

PATENT SPECIFICATION

(11) 1379845

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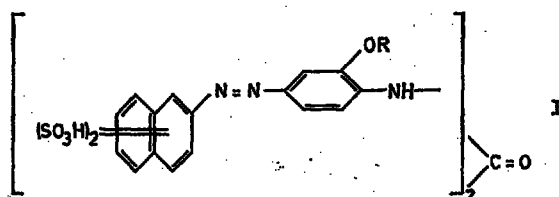
- (21) Application No. 4809/72 (22) Filed 2 Feb. 1972
 (61) Patent of Addition to No. 1202798 dated 25 June 1968
 (31) Convention Application No. 1735/71 (32) Filed 5 Feb. 1971 in
 (33) Switzerland (CH)
 (44) Complete Specification published 8 Jan. 1975
 (51) INT CL² D06P 1/39 D21H 3/80
 (52) Index at acceptance D1B 2D
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(54) PAPER DYEING PROCESS AND PREPARATION THEREFOR

(71) We, SANDOZ LTD., of 35 Lichtstrasse, 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 a paper dyeing process and preparation therefore and is an improvement on the process described in British Patent No. 1,202,798. More particularly, the present invention relates to a process for dyeing paper using compounds of formula I,



in which R signifies an alkyl radical of 1 to 4 carbon atoms, and the two SO₃H groups occupy the 1,5-, 3,6-, 4,8-, 5,7- or 6,8-positions in the naphthyl ring, or a water-soluble salt thereof.

Accordingly, the present invention provides a liquid dye concentrate preparation containing one part by weight of a dye component containing a compound of formula I, as defined above, or a water-soluble salt thereof, two to eight parts by weight of water, 0.5 to five parts by weight of an acid amide and an alkali metal salt, the alkali metal salt being present in an amount of from 0.5 to two parts by weight for each ten parts by weight of the compound of formula I or the water-soluble salt thereof.

The invention also provides a process for dyeing paper comprising applying to paper or adding to the stock, a liquid dye concentrate as hereinabove set forth.

Preferred water-soluble salts of the compounds are alkali metal and ammonium salts. Mono-, di-, tri-, and particularly the tetra-alkali metal or ammonium salts may be used, the sodium salts being preferred.

The preferred compounds of formula I and their salts are those which are symmetrical. Also preferred are those in which R represent a methyl or ethyl radical, particularly a methyl radical, and those in which the naphthalene component is a 2-naphthyl-4,8-disulphonic acid or salt radical.

The liquid dye concentrate of the compounds of formula I may, for example, be applied in solution or dispersion form for the continuous or discontinuous dyeing of paper in sized or unsized form, either by application in the stock prior to sheet formation or by a coating, dipping or other suitable technique on the sheet. The concentrate may also be added in powder or granule form to the paper stock.

The paper may be dyed at a pH value ranging from 1 to 14, preferably at a pH value of 4 to 9, optimally at a pH value of 5.5 to 6.5. Suitable dyeing temperatures are from 5° to 60°C, preferably 20° to 30°C, e.g. at room temperature.

During the application of the dye to the paper, other additives, commonly used in paper manufacture, e.g. fillers, rosin milk, optical brightening agents and other sheet property modifying agents may be added.

After application of the dye, it is preferably fixed on the paper using a cationic fixing agent such as are described in French Patent No. 956,501 and German Patents Nos. 671,704 and 918,743.

The compounds of formula I may be prepared in known manner, for example as described in German Patent No. 212,666.

In a preferred embodiment, a solution or dispersion is used which has been obtained from a liquid dye concentrate preparation containing one part by weight of dye component, two to eight parts by weight of water and 0.5 to five parts by weight of an acid amide, the dye component containing a compound of formula I, or a water soluble salt thereof, and an alkali metal salt, the alkali metal salt being present in an amount of from 0.5 to two parts by weight for each ten parts by weight of the compound of formula I or water soluble salt thereof.

The dye component preferably contains the tetra-sodium salt of a compound of formula I.

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

The acid amide is suitably a carboxylic acid amide, preferably of low molecular weight, i.e., those containing 2 to 4 carbon atoms. Examples include urea, and derivatives thereof, such as substituted or unsubstituted alkyl ureas, guanidine and derivatives thereof, formamides, e.g. alkyl formamides, and acetamide. Sulphonic acid amides may also suitably be used.

The preparation may contain other components, for example auxiliary dyeing agents, pH stabilizers and dispersing agents.

The above-described liquid dyeing concentrate may suitably be added to the paper stock.

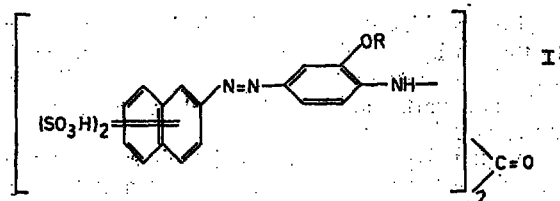
The preparation of the liquid dye concentrate also forms part of the present invention and comprises admixing the stated components in the stated proportions, if necessary with heating for a short time, followed by a filtration step. Preferably it is obtained from aqueous press-cakes of low electrolyte content, as obtained in bulk manufacture, or alternatively from dry concentrates free from stabilizing agents.

The press-cakes or dry concentrates suitably contain from 0.5 to two parts by weight of the alkali metal salt for each ten parts by weight of the compound of formula I, or water-soluble salt thereof. Preferably they contain 0.8 to 1.8, more preferably 1.0 to 1.5 parts by weight of the alkali metal salt and ten parts by weight of said tetrasodium salt.

The press-cakes normally contain from 40% to 60% by weight of water.

The liquid dyeing concentrate preparations provided by the present invention have the advantage of being easy to handle, being free from inconvenient dusting that occurs in weighing out powder dyes and being suitable for both discontinuous and continuous dyeing methods. The preparations are stable over several months storage at room temperature, are unaffected by frost and are immune to mould growth.

The present invention still further provides a process for dyeing paper comprising applying a compound of formula I',



in which

R signifies an alkyl radical of 1 to 4 carbon atoms and the two SO_3H groups occupy the 1,5-, 3,6-, 4,8-, 5,7- or 6,8-positions in the naphthyl ring, with the proviso that, when the compound is symmetrical and the SO_3H groups occupy the 4,8-positions, then

R signifies other than a methyl radical, or a water-soluble salt thereto.

The compounds of formula I' may be applied in conventional manner, e.g. in solution or dispersion form or in powder or granule form.

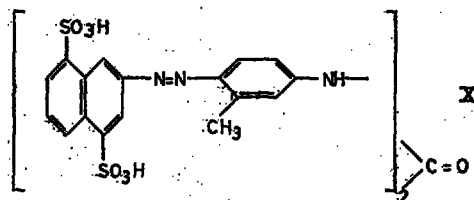
The water-soluble salts of the compounds of formula I' are suitably those as set forth above for the compounds of formula I.

The compounds of formula I dye paper yellow. Paper dyeings produced in accordance with the present invention are markedly fast to light and water, and are resistant to milk, alcoholic drinks, fruit juices and mineral water. The wet and alcohol

fastness of heavy dyeings on sized and unsized grades of paper can be considerably improved by treatment with cationic fixing agents.

The compounds of formula I are highly substantive to the paper, the white water from the wire of the paper machine being colourless or, when high concentrations are used for deep shades, no more than faintly coloured. Dyes containing compounds of formula I have good serviceability, being bleachable by reduction and oxidation bleaching methods.

In relation to comparable known yellow dyes, e.g. the known dye of formula X,

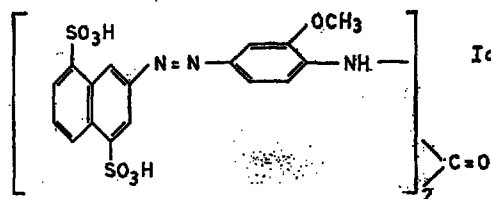


the compounds of formula I have noteworthy wet and alcohol fastness, particularly when dyed paper is treated with conventional cationic fixing agents.

The following Examples illustrate the invention. In the Examples, all parts and percentages are by weight and the temperatures in degrees Centigrade. Examples 1, 2, 4 and 5 are merely present to indicate dyeing procedures and do not themselves illustrate the invention.

EXAMPLE 1:

100 Parts of chemically bleached sulphite stock from softwood pulp in 2000 parts of water are beaten in a hollander beater. A solution of 0.1 part of a sodium salt of the disazo dye of formula Ia,



in 10 parts of water is added. It is believed that the salt is the tetrasodium salt. After 15 minutes the stock is sized which fixes the dye. Paper manufactured from this stock is dyed in a reddish yellow shade. The dye has good power of build-up and is almost quantitatively absorbed by the paper fibre; the dyeing has good fastness properties and the water from the wire is colourless.

EXAMPLE 2

A mixture of 70 parts of chemically bleached sulphite stock from softwood and 30 parts of chemically bleached sulphate stock from birch suspended in 2000 parts of water is beaten in a pulper. 0.1 Part of the sodium salt of compound of formula Ia, described in Example 1, is sprinkled into the stock in dry powder form. The stock is mixed for a further 5—10 minutes, during which time the dye dissolves, is evenly distributed in the stock and absorbed by the paper fibre. The paper sheet formed from the stock has a bright reddish yellow shade which is light and alcohol fast. The water from the wire is almost colourless.

EXAMPLE 3

98.8 Parts of the sodium salt of the compound of formula Ia, described in Example 1, and 10 to 15 parts of sodium chloride in the form of a 40% aqueous press-cake are stirred into 450 parts of water. When the dye is homogeneously distributed 175 parts of urea are added and the temperature is increased to 80—90°, on which the dye goes into solution. 6 Parts of "Hyflo" (Registered Trade Mark) filter earth are added and the solution filtered. The filtrate consists of 872 parts of dye solution which is storable for several months.

If 0.6 parts of the dye solution described in this Example are used in the procedure of Example 2 in place of 0.1 part of the powder dye, a bright yellow paper dyeing of medium depth is obtained which has comparable fastness properties.

EXAMPLE 4

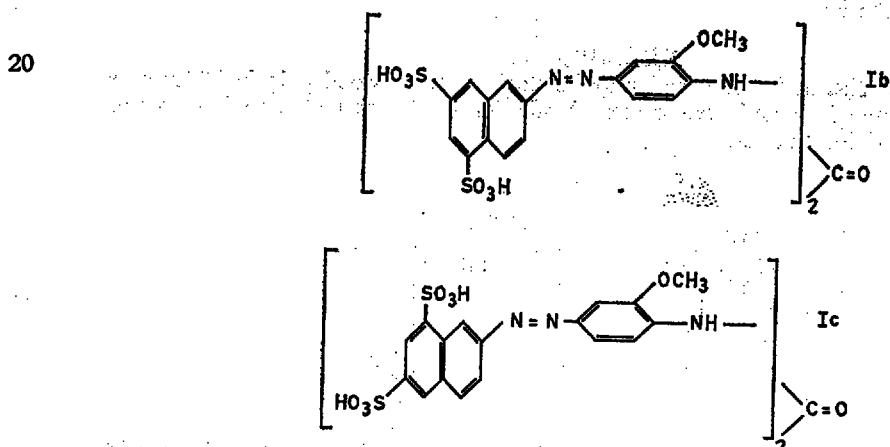
A stock suspension of 70 parts of bleached softwood pulp and 30 parts of bleached hardwood pulp at 2.5% consistency is adjusted to pH 9 with caustic soda. Its freeness value is 20° Schopper-Riegler. 0.3 Parts of the dye of Example 1 are added, the stock stirred further for 2 minutes and the sheet formed at 0.5% consistency (pH 9). The absorbent paper is dyed in a reddish yellow shade showing very good water and alcohol fastness. The water from the wire is colourless.

EXAMPLE 5

For the production of coloured decorative paper, a continuous sheet of absorbent (unsized) paper is conveyed through a solution of 0.5 parts of the dye of Example 1 and 0.5 parts of starch in 99 parts of water. The excess solution is expressed by a pair of rollers and the moist sheet dried and creped on cylinders. It is of advantage to heat the dye solution to 40°—50° to obtain better penetration of the sheet.

EXAMPLE 6

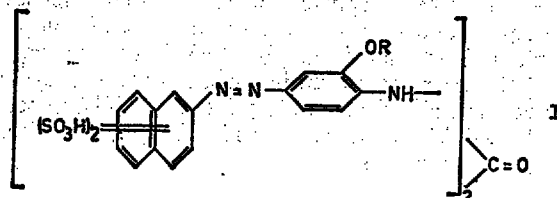
By repeating the process of any one of Examples 1 to 5 but replacing the sodium salt of the compound of formula Ia thereof with a compound of formula Ib or Ic,



or a water-soluble salt thereof, paper dyeings of similarly good quality with a reddish-yellow shade are obtained.

WHAT WE CLAIM IS:—

- 25 1. A liquid dye concentrate preparation comprising a dye component, water and acid amide, for each part by weight of dye component there being present 2 to 8 parts by weight of water and 0.5 to 5 parts by weight of acid amide, the dye component comprising a compound of formula I,



in which

R signifies an alkyl radical of 1 to 4 carbon atoms, and the two SO₃H groups occupy the 1,5-, 3,6-, 4,8-, 5,7- or 6,8-positions in the naphthyl ring, or a water-soluble salt thereof, and an alkali metal salt, the alkali metal salt being present in an amount of from 0.5 to two parts by weight for each ten parts by weight of the compound of formula I or the water-soluble salt thereof.

- 35 2. A preparation according to Claim 1, wherein the acid amide is a carboxylic acid amide of 2 to 4 carbon atoms.



If 0.6 parts of the dye solution described in this Example are used in the procedure of Example 2 in place of 0.1 part of the powder dye, a bright yellow paper dyeing of medium depth is obtained which has comparable fastness properties.

EXAMPLE 4

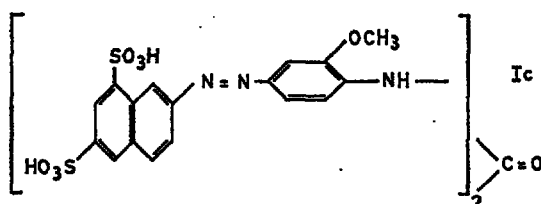
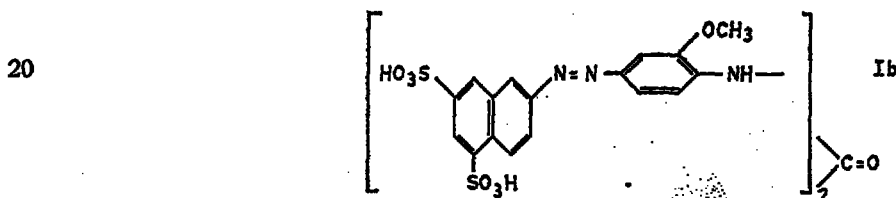
5 A stock suspension of 70 parts of bleached softwood pulp and 30 parts of bleached hardwood pulp at 2.5% consistency is adjusted to pH 9 with caustic soda. Its freeness value is 20° Schopper-Riegler. 0.3 Parts of the dye of Example 1 are added, the stock stirred further for 2 minutes and the sheet formed at 0.5% consistency (pH 9). The absorbent paper is dyed in a reddish yellow shade showing very good water and alcohol fastness. The water from the wire is colourless.

EXAMPLE 5

15 For the production of coloured decorative paper, a continuous sheet of absorbent (unsized) paper is conveyed through a solution of 0.5 parts of the dye of Example 1 and 0.5 parts of starch in 99 parts of water. The excess solution is expressed by a pair of rollers and the moist sheet dried and creped on cylinders. It is of advantage to heat the dye solution to 40°—50° to obtain better penetration of the sheet.

EXAMPLE 6

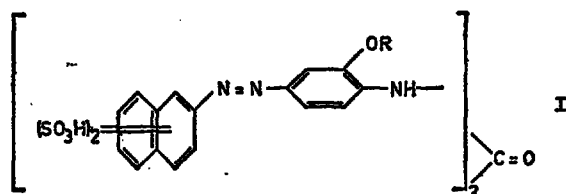
By repeating the process of any one of Examples 1 to 5 but replacing the sodium salt of the compound of formula Ia thereof with a compound of formula Ib or Ic,



or a water-soluble salt thereof, paper dyeings of similarly good quality with a reddish-yellow shade are obtained.

WHAT WE CLAIM IS:—

25 1. A liquid dye concentrate preparation comprising a dye component, water and acid amide, for each part by weight of dye component there being present 2 to 8 parts by weight of water and 0.5 to 5 parts by weight of acid amide, the dye component comprising a compound of formula I,



30 in which

R signifies an alkyl radical of 1 to 4 carbon atoms, and the two SO₃H groups occupy the 1,5-, 3,6-, 4,8-, 5,7- or 6,8-positions in the naphthyl ring, or a water-soluble salt thereof, and an alkali metal salt, the alkali metal salt being present in an amount of from 0.5 to two parts by weight for each ten parts by weight of the compound of formula I or the water-soluble salt thereof.

35 2. A preparation according to Claim 1, wherein the acid amide is a carboxylic acid amide of 2 to 4 carbon atoms.



3. A preparation according to Claim 1 or Claim 2, wherein the water-soluble salt of the compound of formula I is a mono-, di-, tri or tetra-alkali metal or ammonium salt.

5 4. A preparation according to Claim 3, wherein the water-soluble salt of the compound of formula I is the tetrasodium salt. 5

5. A preparation according to any one of the preceding claims, wherein the compound of formula I is symmetrical.

10 6. A preparation according to any one of the preceding claims, wherein, in the compound of formula I, R signifies a methyl or ethyl radical. 10

7. A preparation according to Claim 6, wherein R signifies a methyl radical.

8. A preparation according to any one of the preceding Claims, wherein, in the compound of formula I, the naphthalene component is a 2-naphthyl-4,8-disulphonic acid radical.

15 9. A preparation according to any one of the preceding Claims, wherein the alkali metal salt is sodium chloride or sodium sulphate. 15

10. A liquid dye concentrate preparation according to Claim 1 substantially as hereinbefore described with reference to Example 3 or Example 6.

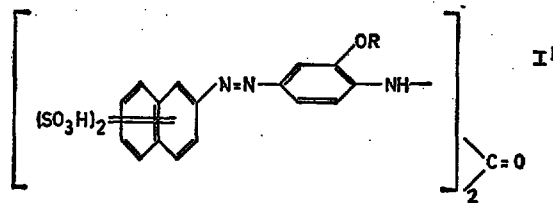
11. A process for dyeing paper comprising adding a preparation according to any one of the preceding claims to the paper stock.

20 12. A process for dyeing paper comprising applying to the paper or to the paper stock a diluted preparation according to any one of Claims 1 to 10. 20

13. A process according to Claim 11 or 12, wherein, after dyeing the paper, the paper is treated with a cationic fixing agent.

25 14. A process according to Claim 11, 12 or 13, substantially as hereinbefore described with reference to Example 3 or Example 6. 25

15. A process for dyeing paper which comprises applying to the paper a compound of formula I',



in which

30 R signifies an alkyl radical of 1 to 4 carbon atoms and the two SO₃H groups occupy the 1,5-, 3,6-, 4,8-, 5,7- or 6,8-positions in the naphthyl ring, with the proviso that, when the compound is symmetrical and the SO₃H groups occupy the 4,8-positions, then 30

R signifies other than a methyl radical,

35 or a water-soluble salt thereof. 35

16. A process according to Claim 15, wherein the water-soluble salt is a sodium salt.

17. A process according to Claim 16, wherein the salt is the tetrasodium salt.

40 18. A process according to any one of Claims 15 to 17, wherein the compound of formula I' or the salt thereof is applied in solution or dispersion form to the paper in stock, sized or unsized form. 40

19. A process according to any one of Claims 15 to 17, wherein the compound of formula I' or the salt thereof is added, in powder form, to the paper stock.

45 20. A process according to any one of Claims 11 to 13 or 15 to 19, wherein the paper is dyed at a pH value of from 5.5 to 6.5 and at a temperature of from 20° to 30°C. 45

21. A process according to Claim 15, substantially as hereinbefore described.

22. Paper when dyed by a process according to any one of Claims 11 to 21.

50 23. A method of preparing a liquid dye concentrate comprising admixing a dye component, water, acid amide and an alkali metal salt, for each part by weight of the dye component there being 2 to 8 parts by weight of water and 0.5 to 5 parts by weight of acid amide, for each ten parts by weight of the dye component there being 0.5 to 2 parts by weight of the alkali metal salt, the dye component comprising a compound of formula I, 50

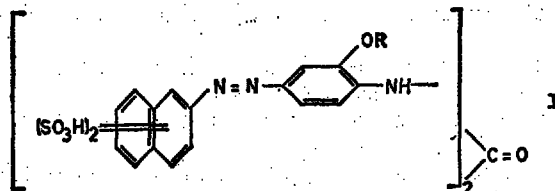


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in which

R signifies an alkyl radical of 1 to 4 carbon atoms, and the two SO₃H groups occupy the 1,5-, 3,6-, 4,8-, 5,7- or 6,8-positions in the naphthyl ring, or a water-soluble salt thereof, followed by a filtration step to remove any filterable solids therefrom.

24. A method according to Claim 23, in which the admixing is carried out with the aid of heating.

25. A method of preparing a liquid dye concentrate as defined in Claim 1, substantially as hereinbefore described with reference to Example 3.

26. A liquid dye concentrate whenever prepared by the process according to any one of Claims 23 to 25.

27. A process for dyeing paper comprising employing a liquid dye concentrate whenever prepared by a process according to any one of Claims 23 to 25.

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Printed for Her Majesty's Stationery Office, by the Courier Press, Leamington Spa, 1975.
Published by The Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from which copies may be obtained.