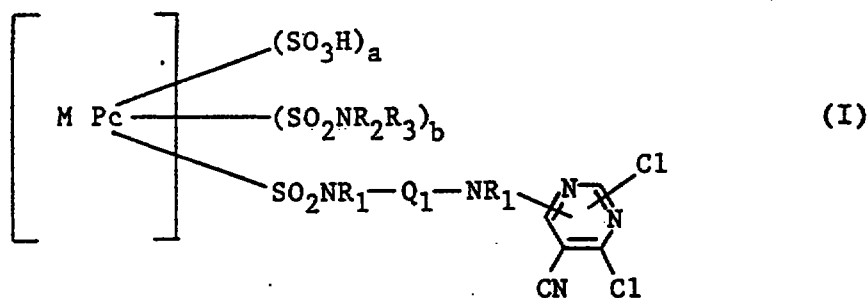


Phthalocyanine fibre-reactive dyes

The invention relates to phthalocyanine compounds which contain a heterocyclic reactive radical, a process for their production and their use as fibre reactive dyes in dyeing and printing processes.

According to the invention there is provided a compound of formula I



in free acid or salt form and mixtures thereof, in which

Pc is the phthalocyanine radical;

M is Cu, Ni, Co, Fe or Al;

a is 1, 2 or 3;

b is 0, 1 or 2;

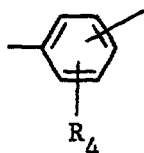
R₂ and R₃ independently are selected from hydrogen and C₁₋₆alkyl, or together with the nitrogen atom to which they are attached they form a five or six membered cyclic ring system which may contain a O- or N- atom;

each R₁ independently is hydrogen, unsubstituted C₁₋₄alkyl or C₁₋₄alkyl which is monosubstituted by hydroxy, halogen,

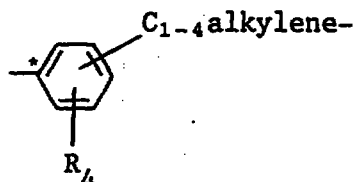
$-\text{SO}_3\text{H}$, $-\text{OSO}_3\text{H}$ or $-\text{COOH}$ and

Q_1 is C_{2-6} alkylene uninterrupted or interrupted by $-\text{O}-$ or $-\text{NR}_1-$, monohydroxy-substituted C_{3-6} alkylene, a group of one of the formulae i) to iv),

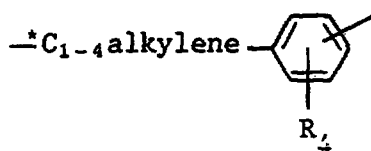
i)



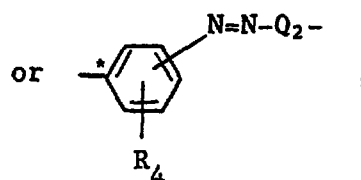
ii)



iii)



iv)



in which * identifies the atom attached to the $-\text{SO}_2\text{NR}_1-$ group; or

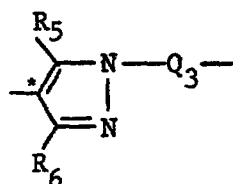
$-\text{SO}_2\text{NR}_1-\text{Q}_1-\text{NR}_1-$ is $-\text{SO}_2-\text{N} \begin{array}{c} \diagup \quad \diagdown \\ \text{ } \end{array} \text{N}-$, $-\text{SO}_2-\text{N} \begin{array}{c} \diagup \quad \diagdown \\ \text{ } \end{array} \text{N}-\text{C}_{2-4}\text{alkylene}-\text{NR}_1-$

or $-\text{SO}_2\text{NR}_1-\text{C}_{2-4}\text{alkylene}-\text{N} \begin{array}{c} \diagup \quad \diagdown \\ \text{ } \end{array} \text{N}-$;

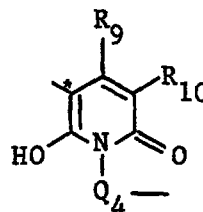
R_4 is hydrogen, halogen, hydroxy, C_{1-4} alkyl, C_{1-4} alkoxy, $-\text{COOH}$ or $-\text{SO}_3\text{H}$;

Q_2

is

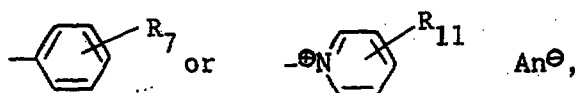
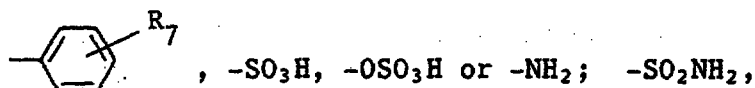


or



in which * indicates the coupling position;

- R₅ is -OH or -NH₂;
 R₆ is C₁₋₄alkyl or -COR₈;
 R₈ is -OH, -O-C₁₋₄alkyl or -NH₂;
 Q₃ is a divalent bridging group;
 R₉ is hydrogen, C₁₋₄alkyl, C₅₋₆cycloalkyl, phenyl or phenyl-(C₁₋₄alkyl), in which any phenyl radical in R₉ is unsubstituted or is substituted by one to three substituents selected from C₁₋₄alkyl, C₁₋₄alkoxy, halogen, -COOH and -SO₃H; -COR₈, -C₁₋₄alkyl-SO₃H, -C₁₋₄alkyl-OSO₃H or -C₁₋₄alkyl-COR₈;
 R₁₀ is hydrogen, -CN, -SO₃H, -COR₈, C₁₋₄alkyl, C₁₋₄alkyl which is monosubstituted by -OH, halogen, -CN, C₁₋₄alkoxy,

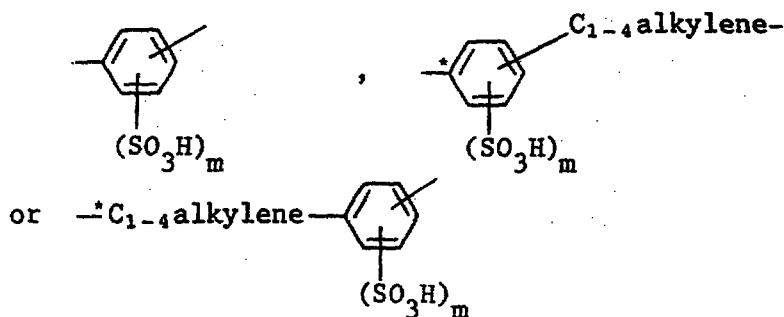


wherein R₇ is hydrogen, halogen, C₁₋₄alkyl, C₁₋₄alkoxy, -COOH or -SO₃H;

R₁₁ is hydrogen, C₁₋₄alkyl or hydroxy-C₂₋₄alkyl;
 and

An[⊖] is a non-chromophoric anion; and

- Q₄ is C₂₋₆alkylene uninterrupted or interrupted by -O- and -NR₁-, monohydroxy-substituted C₃₋₆alkylene,



in which m is 0 or 1 and * indicates the carbon atom attached to the nitrogen atom of the pyridone ring; or

$-Q_4-NR_1-$ is a group $-C_{2-4}$ alkylene-N  N- ;
with the provisos that

α) the sum of a + b is a maximum of 3; and

β) when Q_1 is C_{2-6} alkylene uninterrupted or interrupted by $-O-$ or $-NR_1-$, monohydroxy-substituted C_{3-6} alkylene or a group of formulae i) to iii) defined above;

or $-SO_2NR_1-Q_1-NR_1-$ is $-SO_2-N$  N- , $-SO_2-N$  N- C_{2-4} alkylene- NR_1-

or $-SO_2NR_1-C_{2-4}$ alkylene-N  N- ,

then when b is 1 or 2 and R_2 is hydrogen, R_3 is not hydrogen.

In the present application references to any alkyl or any alkylene group capable of being linear or branched is linear and branched unless indicated to the contrary. In a hydroxy-substituted alkyl or alkylene group which is bonded to nitrogen, the hydroxy group is preferably located at a C-atom which is not directly bonded to nitrogen.

Halogen is fluorine, chlorine or bromine; preferably chlorine or bromine and especially chlorine.

Due to the non-selectivity of the reaction of 5-cyano-2,4,6-trichloropyrimidine at the $-NR_1$ group of the chromophore which occurs by displacement of any one of the chloro atoms on pyrimidine, the site of attachment of the pyrimidine group is not fixed.

Preferably the compounds of formula I are isomeric mixtures in which the positions of the substituents on the phthalocyanine group and the site attachment of the pyrimidine group are not fixed.

Preferably M is M' in which M' is Cu or Ni.

Preferably R_1 is hydrogen, C_{1-2} alkyl or C_{1-3} alkyl substituted by a group selected from hydroxy, $-SO_3H$, $-OSO_3H$ and $-COOH$, (of which hydroxy is most preferred).

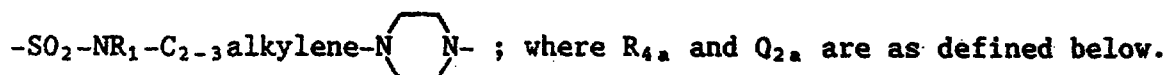
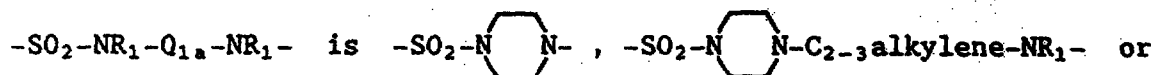
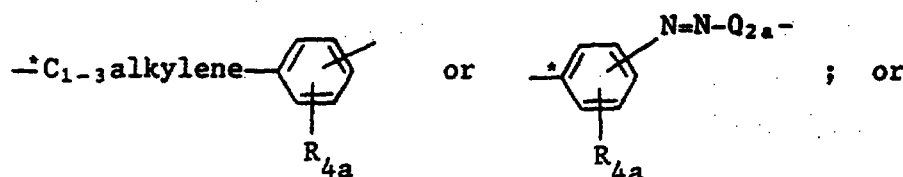
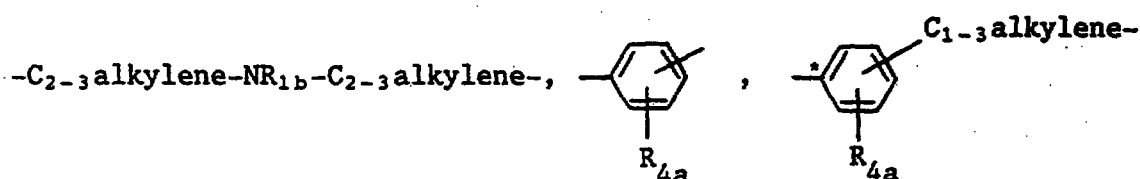
Preferably R_1 is R_{1a} , in which each R_{1a} independently is hydrogen, methyl, ethyl, 2-hydroxyethyl, $-(CH_2)_pSO_3H$, $-(CH_2)_pOSO_3H$ or $-(CH_2)_qCOOH$, and p is 1 or 2 and q is 1, 2 or 3.

More preferably R_1 is R_{1b} , in which each R_{1b} independently is hydrogen, methyl, ethyl or 2-hydroxyethyl.

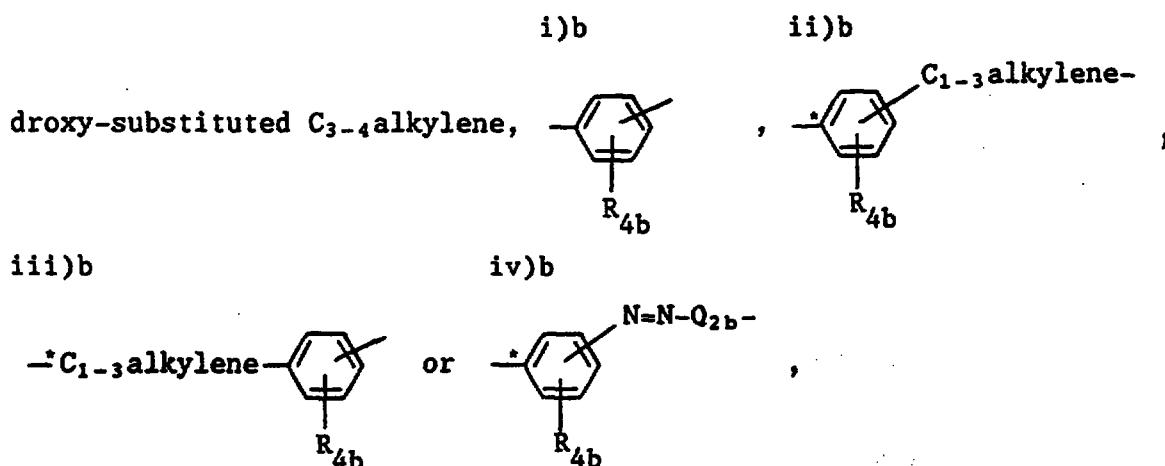
Most preferably R_1 is R_{1c} where R_{1c} is hydrogen or methyl.

Preferably R_2 and R_3 are R_{2a} and R_{3a} , in which each R_{2a} and R_{3a} independently is hydrogen or C_{1-4} alkyl, or R_{2a} and R_{3a} , together with the N-atom to which they are attached form a pyrrolidine, piperidine, morpholine or piperazine ring. More preferably R_2 and R_3 are R_{2b} and R_{3b} , in which each R_{2b} and R_{3b} independently is hydrogen, methyl or ethyl.

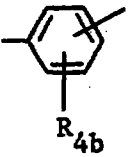
Preferably Q_1 is Q_{1a} in which Q_{1a} is C_{2-3} alkylene, monohydroxy-substituted C_{3-4} alkylene, $-C_{2-3}$ alkylene-O- C_{2-3} alkylene-,

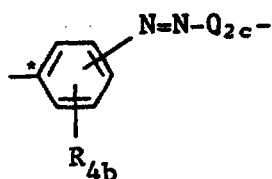


More preferably Q_1 is Q_{1b} in which Q_{1b} is C_{2-3} alkylene, monohy-



where R_{4b} and Q_{2b} are as defined below; or -SO₂-NR₁-Q_{1b}-NR₁- forms a group -SO₂-NN- .

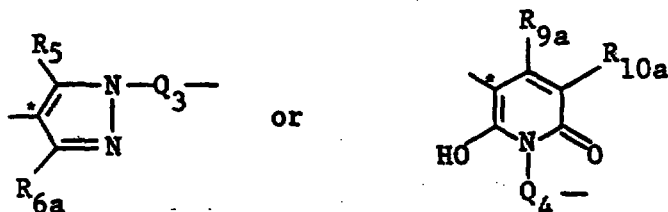
Most preferably Q₁ is Q_{1c} in which Q_{1c} is  or



where R_{4b} and Q_{2c} are as defined below.

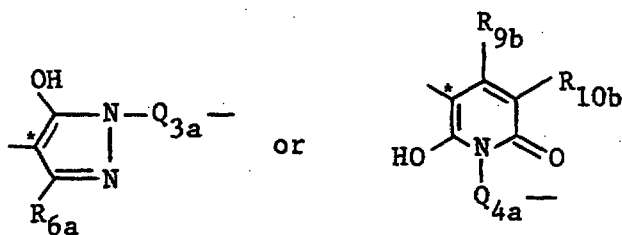
Preferably R₄ is R_{4a} in which R_{4a} is hydrogen, methyl, methoxy, -COOH or -SO₃H. More preferably R₄ is R_{4b} in which R_{4b} is hydrogen, -COOH or -SO₃H.

Preferably the radical Q₂ is Q_{2a} in which Q_{2a} is



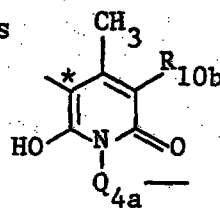
in which R_{6a}, R_{9a} and R_{10a} are as defined below.

More preferably Q₂ is Q_{2b} in which Q_{2b} is



in which R_{6a} , R_{9b} , R_{10b} , Q_{3a} and Q_{4a} are as defined below.

Most preferably Q_2 is Q_{2c} in which Q_{2c} is



in which R_{10b} and Q_{4a} are as defined below.

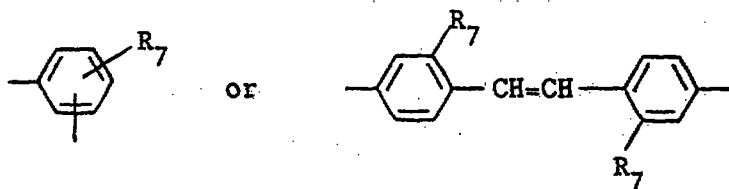
Preferably R_5 is $-OH$.

Preferably R_6 is R_{6a} in which R_{6a} is methyl, $-COOH$ or $-CONH_2$.

Preferably R_7 is R_{7a} in which R_{7a} is hydrogen, chlorine, methyl, methoxy, $-COOH$ or $-SO_3H$.

Preferably R_8 is R_{8a} in which R_{8a} is $-OH$ or $-NH_2$.

Preferably Q_3 is a group Q_{3a} in which Q_{3a} is



and R_7 is as defined above.

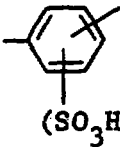
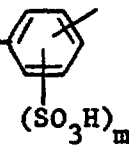
More preferably in Q_{3a} , R_7 is R_{7a} as defined above.

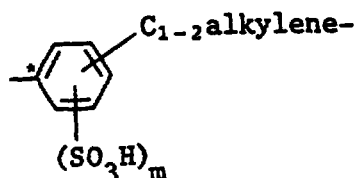
Most preferably in Q_{3a} , R_7 is $-SO_3H$.

Preferably R_9 is R_{9a} in which R_{9a} is hydrogen, methyl, ethyl, phenyl, $-COR_{8a}$, $-CH_2SO_3H$ or $-CH_2OSO_3H$. More preferably R_9 is R_{9b} in which R_{9b} is methyl or ethyl, most preferably methyl.

Preferably R_{10} is R_{10a} in which R_{10a} is hydrogen, $-CN$, $-SO_3H$, $-COR_{8a}$ or $-CH_2SO_3H$. More preferably R_{10} is R_{10b} in which R_{10b} is

hydrogen or $-\text{CONH}_2$.

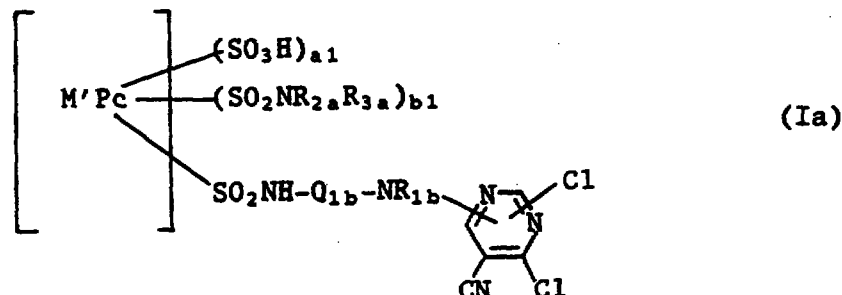
Preferably Q_4 is Q_{4a} in which Q_{4a} is C_{2-4} alkylene, monohydroxy-substituted C_{3-4} alkylene, , $-\text{C}_{1-2}$ alkylene- or



in which m is 0 or 1 and $*$ indicates the carbon atom attached to the nitrogen atom of the pyridone ring, or

$-Q_{4a}-\text{NR}_1-$ forms $-\text{C}_{2-3}$ alkylene--.

Preferred compounds of formula I are those of formula Ia and mixtures thereof



in which the symbols are as defined above; and

a_1 is 2 or 3;

b_1 is 0 or 1;

provided that the sum of a_1 and b_1 is a maximum of 3;

with the proviso that

when Q_{1b} is C_{2-3} alkylene, monohydroxy-substituted C_{3-4} alkylene or a group of formulae i)b to iii)b defined above; or

$-\text{SO}_2\text{NH}-Q_{1b}-\text{NR}_{1b}-$ is $-\text{SO}_2-\text{N}$ - ,

then when b_1 is 1 and R_{2a} is hydrogen, R_{3a} is not hydrogen.

Preferably, in compounds of formula Ia Q_{1b} is Q_{1c} .

More preferred compounds of formula Ia are those in which b_1 is 0 and a_1 is 2 or 3.

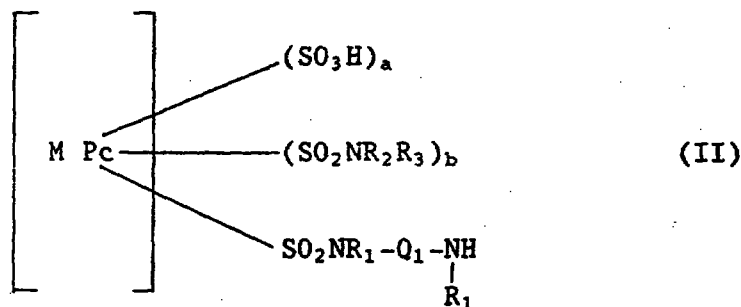
Most preferably, in compounds of formula Ia R_{1b} is hydrogen or methyl and Q_{1b} is Q_{1c} .

Dyestuffs in the form of salts of compounds of formula I are suitably water-soluble and include any non-chromophoric cation common in the chemistry of reactive dyes. Suitable cations are associated with the sulpho groups, and any carboxy groups that are present in the compound of formula I. Examples of suitable cations are alkali metal ions or unsubstituted or substituted ammonium ions, for example lithium, sodium, potassium, ammonium, mono-, di-, tri- and tetra-methylammonium, triethylammonium and mono-, di- and tri-ethanolammonium.

Preferably the cations are selected from the alkali metal ions and ammonium, more preferably sodium.

Dyestuffs according to the invention may be single or mixed salts of compounds of formula I. By mixed salt is meant a salt of two or more different cations.

The invention further provides a process for preparing a compound of formula I or a mixture thereof, which comprises reacting a compound of formula II,



in which R_2 , R_3 , R_1 , Q_1 , a , b , M and Pc are as defined above including the provisos α) and β) as defined above, or a mixture of compounds of formula II, with 5-cyano-2,4,6-trichloropyrimidine, in appropriate molar amounts.

The reaction is suitably carried out at 0° to 40°C and at pH 6.5 to 9. Water is normally used as the reaction medium, but an organic solvent such as acetone can be used as solvent for the 5-cyano-2,4,6-trichloropyrimidine.

The compounds of formula I may be used in free acid form or preferably may be isolated as a single or mixed salt using conventional isolation methods for example, salting out with alkali metal salts, filtering off and drying (in a vacuum) at a slightly elevated temperature.

The starting compounds of formula II are either known or may be obtained by known methods from known compounds.

The compounds of formula I and mixtures thereof are reactive dyes. They are suitable for dyeing or printing hydroxy-group-containing or nitrogen-containing organic substrates. They can for example be used for dyeing or printing fibres, filaments or textiles produced therefrom which consist of or contain natural or synthetic polyamides or natural or regenerated cellulose material, e.g. cotton, viscose or rayon staple fibre, and preferably textile material which consists of or contains cotton. They may also be used for dyeing or printing leather, preferably chrome-tanned types of leather, by known methods.

Methods for dyeing include dye baths or printing pastes commonly used with reactive dyes. For example cotton is preferably dyed by the exhaust process, for example from a long or short bath and at a temperature from 30 to 80°C .

Preferred compounds according to the invention are those which

have good cold dyeing properties and may be used for cold-dyeing at temperatures of about 60°C.

The compounds according to the invention may be used on their own or in combination with other reactive dyes of the same class, which possess comparable dyeing properties, e.g. all-round fastness, exhaust value etc. The combination dyeings obtained have fastness which is as good as that of dyeings made with individual dyes.

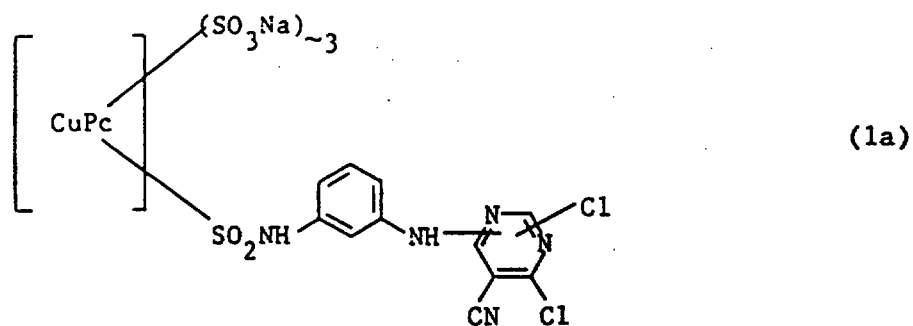
Good exhaust and fixing values are obtained with the compounds of formula I. The unfixed part of the dye can be easily washed out. The dyeings and prints obtained have good light fastness. In addition, they have good washing fastness and wet fastness properties for example to water, sea water and perspiration, and have good resistance to oxidation caused by for example chlorine-containing water, hypochlorite bleaches, peroxide bleaches and perborate-containing detergents.

The following examples illustrate the invention. All parts and percentages are by weight and all temperatures are given in degrees celsius unless indicated to the contrary.

Example 1

25.7 parts (0.025 mols) of a copper phthalocyanine dyestuff base compound containing per molecule on average 2.5 to 3 sulphonic acid groups and 1 sulphamide group, produced by sulphochlorinating copper phthalocyanine and subsequently reacting with 1,3-diaminobenzene, are dissolved in 200 parts of water at pH 6.5 to 7.0. 150 parts of ice are added and an acetic solution of 6.3 parts of 5-cyano-2,4,6-trichloropyrimidine in acetone (20% excess) is added as a single addition. The pH of the reaction mixture drops and is held at pH 7 to 7.5 for the duration of the reaction by the continuous addition of 20% soda solution. At the same time the reaction temperature is raised to and maintained at 25°C. After 3 to 4 hours, the reaction is complete. The mixture is salted out with 45 parts of

sodium chloride, and the dyestuff deposit obtained is filtered off under suction and dried at 35°. The dyestuff obtained is of formula 1a



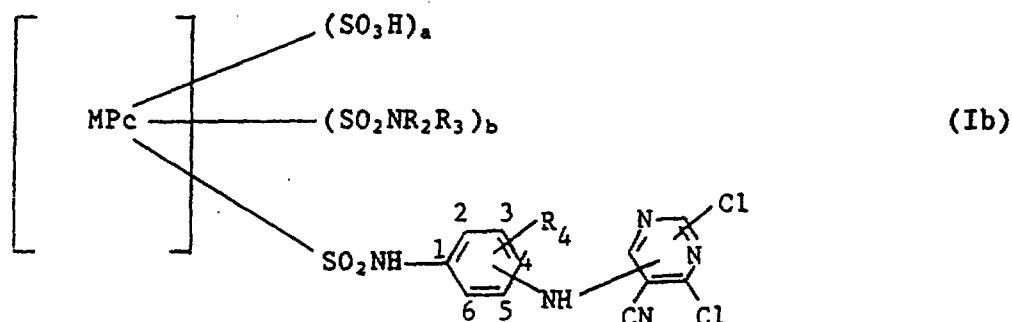
and dyes cellulose material, especially cotton, brilliant turquoise shades. The dyeings have good light fastness and wet fastness.

Example 2

By using, instead of the 25.7 parts of copper phthalocyanine dyestuff base compound of example 1, an equivalent amount of nickel phthalocyanine dyestuff base compound having 2.5 to 3 sulphonic acid groups per molecule of dyestuff base compound, [i.e. 25.5 parts (= 0.025 mols)], the nickel analogue of dyestuff of formula 1a is obtained, which dyes cotton a blue-green shade and produces dyeings with good fastness properties.

Examples 3-16

Using a method analogous to that described in examples 1 and 2, and starting with the appropriate starting compounds, the following compounds of formula Ib (represented in the free acid form)



in which the significances are as defined in Table 1 are prepared.

The values given for a and b are average values.

The table gives the shade of dyeing on cotton of the examples, in which

bt = brilliant turquoise

bg = blue-green.

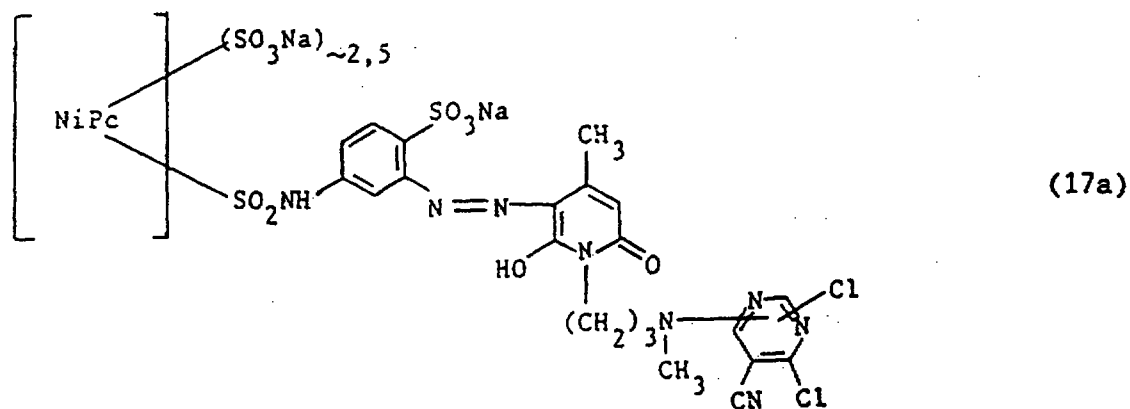
These cotton dyeings have good fastness.

Table 1 Compounds of formula Ib

Ex.No.	M	a	b	R ₂	R ₃	R ₄ (position in ring)	position of -NH- in ring	Shade of dyeing
3	Cu	2.5	0	-	-	H	3	bt
4	Cu	2	1	CH ₃	CH ₃	H	3	bt
5	Cu	2	1	C ₂ H ₅	C ₂ H ₅	H	3	bt
6	Cu	3	0	-	-	4-SO ₃ H	3	bt
7	Cu	2	1	C ₂ H ₅	H	do.	3	bt
8	Cu	2	1	CH ₃	H	2-COOH	4	bt
9	Cu	3	0	-	-	H	4	bt
10	Cu	2	1	C ₂ H ₅	C ₂ H ₅	H	4	bt
11	Ni	2.5	0	-	-	H	3	bg
12	Ni	3	0	-	-	H	4	bg
13	Ni	2	1	CH ₃	CH ₃	H	3	bg
14	Ni	2	1	C ₂ H ₅	C ₂ H ₅	H	4	bg
15	Ni	3	0	-	-	4-SO ₃ H	3	bg
16	Ni	2	1	C ₂ H ₅	H	3-SO ₃ H	4	bg

Example 17

25.5 parts of a nickel phthalocyanine dyestuff base compound containing on average 2.5 sulphonic acid groups and 1 sulphamide group per molecule produced by sulphochlorinating nickel phthalocyanine and subsequently reacting with 1,3-diaminobenzene-4-sulphonic acid, are mixed by stirring with 1.8 parts of sodium nitrite in 150 parts of water. The solution is cooled to 0-2° and is added in drops to a solution of 12 parts of 30% hydrochloric acid in 100 parts of ice/water. The diazonium salt suspension obtained is maintained at a temperature of 0-5° and is passed into a solution consisting of 300 parts of ice/water and 5.9 parts of 1-(3-methyl-aminopropyl)-6-hydroxy-4-methyl-2-pyridone. During the coupling reaction, the pH is maintained at 9 - 9.5 by adding 20% sodium hydroxide solution. Following the method of example 1, the resultant green solution is reacted with 5-cyano-2,4,6-trichloropyrimidine and the product isolated. The dyestuff of formula 17a

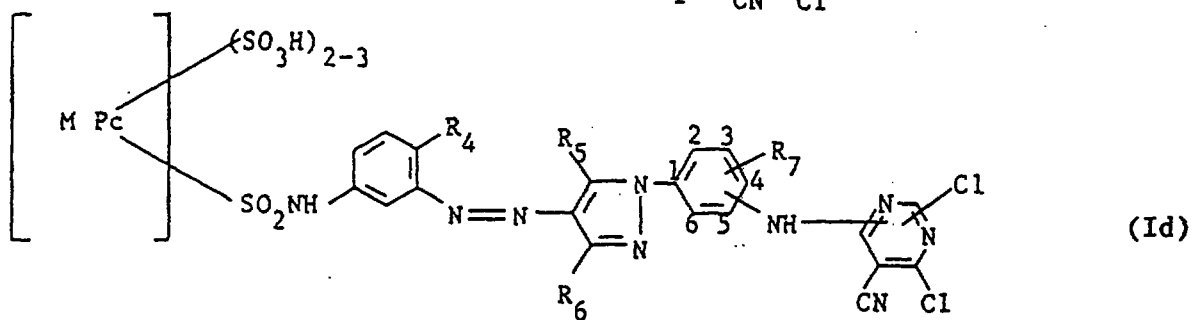
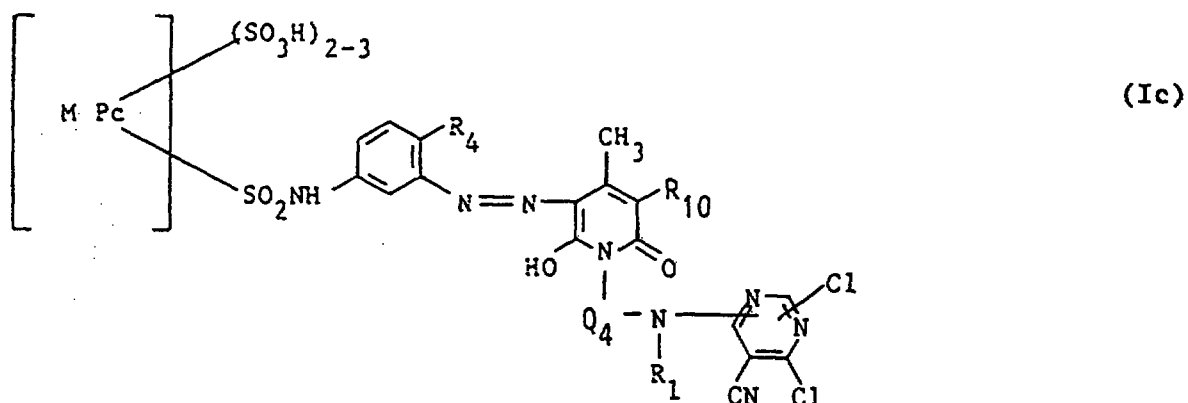


is obtained. It dyes cellulose material, especially cotton, in brilliant green shades. These dyeings have good light fastness and excellent wet fastness.

Examples 18-56

Using a method analogous to that of example 17 and using appropriate starting materials the following compounds of formula Ic

and Id (represented in their free acid form) in which the significances are as defined in Tables 2 and 3, are prepared.



The dyestuffs of examples 18-56 give green dyeings on cotton which have high fixing values and good fastness properties, such as good light and wet fastness. Compounds in which M is nickel give particularly brilliant dyeings.

Table 2 **Compounds of formula Ic**

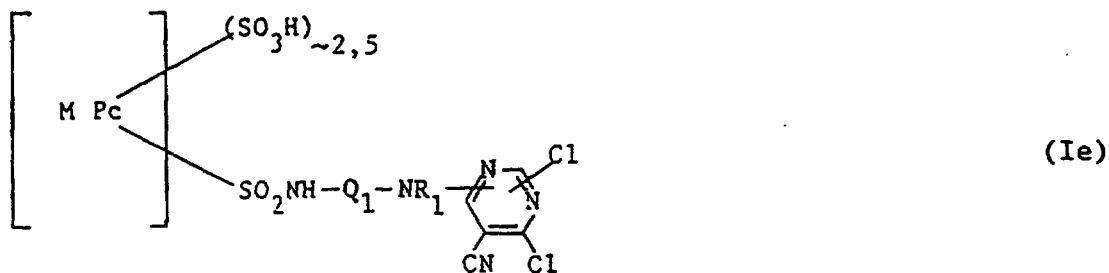
Ex.No.	M	R ₄	R ₁₀	-Q ₄ -NR ₁ -
18	Cu	H	H	$-(CH_2)_3N-CH_3$
19	Cu	SO ₃ H	H	do.
20	Cu	do.	-CONH ₂	do.
21	Cu	H	CN	do.
22	Ni	H	H	do.
23	Ni	H	 Cl [⊖]	do.
24	Ni	H	-CONH ₂	do.
25	Ni	SO ₃ H	do.	do.
26	Ni	H	CN	do.
27	Ni	SO ₃ H	-CONH ₂	$-(CH_2)_2NH-$
28	Ni	do.	H	do.
29	Cu	do.	H	do.
30	Ni	H	H	do.
31	Cu	H	H	do.
32	Ni	H	H	$-(CH_2)_2N$  $N-$
33	Ni	SO ₃ H	H	do.
34	Ni	do.	-CONH ₂	do.
35	Ni	do.	do.	$-(CH_2)_3NH-$
36	Cu	H	do.	do.
37	Ni	SO ₃ H	H	do.
38	Ni	do.	H	$-(CH_2)_2N-C_2H_5$

Table 3**Compounds of formula Id**

Ex.No.	M	R ₄	R ₅	R ₆	R ₇ (Link position)	Link position of -NH-
39	Cu	SO ₃ H	OH	CH ₃	H	3
40	Cu	H	OH	do.	2-SO ₃ H	5
41	Cu	SO ₃ H	OH	do.	do.	5
42	Cu	do.	OH	-COOH	H	3
43	Cu	do.	NH ₂	CH ₃	H	3
44	Ni	do.	OH	do.	H	3
45	Ni	H	OH	do.	2-SO ₃ H	5
46	Ni	SO ₃ H	OH	do.	do.	5
47	Ni	do.	OH	-COOH	H	4
48	Ni	do.	NH ₂	CH ₃	H	3
49	Ni	do.	do.	do.	2-SO ₃ H	5
50	Ni	do.	do.	do.	H	4
51	Ni	do.	OH	-COOH	H	3
52	Ni	do.	OH	CH ₃	2-SO ₃ H	4
53	Ni	do.	OH	do.	H	4
54	Ni	H	OH	-COOH	H	3
55	Cu	H	OH	CH ₃	H	4
56	Ni	H	OH	do.	H	3

Examples 57-64

Using a method analogous to that of examples 1 and 2 and using appropriate starting materials the following compounds of formula Ie in which the significances are as defined in Table 4, are prepared.



The shade of dyeing produced on cotton by the dyestuff is given in Table 4 wherein:

bt = brilliant turquoise

bg = blue-green.

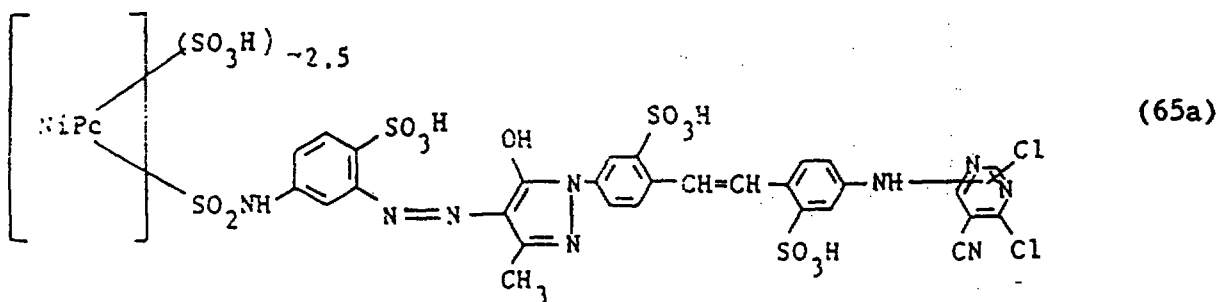
These dyeings have good fastness.

Table 4 Compounds of formula Ie

Ex.No.	M	-Q ₁ -NR ₁ -	Shade of dyeing
57	Cu	-CH ₂ CH ₂ NH-	bt
58	Ni	do.	bg
59	Cu	-CH ₂ CHNH- CH ₃	bt
60	Ni	do.	bg
61	Cu	-(CH ₂) ₃ N- CH ₃	bt
62	Ni	do.	bg
63	Cu	-(CH ₂) ₂ N  N-	bt
64	Ni	do.	bg

Example 65

Using a method analogous to that described in example 17 and using appropriate starting compounds the dyestuff of formula 65a represented in free acid form



is prepared and isolated. Using this dyestuff, brilliant green cotton dyeings are obtained, which have good light and wet fastness.

The dyestuffs of examples 1 to 65 prepared by the above methods are obtained as sodium salts.

The dyestuffs of Example 1 to 65 are isomeric mixtures of a) the compound in which the floating chlorine substituent is located in the 2-position of the pyrimidine ring and the corresponding compound in which the chlorine substituent is located in the 6-position; and b) of the positional isomers which differ with respect to the position of all substituents of the phthalocyanine group.

In general it is preferred to use the mixtures of the dyestuffs of Examples 1 to 65, as such. Thus a separation into individual isomers is not necessary but if desired can be effected by conventional methods.

The following Application Examples illustrate suitable applications for compounds according to the invention and their liquid-aqueous dyeing preparations.

Application Example A

10 parts of bleached cotton fabric are added to a dye bath, which contains 0.3 parts of the dyestuff of formula 1a (Example 1) and 15 parts of Glauber's salt (calcined) in 300 parts of demineralised water. The dyebath is maintained at a temperature of 40° for 30 minutes and subsequently during the addition at intervals of 10 minutes of a total of 6 parts of soda (calcined) in portions of 0.2, 0.6, 1.2 and 4 parts. Dyeing is continued at 40° for one hour. The dyed material is rinsed for 3 minutes under cold running water, for 3 minutes under hot running water, and is then washed for 15 minutes in 500 parts of boiling demineralised water in the presence of 0.25 parts of Marseille soap. The dyeing is again rinsed for 3 minutes under hot running water, spun and dried in a drying chamber at 70°. A brilliant turquoise cotton dyeing is obtained with good fastness. It has especially good light and wet fastness and is stable towards oxidation.

Application Example B

10 parts of bleached cotton material are added to a dyebath containing 10 parts of Glauber's salt (calcined) in 300 parts of demineralised water. The bath is heated to 40° over the course of 10 minutes, then 0.5 parts of the dyestuff of formula 1a (Example 1) are added. After a further 30 minutes at 40°, 3 parts of soda (calcined) are added and dyeing is subsequently continued for 45 minutes at 40°. The dyed material is rinsed, washed and dried according to the procedure given in application example A. A brilliant turquoise cotton dyeing is obtained, with similar properties to the dyeing obtained in application example A.

Application Example C

Using the method of application example A, cotton fabric is dyed in a dyebath of 0.3 parts of the dyestuff of formula 24a (Example 24) with the addition of only 2 parts of soda (calcined) in one portion. The initial temperature of 40° is then increased to 60° and dyeing is continued for one hour at 60°. The dyed material is rinsed, washed and dried according to the procedure given in application example A. A brilliant green cotton dyeing with good build-up and especially good light fastness is obtained.

Application Example D

2.5 parts of the dyestuff of example 6 are dissolved in 2000 parts of water. 100 parts of cotton fabric are added to the dye bath, and the temperature is maintained at 80° over a period of 10 minutes. 100 parts of Glauber's salt (calcined) are added to the dyebath followed by the addition 30 minutes later of 20 parts of soda (calcined). Dyeing is continued for one hour at 80°. The dyed material is rinsed, washed and dried according to the procedure given in application example A. A brilliant turquoise dyeing with good fastness is obtained.

Application Example E

A printing paste comprising:

40 parts of the dyestuff of formula 1a (Example 1)
100 parts of urea
350 parts of water
500 parts of a 4% sodium alginate thickener
10 parts of sodium bicarbonate

1000 parts in all

is applied to cotton material using a known printing process.

The printed material is then steamed for 4-8 minutes at 102-104° and rinsed for 3 minutes under cold running water then 3 minutes under hot running water. The fixed cotton material is subsequently washed and dried according to the procedure given in application example A. The brilliant turquoise print has good all-round fastness.

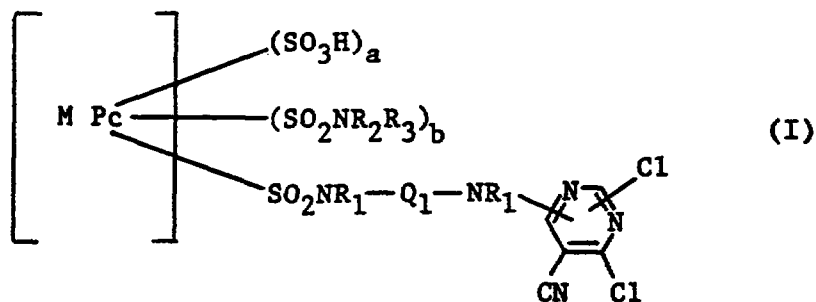
An appropriate amount of any one of the dyestuffs of examples 1 to 65 or dyestuff mixtures thereof may be used in place of the dyestuff or printing paste of example 1, 17 or 6 used in application examples A-E. The dyeings and printings obtained possess similar properties to those of the application examples.

Dyeings obtained with different dyestuffs are of the respective shades indicated in examples 1 to 65.

CLAIMS:



1. A compound of the formula I



in free acid or salt form and mixtures thereof, in which

Pc is the phthalocyanine radical;

M is Cu, Ni, Co, Fe or Al;

a is 1, 2 or 3;

b is 0, 1 or 2;

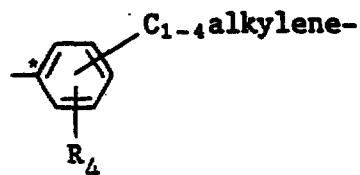
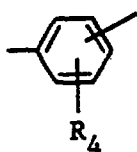
R₂ and R₃ independently are selected from hydrogen and C₁₋₆alkyl, or together with the nitrogen atom to which they are attached they form a five or six membered cyclic ring system which may contain a O- or N- atom;

each R₁ independently is hydrogen, unsubstituted C₁₋₄alkyl or C₁₋₄alkyl which is monosubstituted by hydroxy, halogen, -SO₃H, -OSO₃H or -COOH and

Q₁ is C₂₋₆alkylene uninterrupted or interrupted by -O- or -NR₁-, monohydroxy-substituted C₃₋₆alkylene or a group of one of the formulae i) to iv),

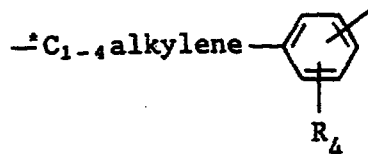
i)

ii)

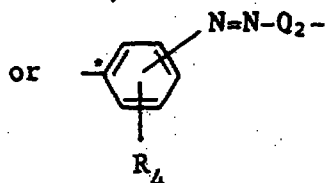




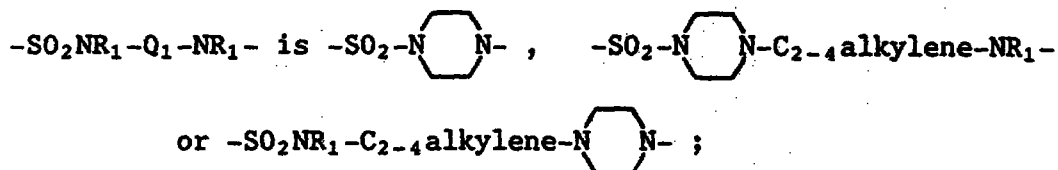
iii)



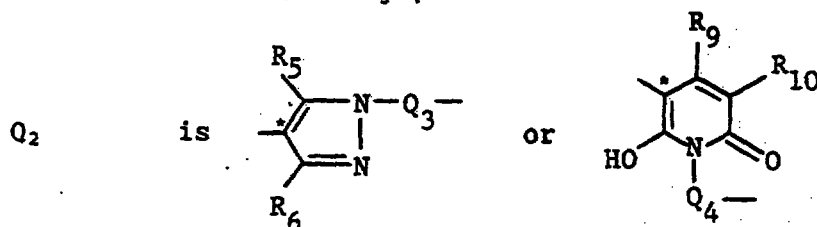
iv)



in which * identifies the atom attached to the $-\text{SO}_2\text{NR}_1-$ group; or



R_4 is hydrogen, halogen, hydroxy, $\text{C}_{1-4}\text{alkyl}$, $\text{C}_{1-4}\text{alkoxy}$, $-\text{COOH}$ or $-\text{SO}_3\text{H}$;



in which * indicates the coupling position;

R_5 is $-\text{OH}$ or $-\text{NH}_2$;

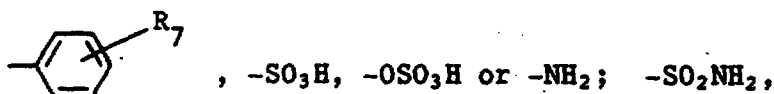
R_6 is $\text{C}_{1-4}\text{alkyl}$ or $-\text{COR}_8$;

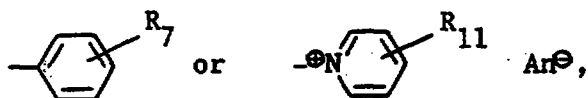
R_8 is $-\text{OH}$, $-\text{O}-\text{C}_{1-4}\text{alkyl}$ or $-\text{NH}_2$;

Q_3 is a divalent bridging group;

R_9 is hydrogen, $\text{C}_{1-4}\text{alkyl}$, $\text{C}_{5-6}\text{cycloalkyl}$, phenyl or phenyl- $(\text{C}_{1-4}\text{alkyl})$, in which any phenyl radical in R_9 is unsubstituted or is substituted by one to three substituents selected from $\text{C}_{1-4}\text{alkyl}$, $\text{C}_{1-4}\text{alkoxy}$, halogen, $-\text{COOH}$ and $-\text{SO}_3\text{H}$; $-\text{COR}_8$, $-\text{C}_{1-4}\text{alkyl}-\text{SO}_3\text{H}$, $-\text{C}_{1-4}\text{alkyl}-\text{OSO}_3\text{H}$ or $-\text{C}_{1-4}\text{alkyl}-\text{COR}_8$;

R_{10} is hydrogen, $-\text{CN}$, $-\text{SO}_3\text{H}$, $-\text{COR}_8$, $\text{C}_{1-4}\text{alkyl}$, $\text{C}_{1-4}\text{alkyl}$ which is monosubstituted by $-\text{OH}$, halogen, $-\text{CN}$, $\text{C}_{1-4}\text{alkoxy}$,



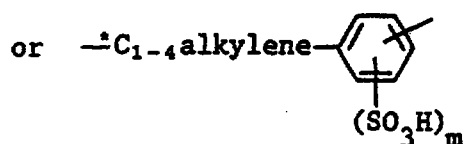
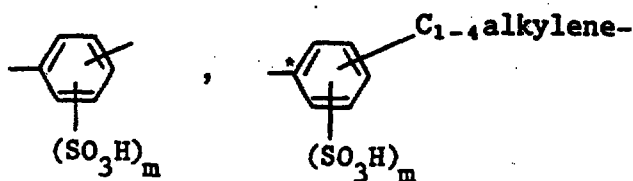


wherein R_7 is hydrogen, halogen, C_{1-4} alkyl, C_{1-4} alkoxy, $-\text{COOH}$ or $-\text{SO}_3\text{H}$;

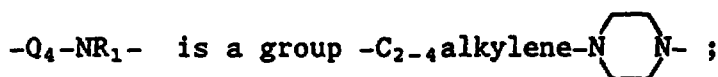
R_{11} is hydrogen, C_{1-4} alkyl or hydroxy- C_{2-4} alkyl; and

$\text{An}^{\ominus}$ is a non-chromophoric anion; and

Q_4 is C_{2-6} alkylene uninterrupted or interrupted by $-\text{O}-$ and $-\text{NR}_1-$, monohydroxy-substituted C_{3-6} alkylene,



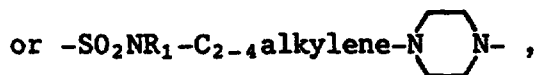
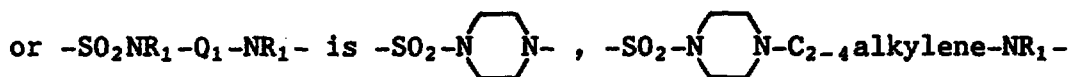
in which m is 0 or 1 and $*$ indicates the carbon atom attached to the nitrogen atom of the pyridone ring; or



with the provisos that

α) the sum of $a + b$ is a maximum of 3; and

β) when Q_1 is C_{2-6} alkylene uninterrupted or interrupted by $-\text{O}-$ or $-\text{NR}_1-$, monohydroxy-substituted C_{3-6} alkylene or a group of formulae i) to iii) defined above;



then when b is 1 or 2 and R_2 is hydrogen, R_3 is not hydrogen.

2. A compound of formula I according to Claim 1 in which M is M' in which M' is Cu or Ni.

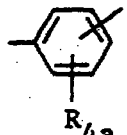
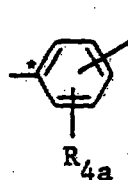


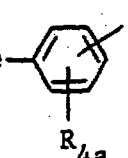
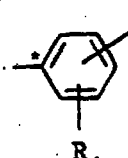
3. A compound of formula I according to Claim 1 or 2 in which R_1 is R_{1c} where R_{1c} is hydrogen or methyl.

4. A compound of formula I according to any of the preceding claims in which R_2 and R_3 are R_{2b} and R_{3b} , in which each R_{2b} and R_{3b} independently is hydrogen, methyl or ethyl.

5. A compound of formula I according to any of the preceding claims in which

Q_1 is Q_{1a} in which Q_{1a} is C_{2-3} alkylene, monohydroxy-substituted C_{3-4} alkylene, $-C_{2-3}$ alkylene- O - C_{2-3} alkylene-,

$-C_{2-3}$ alkylene- NR_{1b} - C_{2-3} alkylene-, , , C_{1-3} alkylene-

$-C_{1-3}$ alkylene- or  $N=N-Q_{2a}-$; or

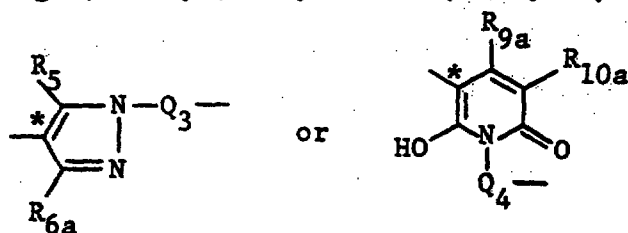
$-SO_2-NR_1-Q_{1a}-NR_1-$ is $-SO_2-N$  $-$, $-SO_2-N$  $-C_{2-3}$ alkylene- NR_1- or

$-SO_2-NR_1-C_{2-3}$ alkylene- N  $-$;

R_{4a} is hydrogen, methyl, methoxy, $-COOH$ or $-SO_3H$;

R_{1b} is hydrogen, methyl, ethyl or 2-hydroxyethyl;

Q_{2a} is



in which R_5 , Q_3 and Q_4 are as defined in Claim 1;

R_{6a} is methyl, $-COOH$ or $-CONH_2$,

R_{9a} is hydrogen, methyl, ethyl, phenyl, $-COR_{8a}$, $-CH_2SO_3H$ or $-CH_2OSO_3H$,

R_{10a} is hydrogen, $-CN$, $-SO_3H$, $-COR_{8a}$ or $-CH_2SO_3H$ and

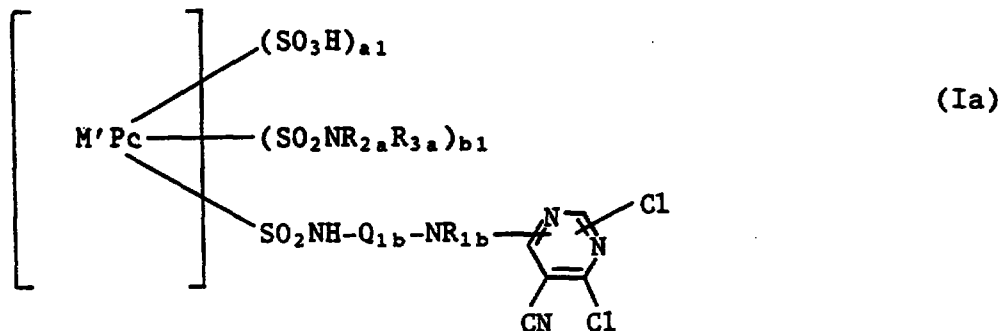
R_{8a} is $-OH$ or $-NH_2$.



6. A compound of formula I according to any of the preceding claims in which R_4 is R_{4b} in which R_{4b} is hydrogen, $-COOH$ or $-SO_3H$.

7. A compound of formula I according to any of the preceding claims in which Q_2 is Q_{2a} in which Q_{2a} is as defined in Claim 5.

8. A compound according to Claim 1, having the formula Ia



in free acid or salt form and mixtures thereof,
in which

Pc is the phthalocyanine radical,

M' is Cu or Ni,

each of R_{2a} and R_{3a} is independently hydrogen or C_{1-4} alkyl, or R_{2a} and R_{3a} together with the N-atom to which they are attached form a pyrrolidine, piperidine, morpholine or piperazine ring;

a_1 is 2 or 3,

b_1 is 0 or 1,

provided that the sum of a_1 and b_1 is a maximum of 3;

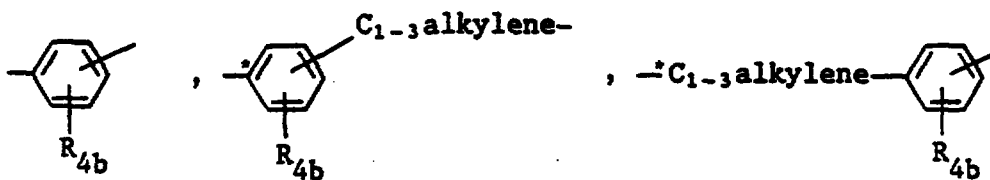
R_{1b} is hydrogen, methyl, ethyl or 2-hydroxyethyl,

Q_{1b} is C_{2-3} alkylene, monohydroxy-substituted C_{3-4} alkylene,

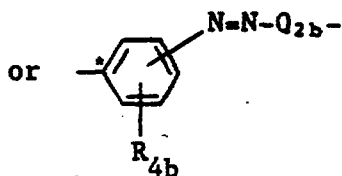
i)b

ii)b

iii)b



iv)b



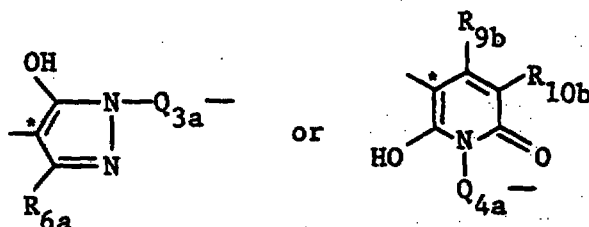


in which * identifies the carbon atom attached to the $-\text{SO}_2\text{NH}-$ group, and

R_{4b} is hydrogen, $-\text{COOH}$ or $-\text{SO}_3\text{H}$;

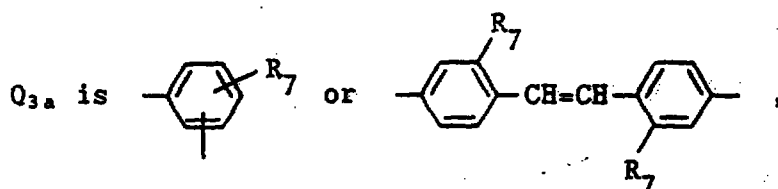
or $-\text{SO}_2\text{NH}-\text{Q}_{1b}-\text{NR}_{1b}-$ is $-\text{SO}_2-\text{N} \begin{array}{c} \diagup \quad \diagdown \\ \text{ } \quad \text{ } \end{array} \text{N}-$,

Q_{2b} is



in which * indicates the coupling position;

R_{6a} is methyl, $-\text{COOH}$ or $-\text{CONH}_2$,

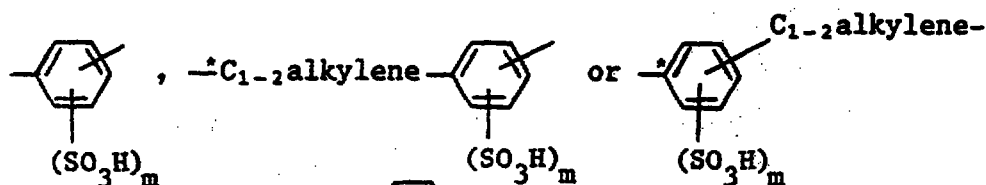


R_7 is hydrogen, halogen, C_{1-4} alkyl, C_{1-4} alkoxy, $-\text{COOH}$ or $-\text{SO}_3\text{H}$,

R_{9b} is methyl or ethyl,

R_{10b} is hydrogen or $-\text{CONH}_2$,

Q_{4a} is C_{2-4} alkylene, monohydroxy-substituted C_{3-4} alkylene,



or $-\text{Q}_{4a}-\text{NR}_{1b}-$ is $-\text{C}_{2-3}$ alkylene- $\text{N} \begin{array}{c} \diagup \quad \diagdown \\ \text{ } \quad \text{ } \end{array} \text{N}-$,

in which * denotes the carbon atom attached to the nitrogen atom of the pyridone ring and m is 0 or 1;

with the proviso that when Q_{1b} is C_{2-3} alkylene, monohydroxy-substituted C_{3-4} alkylene or a group of formulae i)b to iii)b defined above; or

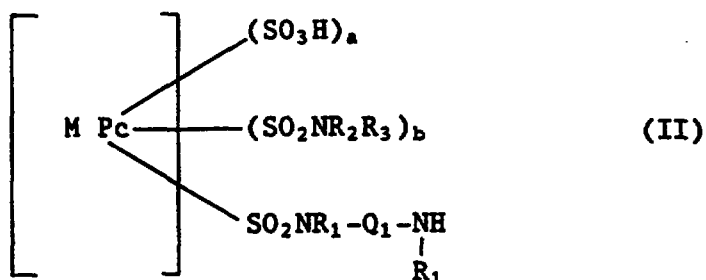
$-\text{SO}_2\text{NH}-\text{Q}_{1b}-\text{NR}_{1b}-$ is $-\text{SO}_2-\text{N} \begin{array}{c} \diagup \quad \diagdown \\ \text{ } \quad \text{ } \end{array} \text{N}-$,

then when b_1 is 1 and R_{2a} is hydrogen, R_{3a} is not hydrogen.



9. A compound according to Claim 8 in which b_1 is 0 and a_1 is 2 or 3.

10. A process for preparing a compound of formula I defined in Claim 1 which comprises reacting a compound of formula II,



in which R_2 , R_3 , R_1 , Q_1 , a , b , M and Pc are as defined in Claim 1 including the provisos α) and β) of Claim 1, with the appropriate molar amount of 5-cyano-2,4,6-trichloropyrimidine.

11. A process for dyeing or printing hydroxy group-containing or nitrogen-containing organic substrates, comprising applying to the substrate a compound of formula I, as defined in any one of Claims 1 to 9, in water-soluble salt form.

12. A process according to Claim 11, in which the substrate used is paper, leather or a textile material which comprises natural or synthetic polyamides or natural or regenerated cellulose.

13. A compound substantially as hereinbefore described with reference to any one of Examples 1 to 65.

14. A process for dyeing or printing substantially as hereinbefore described with reference to any one of Application Examples A to E.
