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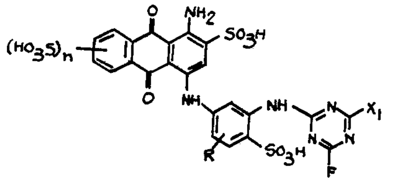
1 564 647

(54) ANTHRAQUINONE REACTIVE DYESTUFFS

(71) We, BAYER AKTIENGESELLSCHAFT, a body corporate, organised under the laws of Germany of Leverkusen, Federal Republic of Germany, 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:—

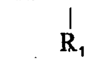
The present invention relates to reactive dyestuffs of the formula



(I)

wherein

R = H, optionally substituted C_1—C_4-alkyl, optionally substituted C_1—C_4-alkoxy or halogen,



$X = \underset{R_1}{\underset{|}{N}}—R_2$, —$OR_3$, —$SR_4$ or optionally substituted hydrazino,

wherein

R_1 = H or optionally substituted C_1—C_4-alkyl,

R_2 = H or optionally substituted C_1—C_4-alkyl; phenyl which is optionally substituted by sulpho, carboxyl, halogen, acylamino, ureido, optionally substituted C_1—C_4-alkyl or optionally substituted C_1—C_4-alkoxy; or optionally substituted naphthyl, it being possible for R_1 and R_2 together also to denote alkylene or alkylene-O-alkylene, and

R_3 and R_4 = optionally substituted alkyl, optionally substituted phenyl or optionally substituted naphthyl and

n = 0 or 1.

Preferred radicals R are, in addition to hydrogen C_1—C_4-alkyl, especially CH_3 and C_2H_5, C_1—C_4-alkoxy, especially OCH_3 as well as Cl, Br and F.

Suitable radicals R_1 are, in addition to H, for example, C_1—C_4-alkyl which is optionally substituted by OH, COOH, SO_3H or OSO_3H.

Suitable radicals R_2 are, in addition to H and the radicals mentioned for R_1, in particular phenyl which is optionally substituted by sulpho, carboxyl, chlorine, methyl, methoxy or ethoxy, ureido and sulphamoyl.

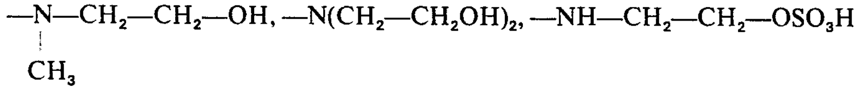
Suitable radicals R_3 are, for example, C_1—C_4-alkyl, especially —CH_3 or —C_2H_5; phenyl which is optionally substituted by sulpho, C_1—C_4-alkyl, chlorine or nitro; and optionally substituted naphthyl.

Suitable radicals R_4 are, in addition to those mentioned for R_3, for example, C_1—C_4-alkyl which is substituted by OH or COOH, such as hydroxyethyl or carboxymethyl.

Examples of substituents X which may be mentioned are:

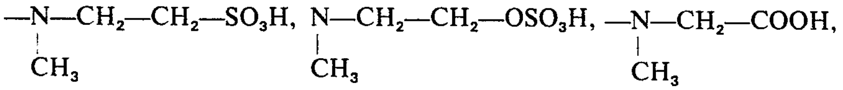
$-NH_2$, $-NHCH_3$, $-N(CH_3)_2$, $-NH-C_2H_5$, $-N(C_2H_5)_2$,

$-NH-C_3H_7$, $-NH-C_4H_9$, $-NH-CH_2-CH_2OH$,

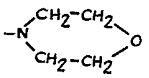


$$-\underset{\underset{CH_3}{|}}{N}-CH_2-CH_2-OH, -N(CH_2-CH_2OH)_2, -NH-CH_2-CH_2-OSO_3H$$

$-NH-CH_2-CH_2-SO_3H$, $-NH-CH_2-COOH$,

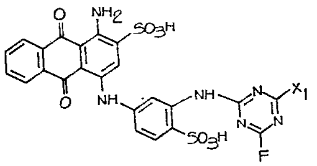


$$-\underset{\underset{CH_3}{|}}{N}-CH_2-CH_2-SO_3H,\ \underset{\underset{CH_3}{|}}{N}-CH_2-CH_2-OSO_3H,\ -\underset{\underset{CH_3}{|}}{N}-CH_2-COOH,$$



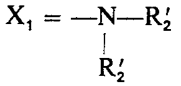
phenylamino, m- and p-sulphophenylamino, 3,4-disulphophenylamino, 3,5-disulphophenylamino, carboxyphenylamino, chloro- or methyl-phenylamino, methoxyphenylamino, ureidophenylamino, sulphamoylphenylamino, N-methyl-N-phenylamino, methoxy, ethoxy, phenoxy, sulphophenoxy, 2,4-disulpho-phenoxy, methylphenoxy, nitrophenoxy, chlorophenoxy,6-,7- or 8-sulpho-2-naphthoxy, 6,8-disulpho-2-naphthoxy, 3,6-disulpho-2-naphthoxy, methylthio, ethylthio, 2-hydroxyethylthio, carboxymethylthio, phenylthio, methylphenylthio and chlorophenylthio.

Preferred dyestuffs are those of the formula



(II)

wherein



$$X_1 = -\underset{\underset{R_2'}{|}}{N}-R_2'$$

in which

R_1' = H or CH_3 and
R_2' = C_1—C_4-alkyl which is optionally substituted by SO_3H, OSO_3H, OH or COOH;

also preferred are those dyestuffs (II)
in which

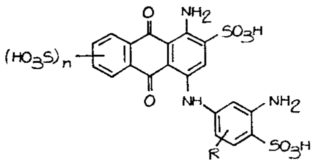
R_1' = H or CH_3,
R_2' = phenyl, carboxyphenyl, m- or p-sulphophenyl, methylphenyl, methoxyphenyl, chlorophenyl, ureidophenyl or sulphamoylphenyl and

$$\left.\begin{matrix} R_1' \\ R_2' \end{matrix}\right\} = -CH_2-CH_2-O-CH_2-CH_2-$$

and also those dyestuffs (II)
in which

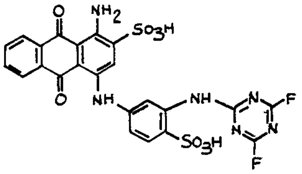
X_1 = phenoxy, sulphophenoxy, chlorophenoxy, nitro-phenoxy, methylphenoxy, sulphonaphthoxy, phenylthio, chlorophenylthio, methylphenylthio, hydroxyethylthio or carboxymethylthio.

The dyestuffs (I) are prepared in a manner which is in itself known (compare German Offenlegungsschrift (German Published Specification) 2,611,550) by reacting compounds of the formula



(III)

with cyanuric fluoride to give the compounds of the formula



(IV)

and further reacting these compounds with compounds of the formula

$$H - X \qquad (V)$$

The reaction of the compounds (III) with cyanuric fluoride is carried out in an aqueous or organic-aqueous medium at temperatures of −10° to +20°, preferably 0° to +10°, in the presence of alkaline condensing agents, such as aqueous alkali metal hydroxide, alkali metal carbonate, alkali metal bicarbonate, alkali metal phosphate or alkali metal hydrogen phosphate solutions, at pH values of 2.0—7.0, preferably 3.0—6.0.

The further reaction of the compounds (IV) with the compounds (V) is carried out at temperatures of −10° to +50°, preferably at 0° to 20°, at pH values of 3 to 10, preferably 5—9, in an aqueous or organic-aqueous medium in the presence of the alkaline condensing agents mentioned above.

It is particularly advantageous immediately to react the compounds (IV) further with the compounds (V) without intermediate isolation.

Suitable compounds (V) are for example, ammonia, methylamine, dimethylamine, ethylamine, diethylamine, propylamine, isopropylamine, butylamine, isobutylamine, 2-amino-ethanol, 2-methylaminoethanol, bis-(2-hydroxyethyl)-amine, sulphuric acid 2-aminoethyl monoester, 2-aminoethanesulphonic acid, 2-methylaminoethanesulphonic acid, aminoacetic acid, methylaminoacetic acid and morpholine, furthermore aniline, 3- or 4-aminobenzenesulphonic acid, 4-aminobenzene-1,2-disulphonic acid, 4-amino-5-methylbenzene-1,2-disulphonic acid, 5-aminobenzene-1,3-disulphonic acid, 2-, 3- or 4-aminobenzoic acid, 2-, 3- or 4-aminotoluene, 2-, 3- or 4-chloroaniline, 2-, 3- or 4-methoxyaniline, N-methylaniline, 2-, 3- or 4-aminobenzenesulphonamide, 3- or 4-aminophenylurea, N-methylaniline, 7-aminonaphthalene-1,3-disulphonic acid and 3-aminonaphthalene-1,5-disulphonic acid, and also phenol, phenol-2-, -3- or -4-sulphonic acid, phenol-2,4-disulphonic acid, 2-, 3- or 4-methylphenol, 2-, 3- or 4-chlorophenol, 2-, 3- or 4-nitrophenol, 2-naphthol-7-, -6- or -8-sulphonic acid, 2-naphthol-6,8- or -3,6-disulphonic acid, methylmercaptan, ethylmercaptan, 2-hydroxyethylmercaptan, mercaptoacetic acid, thiophenol, 2-, 3- or 4-methylthiophenol and 2-, 3- or 4-chlorothiophenol.

The new dyestuffs are extremely valuable products which are suitable for the most diverse applications. As water-soluble compounds, they are of preferred interest for dyeing textile materials containing hydroxyl groups and containing nitrogen, especially textile materials consisting of natural and regenerated cellulose and also those consisting of wool, silk and synthetic polyamide and polyurethane fibres. Because of the reactive fluorine substituent or substituents in the triazine ring, the products are particularly well suited for use as reactive dyestuffs for dyeing cellulose materials by techniques for this process which have been disclosed.

The formulae indicated in the description and examples are those of the free acids. In general, the alkali metal salts, in particular the sodium salts, are obtained.

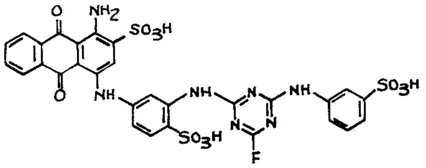
The temperature data are in °C.

Example 1.

A. 12.0 g of 1-amino-4-(3′-amino-phenylamino)-anthraquinone-2,4′-disulphonic acid are dissolved in 240 ml of water. The pH of the solution is adjusted to 4.5 with 1N disodium hydrogen phosphate solution, 3.8 g of 2,4,6-trifluoro-1,3,5-triazine are added dropwise at 0—5° in the course of 5—10 minutes and the pH value of the solution is further kept at 4.5 with the secondary phosphate solution. The reaction has ended 10 minutes after the dropwise addition of the reactive component.

B. A neutralised solution, cooled to 0—5°, or 4.8 g of 3-aminobenzenesulphonic acid in 150 ml of water is now added to the dyestuff solution and the pH value in the mixture is subsequently kept at 5.5—6.0. The condensation reaction of 3-aminobenzenesulphonic acid with the difluorotriazinyl dyestuff has ended after 3 hours.

The dyestuff solution is allowed to warm to room temperature and the dyestuff is salted out with an amount of sodium chloride such that the sodium chloride concentration in the solution is about 18%. The dyestuff which has precipitated is filtered off and washed with 500 ml of 20% strength sodium chloride solution. After drying at 40° in vacuo, a dyestuff of the formula



is obtained, which dyes cotton in blue shades, which are fast to wet processing and light, by the exhaustion process from a long liquor at 40° or by the cold pad-batch, pad-steam or pad-thermofixing process.

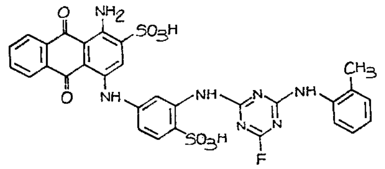
A completely analogous procedure is followed when the dyestuff intermediate product A is to be subjected to a condensation reaction with 4-aminobenzenesulphonic acid. A dyestuff with very similar properties is then obtained.

For the purpose of improved storage stability, the dyesuffs can be made into a paste with a solution of 0.6 g of sodium dihydrogen phosphate ($NaH_2PO_4 . 2H_2O$) and 0.3 g of disodium hydrogen phosphate (calcined Na_2HPO_4) in water before drying.

Example 2.

A. 10.0 g of 1-amino-4-(3′-amino-phenylamino)-anthraquinone-2,4′-disulphonic acid are dissolved in 250 ml of water, with sodium carbonate, at a pH of 4.5. 2.8 g of 2,4,6-trifluoro-1,3,5-triazine are added dropwise at 0.5° in the course of 5—10 minutes and the pH value is kept at 4.2—4.7 with 1N sodium carbonate solution. The reaction has ended 10 minutes after the dropwise addition.

B. 2.4 g of 2-aminotoluene are added to the solution of the above intermediate product and the pH value of the mixture is subsequently kept at 5.0—5.5 with sodium carbonate solution. The condensation reaction has ended after one hour at 0—5°. The resulting dyestuff is salted out with 35 g of sodium chloride at 20° and filtered off and the material on the filter is washed with 400 ml of 10% strength sodium chloride solution. The dyestuff is dried at 40° vacuo. It corresponds to the formula

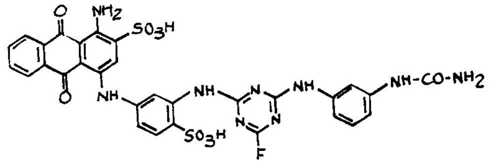


and dyes cotton in blue shades of good fastness to light and wet processing by the exhaustion process from a long liquor or by the pad processes customary in dyeing technology.

Example 3.

A. 10.0 g of 1-amino-4-(3′-amino-phenylamino)-anthraquinone-2,4′-disulphonic acid are reacted, in 250 ml of water, with 2.8 g of 2,4,6-trifluoro-1,3,5-triazine at 0—5° and a pH of 4.2—4.7 analogously to Example 2 A.

B. After the condensation reaction of the cyanuric fluoride has ended, a solution or suspension, cooled to 0—5°, of 3.3 g of 3-aminophenylurea in 200 ml of water is added to the dyestuff solution A. The condensation reaction of the dyestuff intermediate product from A with the urea component is brought to completion in 2 to 3 hours at 0—5°, maintaining a pH value of 5.5—5.8 by adding 1N sodium carbonate solution dropwise. By adding 50 g of sodium chloride to the solution at room temperature, filtering, washing the filter cake with 300 ml of 10% strength sodium chloride solution and drying, a dyestuff is obtained which corresponds to the formula

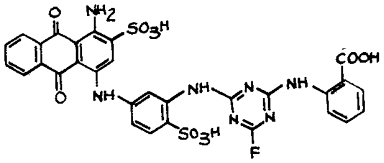


and dyes cotton in blue shades, which are fast to light and wet processing, from a long liquor by the exhaustion process.

Example 4.

A. 10.0 g of 1-amino-4-(3'-amino-phenylamino)-anthraquinone-2,4'-disulphonic acid are reacted, in 250 ml of water, with 2.8 g of 2,4,6-trifluoro-1,3,5-triazine at 0—5° and at a pH of 4.2—4.7 analogously to Example 2 A.

B. After the condensation reaction of the cyanuric fluoride has ended, a solution of 3.0 g of 2-aminobenzoic acid in 200 ml of water, which has been adjusted to pH of 6.0 and to 0—5°, is added to the dyestuff solution. The condensation reaction of the dyestuff intermediate product with 2-aminobenzoic acid is brought to completion in about 3 hours, the pH value being kept between 5.5 and 6.0 by adding 1N sodium carbonate solution dropwise. Adding 15% of potassium chloride to the dyestuff solution at 20°, filtering, washing the residue with 400 ml of 20% strength potassium chloride solution and drying in vacuo at 40° gives a dyestuff which corresponds to the formula

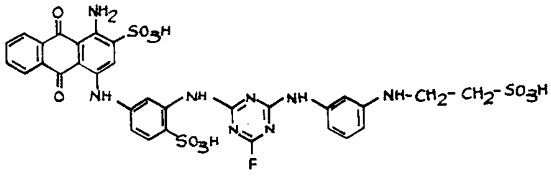


and which gives blue shades on cotton, which are fast to light and wet processing, by the dyeing techniques know for reactive dyestuffs.

Example 5.

A. 12.0 g of 1-amino-4-(3'-amino-phenylamino)-anthraquinone-2,4'-disulphonic acid are subjected to a condensation reaction, in 240 ml of water, with 3.8 g of 2,4,6-trifluoro-1,3,5-triazine at a pH of 4.2—4.7 and at 0—5°, the pH value being maintained with 1N sodium carbonate.

B. A solution which contains 3.2 g of 2-aminoethanesulphonic acid in 150 ml of water and which is adjusted to a pH of 6.5 and cooled to 0—5° is added to the solution in which the condensation reaction has ended. The pH value in the reaction mixture is kept at 6.5—6.8 with 1N sodium carbonate solution. After 3 hours, the reaction mixture is allowed to come to 20°, the product is salted out with 140 g of sodium chloride and filtered off and the dyestuff is washed with 300 ml of 20% strength sodium, chloride solution and dried at 40° in vacuo. It corresponds to the formula



and dyes cotton in blue shades, which are fast to light and to wet processing, by the exhaustion process from a long liquor and by the known pad processes.

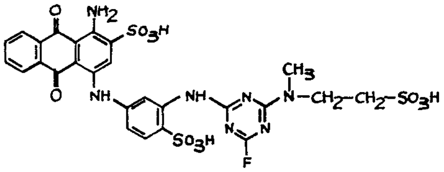
A similar dyestuff is obtained when 4.0 g of sulphuric acid 2-aminoethyl monoester are employed instead of 3.2 g of 2-amino-ethanesulphonic acid.

Example 6.

12.0 g of 1-amino-4-(3′-amino-phenylamino)-anthraquinone-2,4′-disulphonic acid are subjected to a condensation reaction with cyanuric fluoride in the manner described in Example 2 A. An aqueous solution, adjusted to a pH of 7, of 3.9 g of 2-methyl-aminoethanesulphonic acid in 40 ml of water is added to the solution of the reactive intermediate product at 0—5° and the pH value is kept at 6.5—6.8 with 2N sodium carbonate solution.

The condensation reaction has ended after about 2 hours.

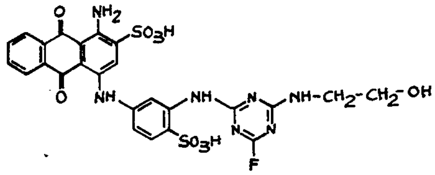
The dyestuff is now salted us at 20° and at a pH of 6.5 with 18 g of potassium chloride, filtered off and the filter lying down is washed with 5% strength potassium chloride solution. After drying in vacuo at 40°, a product is obtained which corresponds to the formula



and dyes cotton in blue shades of good fastness to light and wet processing by exhaustion processes and pad processes.

Example 7.

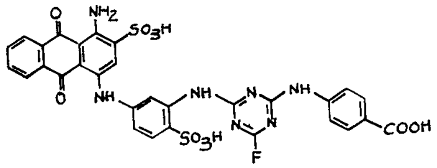
A solution of 1.7 g of 2-aminoethanol in 50 ml of water, which was previously adjusted to a pH of 7.0 with hydrochloric acid, is added to a solution of the condensation product, prepared as in Example 2A, of 12.0 g of 1-amino-4-(3′-amino-phenylamino)-anthraquinone-2,4′-disulphonic acid and 3.8 g of cyanuric fluoride in 280 ml of water, at 0—5°. The acid liberated during the reaction which sets in is buffered by adding 2N sodium carbonate solution dropwise so that a pH value of 6.5—6.8 is maintained in the reaction mixture. The reaction has ended after about 1¼ hours. The mixture is warmed to 20° and the dystuff of the formula



is salted out with 100 g of sodium chloride, filtered off and washed with 20% strength sodium chloride solution. After drying at 40° in vacuo, it dyes cellulose materials in blue shades, which are fast to light and wet processing, by the exhaustion process or the pad-steam or pad-thermofixing process.

Example 8.

A solution of 3.5 g of 4-aminobenzoic acid, which was prepared by neutralising the acid in 200 ml of water to a pH of 6.0 with 2N sodium hydroxide solution, is added to a solution of the condensation product, prepared as in Example 2 A, of 12.0 g of 1-amino-4-(3′-amino-phenylamino)-anthraquinone-2,4′-disulphonic acid and 3.8 g of cyanuric fluoride in 280 ml of water, at 0—5°. A pH value of 5.5—6.0 is maintained in the reaction mixture by adding 1N sodium carbonate solution dropwise at 0—5°. After 2¼ hours, the cooling is removed and the temperature is allowed to rise to 20. After stirring overnight, the pH of the batch is adjusted to 5.7. The dyestuff, which corresponds to the formula



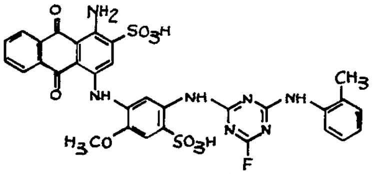
is salted out by adding 150 g of sodium chloride and stirring for a further two hours, filtered off, washed with 15% strength sodium chloride solution and dried at 40° in vacuo. It dyes cellulose materials in blue shades, which are fast to light and wet processing, by the exhaustion process or in pad or printing processes.

A similar dyestuff is obtained when 3.5 g of 3-aminobenzoic acid are employed instead of the 4-aminobenzoic acid.

Example 9.

A. 9.0 g of 1-amino-4-(3′-amino-6′-methoxy-phenylamino)-anthraquinone-2,4′-disulphonic acid are dissolved in 200 ml of water and the solution is adjusted to a pH of 4.5. After cooling to 0—5°, 2.6 g of 2,4,6-trifluoro-1,3,5-triazine are added dropwise in the course of 5 minutes and the pH value is kept at 4.2—4.5 with IN sodium carbonate solution. The mixture is subsequently stirred for a further 10 minutes, after which the condensation reaction has ended.

B. 1.9 g of o-toluidine are now allowed to run into the solution a and the pH value is adjusted to 5.5—5.7. The acid liberated during the reaction is further buffered with IN sodium carbonate solution so that a pH value between 5.5 and 6.0 is maintained. After the condensation reaction has ended, in about 1¼ hours, the reaction mixture is allowed to come to 20° and the dyestuff of the formula



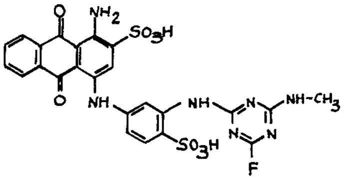
is salted out with 82 g of sodium chloride and filtered off and the product is washed with 15% strength sodium chloride solution.

After drying at 40° in vacuo, a salt-containing dyestuff is obtained which dyes cotton in slightly greenish-tinged blue shades which are fast to light and wet processing.

Example 10.

A. 10.0 g of 1-amino-4-(3′-amino-phenylamino)-anthraquinone-2,4′-disulphonic acid are subjected to a condensation reaction, in 250 ml of water, with 2.8 g of 2,4,6-trifluoro-1,3,5-triazine analogously to Example 2A.

B. After the reaction has ended, a solution, cooled to 0—5°, of 0.7 g of methylamine in 20 ml of water, the pH of which is adjusted to 6.5 with 10% strength hydrochloric acid, is allowed to run into the condensation product. The pH value is further kept at 6.5—7.0 with IN sodium carbonate solution. After the condensation reaction with methylamine has ended, after 3 hours, the mixture is warmed to 20° and the dyestuff which has formed is gradually salted out with 50 g of sodium chloride. Filtering off the precipitate, washing the filter cake with 10% strength sodium chloride solution and drying at 40° in vacuo gives a salt-containing dyestuff of the formula



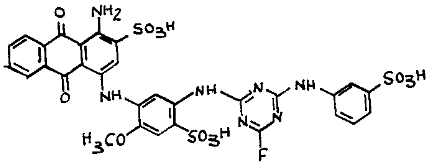
which dyes cellulose materials in blue shades.

A similar dyestuff is obtained when the intermediate product of stage A is subjected to a condensation reaction with 1.0 g of dimethylamine instead of with 0.7 g of methylamine.

Example 11.

A. 9.0 g of 1-amino-4-(3′-amino-6′-methoxy-phenylamino)-anthraquinone-2,4′-disulphonic acid are dissolved in 180 ml of water. The solution is adjusted to a pH of 4.5 by means of 2N sodium carbonate solution and cooled to 0—5°. By adding 2.6 g of 2,4,6-trifluoro-1,3,5-triazine dropwise in the course of 5 minutes and maintaining a pH value of 4.0—4.5 by means of 2N sodium carbonate solution, a condensation reaction to give the difluoro-triazinylamino dyestuff is brought about, which has ended 10 minutes after the dropwise addition of the cyanuric fluoride.

B. A neutralised solution of 3.3 g of 3-aminobenzenesulphonic acid in 70 ml of water is added to the solution thus prepared, of the intermediate product at 0—5°, the pH value of the mixture is subsequently kept at 5.5—5.8 and, after 4 hours, the temperature is allowed to rise to 20°. The dyestuff which has formed, which corresponds to the formula



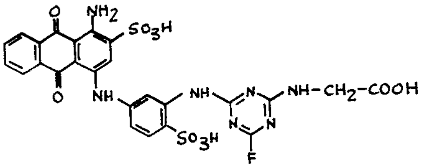
is salted out with 50 g of potassium chloride, filtered off and washed with 15% strength potassium chloride solution. After drying at 40° in vacuo, a salt-containing product is obtained which dyes cellulose fibres in greenish-tinged blue shades.

Example 12

A. 10.0 g of 1-amino-4-(3′-amino-phenylamino)-anthraquinone-2,4′-disulphonic acid are subjected to a condensation reaction, in 200 ml of water, with 2.8 g of 2,4,6-trifluoro-1,3,5-triazine analogously to Example 2 A.

B. A solution, adjusted to a pH of 6.5—6.8, of 1.6 g of aminoacetic acid in 40 ml of water is now added at 0—5° and the pH value in the reaction mixture is kept at 6.8—7.0 with 2N sodium carbonate solution.

After the condensation reaction has ended, the pH value is adjusted to 5.5—5.7 by means of hydrochloric acid, an amount of potassium chloride is added to the solution so that the content of KCl is 19—20 per cent by weight and the mixture is further stirrred at 20° overnight. The dyestuff which has been salted out is filtered off, washed with 25% strength potassium chloride solution and dried at 40° in vacuo. It corresponds to the formula



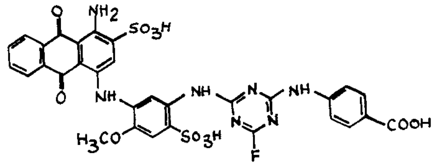
and dyes cellulose materials in blue shades which are fast to light and wet processing.

A very similar dyestuff is obtained by employing 1.9 g of N-methylaminoacetic acid instead of 1.6 g of aminoacetic acid.

Example 13.

A. 9.0 g of 1-amino-4-(3′-amino-6′-methoxy-phenylamino)-anthraquinone-2,4′-disulphonic acid are dissolved in 180 ml of water and subjected to a condensation reaction with 2.6 g of 2,4,6-trifluoro-1,3,5-triazine in the manner indicated in Example 11 A.

B. 2.4 g of 4-aminobenzoic acid are dissolved in 120 ml of water, with sodium hydroxide solution, at a pH of 6.0. After cooling to 0—5°, the solution is run into the condensation product prepared under A and the pH value is kept at 5.6—5.8 with 2N sodium carbonate solution, at 0—5°. When this second condensation reaction has ended, after about 3 hours, the batch is allowed to come to 20° and the dyestuff is salted out with 50 g of potassium chloride. The product, which corresponds to the formula



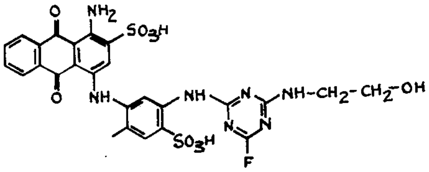
is filtered off, washed with 10% strength potassium chloride solution and dried at 40° in vacuo.

It dyes cellulose fibres in slightly greenish-tinged blue shades of excellent fastness to light and wet processing.

Example 14.

A. 9.0 g of 1-amino-4-(3′-amino-6′-methoxy-phenylamino)-anthraquinone-2,4′-disulphonic acid are reacted, in 180 ml of water, with 2.6 g of 2,4,6-trifluoro-1,3,5-triazine as in Example 11 A.

B. A solution of 1.2 g of 2-aminoethanol in 50 ml of water, which had been previously adjusted to a pH of 7.0 with hydrochloric acid and cooled to 0—5°, is added to the solution of the intermediate product formed. A pH value of 6.5—7.0 is now maintained in the mixture by means of 1N sodium carbonate solution and the condensation reaction is brought to completion by subsequently stirring for one hour. The batch is now warmed to 20° in the course of one hour, whilst further monitoring the pH, and 80 g of sodium chloride are then gradually added. The dyestuff of the formula



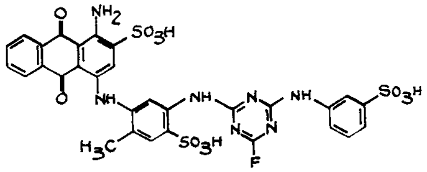
which has precipitated is filtered off and the filter cake is washes with 20% strength sodium chloride solution and dried at 40° in vacuo.

This gives a salt-containing product which dyes cellulose fibres in slightly greenish-tinged blue shades which are fast to wet processing and light.

Example 15.

A. 9.5 g of 1-amino-4-(3′-amino-6′-methyl-phenylamino)-anthraquinone-2,4′-disulphonic acid are dissolved, by neutralisation, in 200 ml of water. 2.7 g of 2,4,6-trifluoro-1,3,5-triazine are added dropwise at 0—5° in the course of 5 minutes and the pH value is kept at 4.2—4.7 by means of 2N sodium carbonate solution. The reaction has ended 10 minutes later.

B. A solution of 3.5 g of 3-aminobenzenesulphonic acid in 100 ml of water, which is adjusted to a pH of 6 and cooled to 0—5°, is added to the solution A. The pH value is kept at 5.5—5.8 by adding 2N sodium carbonate solution dropwise and the temperature is allowed to rise to 20° after 3 hours. The dyestuff of the formula



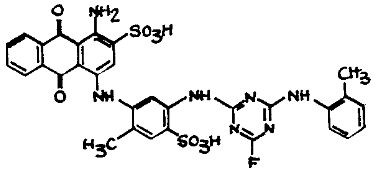
which has formed is salted out with 100 g of sodium chloride, filtered off and washed with 20% strength sodium chloride solution. After drying at 40° in vacuo, a product is obtained which dyes cotton in blue shades which are fast to wet processing and light.

Example 16.

A. 9.5 g of 1-amino-4-(3′-amino-6′-methoxy-phenylamino)-anthraquinone-2,4′-disulphonic acid are subjected to a condensation reaction, in 200 ml of water, with

2.7 g of 2,4,6-trifluoro-1,3,5-triazine at 0—5° and at a pH of 4.2—4.7 as in Example 15 A.

B. 2.1 g of 2-aminotoluene are added to the solution, in which the condensation reaction has ended, and the pH value is kept at 5.5—6.0 with 1N sodium carbonate solution at 0—5°. 2 hours later, the dyestuff of the formula



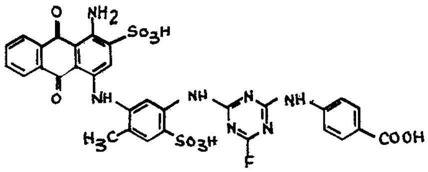
which has formed is salted out with 40 g of sodium chloride at 20° and filtered off and the filter cake is washed with 10% strength sodium chloride solution. Drying at 40° in vacuo gives a salt-containing dyestuff which dyes cellulose materials in blue shades of good fastness to light and wet processing.

A similar dyestuff is obtained if 1.9 g of aniline are employed instead of the 2-aminotoluene.

Example 17.

A. 9.5 g of 1-amino-4-(3′-amino-6′-methyl-phenylamino)-anthraquinone-2,4′-disulphonic acid are subjected to a condensation reaction, in 200 ml of water, with 2.7 g of 2,4,6-trifluoro-1,3,5-triazine at 0—5° and at a pH of 4.2—4.7 analogously to Example 15.

B. A solution, adjusted to a pH of 6, of 2.7 g of 4-aminobenzoic acid in 130 ml of water is added to the resulting solution at 0—5° and the pH value in the mixture is kept at 5.7—6.0 with 2N sodium carbonate solution. After 3 hours, the mixture is warmed to 20° and the dyestuff is salted out with 75 g of potassium chloride and filtered off. After washing with 15% strength potassium chloride solution and drying at 40° in vacuo, a product corresponding to the formula

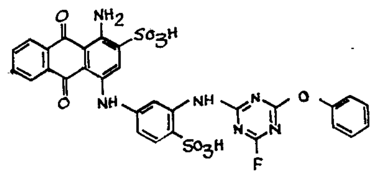


is obtained which dyes cotton in blue shade which are fast to light and wet processing.

Example 18.

A. 10.0 g of 1-amino-4-(3′-amino-phenylamino)-anthraquinone-2,4′-disulphonic acid are subjected to a condensation reaction with 2.8 g of 2,4,6-trifluoro-1,3,5-triazine in the manner described in Example 2 A.

B. A solution of 1.9 g of phenol in 30 ml of water, which is adjusted to pH 7.5 with sodium hydroxide solution, is allowed to run into the dissolved reactive intermediate product at 0—5°. The pH value is kept at 7.3—7.7 with 1N sodium carbonate. The replacement of one fluorine atom by the phenoxy group is completed after about 4 hours. The dyestuff solution is warmed to 20° and 300 ml of saturated potassium chloride, solution are added dropwise. The dyestuff which has precipitated is filtered off and washed with 10% strength potassium chloride solution and made into a paste with a solution of 0.6 g of sodium dihydrogen phosphate (NaH_2HPO_4) and 0.3 g of disodium hydrogen phosphate (calcined Na_2HPO_4). The dyestuff, which corresponds to the formula



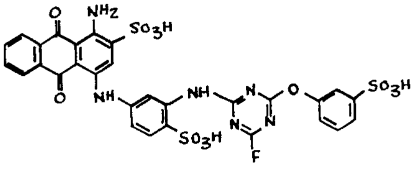
dyes cellulose fibres in blue shades, which are fast to light and wet processing, by exhaustion or pad processes.

Example 19.

A. 10.0 g of 1-amino-4-(3′-amino-phenylamino)-anthraquinone-2,4′-disulphonic acid are subjected to a condensation reaction, in 100 ml of water, with 2.8 g of cyanuric fluoride in the manner described in Example 2 A.

B. A solution, adjusted to a pH of 7.5 with 4N sodium hydroxide solution, of 3.6 g of phenol-3-sulphonic acid in 35 ml of water is added to the solution of the intermediate product at 0—5°. The pH value is kept at 7.5—8.0 with 15% strength sodium carbonate solution and the condensation reaction is brought to completion in the course of 4 hours. The very slightly soluble dyestuff is now precipitated by adding isopropanol and filtered off and the mother liquor is removed by means of isopropanol.

The dyestuff is triturated with 0.6 g of sodium dihydrogen phosphate ($NaH_2PO_4 . 2H_2O$) and 0.3 g of disodium hydrogen phosphate (calcined Na_2HPO_4) in 10 ml of water and dried at 40° in vacuo. It corresponds to the formula



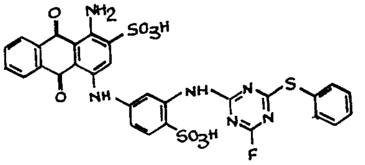
and dyes cellulose fibres in blue shades, which are fast to light and wet processing, by exhaustion or pad processes.

A similar dyestuff is obtained when 3.6 g of phenol-4-sulphonic acid are employed instead of the phenol-3-sulphonic acid.

Example 20.

A. 10.0 g of 1-amino-4-(3′-amino-phenylamino)-anthraquinone-2,4′-disulphonic acid are dissolved in 200 ml of water and, after adjusting the pH value to 4.5 by means of 2N sodium carbonate solution, are reacted analogously to Example 2 A by adding 2.8 g of 2,4,6-trifluoro-1,3,5-triazine dropwise at 0—5°.

B. When this first condensation reaction has ended, 1.8 ml of thiophenol are allowed to run in at 0—5° and the pH value is kept at 6.8—7.3 with 2N sodium carbonate solution. When the reaction has ended, after about 1 hour, 150 ml of saturated potassium chloride solution are added dropwise to the resulting solution, a further 25 g of potassium chloride are added and the precipitate is filtered off. The filter cake is washed with 15% strength potassium chloride solution, triturated with a solution of 0.6 g of sodium dihydrogen phosphate ($NaH_2PO_4 . 2H_2O$) and 0.3 g of disodium hydrogen phosphate (calcined Na_2HPO_4) in 10 ml of water and dried at 40° in vacuo. The dyestuff, which corresponds to the formula

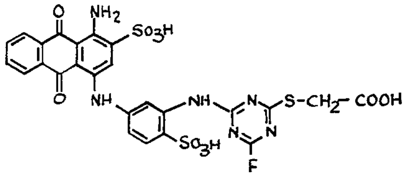


dyes cellulose materials in blue shades which are fast to wet processing and light.

Example 21.

A. 10.0 g of 1-amino-4-(3′-amino-phenylamino)-anthraquinone-2,4′-disulphonic acid are subjected to a condensation reaction, in 100 ml of water, with 2.8 g of 2,4,6-trifluoro-1,3,5-triazine at 0—5° and a pH of 4.5 analogously to Example 2 A.

B. A solution, adjusted to a pH of 7 with sodium hydroxide solution, of 1.8 g of thioglycolic acid in 10 ml of water is added to the solution of the reactive intermediate product at 0—5° and the pH value is kept at 6.7—7.0 with 2N sodium carbonate solution. After 5¼ hours, the temperature is allowed to rise to 20°. the pH value is adjusted to 4.5 with hydrochloric acid and the solution is saturated with potassium chloride. The precipitated dyestuff of the formula

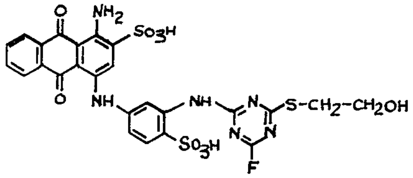


is filtered off, washed with slightly saturated potassium chloride solution and made into a paste with a solution of 0.5 g of sodium dihydrogen phosphate dihydrate and 0.5 g of anhydrous disodium hydrogen phosphate in 10 ml of water. After drying in vacuo at 40°, a product is obtained which dyes cotton in blue shades which are fast to wet processing and light.

Example 22.

A. 10.0 g of 1-amino-4-(3'-amino-phenylamino)-anthraquinone-2,4'-disulphonic acid are reacted with 2.8 g of 2,4,6-trifluoro-1,3,5-triazine at 0—5° and at a pH of 4.2—4.5 analogously to Example 2 A.

B. A solution of 1.6 g of 2-mercaptoethanol in 30 ml of water, which is adjusted to a pH of 6.5, is slowly added dropwise to the resultilng solution at 0—5° and the pH value of the reaction mixture is kept at 6.5—6.8 with 2N sodium carbonate solution. The reaction has ended after 2 hours. The dissolved dyestuff of the formula

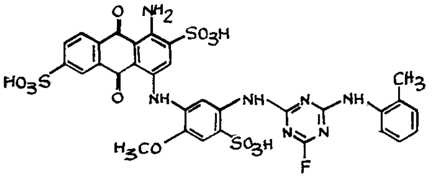


is salted out with 65 g of sodium chloride, the precipitate is filtered off and the filter cake is washed with 10% strength sodium chloride solution. The filter cake is made into a paste with a solution of 0.6 g of sodium dihydrogen phosphate dihydrate and 0.3 g of calcined disodium hydrogen phosphate in 10 ml of water. After drying in vacuo at 40°, a dyestuff is obtained which dyes cotton in blue shades which are fast to light and wet processing.

Example 23.

A. 12.0 g of 1-amino-4-(3'-amino-6'-methoxy-phenylamino)-anthraquinone-2,4'-trisulphonic acid are dissolved in 200 ml at a pH of 4.5.2.8 g of 2,4,6-trifluoro-1,3,5-triazine are added to the solution at 0—5° in the course of 5 minutes and the pH value is kept at 4.2—4.5 with 2N sodium carbonate solution. The condensation reaction is brought to completion in the course of a further 10 minutes.

B. 2.3 g of 2-aminotoluene are added to the solution thus obtained. This second condensation stage is brought to completion by adjusting the pH value to 5.5—5.8 and maintaining this value further with 2N sodium carbonate solution at 0—5°. After 2 hours, the solution is brought to 20° and 80 g of sodium chloride are added. The dyestuff of the formula

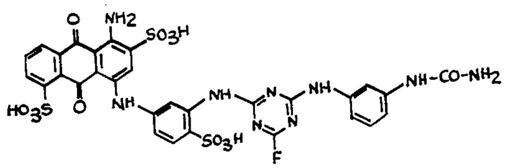


which has precipitated is filtered off and the filter cake is washed with 20% strength sodium chloride solution and dried at 40° in vacuo. The dyestuff dyes cellulose materials in greenish-tinged blue shades which are fast to light and wet processing.

Example 24.

A. 11.5 g of 1-amino-4-(3'-amino-phenylamino)-anthraquinone-2,4'-trisulphonic acid are dissolved in 200 ml of water at a pH of 4.5 and subjected to a condensation reaction with 2.9 g of trifluoro-1,3,5-triazine at 0—5°, whilst maintaining a pH value of 4.2—4.5.

B. 3.1 g of 3-aminophenylurea are dissolved in 180 ml of water at 40°. The solution is allowed to cool and is added dropwise to the solution, prepared under A, of the reactive intermediate product at 0—5°. During the dropwise addition, the pH value of the mixture is kept at 5.5—5.8 and the mixture is subsequently stirred at this pH value for a further 3 hours. The dyestuff is then salted out with 130 g of sodium chloride at 20°, filtered off and washes with 20% strength sodium chloride solution. After drying in vacuo, a dyestuff is obtained which corresponds to the formula

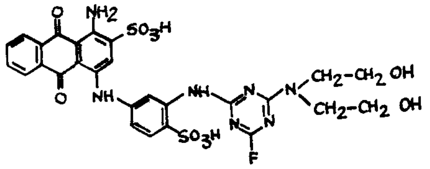


and dyes cellulose materials in slightly greenish-tinged blue shades which are fast to light and wet processing.

Example 25.

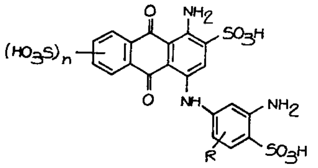
A. 10.0 g of 1-amino-4-(3'-amino-phenylamino)-anthraquinone-2,4'-disulphonic acid are subjected to a condensation reaction, at a pH of 4.5 in 150 ml of water, with 2.8 g of 2,4,6-trifluoro-1,3,5-triazine at 0—5° and at a pH of 4.2—4.7 analogously to Example 2 A.

B. A solution, adjusted to a pH of 7 with hydrochloric acid and cooled to 0—5°, of 2.2 g of bis-(2-hydroxyethyl)-amine in 20 ml of water is added to the solution, in which the condensation reaction has ended, and the pH value is kept at 6.5—6.8 with 2N sodium carbonate solution. After the condensation reaction has ended, in the course of about 1 hour, the temperature is raised to 20° and the solution is saturated with potassium chloride. The dyestuff of the formula



which has separated out is isolated from the solution and dried at 40° in vacuo. It dyes cellulose materials in blue shades which are fast to wet processing and light.

Quite analogously, further dyestuffs are obtained when the anthroquinone compounds of the general formula



wherein

R and n have the meaning illustrated in the general part

given in the left-hand column I of the table are reacted with 2,4,6-trifluoro-1,3,5-triazine and the intermediate products thus obtained are subjected to a condensation reaction with the amino, hydroxy or mercapto compound indicated in the right-hand column II of the table.

TABLE

No.	I	II	Colour shade
26	1-Amino-4-(3′-amino-phenyl-amino)-anthraquinone-2,4′-disulphonic acid	Ammonia	Blue
27	,, ,,	Aniline	,,
28	,, ,,	N-Methylaniline	,,
29	,, ,,	2-Methoxyaniline	,,
30	,, ,,	4-Methoxyaniline	,,
31	,, ,,	4-Aminotoluene	,,
32	,, ,,	3-Aminotoluene	,,
33	,, ,,	3-Amino-4-methyl-benzenesulphonic acid	,,
34	,, ,,	5-Aminobenzene-1,3-disulphonic acid	,,
35	,, ,,	2-Chloroaniline	,,
36	,, ,,	4-Chloroaniline	,,
37	,, ,,	4-Methylthiophenol	,,
38	,, ,,	4-Chlorothiophenol	,,
39	,, ,,	Ethylmercaptan	,,
40	,, ,,	Methylmercaptan	,,
41	,, ,,	4-Hydroxyphenyl-methyl sulphide	,,
42	1-Amino-4-(3′-amino-6′-methoxy-phenylamino)-anthraquinone-2,4′-disulphonic acid	4-Aminobenzene-sulphonic acid	slightly greenish-tinged blue
43	,, ,,	3-Aminobenzoic acid	,,
44	,, ,,	3-Aminobenzene sulphonamide	,,
45	,, ,,	3-Aminotoluene	,,
46	,, ,,	2-Methoxyaniline	,,
47	,, ,,	2-Aminoethane sulphonic acid	,,
48	,, ,,	2-Aminoethanol	,,

TABLE (Continued)

No.	I	II	Colour shade
49	1-Amino-4-(3'-amino-6'-methoxy-phenylamino)-anthraquinone-2,4'-disulphonic acid	Aminoacetic acid	slightly greenish-tinged blue
50	,, ,,	n-Propylamine	,,
51	,, ,,	3-Chloroaniline	,,
52	,, ,,	Diethylamine	,,
53	,, ,,	2-Naphthol-6,8-disulphonic acid	,,
54	,, ,,	1-Naphthol-4-sulphonic acid	,,
55	,, ,,	Phenol	,,
56	,, ,,	Phenol-3-sulphonic acid	,,
57	,, ,,	Phenol-4-sulphonic acid	,,
58	,, ,,	6-Aminonaphthalene-1,3-disulphonic acid	,,
59	,, ,,	Ammonia	,,
60	,, ,,	3-Aminophenylurea	,,
61	,, ,,	Thiophenol	,,
62	,, ,,	2-Hydroxyethyl-mercaptan	,,
63	,, ,,	Thioglycollic acid	,,
64	,, ,,	Ethylmercaptan	,,
65	,, ,,	4-Methylphenol	,,
66	,, ,,	2-Methylphenol	,,
67	,, ,,	Bis-(2-hydroxy-ethyl)-amine	,,
68	,, ,,	2-Methylamino-ethanesulphonic acid	,,
69	,, ,,	4-Aminobenzene-sulphonic acid	Blue
70	,, ,,	3-Aminobenzoic acid	,,

TABLE (Continued)

No.	I	II	Colour shade
71	1-Amino-4-(3′-amino-6′-methyl-phenylamino)-anthraquinone-2,4′-disulphonic acid	2-Aminobenzoic acid	Blue
72	,, ,,	3-Aminophenylurea	,,
73	,, ,,	4-Aminobenzene-sulphonamide	,,
74	,, ,,	N-Methylamino-acetic acid	,,
75	,, ,,	2-Methylamino-ethanol	,,
76	,, ,,	2-Aminoethanol	,,
77	,, ,,	2-Aminoethane-sulphonic acid	,,
78	,, ,,	2-Methylamino-ethanesulphonic acid	,,
79	,, ,,	Phenol	,,
80	,, ,,	Phenol-3-sulphonic acid	,,
81	,, ,,	Phenol-4-sulphonic acid	,,
82	,, ,,	Thiophenol	,,
83	,, ,,	Thioglycollic acid	,,
84	,, ,,	2-Hydroxyethyl-mercaptan	,,
85	,, ,,	4-Amino-5-methyl-benzene-1,2-disulphonic acid	,,
86	1-Amino-4-(3′-amino-phenylamino)-anthra quinone-2,4′-disulphonic acid	3-Aminobenzene-sulphonamide	,,
87	,, ,,	Morpholine	,,
88	,, ,,	4-Amino-5-methyl-benzene-1,2-disulphonic acid	,,
89	,, ,,	Cyclohexylamine	,,

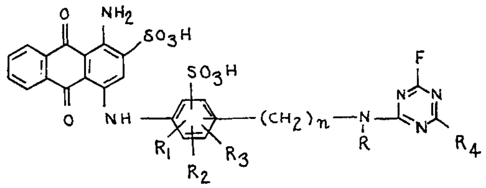
TABLE (Continued)

No.	I	II	Colour shade
90	1-Amino-4-(3'-amino-phenylamino)-anthraquinone-2,4'-disulphonic acid	n-Butylamine	Blue
91	,, ,,	2-Methylamino-ethanol	,,
92	,, ,,	4-Aminobenzene-sulphonamide	,,
93	,, ,,	Piperidine	,,
94	,, ,,	3-Nitroaniline	,,
95	,, ,,	Isopropylamine	,,
96	,, ,,	2-Aminobenzoic acid ethyl ester	,,
97	,, ,,	4-Aminobenzamide	,,
98	,, ,,	4-Methylphenol	,,
99	,, ,,	3-Methylphenol	,,
100	,, ,,	2-Chlorophenol	,,
101	,, ,,	4-Chlorophenol	,,
102	,, ,,	3-Nitrophenol	,,
103	,, ,,	4-Nitrophenol	,,
104	,, ,,	2-Nitrophenol	,,
105	,, ,,	7-Aminonaphthalene-1,3-disulphonic acid	,,
106	,, ,,	3-Aminonaphthalene-1,5-disulphonic acid	,,
107	,, ,,	2-Naphthol-6-sulphonic acid	,,
108	,, ,,	2-Naphthol-7-sulphonic acid	,,
109	,, ,,	3-Aminoglycollic acid anilide	,,
110	,, ,,	2-Amino-5-sulpho-benzoic acid	,,
111	1-Amino-4-(3'-amino-2'-methylphenylamino)-anthraquinone-2,4'-disulphonic acid	2-Aminotoluene	,,

TABLE (Continued)

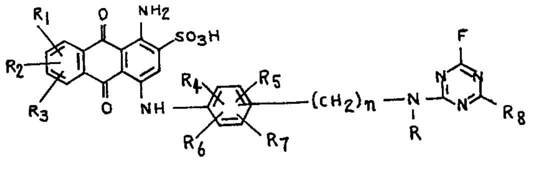
No.	I	II	Colour shade
112	1-Amino-4-(3'-amino-2'-methylphenylamino)-anthraquinone-2,4'-disulphonic acid	3-Aminobenzene-sulphonic acid	Blue
113	1-Amino-4-(3'-amino-phenylamino)-anthraquinone-2,4',6-tri-sulphonic acid	Aniline	slightly greenish-tinged blue
114	,, ,,	2-Aminoethanol	,,
115	,, ,,	3-Aminobenzene-sulphonamide	,,
116	,, ,,	Phenol	,,
117	,, ,,	Thiophenol	,,
118	,, ,,	2-Hydroxyethyl-mercaptan	,,
119	1-Amino-4-(3'-amino-phenylamino)-anthraquinone-2,4',7-tri-sulphonic acid	2-Aminotoluene	,,
120	,, ,,	3-Aminophenylurea	,,
121	1-Amino-4-(3'-amino-6'-methoxy-phenylamino)-anthraquinone-2,4',6-trisulphonic acid	2-Aminotoluene	greenish-tinged blue
122	,, ,,	4-Chloroaniline	,,
123	1-Amino-4-(3'-amino-phenylamino)-anthraquinone-2,4',5-tri-sulphonic acid	4-Aminobenzoic acid	slightly greenish-tinged blue
124	,, ,,	Bis-(2-hydroxy-ethyl)-amine	,,
125	,, ,,	Thioglycollic acid	,,
126	,, ,,	2-Methoxyaniline	,,
127	1-Amino-4-(3'-amino-6'-chloro-phenylamino)-anthraquinone-2,4'-disulphonic acid	3-Aminobenzene-sulphonic acid	Blue
128	,, ,,	2-Aminotoluene	,,
129	,, ,,	4-Aminobenzoic acid	,,

Our Patent, 1,177,437 describes and claims anthraquinone reactive dyestuffs of the formula



in which R_1, R_2 and R_3 represent independently of one another, hydrogen or alkyl, alkoxy or halogen substituents, n is the number 0, 1 or 2, R stands for hydrogen or for an alkyl group having 1 to 5 carbon atoms, F represents a fluorine substituent, and R_4 stands for an amino or hydrozino group or a hydrocarbon radical which may be linked via 0, N or S and which may be further substituted.

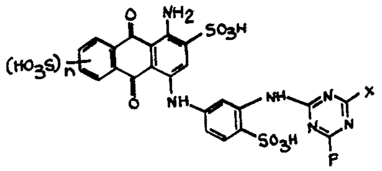
Our Patent 1,181,744 describes and claims anthroquinone reactive dyestuffs of the formula



in which R_1 and R_2 represents, independently of one another, hydrogen or substituents, R_3 stands for a substituent, R_4 to R_7 stand, independently of one another, for hydrogen or substituents, n is the number 0, 1 or 2, R stands for hydrogen or for a substituent, F represents a fluorine substituent, and R_8 stands for an amino or hydrazino group or a hydrocarbon radical which may be linked via 0, N or S and which may be further substituted.

WHAT WE CLAIM IS:—

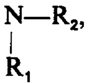
1. A reactive dyestuff of the general formula



(I)

in which

R denotes a hydrogen atom, an optionally substituted C_1 to C_4 alkyl group, on optionally substituted C_1 to C_4 alkoxy group or a halogen atom;
X denotes a

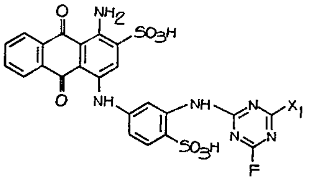


$$\underset{\displaystyle R_1}{\overset{}{N}}\!-\!R_2,$$

$—OR_3$, $—SR_4$ or optionally substituted hydrozino group,
in which

R_1 denotes a hydrogen atom or an optionally substituted C_1 to C_4 alkyl group,
R_2 denotes a hydrogen atom, an optionally substituted C_1 to C_4 alkyl group; a phenyl radical which is optionally substituted by sulpho, carboxyl, halogen, ureido, acylamino, optionally substituted C_1 to C_4 alkyl or optionally substituted naphthyl radical; or R_1 and R_2 together denote an alkylene or alkylene-O-alkylene radical, and
R_3 and R_4 independently denote an optionally substituted alkyl, phenyl or naphthyl radical and
n is 0 or 1.

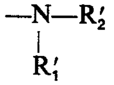
2. A reactive dyestuff of the general formula



(II)

in which

X_1 denotes a



$$\begin{array}{l}-\mathrm{N}-\mathrm{R}_2' \\ \;\;\;| \\ \;\;\mathrm{R}_1'\end{array}$$ radical

in which

R_1' denotes a hydrogen atom or a methyl group,

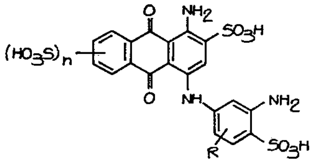
R_2' denotes a C_1 to C_4 alkyl group which is optionally substituted by SO_3H, OSO_3H, OH or COOH; or a phenyl, carboxyphenyl, m- or p-sulphophenyl, methylphenyl, methoxyphenyl, chlorophenyl, ureidophenyl or sulphamoylphenyl radical, or

R_1' and R_2' together denote a $—CH_2—CH_2—O—CH_2—CH_2—$ radical, or

X_1 denotes a phenoxy, sulphophenoxy, chlorophenoxy, nitrophenoxy, methylphenoxy, sulphonaphthoxy, phenylthio, chlorophenylthio, methylphenylthio, hydroxyethylthio or carboxymethylthio radical.

3. A reactive dyestuff according to claim 1, as hereinbefore specifically identified.

4. A process for the production of a reactive dystuff as claimed in claim 1, comprising reacting a compound of the general formula



(III)

in which r and n have the same meanings as in claim 1, with cyanuric fluoride, and then reacting the product with a compound of the general formula H—X (V) in which X has the same meaning as in claim 1.

5. A process according to claim 4, in which the compound of formula (V) is any of those hereinbefore specifically mentioned.

6. A process for the production of a reactive dyestuffs as claimed in claim 1, when carried out substantially as described in any one of the Examples.

7. A reactive dyestuff as claimed in claim 1, when produced by the process of any of claims 4 to 6.

8. A process for dyeing or printing a material containing hydroxyl groups or nitrogen comprising treating the material with a reactive dyestuff as claimed in any of claims 1 to 3 and 7.

9. A material containing hydroxyl groups or nitrogen when dyes or printed by the process of claim 8.

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