

PATENT SPECIFICATION

(11) 1 241053

NO DRAWINGS

- (21) Application No. 40772/68 (22) Filed 26 Aug. 1968
 (31) Convention Application No. 13321 (32) Filed 22 Sept. 1967 in
 (33) Switzerland (CH)
 (45) Complete Specification published 28 July 1971
 (51) International Classification D 06 p 1/06, 1/14, 1/16
 (52) Index at acceptance D1B 2F 2G 2J
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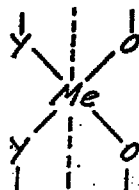
(54) SOLID DYE PREPARATIONS AND THEIR USE

(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 solid dye preparations comprising granules having an average particle size of at least 20 microns, said granules having a core comprising essentially pure dyestuff material which is soluble in water at 25° C. to at least 2% by weight and having a coating comprising a water-soluble salt, the salt comprising up to 50% by weight of the preparation.

By essentially pure dyestuff material we mean dyestuff material (whether a single dye or a mixture of component dyes) that is substantially free of the starting materials used in its production and/or by-products formed during its preparation. In general such essentially pure dyestuff material can be obtained by a conventional recrystallisation or salting out technique. Mixtures of dyes purified individually by such conventional techniques may be used. The preparations of the invention comprising granules which have an average particle size of at least 20 microns and which comprise essentially pure dyestuff material having a water solubility at 25° C. of at least 2% by weight and up to 50% by weight of the preparation of a water-soluble salt, can be prepared by a process which comprises the steps of forming an aqueous suspension of said essentially pure dyestuff material in the presence of said salt, homogenising the suspension and spray-drying the homogenised suspension. It will be readily apparent that, because we operate the process with any form of conventional spray dryer by starting with a suspension of the dye, the granules (or at least a large proportion of them) will have a core of essentially pure dyestuff material and a coating of the water-soluble salt and any other ingredients present. This invention relates further to a process for the preparation of dyebaths, padding liquors and printing pastes for the exhaustion dyeing, pad dyeing and printing of textiles, and to a process for the production of liquid dye preparations for paper dyeing which comprises dissolving in water the afore-stated solid dye preparations.

The dyes which have a water solubility at 25° C. of at least 2% by weight may be of anionic, cationic or nonionic character. The anionic dyes may contain as water-solubilizing groups any one of the following: $-\text{PO}_3\text{H}_2$, $-\text{AsO}_3\text{H}_2$, $-\text{COOH}$, $-\text{SO}_2\text{NH-acyl}$, $-\text{SO}_2-\text{NH}_2$, $-\text{SO}_2-\text{NH-alkyl}$, or

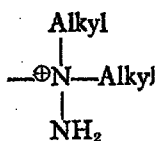


where Me stands for a cobalt or chromium atom and Y for $-\text{O}-$ or $-\text{COO}-$.

Preferred water-solubilizing groups are $-\text{O}-\text{SO}_3\text{H}$ and $-\text{SO}_3\text{H}$. These groups are generally present in the form of salts of alkali metals (sodium, potassium), or as ammonium or water soluble amine salts.

[Price 25p]

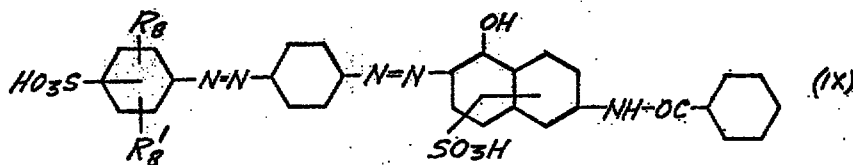
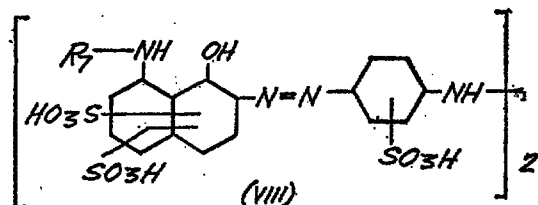
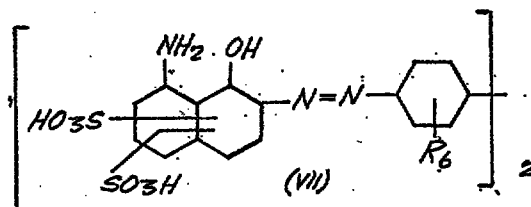
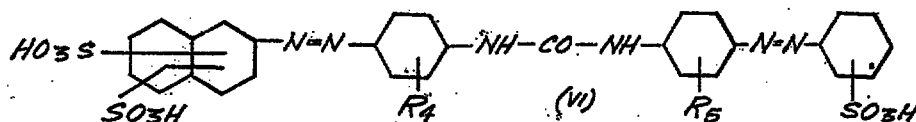
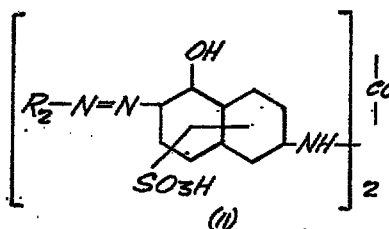
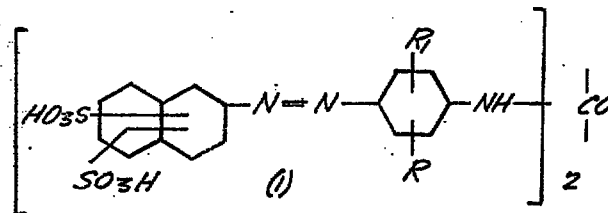
The cationic dyes may bear as water-solubilizing substituents, for example, hydrazinium groups such as

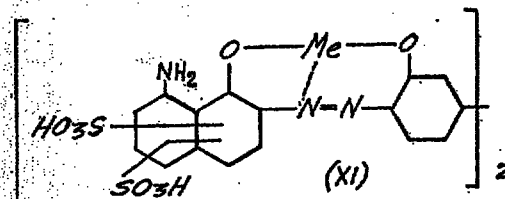
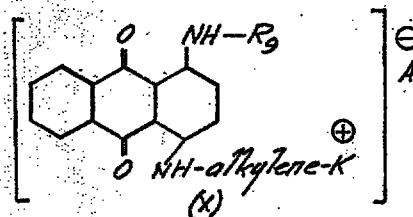


or quaternary ammonium or phosphonium groups.

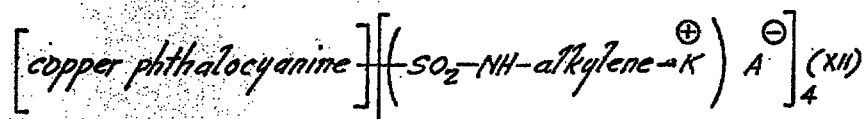
The non-ionic dyes may contain, for example, one or two polyethylene oxide chains $(\text{---CH}_2\text{---CH}_2\text{---O})_n\text{---H}$ or polyol radicals, in particular sugar radicals.

Particularly good dye preparations are obtained with the dyes of the following formulae:

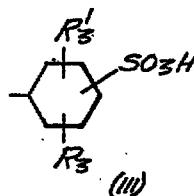




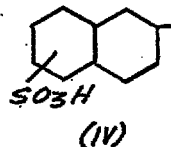
and



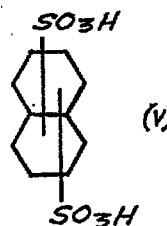
in the above formulae R stands for hydrogen, alkyl or alkoxy, R₁ for hydrogen or alkyl, R₂ for a radical of formula



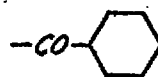
where R₂ represents hydrogen or an alkyl radical and R'₁, hydrogen or a sulphonic acid group, or



or



R₃ for an alkyl radical, R₄ for alkoxy radical, R₅ for hydrogen, alkyl or alkoxy, R₆ for hydrogen or



R₇ for hydrogen or an alkyl radical, R'₂ for hydrogen or a sulphonic acid group, R₈

	for hydrogen, alkyl, cycloalkyl, e.g. cyclohexyl, or aryl, e.g. phenyl, K for a substituted or unsubstituted hydrazinium or ammonium radical, A [⊖] for an anion, e.g. a chloride, bromide, sulphate, disulphate, acetate or methylsulphate ion, and Me for a metal atom. The alkylene radical contains 1 to 6 or preferably 1 to 3 carbon atoms. Alkyl and alkoxy radicals may contain 1 to 4 but preferably 1 and 2 carbon atoms; thus alkyl may stand for methyl or ethyl. The dyes may be members of any class, e.g. monoazo, disazo or polyazo dyes and the complex compounds of these dyes with metals such as chromium, cobalt, copper or nickel; anthraquinone dyes, e.g. 1-amino-2-sulpho-4-arylamino-, 1,4- and 1,5-diarylamino-, 1-amino-2-aryloxy-4-arylamino-anthraquinones and 4-alkylaminoanthraquinonyl-1-amino-trialkylammonium salts; nitro dyes; copper and nickel phthalocyanine dyes; triarylmethane, oxazine, thiazine, dioxazine, xanthine, quinophthalone, diazine or naphthazarine dyes; and the solubilized vat dyes of the indigoid and anthraquinone series. The anionic dyes may be members of the acid class used for dyeing and printing wool, silk, polyamide and polyurethane fibres, or of the direct class used for dyeing and printing cotton, linen and other natural cellulosic fibres and regenerated cellulosic fibres such as viscose and cuprammonium rayon. Other cationic dyes are the solubilized vat dyes. Also suitable are reactive dyes containing a group which forms a chemical linkage with the fibres. Examples of such groups are those of the heterocyclic series (triazines, diazines, oxazines and thiazines), mono- and di-halogenotriazinyl, mono-, di- and tri-halogenopyrimidyl, 2,3-dihalogenoquinoxalyl-5- and -6-carbonyl-, -sulphonyl- and -aminocarbonyl-, 2-halogenobenzoxazol- and -benzthiazole-5-carbonyl- and -6-sulphonyl-, dihalogenopyrimidyl-5-carbonyl- and dihalogenopyrimidyl-5-methylene groups. Suitable groups of the aliphatic series are halogenalkanoyl, halogenalkenoyl, alkenoyl, sulphato-alkanoyl, alkyl- and alkenesulphonyl groups. These groups may be attached to the dye molecule through an optionally substituted imino group and possibly an aliphatic chain. For the mono- and di-halogenotriazinyl- mono-, di- and tri-halogenopyrimidyl and dihalogenopyrimidyl-5-methylene groups, the —O— and —S— bridges are available besides the imino bridge while the halogeno- or sulphato-alkylsulphonyl group and the alkenylsulphonyl group may be bound directly to the dye molecule. Further reactive groups such as sulphatoalkylaminosulphonyl and N-sulphato-alkyl-N-alkyl-aminoalkylene groups are as a rule attached directly to the dye molecule. The aforementioned reactive groups may contain bromine and fluorine atoms and in particular chlorine atoms.		
5		5	5
10		10	10
15		15	15
20		20	20
25		25	25
30		30	30
35	The dyes employed for the preparations of this invention must bear a sufficient number of water-solubilizing groups to impart a solubility of at least 2% by weight in water at 25° C. Thus the anionic azo dyes must contain at least 1 and preferably 2 to 6 sulphonic acid groups and the anionic anthraquinone and phthalocyanine dyes 2 to 4 sulphonic acid groups; the sulphonic acid groups may be partly replaced by —COOH— or —SO ₂ —NH ₂ —groups. The cationic dyes contain, for example, at least 1 and preferably 2 to 4 hydrazinium or ammonium groups.	35	35
40	The substantive disazo dyes, whether metal free or copper or nickel containing, together with the substantive reactive dyes form the preferred group of dyes for employment in the present process.	40	
45	The salts dissociable in water which are used for these dye preparations are primarily the neutral salts of alkali metals, preferably NaCl, KCl, Na ₂ SO ₄ , K ₂ SO ₄ and NaPO ₃ .	45	
50	Salts of alkaline reaction such as Na ₂ CO ₃ , K ₂ CO ₃ , Na ₂ HPO ₄ , Na ₄ P ₂ O ₇ and K ₄ P ₂ O ₇ can be employed for preparations intended for the dyeing of cellulosic fibres or paper, while salts of acid reaction such as KH ₂ PO ₄ , K ₂ H ₂ P ₂ O ₇ and (NH ₄) ₂ SO ₄ or NH ₄ Cl are suitable for dye preparations formulated for application to wool, silk and polyamide fibres. Salts of alkaline or acid reaction however are normally used only in small amounts, for example as standardizing material along with neutral salts. Other suitable non-ionic standardizing agents are, for example, urea, dextrin, sulphite cellulose decomposition products, dispersing agents such as dinaphthylmethanedi-	50	45
55	sulphonic acid and ligninsulphonic acid in the form or their alkali metal salts, and alkanoylaminophenyl, alkenoylaminophenyl, alkanoylaminoalkyl and alkenoylamino-alkyltrialkyl-ammonium or -dialkylbenzyl-ammonium salts (chlorides, bromides or sulphates), alkylpolyglycol ethers, alkenylpolyglycol ethers and alkylphenylpolyglycol ethers with more than 20 moles ethylene oxide, and condensation products of poly-	55	
60	propylene glycol of molecular weight about 1700 with about 140—150 moles ethylene oxide. The alkanoyl and alkenoyl radicals in cationic dispersing agents are derived from higher fatty acids, whilst alkyl stands preferably for methyl, ethyl, propyl or butyl. The alkyl or alkenyl groups in non-ionic dispersing agents contain preferably 12	60	50

to 22 carbon atoms and the alkylphenyl groups are preferably octylphenyl, nonylphenyl or dodecylphenyl groups.

The dispersing agents, when present, are employed in amounts of not more than about 10% of the final dye preparation, the optimum amounts ranging from 2 to 5%. The selected dispersing agent must be of the same ionic character as the dye, either anionic or cationic as the case may be, in order to preclude precipitation. This does not of course apply with non-ionic dispersing agents which can be employed with dyes of any class.

The dyes can be employed singly or in mixtures of two or more components, and the salts likewise. Cationic and anionic dyes must not however be combined in such mixtures since they interact and form precipitates.

The dye preparations of this invention can be produced by suspending the selected dye or dyes, the salt or salts, and, as required, one or more standardizing agents in amounts of about two to ten times or preferably two and a half to five times by weight of water greater than the combined weight of the afore-mentioned solid components. The suspension is homogenized and spray dried, on which the dye preparations are obtained in the form of granules which dust very little and dissolve rapidly in water.

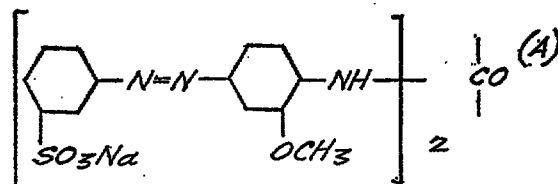
In comparison with the dye preparations in powder form which have hitherto been used, these preparations have the advantage of being more readily wettable with water and more highly soluble in water, this being particularly true of preparations containing a salt which dissociates in water to a maximum of 50%. With such preparations concentrated stock solutions can be prepared.

The transportation costs for the dry preparations of this invention are less than for liquid preparations. They are much stronger than the latter, show better storage stability, and are more suitable for paper dyeing methods in which a dry dye preparation is metered into the paper stock. They are suitable for the exhaustion dyeing, pad dyeing and printing of wool, silk, polyamide, polyurethane, natural cellulosic and regenerated cellulosic fibres, of leather and in particular of paper.

In the following Examples the parts are by weight and temperatures in degrees Centigrade. The granules produced in Examples 1 to 20 and 24 to 26 have an average particle size of at least 20 microns.

EXAMPLE 1

62.5 Parts of the dye of formula



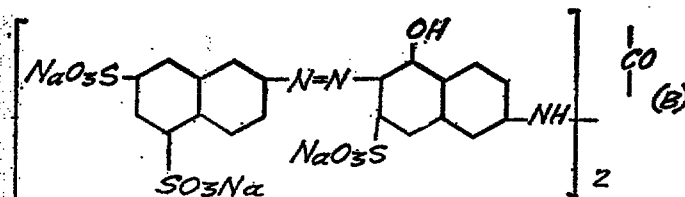
33.5 parts of anhydrous sodium sulphate and 4 parts of sodium ligninsulphonate are stirred into 300 parts of water at room temperature. The resulting dye suspension is homogenized and spray dried. The granules thus formed dissolve readily in water and are highly suitable for dyeing paper in yellow shades.

Dyeing Example A

A solution of 0.1 part of the dye preparation of Example 1, in 5 parts of water is added to a charge of 100 parts of chemically bleached sulphite cellulose in 2000 parts of water after it has been beaten to suitable fineness. After 15 minutes the stock is sized which fixes the dye. Paper made from this stock is dyed in a yellow shade of medium depth which has good fastness properties. The backwater from the paper machine is colourless.

EXAMPLE 2

60 Parts of the dye of formula



are suspended in a solution of 40 parts of anhydrous sodium sulphate in 200 parts

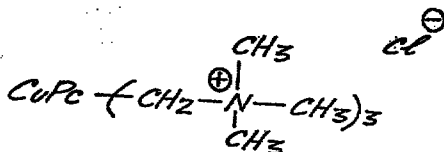
of water at room temperature, and the suspension is homogenized and spray dried. Red granules are obtained which dissolve readily in water and which dye paper in red shades.

Dyeing Example B

A charge of 70 parts of chemically bleached sulphite cellulose and 30 parts of chemically bleached sulphate cellulose in 2000 parts of water is beaten in a pulper, and 0.05 parts of the dye preparation of Example 2 are strewn into the stock at a suitable point. After 20 minutes the stock is converted into an absorbent paper of pale scarlet shade.

EXAMPLE 3

20 Parts of sodium sulphate are dissolved in a solution of 44 parts of the dye of formula



in 150 parts of water, and the dye solution is spray dried. The granules formed dissolve well in water and are eminently suitable for dyeing paper to give absorbent papers of turquoise shade which have good wet and alcohol fastness.

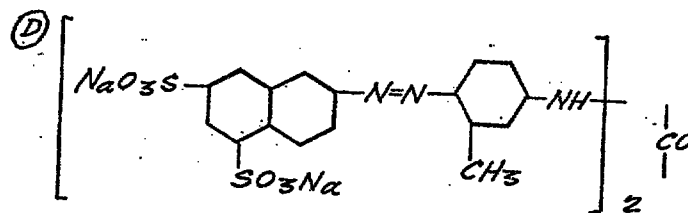
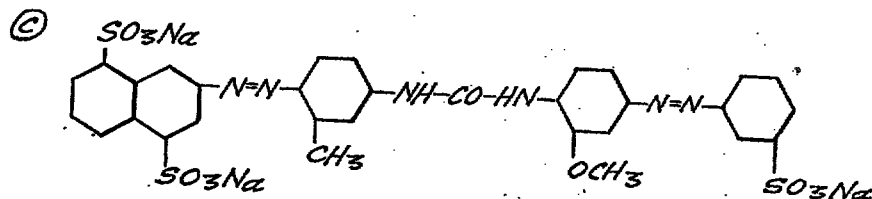
The dye preparations listed in the following table produced in accordance with the procedures of Examples 1 to 3 and are specified by their composition and the shade of their dyeings on paper.

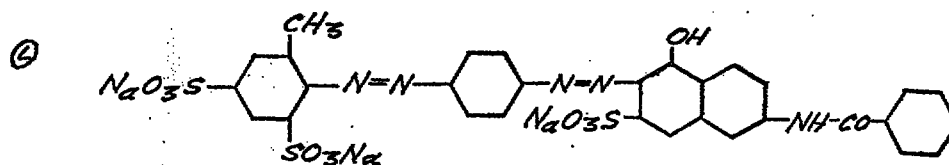
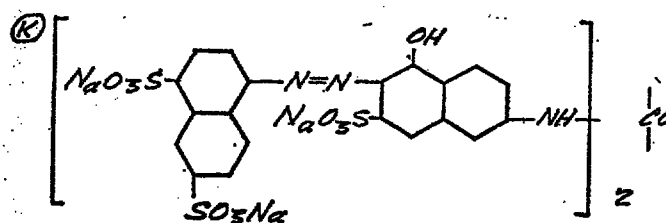
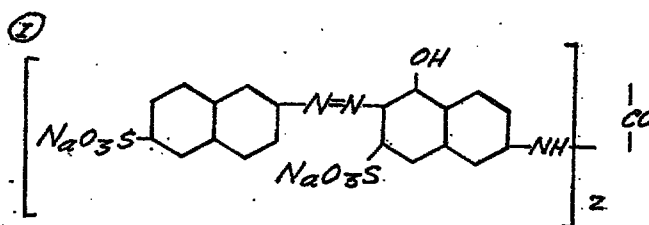
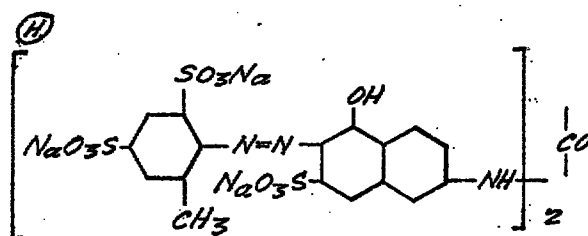
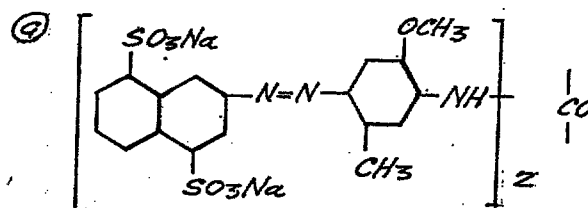
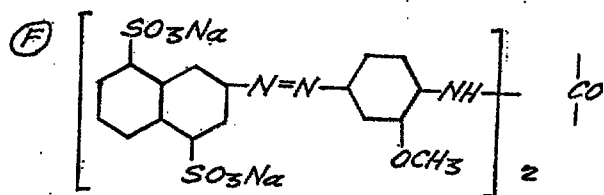
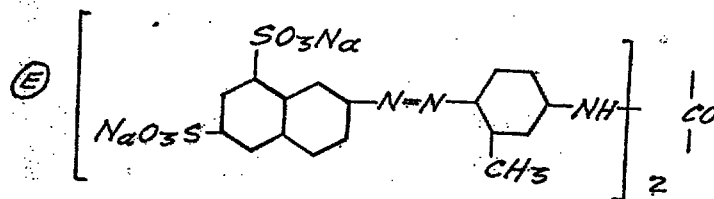
TABLE

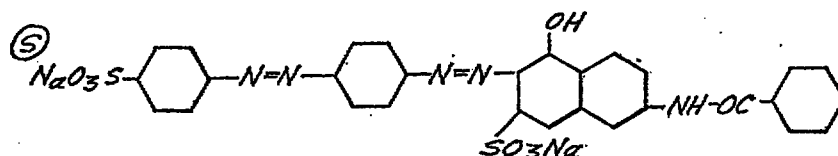
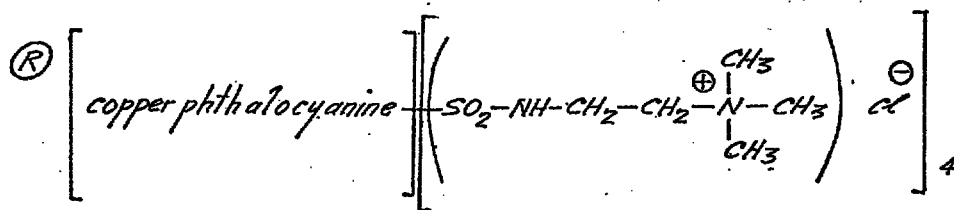
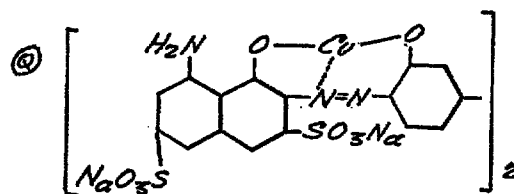
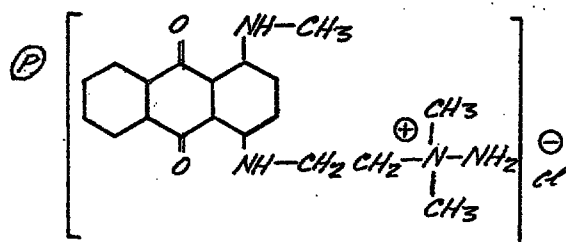
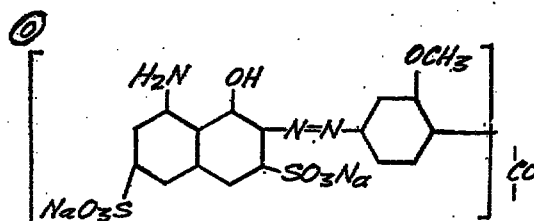
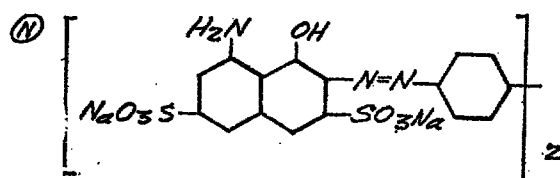
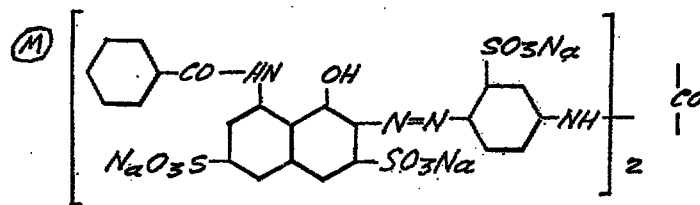
Example No	Dye parts		Na ₂ SO ₄ calc parts	Dispersing agents parts	Shade of paper dyeing
4	(C)	78	22	—	yellow
5	(D)	65	35	—	do
6	(E)	65	35	—	do
7	(F)	70	27	3 parts sodium lignin-sulphonate	reddish yellow
8	(G)	68	32	—	do
9	(H)	65	35	—	yellowish red
10	(I)	50	50	—	red
11	(K)	50	50	—	do
12	(L)	80	20	—	bluish red
13	(M)	75	25	—	violet
14	(N)	60	40	—	blue
15	(O)	60	40	—	do
16	(P)	80	20	—	do
17	(Q)	70	30	—	greenish blue
18	(R)	80	20	—	turquoise
19	(S)	60	40	—	bluish red
20	(T)	60	40	—	blue

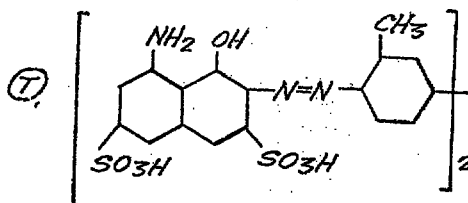
Dye preparations of very good quality are obtained with the dyes of Examples 1, 3, 8, 10, 14, 15, and 17.

The dyes specified in the Table have the following formulae:









EXAMPLE 21

(Preparation of a dyebath)

1.5 Parts of the dye preparation produced as described in Example 1 are dissolved in 2000 parts of water.

EXAMPLE 22

4 Parts of the dye preparation of Example 8 and 20 parts of urea are dissolved in 400 parts of water, and 2 parts of locust bean gum are strewn into the solution. To the thickened solution are added 3 parts of laurylglycoether sulphonate containing 3 moles ethylene oxide groups and 3 parts of nonylphenylpolyglycoether containing 4.5 moles ethylene oxide groups. Finally 5 parts of glacial acetic acid are added.

EXAMPLE 23

10 Parts of the dye preparation produced as described in Example 1 are dissolved by the addition of 280 parts of water at 40°. The solution is stirred into 550 parts of a 30% aqueous crystal gum solution containing 50 parts of urea, 50 parts of thiodiethylene glycol and 60 parts of a 30% aqueous ammonium sulphate solution.

The dye preparations employed in Examples 19, 20 and 21 can be replaced by any of those listed in the Table to give equally good dyebaths, padding liquors or printing pastes.

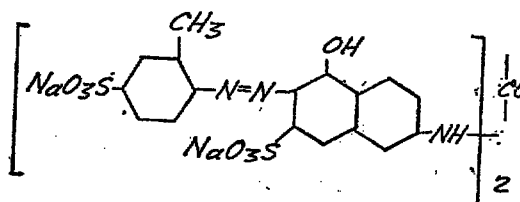
EXAMPLE 24

95 Parts of the dye of formula (A) as used in Example 1 and 5 parts of sodium chloride are stirred into 400 parts of water at room temperature to form a dye suspension which is homogenized and spray dried. Yellow granules are formed which dissolve readily in water. They are highly suitable for dyeing paper in yellow shades.

The 5 parts of sodium chloride used in this Example can be replaced by 5 parts of sodium metaphosphate, which gives yellow granules showing similarly good properties.

EXAMPLE 25

95 Parts of the dye of formula



are stirred into a solution of 5 parts of sodium carbonate in 350 parts of water at room temperature. The solution is then homogenized and spray dried to yield red granules. These dissolve well in water and are very suitable for producing reddish orange shades on paper.

Red granules with similarly good properties are obtained when the 5 parts of sodium carbonate used in this Example are replaced by 10 parts of sodium carbonate or by 5 parts of potassium carbonate.

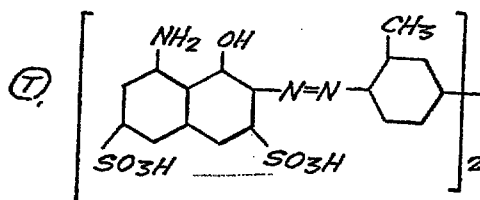
EXAMPLE 26

50 Parts of the dye of formula (A) as used in Example 1 are stirred into a mixture of 250 parts of water, 5 parts of sodium chloride and 20 parts of dextrin, and the solution is homogenized and spray dried to granulate form. The granules dissolve readily in water and dye paper in yellow shades.

The 20 parts of dextrin used in this Example can be replaced by 20 parts of urea to give granules with similarly good properties.

WHAT WE CLAIM IS:—

1. A process for the preparation of a solid dy preparation which comprises the



EXAMPLE 21

(Preparation of a dyebath)

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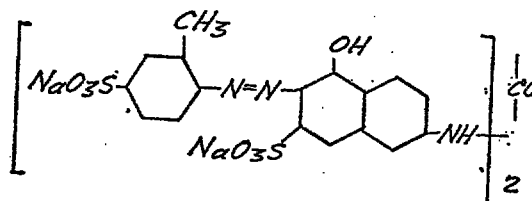
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WHAT WE CLAIM IS:—

1. A process for the preparation of a solid dy preparation which comprises the

steps of forming an aqueous suspension of essentially pure dyestuff material, said dyestuff material having a water solubility at 25° C. of at least 2% by weight, in the presence of a water-soluble salt, homogenising the suspension and spray-drying the homogenised suspension to form a granular preparation, the granules of which have an average particle size of at least 20 microns and contain the dyestuff material and the salt, the salt comprising up to 50% by weight of the preparation.

2. A process according to claim 1, in which the aqueous suspension further includes a dispersing agent.

3. A process according to claim 1 or claim 2 in which the aqueous suspension further includes a standardizing agent.

4. A process according to claim 3 in which urea, dextrin or a sulphite cellulose decomposition product is used as a standardizing agent.

5. A process according to any one of the preceding claims in which a neutral salt is used.

6. A process according to claim 5 in which sodium chloride, sodium sulphate or sodium metaphosphate is used.

7. A process according to any one of claims 1 to 4 in which a salt of alkaline reaction is used.

8. A process according to claim 7 in which sodium or potassium carbonate is used.

9. A process according to claim 1 substantially as herein described with reference to any of Examples 1 to 20 or 24 to 26.

10. A solid dye preparation prepared by a process according to any one of the preceding claims.

11. A solid dye preparation comprising granules having an average particle size of at least 20 microns, said granules having a core comprising essentially pure dyestuff material which is soluble in water at 25° C. to at least 2% by weight and having a coating comprising a water-soluble salt, the salt comprising up to 50% by weight of the preparation.

12. A preparation according to claim 11, in which the coating further includes a dispersing agent.

13. A preparation according to claim 11 or claim 12, in which the coating further includes a standardizing agent.

14. A preparation according to claim 13, in which the standardizing agent is urea, dextrin or a sulphite cellulose decomposition product.

15. A solid dye preparation comprising granules which have an average particle size of at least 20 microns and which comprise essentially pure dyestuff material having a water solubility at 25° C. of at least 2% by weight and up to 50% by weight of the preparation of a water-soluble salt.

16. A preparation according to claim 15, in which the granules further comprise a dispersing agent.

17. A preparation according to claim 15 or claim 16, in which the granules further comprise a standardizing agent.

18. A preparation according to claim 17, in which the standardizing agent is urea, dextrin or a sulphite cellulose decomposition product.

19. A preparation according to any one of the claims 11 to 18, in which the salt comprises from 5 to 50% by weight of the preparation.

20. A preparation according to any one of claims 11 to 19, containing a neutral salt.

21. A preparation according to claim 20, in which the neutral salt is sodium chloride, sodium sulphate or sodium metaphosphate.

22. A preparation according to any one of claims 11 to 19, containing a salt of alkaline reaction.

23. A preparation according to claim 22, in which the salt of alkaline reaction is sodium carbonate or potassium carbonate.

24. A preparation according to any one of claims 11 to 23, which contains a dye of formula

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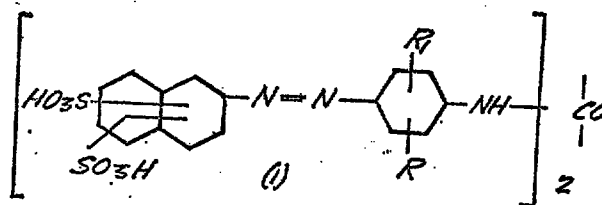
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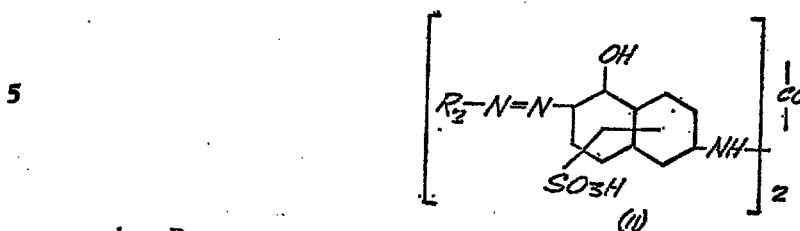
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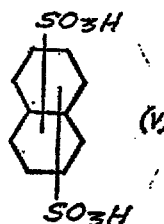
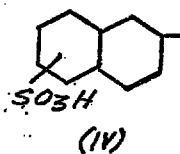
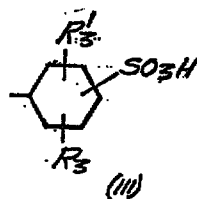


where R represents hydrogen, alkyl or alkoxy and R₁ hydrogen or alkyl.

25. A preparation according to any one of Claims 11 to 23, which contains a dye of formula

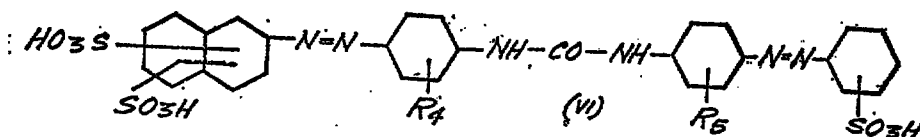


where R₂ represents a radical of formula



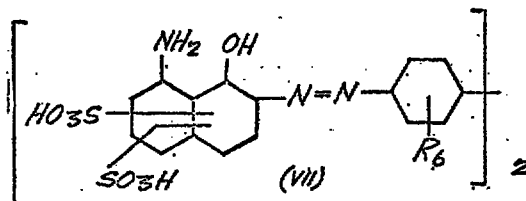
and where R₃ in formula (III) represents hydrogen or an alkyl radical and R'₃ hydrogen or a sulphonic acid group.

26. A preparation according to any one of claims 11 to 23, which contains a dye of formula



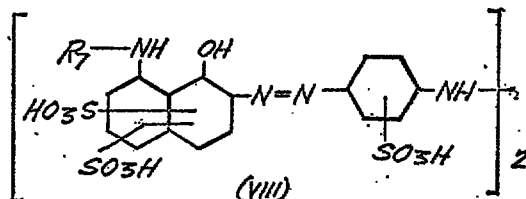
where R₄ represents an alkyl radical and R₅ an alkoxy radical.

27. A preparation according to any one of Claims 11 to 23, which contains a dye of formula

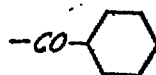


where R_6 represents hydrogen, alkyl or alkoxy.

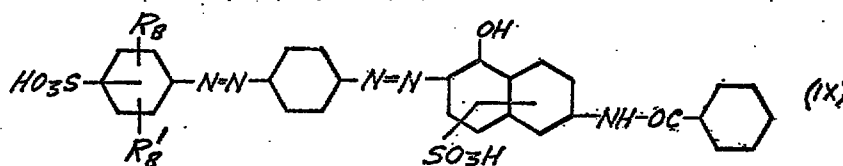
28. A preparation according to any one of Claims 11 to 23, which contains a dye of formula



where R_7 represents hydrogen or

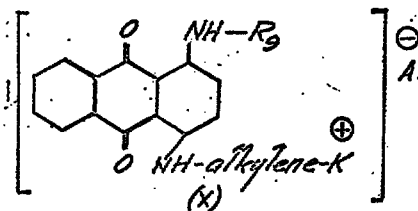


29. A preparation according to any one of Claims 11 to 23 which contains a dye of formula



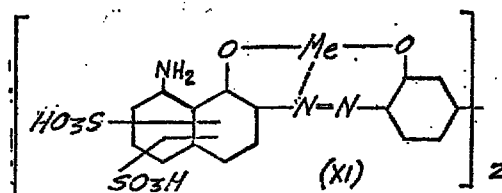
where R_8 represents hydrogen or an alkyl radical and R'_8 hydrogen or a sulphonic acid group.

30. A preparation according to any one of Claims 11 to 23, which contains a dye of formula



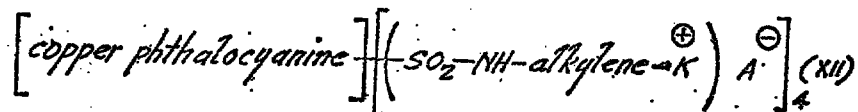
where R_9 represents hydrogen, alkyl, cycloalkyl or aryl, K^+ a hydrazinium or ammonium radical and A^- an anion.

31. A preparation according to any one of Claims 11 to 23, which contains a dye of formula



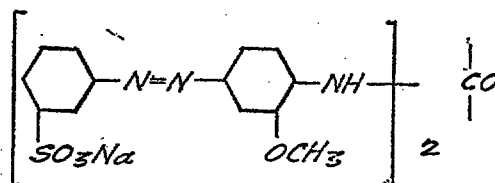
where Me represents a metal atom.

32. A preparation according to any one of Claims 11 to 23, which contains a dye of formula

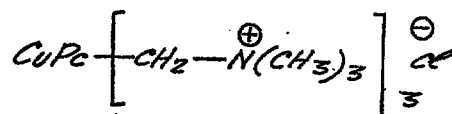


5 where $\text{K}^{\oplus}$ represents a substituted or unsubstituted hydrazinium or ammonium radical and $\text{A}^{\ominus}$ an anion. 5

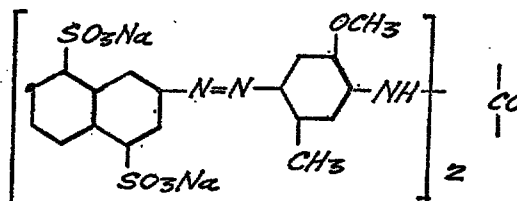
33. A preparation according to any one of Claims 11 to 23, which contains the dye of formula



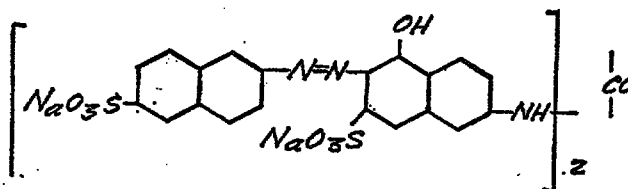
10 34. A preparation according to any one of Claims 11 to 23, which contains the dye of formula 10



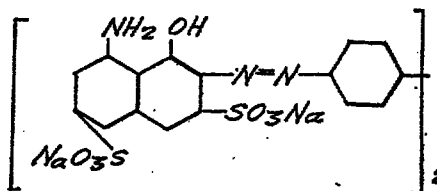
35. A preparation according to any one of Claims 11 to 23, which contains the dye of formula



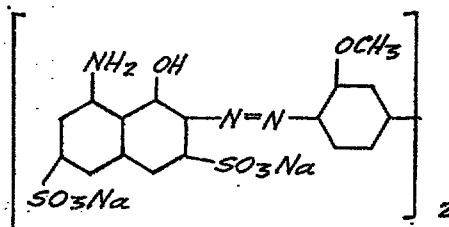
15 36. A preparation according to any one of Claims 11 to 23, which contains the dye of formula 15 20



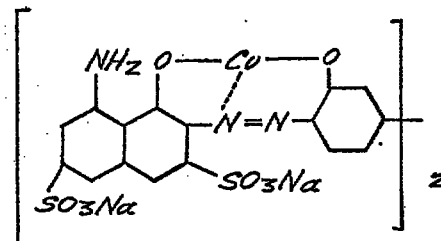
20 37. A preparation according to any one of Claims 11 to 23, which contains the dye of formula 20



38. A preparation according to any one of Claims 11 to 23, which contains the dye of formula



39. A preparation according to any one of Claims 11 to 23, which contains the dye of formula



40. Solid dye preparations substantially as herein described with reference to any of Examples 1 to 20 or 24 to 26.

41. A process for the preparation of a dyebath, padding liquor or printing paste for the exhaustion dyeing, pad dyeing or printing of textiles, which comprises dissolving in water a preparation according to any one of claims 10 to 40.

42. A process for the preparation of a dyeing solution for dyeing paper which comprises dissolving in water a preparation according to any one of claims 10 to 40.

43. A process according to claim 41 or claim 42 substantially as herein described and exemplified.

44. Dyebaths, padding liquor and printing pastes for the exhaustion dyeing, pad dyeing and printing of textiles, and dyeing solutions for dyeing paper, prepared by dissolving in water a preparation according to any one of claims 10 to 40.

45. Textiles dyed, padded or printed, and paper dyed, using a dyebath, padding liquor, printing paste or dyeing solution according to claim 44.

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Printed for Her Majesty's Stationery Office by the Courier Press, Leamington Spa, 1971.
Published by the Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from
which copies may be obtained.