

AMENDED SPECIFICATION

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PATENT SPECIFICATION

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NO DRAWINGS

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(54) CONCENTRATED, LIQUID DYE PREPARATIONS

(71) We, SANDOZ LTD. of Lichtstrasse 35, Basle, Switzerland, a Body Corporate organised according to the laws of Switzerland, 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:—

This invention relates to concentrated, liquid preparations of metal-free direct disazo dyes comprising storable aqueous solutions containing 1 part by weight of dye, 1 to 8 parts by weight of water, and 0.5 to 5 or preferably 0.5 to 2 parts by weight of an acid amide. Mixtures of acid amides may be employed if desired.

The disazo dyes are represented by the Formulae I or II below:



(I)

where F_1 and F_2 represent radicals of identical or different monoazo dyes each bearing 1 to 4 water solubilizing groups and A represents an imino group or the radical of a diamide of carbonic, fumaric or cyanuric acid.



(II),

where B represents the radical of a tetrazotizable diamine of the diphenyl series and K_1 and K_2 represent identical or different azo components, and the dye bearing 1 to 4 water solubilizing groups to each azo group. Suitable water solubilizing groups are carboxylic and sulphonic acid amide groups and preferably the sulphonic acid group.

Mixtures of such dyes are suitable for the production of these preparations.

The amides of inorganic or organic acids may be employed as acid amides, but carboxylic acid amides are preferred, e.g. those of monobasic or dibasic carboxylic acids such as the amides of carboxylic acids containing up to 8 carbon atoms, e.g. 2 to 4 carbon atoms, e.g. acetamide, propionic acid amide, butyric acid amide and malonic acid diamide. Urea and urea derivatives are particularly suitable; examples, besides urea itself, are substituted or unsubstituted alkyl-urea compounds such as methyl and ethyl urea, N,N' -dimethyl urea, and dihydroxyalkyl ureas. Further, guanidine and its derivatives such as methyl guanidine are suitable, and so are the formamides, e.g. formamide itself and alkyl formamides such as methyl and dimethyl formamide. Sulphonic acid amides, e.g. sulphonic acid diamides, are also suitable for the production of the dye preparations of this invention.

The dye preparations are produced by mixing the aforementioned components and heating the mixture for a short time if necessary. The preparations may contain further assistants if desired, for instance dyeing assistants if used for textile dyeing or paper

auxiliary products if used for paper dyeing, such as pH-stabilizing agents, e.g. amino acids, and acetates. The urea component itself can be employed as a pH-stabilizing agent. Other additions which the preparations may contain are softeners, water repellent agents and agents for improving the wet tensile strength.

In French Patent 1,420,403 dyeing preparations are described which contain 1 part by weight of dye, 0.01 to 75 parts by weight of water and 2 to 100 parts by weight of an acid amide. These preparations are employed solely for the dyeing of leather and accordingly they contain only leather dyes, in particular metal complex dyes. In all the examples of the named French Patent metal complex dyes are employed. No mention is made of metal-free direct dyes.

The advantage of the new preparations is that they contain substantially smaller amounts of acid amide. Hence they are more economical and the waste water from dyeing is less heavily contaminated.

The new preparations can be employed for the dyeing of paper, as true aqueous solutions diluted with water as necessary. They are equally suitable for dyeing paper in the stock and by dipping and coating techniques.

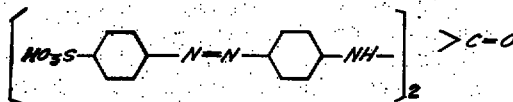
Another advantage of the dyeing preparations here disclosed is that they are easier to handle. There is no inconvenient dusting in weighting out as with powder dyes and the liquid form makes them well suitable for application in continuous dyeing processes.

The preparations are storable that is to say they are storable for several months at room temperature without precipitation of dyestuff. They are not affected by frost and are immune to mould growth.

In the following Examples the parts and percentages are by weight and the temperatures in degrees centigrade.

Example 1.

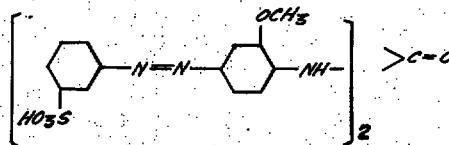
62.4 Parts of the sodium salt of the disazo dye of formula



are formed into a 50% aqueous paste with an equal weight of water. This paste is then stirred into 275 parts of water to form a homogeneous mixture and dissolved by the addition of 100 parts of urea to give approximately 500 parts of dye solution which is storable for several months at room temperature. When employed for dyeing paper in the stock, this liquid preparation gives bright yellow dyeings.

Example 2.

68.4 Parts of the sodium salt of the disazo dye of formula



are pasted with 55.8 parts of water to form a 55% aqueous paste which is entered into 275 parts of water at 40° and stirred to form a homogeneous mixture. The dye is then brought into solution by adding 100 parts of urea. The solution is filtered to eliminate small amounts of insoluble impurities, after which approximately 500 parts of a preparation are obtained which is storable for several months at room temperature. With this liquid preparation bright yellow paper dyeings are obtained.

Example 3.

A 40% aqueous paste of 95.6 parts of the sodium salt of the disazo dye C.I. Direct Yellow 50 (Colour Index, 2nd ed., No. 29025) are homogeneously mixed with 160 parts of water, with the subsequent addition of 200 parts of urea. On heating to 70—80° the dye goes into solution. The solution is filtered with the addition of 5 parts of "Hyflo" (registered trade mark) filter earth and cooled. Approximately 600 parts

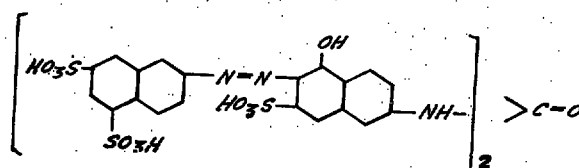
of a liquid preparation are obtained which is storable for several months at room temperature. It gives bright reddish yellow dyeings on paper.

Example 4.

101.6 Parts of the sodium salt of the disazo dye C.I. Direct Yellow 34 (Colour Index, 2nd ed., No. 29060) in the form of a 37% aqueous paste are homogeneously mixed with 415 parts of water, after which 175 parts of urea are added and the temperature increased to 85–90°, at which temperature the dye goes into solution. 6 Parts of "Hyflo" filter earth are added and the solution is filtered to give about 865 parts of a liquid dye preparation. The preparation is storable for several months at room temperature and gives bright golden-yellow dyeings on paper.

Example 5.

126.4 Parts of the sodium salt of the disazo dye of formula



as a 40% aqueous paste are entered with stirring into a solution of 250 parts of urea and 310 parts of water and dissolved by raising the temperature to 60–70°. 5 Parts of "Hyflo" filter earth are added and the solution filtered to yield about 875 parts of a liquid dye preparation which is storable for several months at room temperature. With this preparation bright scarlet paper dyeings can be produced.

Example 6.

99.2 Parts of the sodium salt of the disazo dye C.I. Direct Blue 15 (Colour Index, 2nd ed., No. 24400) in the form of a 50% aqueous paste are dissolved in a solution of 152 parts of urea and 410 parts of water at room temperature. After the addition of 4 parts of "Hyflo" filter earth the solution is filtered. About 760 parts of a dye preparation are obtained which is storable at room temperature for several months. It gives bright blue dyeings on paper.

Example 7.

99.2 Parts of the sodium salt of the disazo dye C.I. Direct Blue 1 (Colour Index, 2nd ed., No. 24410) as a 50% aqueous paste are homogeneously mixed with 402 parts of water and dissolved at room temperature by the addition of 200 parts of urea. The solution is clarified by filtration using 5 parts of "Hyflo" filter earth. The product is about 800 parts of a dye preparation which is storable for several months at room temperature and gives bright blue paper dyeings.

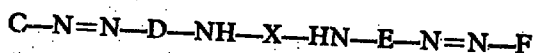
Dyeing Example A.

0.3 Parts of the dyeing preparation as described in Example 2 are added to a stock of 100 parts of chemically bleached sulphite cellulose in 2000 parts of water while it is being beaten in the beater. After 15 minutes the stock is sized which fixes the dyeing. Paper fabricated from this stock is dyed in a yellow shade of medium depth and the fastness properties of the dyeing are good. The back-water is colourless.

Dyeing Example B.

A charge of 70 parts of chemically bleached sulphite cellulose from coniferous wood pulp and 30 parts of chemically bleached sulphate cellulose from birchwood pulp in 2000 parts of water is mechanically treated in the pulper and at a suitable point 0.2 parts of the liquid dye preparation of Example 4 are added to it. After a further 20 minutes' processing the stock is converted into absorbent paper dyed in a golden yellow shade of medium depth.

Further liquid dye preparations of similarly good quality can be prepared in accordance with the procedures of Examples 1 to 7 with the dyes of the following Table 1, which are of the general formula



The meanings of C, D, E, F and X are noted in the appropriate columns of the table.

TABLE 1

Example No.	C =Radical of	D =Radical of	E =Radical of	F =Radical of	X =Radical of	Shade on paper
8	1-Aminobenzene-3-sulphonic acid	1-Amino-2-methoxybenzene	1-Amino-3-methylbenzene	2-Aminonaphthalene-4,8-disulphonic acid	Phosgene	yellow
9	2-Aminonaphthalene-5,7-disulphonic acid	1-Amino-3-methylbenzene	as D	as C	do.	do.
10	2-Aminonaphthalene-6,8-disulphonic acid	do.	as D	as C	do.	do.
11	do.	do.	1-Amino-3-methylbenzene	as C	Fumaric acid	do.
12	1-Amino-2-methylbenzene-4,6-disulphonic acid	2-Amino-5-hydroxynaphthalene-7-sulphonic acid	as D	as C	Phosgene	orange
13	1-Amino-2-methylbenzene-4-sulphonic acid	do.	as D	as C	do.	yellowish scarlet
14	1-Amino-4-methylbenzene-3-sulphonic acid	do.	as D	as C	do.	do.
15	1-Amino-4-methoxybenzene-3-sulphonic acid	do.	as D	as C	do.	scarlet
16	1-Amino-4-methoxybenzene-2-sulphonic acid	2-Amino-5-hydroxynaphthalene-7-sulphonic acid	as D	as C	Phosgene	scarlet
17	1-Amino-2-methoxybenzene-4-sulphonic acid	do.	as D	as C	do.	do.

TABLE 1 (Continued)

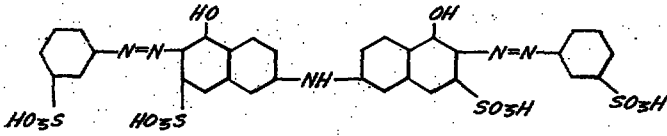
Example No.	C =Radical of	D =Radical of	E =Radical of	F =Radical of	X =Radical of	Shade on paper
18	2-Aminonaphthalene-4,8-disulphonic acid	2-Amino-5-hydroxy-naphthalene-7-sulphonic acid	as D	as C	Phosgene	scarlet
19	2-Aminonaphthalene-6,8-disulphonic acid	do.	as D	as C	do.	do.
20	2-Aminonaphthalene-4,8-disulphonic acid	do.	as D	2-Aminonaphthalene-6-sulphonic acid	do.	do.
21	3-Acetylamino-1-aminobenzene-6-sulphonic acid	do.	as D	as C	do.	do.
22	2-Aminonaphthalene-4,8-disulphonic acid	do.	as D	as C	2-Amino-4,6-dichloro-1,3,5-triazine	do.
23	do.	do.	as D	as C	2-Phenylamine-4,6-dichloro-1,3,5-triazine	do.
24	2-Aminonaphthalene-5,7-disulphonic acid	do.	as D	as C	2-Phenylamino-4,6-dichloro-1,3,5-triazine-3'-sulphonic acid	do.
25	2-Aminonaphthalene-6-sulphonic acid	do.	as D	as C	Phosgene	do.
26	1-Aminonaphthalene-4,6-disulphonic acid	do.	as D	as C	do.	red
27	1-Aminonaphthalene-5-sulphonic acid	do.	as D	as C	do.	do.

Similarly good dye preparations can be prepared in accordance with Examples 1 to 7 using the dyes set out in the following Table 2, which are of formula (II) and in which the symbols K₁, K₂ and B have the meanings assigned to them in the appropriate columns.

TABLE 2

Example No.	K ₁ =Radical of	K ₂ =Radical of	B =Radical of	Shade on paper
28	1-Amino-8-hydroxy-naphthalene-3,6-di-sulphonic acid	1-Amino-8-hydroxy-naphthalene-3,6-di-sulphonic acid	4,4'-Diamino-1,1'-diphenyl	reddish blue
29	do.	do.	4,4'-Diamino-3,3'-dimethyl-1,1'-diphenyl	blue
30	1,8-Dihydroxy-naphthalene-3,6-disulphonic acid	do.	4,4'-Diamino-3,3'-dimethoxy-1,1'-diphenyl	do.
31	do.	1,8-Dihydroxy-naphthalene-3,6-disulphonic acid	do.	do.
32	do.	do.	4,4'-Diamino-3,3'-dimethyl-1,1'-diphenyl	do.

Similarly good liquid dye preparations can be prepared in accordance with Examples 1 to 7 with the dye given in the following Table 3.

Example No.	Dye Constitution	Shade on paper
33		blue red

The composition of further liquid dye preparations conforming to the invention is set forth in Table 4 below. The tabulation gives the number of parts by weight of dye in the preparation and the number of the Example in Table 1, 2 or 3 which identifies the dye, the number of parts of acid amide or acid amide mixture, and the number of parts of water.

TABLE 4

Example No.	Parts Dye of Example	Parts Acid amide	Parts Water
34	1.0 No. 2	0.5 Urea	8.0
35	1.0 No. 4	0.5 „	8.0
36	1.0 No. 6	0.5 „	8.0
37	1.0 No. 1	5.0 „	6.0
38	1.0 No. 2	5.0 „	6.0
39	1.0 No. 9	5.0 „	6.0
40	1.0 No. 2	2.5 „	3.5
41	1.0 No. 4	1.0 „	6.0
42	1.0 No. 11	3.0 „	6.0
43	1.0 No. 25	2.0 „	7.0
44	1.0 No. 33	2.0 „	4.0
45	1.0 No. 16	5.0 „	8.0
46	1.0 No. 24	5.0 „	8.0
47	1.0 No. 8	5.0 „	8.0
48	1.0 No. 28	5.0 „	8.0
49	1.0 No. 2	2.0 „	6.0
50	1.0 No. 4	2.0 „	6.0
51	1.0 No. 2	0.5 Formamide	8.0
52	1.0 No. 4	0.5 „	8.0
53	1.0 No. 5	0.5 „	8.0
54	1.0 No. 6	0.5 „	8.0
55	1.0 No. 13	0.5 „	8.0
56	1.0 No. 25	0.5 „	8.0
57	1.0 No. 2	5.0 „	1.0

TABLE 4 (Continued)

Example No.	Parts Dye of Example	Parts Acid amide	Parts Water
58	1.0 No. 4	5.0 Formamide	1.0
59	1.0 No. 7	5.0 „	1.0
60	1.0 No. 27	5.0 „	1.0
61	1.0 No. 1	5.0 „	8.0
62	1.0 No. 3	5.0 „	8.0
63	1.0 No. 5	5.0 „	8.0
64	1.0 No. 7	5.0 „	8.0
65	1.0 No. 2	1.0 „	4.0
66	1.0 No. 4	2.0 „	4.0
67	1.0 No. 7	2.0 „	4.0
68	1.0 No. 25	3.0 „	5.0
69	1.0 No. 26	4.0 „	5.0
70	1.0 No. 25	2.0 „	8.0
71	1.0 No. 2	0.5 Acetamide	8.0
72	1.0 No. 6	0.5 „	8.0
73	1.0 No. 27	0.5 „	8.0
74	1.0 No. 2	5.0 „	4.0
75	1.0 No. 7	5.0 „	4.0
76	1.0 No. 4	5.0 „	8.0
77	1.0 No. 30	5.0 „	8.0
78	1.0 No. 32	3.0 „	6.0
79	1.0 No. 2	1.2 Urea 0.8 Formamide	4.0
80	1.0 No. 4	1.5 Urea 0.5 Ethyl urea	7.0
81	1.0 No. 13	3.0 Formamide 1.0 Methylformamide	3.0
82	1.0 No. 25	2.0 Urea 1.0 Formamide	8.0
83	1.0 No. 27	1.0 Formamide 1.0 Methylformamide	6.0
84	1.0 No. 25	1.5 Urea 0.3 Formamide	8.0

The dyes of formula (I) can be produced by the method described in German Patents 122,904; 132,511 and 216,666. Dyes of formula (I) in which A stands for e.g. the radical of a cyanuric acid can be produced in accordance with German Patent 436,179.

Dyes of formula (II) can be obtained by the process of German Patent 74,593.

The dye of Example 33 is produced in accordance with German Patent 114,841.

The dye of Example 25 is described in our copending patent application No. 47066/69 (Serial No. 1,202,799) which was divided out of this application.

The use of the dyes of Examples 2, 4 and 25 for dyeing paper is described in our copending patent application No. 47067/69 (Serial No. 1,202,800) which was also divided out of this application.

Similarly good dye preparations are obtained by using lactams or lactam mixtures. For example, the urea used in Examples 1 to 7 can be replaced by lactams or mixtures of lactams; such a preparation can be produced as follows:

Example 85.

106 parts of the sodium salt of the disazo dye of Example 25 are formed into a 38% aqueous paste with 173 parts of water. This is then homogeneously stirred in 665 parts of water, and after the addition of 350 parts of γ -butyrolactam the mixture is raised to 85–90°, on which the dye goes into solution. 5 parts of "hyflo" filter earth are added and the solution filtered clear, giving about 1294 parts of a liquid dye preparation which is storable for several months at room temperature. Bright red paper dyeings can be produced with this preparation.

Dye preparations of similarly good quality are obtained when the butyrolactam is replaced by ϵ -caprolactam.

WHAT WE CLAIM IS:—

1. A concentrated liquid preparation of a metal-free direct disazo dye of formula



where F_1 and F_2 represent radicals of identical or different monoazo dyes each bearing 1 to 4 water-solubilizing groups and A represents an imino group or the radical of a diamide of carbonic, fumaric or cyanuric acid, the preparation comprising a storable aqueous solution containing 1 part by weight of dye, 1 to 8 parts by weight of water and 0.5 to 5 parts by weight of an acid amide.

2. A concentrated liquid preparation of a metal-free direct disazo dye of formula



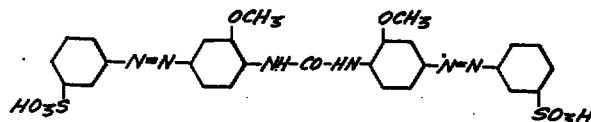
where B represents the radical of a tetrazotizable diamine of the diphenyl series and K_1 and K_2 represent radicals of identical or different azo components, and the dye bearing 1 to 4 water solubilizing groups to each azo group, the preparation comprising a storable aqueous solution containing 1 part by weight of dye, 1 to 8 parts by weight of water and 0.5 to 5 parts by weight of an acid amide.

3. A preparation according to claim 1 or claim 2 containing 0.5 to 2 parts by weight of an acid amide.

4. A preparation according to any one of claims 1 to 3 wherein said acid amide comprises a carboxylic acid amide.

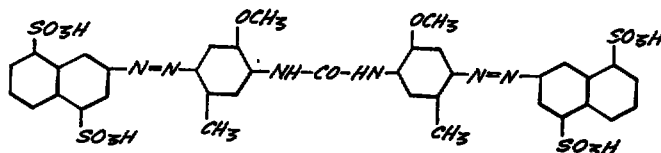
5. A preparation according to claim 4 wherein said carboxylic acid amide is urea.

6. A preparation according to claim 1, containing the dye of formula



(a).

7. A preparation according to claim 1, containing the dye of formula



(b).



The dyes of formula (I) can be produced by the method described in German Patents 122,904; 132,511 and 216,666. Dyes of formula (I) in which A stands for e.g. the radical of a cyanuric acid can be produced in accordance with German Patent 436,179.

Dyes of formula (II) can be obtained by the process of German Patent 74,593. The dye of Example 33 is produced in accordance with German Patent 114,841. The dye of Example 25 is described in our copending patent application No. 47066/69 (Serial No. 1,202,799) which was divided out of this application.

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2. A concentrated liquid preparation of a metal-free direct disazo dye of formula



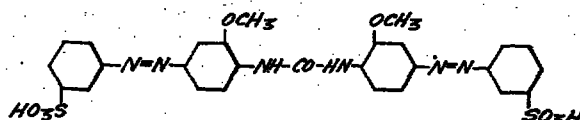
where B represents the radical of a tetrazotizable diamine of the diphenyl series and K_1 and K_2 represent radicals of identical or different azo components, and the dye bearing 1 to 4 water solubilizing groups to each azo group, the preparation comprising a storable aqueous solution containing 1 part by weight of dye, 1 to 8 parts by weight of water and 0.5 to 5 parts by weight of an acid amide.

3. A preparation according to claim 1 or claim 2 containing 0.5 to 2 parts by weight of an acid amide.

4. A preparation according to any one of claims 1 to 3 wherein said acid amide comprises a carboxylic acid amide.

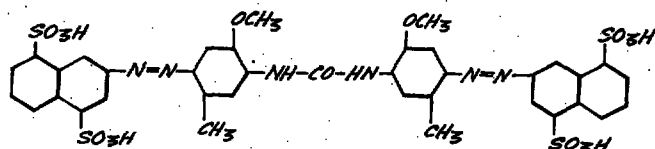
5. A preparation according to claim 4 wherein said carboxylic acid amide is urea.

6. A preparation according to claim 1, containing the dye of formula



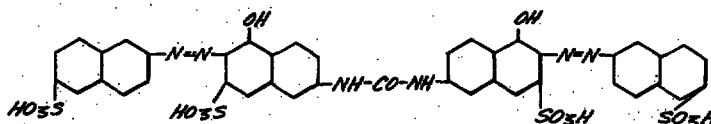
(a).

7. A preparation according to claim 1, containing the dye of formula



(b).

8. A preparation according to claim 1, containing the dye of formula



(c).

9. A preparation according to claim 1 or claim 2 substantially as herein described with reference to any one of Examples 1 to 85.

10. A process for dyeing paper in which there is used a preparation according to any one of claims 1 to 9.

11. A process for dyeing paper substantially as herein described with reference to Dyeing Example A or Dyeing Example B.

12. Paper dyed by a process according to claim 10 or claim 11.

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