15 parts of a carrier based on reaction products of ethylene oxide with dichlorophenols, and the liquor is buffered with an acid buffer solution to a pH-value of 6, and is entered into a dye bath at a liquor ratio of 1:80 with 100 parts of acid modified polyamide fabric. The bath is heated to 98° over the course of 45 minutes, boiled for one hour and the fabric removed, rinsed under flowing water at 70°—80° and subsequently under cold water. The fabric is dried e.g. by spin-drying and is subsequently ironed. A greenish-blue dyeing is obtained which has good fastness properties.

## Example 2.

42.7 Parts of 1 - (3' - dimethylamino-propyl) - amino - 4 - (2'',4'' - dimethylphenyl) - aminoanthraquinone are stirred with 150 parts of water and 8 parts of 95% sulphuric acid are added. Over the course of 5 hours, 14 parts of propylene oxide are passed into the suspension which is heated to 75—80°, and the resultant quaternary dyestuff goes into solution. After stirring for 2 hours at 75—80°, a chromatogram indicates quaternisation to be practically complete. 30 Parts of sodium chloride are then added to the solution at 40° over the course of 30 minutes. In order completely to precipitate the dyestuff, the resultant suspension is stirred for a further 3 hours at 25—30°. The deposit is then suctioned off, washed with 300 parts of 10% sodium chloride solution and dried in a vacuum drying chamber.

## Example 3.

42.7 Parts of 1 - (3' - dimethylamino-propyl) - amino - 4 - (2'',4'' - dimethylphenyl) - aminoanthraquinone are dissolved in 400 parts of toluene at 80°. 11 Parts of hydrogen chloride gas are passed into this with stirring over the course of 3 hours, and the protonised product is precipitated. It is filtered off at 60°, washed out with 200 parts of toluene and vacuum dried at 80°.

## Example 4.

41.8 Parts of 4 - (3'' - chloropropyl) - amino - 1 - (2',4' - dimethylphenyl) - aminoanthraquinone are stirred in 400 parts of pyridine for 8 hours at 100—110° until the chromatogram indicates only a trace of the initial substance in a test of the reaction mixture. The resultant crystal mass is diluted with 200 parts of chlorobenzene and is subsequently filtered off at 60°. After washing out with chlorobenzene until the outflow becomes

colourless, the dyestuff is dried in a vacuum at 100°. 4 - (3'' - chloropropyl) - amino - 1 - (2',4' - dimethylphenyl) - aminoanthraquinone is produced by reacting 4 - (3'' - hydroxypropyl) - amino - 1 - (2',4' - dimethylphenyl) - aminoanthraquinone with thionyl chloride at 60—70° in chlorobenzene.

## Example 5.

50—2 Parts of N - 3- (4' - bromoanthraquinonyl - 1' - amino) - propylpyridinium bromide are stirred at 90°—100° for 8—10 hours in 200 parts of 1 - amino - 2,5-dimethylbenzene, with the addition of 19 parts of anhydrous potassium acetate and 1 part of copper sulphate. The initial red colouration of the reaction medium alters to violet and then to blue as condensation takes place. When a chromatogram indicates the end of condensation, the reaction product is diluted with 100 parts of 1,2-dichlorobenzene and the precipitated dyestuff is isolated by filtration at 60°. The residue is washed out with 1,2-dichlorobenzene and may be recrystallised from n-butanol for further purification. It is vacuum dried at 100°.

The starting material is obtained by bromination of 1 - (3' - bromopropyl) - aminoanthraquinone, e.g. in an aqueous hydrochloric acid suspension, with subsequent reaction of the product obtained with pyridine in known manner.

In the following table are given further dyestuffs of formula I which may be produced in a similar manner to those of the previous Examples. The column headed 'Q' gives the structure of the xylol group.

The dyestuffs of Examples 2—19 and 21 give greenish-blue dyeings on polyacrylonitrile and on acid modified polyester and nylon fabrics, and the dyestuff of Example 20 gives a reddish-blue dyeing on the same fabrics.

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TABLE

| Ex. No. | Q                   | K                                                              | R <sub>1</sub>                 | R <sub>2</sub>                 | R <sub>3</sub>                                   | A <sup>⊖</sup>                                              |
|---------|---------------------|----------------------------------------------------------------|--------------------------------|--------------------------------|--------------------------------------------------|-------------------------------------------------------------|
| 6       | 3,4-dimethyl-phenyl | pyridinium                                                     | —                              | —                              | —                                                | Cl <sup>⊖</sup>                                             |
| 7       | 2,5-dimethyl-phenyl | <sup>⊕</sup><br>—NR <sub>1</sub> R <sub>2</sub> R <sub>3</sub> | —CH <sub>3</sub>               | —CH <sub>3</sub>               | benzyl                                           | Cl <sup>⊖</sup>                                             |
| 8       | do.                 | do.                                                            | do.                            | do.                            | —CH <sub>2</sub> CH=CH <sub>2</sub>              | Cl <sup>⊖</sup>                                             |
| 9       | do.                 | do.                                                            | —C <sub>2</sub> H <sub>5</sub> | —C <sub>2</sub> H <sub>5</sub> | —C <sub>2</sub> H <sub>5</sub>                   | C <sub>2</sub> H <sub>5</sub> SO <sub>4</sub> <sup>⊖</sup>  |
| 10      | 2,4-dimethyl-phenyl | do.                                                            | —CH <sub>3</sub>               | —CH <sub>3</sub>               | —CH <sub>2</sub> CH(OH)CH <sub>3</sub>           | CH <sub>3</sub> COO <sup>⊖</sup>                            |
| 11      | do.                 | do.                                                            | do.                            | do.                            | —C <sub>2</sub> H <sub>4</sub> OH                | Cl <sup>⊖</sup>                                             |
| 12      | do.                 | do.                                                            | do.                            | do.                            | —C <sub>2</sub> H <sub>4</sub> CONH <sub>2</sub> | Cl <sup>⊖</sup>                                             |
| 13      | do.                 | do.                                                            | —C <sub>2</sub> H <sub>5</sub> | —C <sub>2</sub> H <sub>5</sub> | —CH <sub>3</sub>                                 | CH <sub>3</sub> SO <sub>4</sub> <sup>⊖</sup>                |
| 14      | do.                 | do.                                                            | —CH <sub>3</sub>               | —CH <sub>3</sub>               | —CH <sub>3</sub>                                 | p-toluene-sulphonate                                        |
| 15      | 3,4-dimethyl-phenyl | do.                                                            | do.                            | do.                            | —C <sub>2</sub> H <sub>5</sub>                   | C <sub>2</sub> H <sub>5</sub> —SO <sub>4</sub> <sup>⊖</sup> |
| 16      | 2,4-dimethyl-phenyl | do.                                                            | do.                            | do.                            | —CH <sub>3</sub>                                 | Br <sup>⊖</sup>                                             |
| 17      | do.                 | do.                                                            | do.                            | do.                            | do.                                              | Cl <sup>⊖</sup>                                             |
| 18      | do.                 | do.                                                            | do.                            | do.                            | —C <sub>2</sub> H <sub>5</sub>                   | C <sub>2</sub> H <sub>5</sub> —SO <sub>4</sub> <sup>⊖</sup> |
| 19      | do.                 | do.                                                            | do.                            | do.                            | benzyl                                           | Cl <sup>⊖</sup>                                             |
| 20      | 2,6-dimethyl-phenyl | do.                                                            | do.                            | do.                            | —CH <sub>3</sub>                                 | Cl <sup>⊖</sup>                                             |
| 21      | 3,5-dimethyl-phenyl | do.                                                            | do.                            | do.                            | do.                                              | Cl <sup>⊖</sup>                                             |

## WHAT WE CLAIM IS:—

1. Cationic 1,4-diamino-anthraquinone dye-stuffs, free from sulpho groups and in which the 4-amino group is substituted by a xylyl group and the 1-amino group is substituted by a propylene group carrying in the  $\gamma$ -position a radical of formula (a) or (b),



or

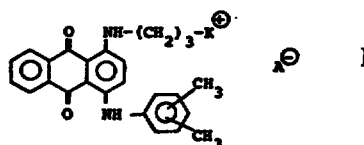


10 wherein

R<sub>1</sub> and R<sub>2</sub>, independently, signify a C<sub>1-4</sub> alkyl radical, and

15 R<sub>3</sub> is hydrogen, C<sub>1-4</sub>alkyl, 2-hydroxypropyl or 2-hydroxy-ethyl, allyl, benzyl or 2-amino-carbonyl-ethyl.

2. A compound of formula I,



in which K<sup>⊕</sup> is a radical of formula (a) or (b), defined in Claim 1, and A<sup>⊖</sup> is an anion.

3. A compound of Claim 2, wherein the methyl groups in the xylydino radical are in the 2- or 5- or in the 2- and 4-positions.

4. A compound of Claim 3, wherein said methyl groups are in the 2- and 4-positions.

5. A compound of any one of Claims 2 to 4, wherein R<sub>1</sub> and R<sub>2</sub>, independently, are methyl or ethyl.



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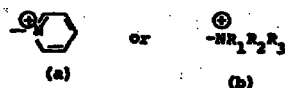
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TABLE

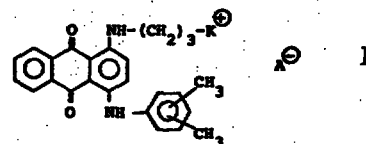
| Ex. No. | Q                   | K                                                              | R <sub>1</sub>                 | R <sub>2</sub>                 | R <sub>3</sub>                                   | A <sup>⊖</sup>                                              |
|---------|---------------------|----------------------------------------------------------------|--------------------------------|--------------------------------|--------------------------------------------------|-------------------------------------------------------------|
| 6       | 3,4-dimethyl-phenyl | pyridinium                                                     | —                              | —                              | —                                                | Cl <sup>⊖</sup>                                             |
| 7       | 2,5-dimethyl-phenyl | <sup>⊕</sup><br>—NR <sub>1</sub> R <sub>2</sub> R <sub>3</sub> | —CH <sub>3</sub>               | —CH <sub>3</sub>               | benzyl                                           | Cl <sup>⊖</sup>                                             |
| 8       | do.                 | do.                                                            | do.                            | do.                            | —CH <sub>2</sub> CH=CH <sub>2</sub>              | Cl <sup>⊖</sup>                                             |
| 9       | do.                 | do.                                                            | —C <sub>2</sub> H <sub>5</sub> | —C <sub>2</sub> H <sub>5</sub> | —C <sub>2</sub> H <sub>5</sub>                   | C <sub>2</sub> H <sub>5</sub> SO <sub>4</sub> <sup>⊖</sup>  |
| 10      | 2,4-dimethyl-phenyl | do.                                                            | —CH <sub>3</sub>               | —CH <sub>3</sub>               | —CH <sub>2</sub> CH(OH)CH <sub>3</sub>           | CH <sub>3</sub> COO <sup>⊖</sup>                            |
| 11      | do.                 | do.                                                            | do.                            | do.                            | —C <sub>2</sub> H <sub>4</sub> OH                | Cl <sup>⊖</sup>                                             |
| 12      | do.                 | do.                                                            | do.                            | do.                            | —C <sub>2</sub> H <sub>4</sub> CONH <sub>2</sub> | Cl <sup>⊖</sup>                                             |
| 13      | do.                 | do.                                                            | —C <sub>2</sub> H <sub>5</sub> | —C <sub>2</sub> H <sub>5</sub> | —CH <sub>3</sub>                                 | CH <sub>3</sub> SO <sub>4</sub> <sup>⊖</sup>                |
| 14      | do.                 | do.                                                            | —CH <sub>3</sub>               | —CH <sub>3</sub>               | —CH <sub>3</sub>                                 | p-toluene-sulphonate                                        |
| 15      | 3,4-dimethyl-phenyl | do.                                                            | do.                            | do.                            | —C <sub>2</sub> H <sub>5</sub>                   | C <sub>2</sub> H <sub>5</sub> —SO <sub>4</sub> <sup>⊖</sup> |
| 16      | 2,4-dimethyl-phenyl | do.                                                            | do.                            | do.                            | —CH <sub>3</sub>                                 | Br <sup>⊖</sup>                                             |
| 17      | do.                 | do.                                                            | do.                            | do.                            | do.                                              | Cl <sup>⊖</sup>                                             |
| 18      | do.                 | do.                                                            | do.                            | do.                            | —C <sub>2</sub> H <sub>5</sub>                   | C <sub>2</sub> H <sub>5</sub> —SO <sub>4</sub> <sup>⊖</sup> |
| 19      | do.                 | do.                                                            | do.                            | do.                            | benzyl                                           | Cl <sup>⊖</sup>                                             |
| 20      | 2,6-dimethyl-phenyl | do.                                                            | do.                            | do.                            | —CH <sub>3</sub>                                 | Cl <sup>⊖</sup>                                             |
| 21      | 3,5-dimethyl-phenyl | do.                                                            | do.                            | do.                            | do.                                              | Cl <sup>⊖</sup>                                             |

WHAT WE CLAIM IS:—

1. Cationic 1,4-diamino-anthraquinone dye-stuffs, free from sulpho groups and in which the 4-amino group is substituted by a xylyl group and the 1-amino group is substituted by a propylene group carrying in the γ-position a radical of formula (a) or (b),



2. A compound of formula I,
3. A compound of Claim 2, wherein the methyl groups in the xylylino radical are in the 2- or 5- or in the 2- and 4-positions.
4. A compound of Claim 3, wherein said methyl groups are in the 2- and 4-positions.
5. A compound of any one of Claims 2 to 4, wherein R<sub>1</sub> and R<sub>2</sub>, independently, are methyl or ethyl.



in which K<sup>⊕</sup> is a radical of formula (a) or (b), defined in Claim 1, and A<sup>⊖</sup> is an anion.

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6. A compound of Claim 5, wherein  $R_1$  and  $R_2$  are both methyl.

7. A compound of any one of Claims 2 to 6, wherein  $R_3$  is  $C_{1-4}$  alkyl or benzyl.

8. A compound of Claim 7, wherein  $R_3$  is methyl, ethyl or benzyl.

9. A compound of Claim 8, wherein  $R_3$  is methyl.

10. A compound of Claim 2, wherein the methyl groups in the xylidino radical are in 2- and 5- or in the 2- and 4-positions and  $K^\oplus$  is a radical of formula (a) or a radical of formula (b), in which  $R_1$  and  $R_2$ , independently, are methyl or ethyl and  $R_3$  is  $C_{1-4}$  alkyl or benzyl.

11. A compound of Claim 10, wherein the methyl groups in the xylidino radical are in the 2- and 4-positions, and  $K^\oplus$  is a radical of formula (b), in which  $R_1$  and  $R_2$  are both methyl and  $R_3$  is methyl, ethyl or benzyl.

12. A compound of Claim 11, wherein  $R_3$  is methyl.

13. A compound of Claim 11, wherein  $R_3$  is ethyl.

14. A compound of Claim 11, wherein  $R_3$  is benzyl.

15. A compound of Claim 10, in which said methyl groups are in the 2- and 4-positions and  $K^\oplus$  is a radical of formula (b), in which  $R_1$  and  $R_2$  are both ethyl and  $R_3$  is methyl.

16. A compound of Claim 4, wherein  $K^\oplus$  is a radical of formula (b), in which  $R_1$  and  $R_2$  are both methyl and  $R_3$  is hydrogen.

17. The compound of Claim 12, wherein  $A^\ominus$  is the methyl sulphate anion.

18. The compound of Claim 13, wherein  $A^\ominus$  is the ethyl sulphate anion.

19. The compound of Claim 14, wherein  $A^\ominus$  is the chloride anion.

20. The compound of Claim 15, wherein  $A^\ominus$  is the methyl sulphate anion.

21. The compound of Claim 16, wherein  $A^\ominus$  is the chloride anion.

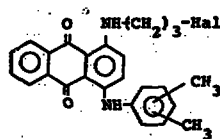
22. A compound of any one of the foregoing Examples 1 to 21.

23. A process for the production of the dyestuffs of Claim 1, which comprises reacting a 1 - halopropylamino - 4 - xylidino - anthraquinone with a secondary or tertiary amine or with pyridine.

24. A process for the production of the dyestuffs of Claim 1, which comprises quaternising or protonising a 1 - aminopropylamino - 4 - xylidino - anthraquinone.

25. A process for the production of the dyestuffs of Claim 1, which comprises reacting an anthraquinone, substituted in the 4-position by a halogen and in the 1-position by a n-propylamino group carrying in the  $\gamma$ -position a radical of formula (a) or (b) as defined in Claim 1, with a xylidine.

26. A process for the production of a compound of formula I, stated in Claim 2, comprising reacting a compound of formula II,



II

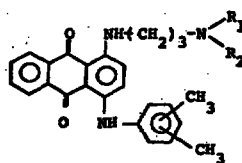
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in which Hal signifies a halogen atom with pyridine or an amine of formula



in which  $R_1$ ,  $R_2$  and  $R_3$  are as defined in Claim 1.

27. A process for the production of a compound of formula I, stated in Claim 2, comprising obtaining a compound of formula I in which  $K^\oplus$  is a radical of formula (b), defined in Claim 1, by reacting a compound of formula III,



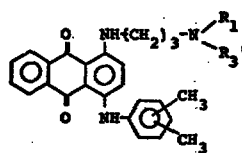
III

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with an agent capable of generating  $R_3^\oplus$  and  $A^\ominus$  ions.

28. A process for the production of a compound of formula I, stated in Claim 2, comprising obtaining a compound of formula I, in which  $K^\oplus$  is a radical of formula (b), defined in Claim 1, in which  $R_3$  is other than hydrogen, by reacting a compound of formula IV



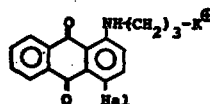
IV

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in which  $R_3'$  has the same significance as  $R_3$ , defined in Claim 1, provided that  $R_3'$  can not be hydrogen, with a compound  $R_2A$  in which A is a radical convertible into  $A^\ominus$ .

29. A process for the production of a compound of formula I, stated in Claim 2, comprising reacting a compound of formula V,



V

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with a xylidine.

30. A process according to any one of Claims 23 to 29, substantially as hereinbefore described, with reference to any one of the foregoing Examples 1 to 21.

31. A dyestuff of Claim 1, whenever obtained by a process according to any one of Claims 23 to 30.

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5 32. A process for dyeing or printing substrates comprising homo- or mixed polymers of acrylonitrile or of asymmetrical dicyanoethylene, of acid modified polyamide or polyester, or a paper or leather comprising employing, as dyestuff, a compound of any one of Claims 1 to 22 or 31.

10 33. A process according to Claim 32, substantially as hereinbefore described, with reference to any one of the foregoing Application Examples A to C.

34. Substrates comprising homo- or mixed polymers of acrylonitrile or of asymmetrical dicyanoethylene, of acid modified polyamide or polyester, paper or leather, whenever dyed or printed by the process of Claim 32 or 33.

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