

PATENT SPECIFICATION

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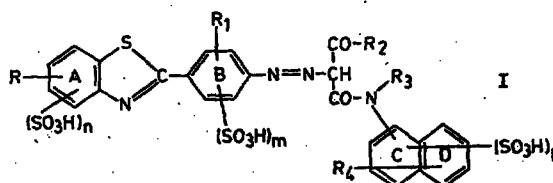
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(54) AZO DYES, THEIR PRODUCTION AND USE

(71) We, SANDOZ LTD., of 35 Lichtstrasse, 4000 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 present invention relates to azo dyes.

According to the present invention, there are provided monoazo dyes of formula I,



in which

R, R₁ and R₂, which may be the same or different, each signify a hydrogen atom, an alkyl radical of 1 to 6 carbon atoms or an alkoxy radical of 1 to 6 carbon atoms,

R₃ signifies an alkyl radical of 1 to 6 carbon atoms;

R₄ signifies a hydrogen atom or an alkyl radical of 1 to 6 carbon atoms, rings A, B, C and D may be further substituted,

n signifies 0 or 1

m signifies 0 or 1, and

p signifies 0 to 3

with the proviso that the compounds contain at least one sulphonic acid group; and water-soluble salts thereof.

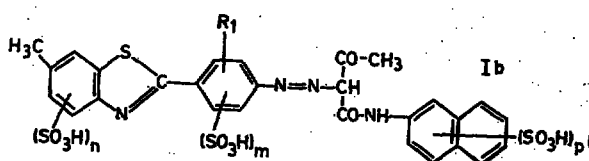
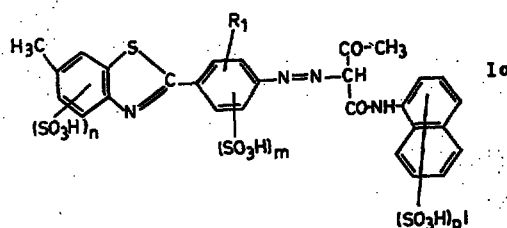
The water-soluble salts of the compounds of formula I may, for example, be the alkali-metal or ammonium salts thereof, preferably sodium salts.

In the compounds of formula I, any alkyl or alkoxy radicals are preferably of 1 to 3 carbon atoms, R is preferably in the *para* position to the nitrogen atom and most preferably signifies a methyl radical. R₁ and R₂ preferably signify a hydrogen atom. R₃ most preferably signifies a methyl radical. R₄ preferably signifies a hydrogen atom or a methyl or ethyl radical.

The preferred compounds of formula I have 2 to 4 sulphonic acid groups if ring D bears 2 such groups, or 2 or 3 sulphonic acid groups if ring D bears only 1 such group.

The further substituents in rings A, B, C and D may, for example, be halogen atoms or nitro, cyano, carboxylic acid or substituted or unsubstituted amino groups. The preferred compounds of formula I, however, contain no such further substituents.

Representative of the compounds of formula I are the compounds of formulae Ia and Ib,

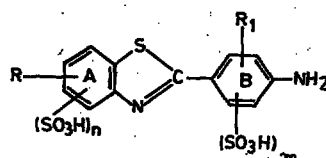


in which formulae,

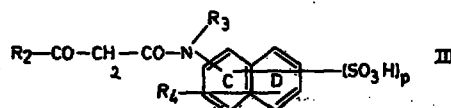
R_1 , n and m are as defined above and
 p' is 1 to 3.

Preferred compounds of formula Ia and Ib, are those in which R_1 signifies a hydrogen atom.

The invention also provides a process for the production of a compound of formula I, stated above, characterised by reacting a diazo derivative of an amine of formula II,



in which R , R_1 , n , m and rings A and B are as defined above in connection with formula I, with a compound of formula III,



in which R_2 , R_3 , R_4 , p and rings C and D are as defined above in connection with formula I.

The reaction may be carried out according to known methods, for example in an aqueous, weakly acid, neutral or alkaline medium, preferably in a neutral to weakly alkaline medium. Similarly, the diazo derivative of the amine of formula II may be obtained in known manner.

The amines of formula II, as defined above, are either known or can be produced in analogous manner to that for known compounds, for example as described in *Berichte* 22 (1889) 970, *Annalen* 558, 16 (1947) or German Patent No. 281,048.

Similarly, the compounds of formula III are known or can be produced in analogous manner to that for known compounds, for example, as described in German Patent No. 749,975 or in U.S. Patent No. 2,328,353.

The water-soluble salts of the compounds of formula I may be obtained in manner known *per se*, for example by carrying out the reaction in the presence of, or by treating the resulting compounds of formula I with, an ammonium hydroxide or aqueous alkali metal salt solution. Alternatively, salt forms of the compounds of formulae II and III may be used.

The compounds of formula I and the water-soluble salts thereof may be isolated in manner known *per se*.

The compounds of formula I and the water-soluble salts thereof possess good solubility properties, having notably good solubility in cold water.

The invention also provides a process for dyeing paper, characterised by applying to the paper a compound of formula I or a water-soluble salt thereof.

The compound of formula I or water-soluble salt thereof may be added to the paper stock as dry powder or as granules, or the paper, insized or unsized sheet form may be dyed by dipping methods using a solution or dispersion of the compound of formula I or water-soluble salt thereof.

Preferably, after the paper has been dyed, it is treated with a cationic fixing agent, for example, with one of such agents disclosed in French Patent No. 956,501 or in German Patents Nos. 671,704 and 918,743.

The dry powder or granule form of the dye may be produced by known methods, for example as described in French Patent No. 1,581,900. The granulated form preferably contains, in addition to the compound of formula I or water-soluble salt thereof, 0.1% to 50% by weight of a salt which dissociates in water, e.g. sodium chloride or sodium sulphate, the average size of the granules being at least 20 microns.

The solution or dispersion of the compound of formula I or water-soluble salt thereof is preferably obtained by diluting a liquid dye concentrate preparation which contains one part by weight of a dye component, two to eight parts by weight of water and 0.5 to 5 parts by weight of an acid amide, the dye component containing 0.5 to two parts by weight of an alkali metal salt to ten parts by weight of a compound of formula I or water-soluble salt thereof.

The alkali metal salt may, for example, be sodium chloride or sodium sulphate.

The acid amide is preferably a carboxylic acid amide of 1 to 4 carbon atoms, for example urea.

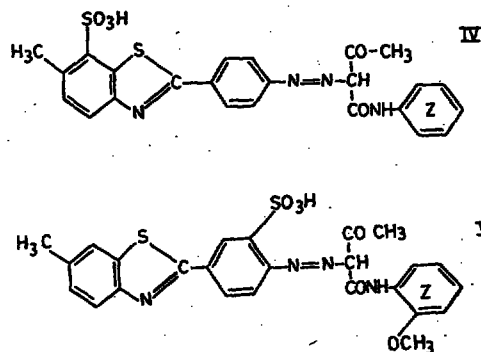
The above described liquid dye concentrate preparation forms part of the present invention and is particularly suitable for use in dyeing paper, it being stable in storage for notably long periods. It may be obtained by mixing the stated ingredient, if necessary heat being applied to aid the mixing. Preferably the preparation is prepared from an aqueous press-cake, as obtained in manufacture, containing 0.5 to 2 parts by weight of the alkali-metal salt to ten parts by weight of the compound of formula I or water-soluble salt thereof.

Preferably, the press-cake and the liquid dye concentrate preparation contain 0.8 to 1.8, more preferably only 1.0 to 1.5 parts by weight of the alkali-metal salt to the ten parts of the compound of formula I or water-soluble salt thereof.

The compounds of formula I and the water-soluble salts thereof are highly substantive to paper, white water from the paper machine during the dyeing of paper being only slightly coloured.

The dyes are substantially unaffected by pH conditions and dyed paper is free from mottled and so-called "two-sided" effects. The dyeings produced are of good shade and are light fast, showing a tone-in-tone fade after a long period of exposure to light. The dyed paper has good fastness to water, milk, fruit juices, sweetened mineral water and is stable to alcohol. Paper dyed with compounds of formula I or their water-soluble salts can be bleached by oxidation and reduction bleaching methods.

In comparison with the known similar dyes of formulae IV and V,

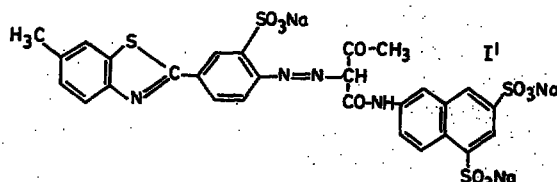


the compounds of formula I have notable solubility properties, are particularly suitable for dry addition to paper stock and have noteworthy properties after fixing with cationic fixing agents. Moreover, in comparison to known compounds similar to those of formula V, but which are sulphonated in the benzene radical Z, the com-

pounds of formula I and the water-soluble salts thereof show marked substantivity to paper and notable wet and alcohol fastness, especially when fixed with a cationic fixing agent.

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

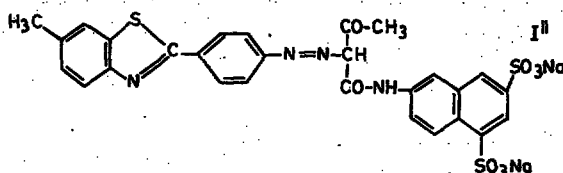
EXAMPLE 1. Production of a compound of formula I'



A mixture of 34 parts of the sodium salt of 2-(4'-amino-3'-sulphophenyl)-6-methylbenzothiazole, 7 parts of sodium nitrite and 1000 parts of water is stirred to form a homogeneous suspension. The suspension is run slowly into a mixture of 25 parts of 30% hydrochloric acid and 100 parts of ice. The corresponding diazo compound is formed. It is added with vigorous stirring to a solution of 43 parts of the disodium salt of 2-acetoacetylaminonaphthalene-5,7-disulphonic acid and 20 parts of sodium carbonate in 400 parts of water. The monoazo dye of formula I', thus formed is precipitated from the solution at 50° by the addition of 200 parts of sodium chloride, and is isolated by filtration.

The filtercake can be used as it is to produce the dye preparations described in Examples 6 and 7. In the dry state the dye is a yellow powder, which dissolves in water with a yellow colour and dyes paper greenish yellow shades.

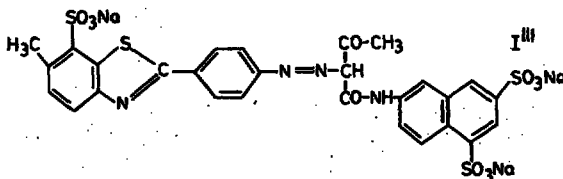
EXAMPLE 2. Production of a compound of formula I''



Over a period of 2 hours, a solution of 7 parts of sodium nitrite in 25 parts of water is allowed to run into a mixture of 24 parts of 2-(4-aminophenyl)-6-methylbenzothiazole, 200 parts of water, 25 parts of 30% hydrochloric acid and 100 parts of ice. The diazo compound formed is added to a solution of 43 parts of the disodium salt of 2-acetoacetylaminonaphthalene-5,7-disulphonic acid and 25 parts of sodium bicarbonate in 200 parts of water and 200 parts of ice. When the coupling reaction is complete the suspension is heated and the dye of formula I'' is precipitated by the addition of sodium chloride and is isolated by filtration.

The filtercake can be used, as obtained, to produce the dye preparations described in Examples 6 and 7. Alternatively it can be dried to give a yellow powder which dissolves readily in water with a yellow colour and which dyes paper brilliant greenish yellow shades.

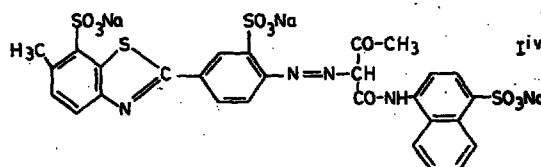
EXAMPLE 3. Production of a compound of formula I'''



32 Parts of 2-(4'-aminophenyl)-6-methylbenzothiazole-7-sulphonic acid are dissolved in 600 parts of water with the aid of 15 parts of 30% sodium hydroxide solution. After the addition of 7 parts of sodium nitrite, the solution is run into a thoroughly stirred mixture of 25 parts of 30% hydrochloric acid and 100 parts of ice. The diazo compound formed is added slowly to a solution of 43 parts of the disodium salt of 2-acetoacetylaminonaphthalene-5,7-disulphonic acid in 250 parts of water. During the addition the pH is maintained between 7.5 and 8.5 by the gradual addition of 20 parts of sodium carbonate while the temperature is held below 10° by adding ice. A solution of yellowish brown colour is formed. It is raised to a temperature of 60°, and 200 parts of sodium chloride are added, where upon dye of formula I''' is precipitated and isolated by filtration.

The filtercake can be used directly to produce the dyeing preparations described in Examples 6 and 7. If, instead, it is dried, a yellow powder is obtained which dissolves readily in water to give solutions of yellow colour which dye paper brilliant greenish yellow shades.

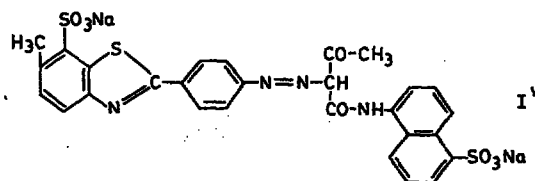
EXAMPLE 4. Production of a compound of formula I^{iv}



A solution of 40 parts of 2-(4'-amino-3'-sulphophenyl)-6-methyl-benzothiazole-7-sulphonic acid in 800 parts of water is prepared. 30 Parts of 30% hydrochloric acid and 300 parts of ice are added, then a solution of 7 parts of sodium nitrite in 50 parts of water is allowed to run in at a slow rate. The solution of the diazo component thus formed is added to a solution of 33 parts of the sodium salt of 1-acetoacetylaminonaphthalene-4-sulphonic acid and 25 parts of sodium carbonate in 200 parts of water. From the final yellowish brown solution the dye of formula I^{iv} is precipitated at 60° by addition of 300 parts of sodium chloride, and is isolated by filtration.

The filtercake can be used as obtained to produce the dyeing preparations described in Examples 6 and 7, or it can be dried to give a yellow powder which dissolves readily in water and which dyes paper brilliant greenish yellow shades.

EXAMPLE 5. Production of a compound of formula I^v



By repeating the procedure of Example 4, but using 1-acetoacetylaminonaphthalene-5-sulphonic acid in place of 1-acetoacetylaminonaphthalene-4-sulphonic acid the compound of formula I^v is obtained. It has comparable properties to the dye of Example 4 and gives greenish yellow dyeings on paper.

EXAMPLE 6:

60 Parts of the compound of formula I' (obtained as in Example 1) in the form of the filtercake are added at room temperature to a solution of 40 parts of sodium sulphate in 300 parts of water and stirred until a homogeneous dispersion is formed. The dispersion is dried in an atomizer. Yellow granules averaging 90 microns in size are obtained. They dissolve readily in water and dye paper in brilliant greenish yellow shades.

The filtercakes of the dyes obtained by the operating procedures of Example 2 to 5 can be converted into granules by the same method.

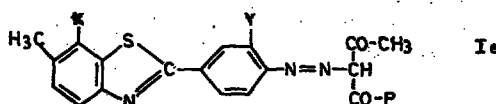
EXAMPLE 7:

120 Parts of the compound of formula I' (obtained as in Example 1) in the form of the filtercake are added to a solution of 200 parts of urea and 500 parts of water,

with stirring until a homogeneous suspension is formed. The temperature is increased to 50°, on which the dye goes into solution. The solution is clarified by filtration in the presence of a filtering aid and is then diluted with water to 1000 parts. This dye solution is stable for several months at room temperature and is used for dyeing paper in bright greenish yellow shades.

If the dyes of Examples 2 to 5 are used in place of the dye of Example 1, dye solutions with equally good storage stability are obtained.

The structural composition of further dyes is shown in the table below. They can be produced in analogy with the reaction procedures of Examples 1 to 5 and agree with formula Ie,



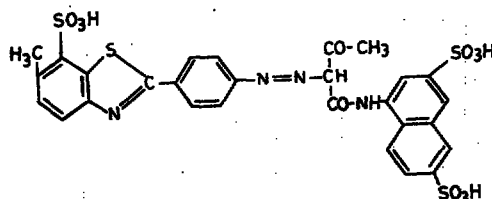
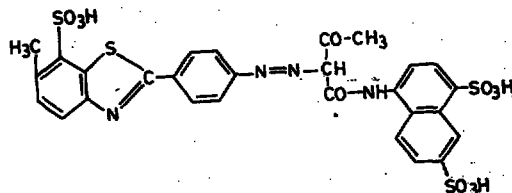
where X, Y and P have the meanings assigned to them in the table. These dyes give dyeings of greenish yellow shade on paper. The compounds are shown in the table, in their free acid form although, as will be appreciated, by the following procedures of Examples 1 to 5, they would be obtained in sodium salt form.

Example No.	X	Y	P
8	SO ₃ H	SO ₃ H	
9	SO ₃ H	SO ₃ H	
10	SO ₃ H	H	
11	H	SO ₃ H	do
12	H	H	do
13	H	SO ₃ H	
14	H	SO ₃ H	
15	SO ₃ H	SO ₃ H	do

Example No.	X	Y	P
16	SO ₃ H	H	
17	SO ₃ H	SO ₃ H	do
18	SO ₃ H	SO ₃ H	
19	H	H	
20	SO ₃ H	H	
21	SO ₃ H	SO ₃ H	do
22	H	SO ₃ H	do
23	SO ₃ H	SO ₃ H	
24	SO ₃ H	SO ₃ H	

Example No.	X	Y	P
25	SO ₃ H	SO ₃ H	
26	SO ₃ H	SO ₃ H	
27	SO ₃ H	SO ₃ H	
28	SO ₃ H	H	
29	SO ₃ H	SO ₃ H	

The full structural formulae of the compounds of Examples 10 and 28, respectively are as follows:



In the foregoing Examples, the resulting compounds are isolated in the form of sodium salts. As will be appreciated such salt forms may be converted into other water-soluble salt forms, e.g. other alkali metal or ammonium salt forms, or into free acid forms in conventional manner.

EXAMPLES OF APPLICATION

EXAMPLE A.

Paper stock consisting of 70 parts of chemically bleached sulphite pulp from softwood and 30 parts of chemically bleached sulphate pulp from birch is suspended in 2000 parts of water and beaten in a hollander beater. 0.2 Parts of the dyeing preparation described in Example 6 are sprinkled into the stock, which is then beaten for a further 20 minutes. On the paper machine the stock is converted into sheet, dyed in a greenish yellow shade. The back water from the wire is virtually colourless.

EXAMPLE B.

A solution of 0.5 parts of the powder dye described in Example 1 is prepared, cooled to room temperature, and added to a suspension of 100 parts of chemically bleached sulphite pulp in 200 parts of water in the beater. After further beating for 15 minutes the stock is sized and the sheet formed. This is dyed in a greenish yellow shade of medium depth which has good wet fastness properties.

EXAMPLE C.

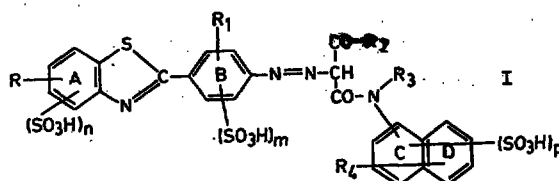
If the 0.2 parts of the dyeing preparation of Example 6 used in Example A are replaced by 1 part of the liquid dyeing preparation of Example 7, the paper is dyed in a similar shade with comparable fastness properties.

EXAMPLE D.

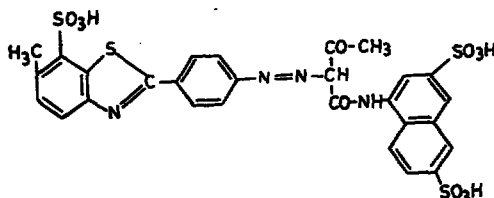
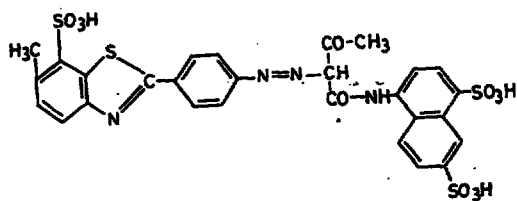
A sheet of absorbent, unsized paper is conveyed through a dye solution at 40—50° consisting of 0.5 parts of the dyeing preparation of Example 6, 0.5 parts of starch and 99 parts of water. The excess solution is expressed by a pair of roller and the sheet dried. It is dyed in a greenish yellow shade.

WHAT WE CLAIM IS:—

1. A monoazo dye of formula I,



The full structural formulae of the compounds of Examples 10 and 28, respectively are as follows:



In the foregoing Examples, the resulting compounds are isolated in the form of sodium salts. As will be appreciated such salt forms may be converted into other water-soluble salt forms, e.g. other alkali metal or ammonium salt forms, or into free acid forms in conventional manner.

EXAMPLES OF APPLICATION

EXAMPLE A.

Paper stock consisting of 70 parts of chemically bleached sulphite pulp from softwood and 30 parts of chemically bleached sulphate pulp from birch is suspended in 2000 parts of water and beaten in a hollander beater. 0.2 Parts of the dyeing preparation described in Example 6 are sprinkled into the stock, which is then beaten for a further 20 minutes. On the paper machine the stock is converted into sheet, dyed in a greenish yellow shade. The back water from the wire is virtually colourless.

EXAMPLE B.

A solution of 0.5 parts of the powder dye described in Example 1 is prepared, cooled to room temperature, and added to a suspension of 100 parts of chemically bleached sulphite pulp in 200 parts of water in the beater. After further beating for 15 minutes the stock is sized and the sheet formed. This is dyed in a greenish yellow shade of medium depth which has good wet fastness properties.

EXAMPLE C.

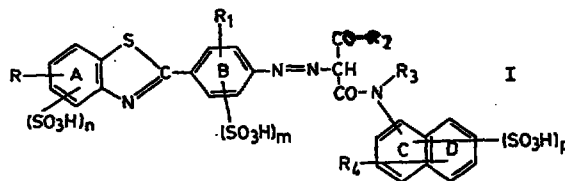
If the 0.2 parts of the dyeing preparation of Example 6 used in Example A are replaced by 1 part of the liquid dyeing preparation of Example 7, the paper is dyed in a similar shade with comparable fastness properties.

EXAMPLE D.

A sheet of absorbent, unsized paper is conveyed through a dye solution at 40—50° consisting of 0.5 parts of the dyeing preparation of Example 6, 0.5 parts of starch and 99 parts of water. The excess solution is expressed by a pair of roller and the sheet dried. It is dyed in a greenish yellow shade.

WHAT WE CLAIM IS:—

1. A monoazo dye of formula I,



in which

R , R_1 and R_2 , which may be the same or different, each signify a hydrogen atom, an alkyl radical of 1 to 6 carbon atoms or an alkoxy radical of 1 to 6 carbon atoms,

R_2 signifies an alkyl radical of 1 to 6 carbon atoms,

R_3 signifies a hydrogen atom or an alkyl radical of 1 to 6 carbon atoms, rings A, B, C and D may be further substituted,

n signifies 0 or 1

m signifies 0 or 1, and

p signifies 0 to 3 with the proviso that the compounds contain at least one sulphonic acid group; or a water-soluble salt thereof.

2. An alkali metal or ammonium salt of a compound of formula I, stated in claim 1.

3. A sodium salt of a compound of formula I, stated in claim 1.

4. A compound according to any one of the preceding claims, wherein any alkyl or alkoxy radical is of 1 to 3 carbon atoms.

5. A compound according to any one of the preceding claims, wherein R is in the *para* position to the nitrogen atom and signifies a methyl radical.

6. A compound according to any one of the preceding claims, wherein R_1 and R_2 each signify a hydrogen atom.

7. A compound according to any one of the preceding claims, wherein R_3 signifies a methyl radical.

8. A compound according to any one of the preceding claims, wherein R_3 signifies a hydrogen atom, a methyl radical or an ethyl radical.

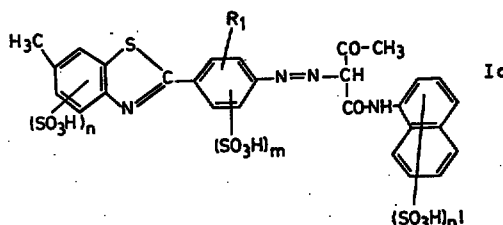
9. A compound according to any one of the preceding claims, bearing two to four sulphonic groups, of which two such groups are contained in ring D.

10. A compound according to any one of claims 1 to 8, bearing two or three sulphonic acid groups, of which one such group is contained in ring D.

11. A compound according to any one of the preceding claims, in which ring A, B, C or D is further substituted by a halogen atom or a nitro, cyano, carboxylic acid or a substituted or unsubstituted amino group.

12. A compound according to any of claims 1 to 10, wherein rings A, B, C or D bear no further substituents than are shown in formula I, stated in claim 1.

13. A compound of formula Ia,

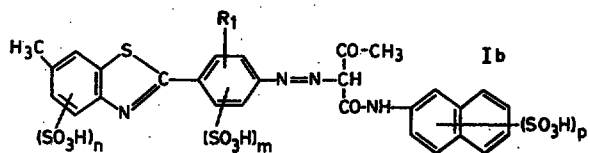


in which

R_1 , n and m are as defined in claim 1, and p' is 1 to 3;

or a water-soluble salt thereof.

14. A compound of formula Ib,



in which

R_1 , n and m are as defined in claim 1, and p' is 1 to 3;

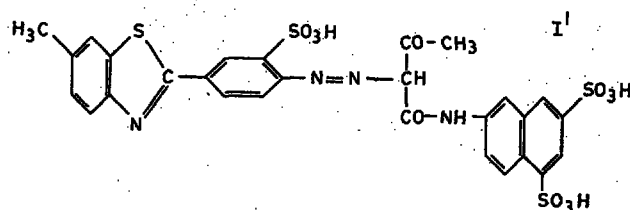
or a water-soluble salt thereof.

15. A compound of claim 13 or 14, in which R_1 signifies a hydrogen atom.

16. An alkali-metal or ammonium salt of a compound of formula Ia, stated in claim 13, or of a compound of formula Ib, stated in claim 14.

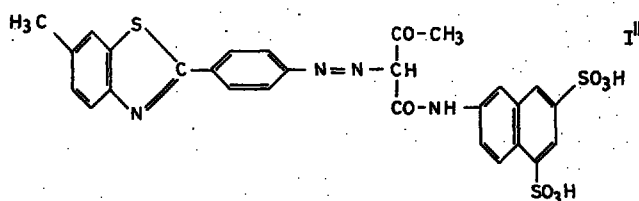
17. A compound of formula I',





or a water-soluble salt thereof.

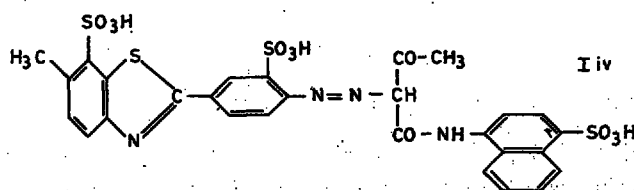
18. A compound of formula I'',



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or a water-soluble salt thereof.

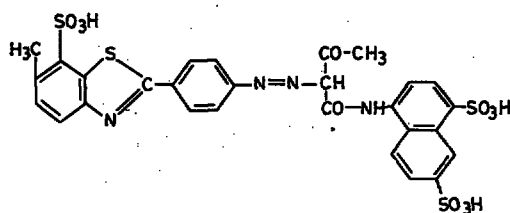
19. A compound of formula I''',



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or a water-soluble salt thereof.

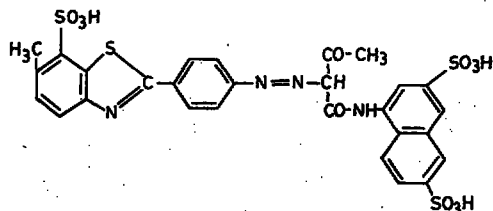
20. A compound of formula,



10

or a water-soluble salt thereof.

21. A compound of formula



10

or a water-soluble salt thereof.

22. A sodium salt of a compound according to any one of claims 17 to 21.

23. A granulated dyeing preparation containing a compound according to any one of the preceding claims and from 0.1% to 50% by weight of a salt which dissociates in water, the average particle size of the granules being at least 20 microns.

24. A granulated dyeing preparation according to claim 23, wherein said salt is sodium chloride or sodium sulphate.

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25. A liquid dye concentrate preparation containing one part by weight of a dye component, two to eight parts by weight of water and 0.5 to 5 parts by weight of a carboxylic acid amide, the dye component containing 0.5 to two parts by weight of an alkali metal salt to ten parts by weight of a compound of formula I, stated in claim 1, or water-soluble salt thereof.

26. A liquid dye concentrate preparation according to claim 25, wherein the alkali metal salt is sodium chloride or sodium sulphate.

27. A liquid dye concentrate preparation according to claim 25 or 26, wherein the carboxylic acid amide contains 1 to 4 carbon atoms.

28. A liquid dye concentrate preparation according to claim 27, wherein the carboxylic acid amide is urea.

29. A process for dyeing paper comprising applying to the paper a compound according to any one of claims 1 to 22.

30. A process according to claim 29, wherein the compound is added to the paper stock.

31. A process according to claim 30, wherein a granulated dyeing preparation according to claim 23 or 24 is added to the paper stock.

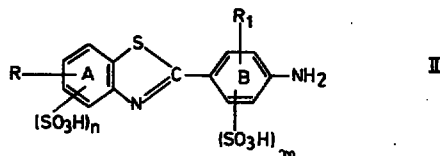
32. A process according to claim 30, wherein a liquid dye concentrate preparation according to any one of claims 25 to 28 is added to the paper stock.

33. A process according to claim 29, wherein the paper in sized or unsized sheet form is dyed by a dipping method with a solution or dispersion of said compound.

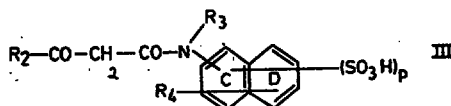
34. A process according to claim 29, substantially as herein before described.

35. Paper when dyed by a process according to any one of claims 29 to 35.

36. A process for the production of a compound of formula I, stated in claim 1, characterised by reacting a diazo derivative of an amine of formula II,



in which R, R₁, n, m and rings A and B are as defined in Claim 1, with a compound of formula III,



in which R₂, R₃, R₄, p and rings C and D are as defined in Claim 1.

37. A process according to claim 36, wherein the reaction is carried out in a neutral to weakly alkaline medium.

38. A process according to claim 36, substantially as hereinbefore described, with reference to any one of Examples 1 to 5.

39. A compound of formula I as defined in claim 1, according to any one of Examples 1 to 5, and 8 to 29.

40. A compound of formula I, as defined in claim 1, according to any one of Examples 1 to 5 and 8 to 27.

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