1310154

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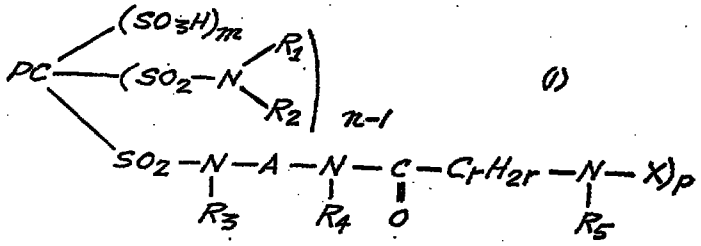
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(54) REACTIVE PHTHALOCYANINE COMPOUNDS

(71) We, SANDOZ LTD. of 4002 Basle/Switzerland, Lichtstrasse 35, 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 reactive phthalocyanine compounds of formula.



(I)

wherein,

PC stands for the radical of a phthalocyanine,

A for a divalent bridge member containing at least two carbon atoms,

R_1 and R_2 each for a hydrogen atom or a hydrocarbon radical, or R_1 and R_2 together with the adjacent nitrogen atom form a heterocyclic ring,

R_3 and R_4 each for a hydrogen atom or a lower alkyl radical which may be substituted, or R_3 and R_4 together with the adjacent nitrogen atoms and the bridge member A form a heterocyclic ring,

R_5 for a hydrogen atom or a lower alkyl radical which may be substituted,

X for a halogenopyrimidyl, halogenotriazinyl or halogenopyrimidylalkylene radical, or for an acyl radical of a heterocyclic acid or of a heterocyclic-substituted aliphatic acid, which acid contains at least one fibre-reactive halogen atom,

m for 1 to 3,

n for 1 to 3,

p for 1 or 2, preferably 1, and

r for 1 to 5, preferably 1,

the sum of m, n and p being 4 or 5.

By the term "fibre-reactive" halogen atom we mean a halogen atom that is capable of reacting with a hydroxyl group of cellulose to form a covalent bond. Preferred compounds of formula (I) are those in which PC stands for a copper or nickel phthalocyanine,

R_1, R_2, R_3, and R_4 each stands for hydrogen, methyl ethyl or hydroxyethyl,

R_5 for hydrogen or methyl,

A for a benzene radical substituted in ortho-position to the $-NR_4-$ group,

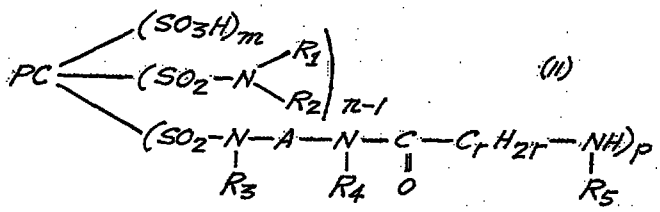
X for a halogenopyrimidyl, halogenotriazinyl, halogenopyrimidylalkylene or halogenopyrimidylcarbonyl group,

m for 1 to 3,

n for 1 to 3, and

p for 1 where the sum of m, n and p is 4 or 5.

The compounds of formula (I) can be produced by reaction of 1 mole of a compound of formula

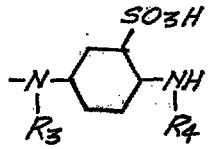


(II)

with p moles of a polyhalogenopyrimidine, polyhalogenotriazine or halogenoalkyl-mono- or -poly-halogenopyrimidine or of an acylating agent capable of introducing an acyl radical of a heterocyclic acid or of a heterocyclic-substituted aliphatic acid, which acid contains at least one fibre-reactive halogen atom. In relation to the nearest comparable phthalocyanine compounds, which do not bear the bridge member

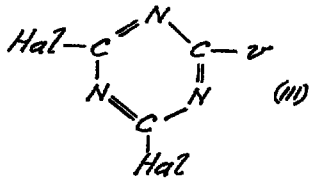
$$—CO—C_rH_{2r}—NR_5—,$$

the compounds of the present invention exhibit major advantages. For example, many compounds in which the bridge member $—CO—C_rH_{2r}—NR_5$ does not occur cannot be produced, or only with great difficulty, if the radical A bears a substituent in ortho position to the $—NR_4—$ group which sets up steric hindrance. Thus compounds which contain the grouping



are virtually non-condensible with halogenopyrimidines. A further advantage of the compounds disclosed herein is that an optionally substituted lower alkyl radical, e.g., an alkyl, hydroxyalkyl or phenylalkyl radical, can be introduced as the R_5 radical with the utmost ease. This advantage resides in the fact that dyes in which the reactive radical is bound to the dye molecule through $—\underset{\displaystyle R}{\overset{|}{N}}—$, where R represents a lower, optionally substituted alkyl radical, possess higher reactivity than those in which R represents hydrogen (cf- H. Ackermann and P. Dussy, Helv. Chim. Acta (1962) p. (1683), and that the unfixed proportion of the applied dye can be more readily washed off the dyed or printed substrate (cf. French patent 1 360 036). With dyes from which the bridge member $—CO—C_rH_{2r}—NR_5—$ of this invention is absent, it is often impossible to give R_4 the significance of a lower alkyl or hydroxyalkyl radical, or if possible only by using laborious methods. Throughout this specification and claims the term "lower alkyl" refers to alkyl radicals containing 1 to 5 carbon atoms. X may be the acyl radical of a heterocyclic acid or of a heterocyclic-substituted aliphatic acid, which acid contains a fibre-reactive halogen atom, such as 2, 4-dichloropyrimidine-or 2, 4-dibromopyrimidine-5-carboxylic acid, 2, 4-dichloro- or 2, 4-dibromo-6-methyl- or -6-chloromethylpyrimidine-5-carboxylic acid, 2, 3-dichloro- or 2, 3-dibromoquinoxaline-5- or -6-carboxylic acid, -sulphonic acid or -imino-carboxylic acid, 2-(3) -monochloroquinoxaline-6-carboxylic acid, 1, 4-dichlorophthalazine-6-carboxylic acid, 2-chlorobenzoxazole-5-, -6- or -7-carboxylic acid, 2-chlorobenzothiazole-5-carboxylic or -5-sulphonic acid, 3- or 4-(4′,5′-dichloro-6′-pyridazonyl-1′)-benzoic acid or β-(4′,5′-dichloro-6′-pyridazonyl-1′)-propionic acid. If the substituent X stands for a radical of a pyrimidine derivative, it may be selected from the radicals of pyrimidines containing at least two easily replaceable halogen atoms, that is to say the radicals obtained on removing a halogen atom therefrom, e.g. the radicals of 2, 4, 6-trichloro-, 2, 4, 6-trifluoro- or 2, 4, 6-tribromo-pyrimidine or their derivatives which may bear a substituent in the 5-position, for example a methyl, ethyl, cyano, carboxy, methoxycarbonyl, ethoxycarbonyl, chlorovinyl, substituted alkyl, e.g., carboxymethyl, chloromethyl, or bromomethyl group; X may also be the radical of 2, 4, 5, 6-tetrachloro-, -tetrafluoro- or -tetrabromo-pyrimidine, 5-bromo-2, 4, 6-trichloropyrimidine, 5-chloro- or 5-bromo-2, 4, 6-trifluoropyrimidine, 2,4-di-

chloro-5-chloromethylpyrimidine, 2,4-dibromo-5-bromoethylpyrimidine, 2,4-dichloro-5-chloromethyl-6-methylpyrimidine or 2,4-dibromo-5-bromomethyl-6-methylpyrimidine. If the substituent X stands for a radical of a triazine derivative, the radicals of polyhalogenotriazines are suitable, that is to say the radicals obtained by removing a halogen atom therefrom, e.g. those of cyanuric chloride, of cyanuric bromide or of a cyanuric halide derivative of formula

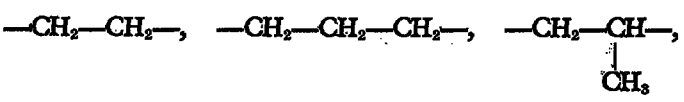


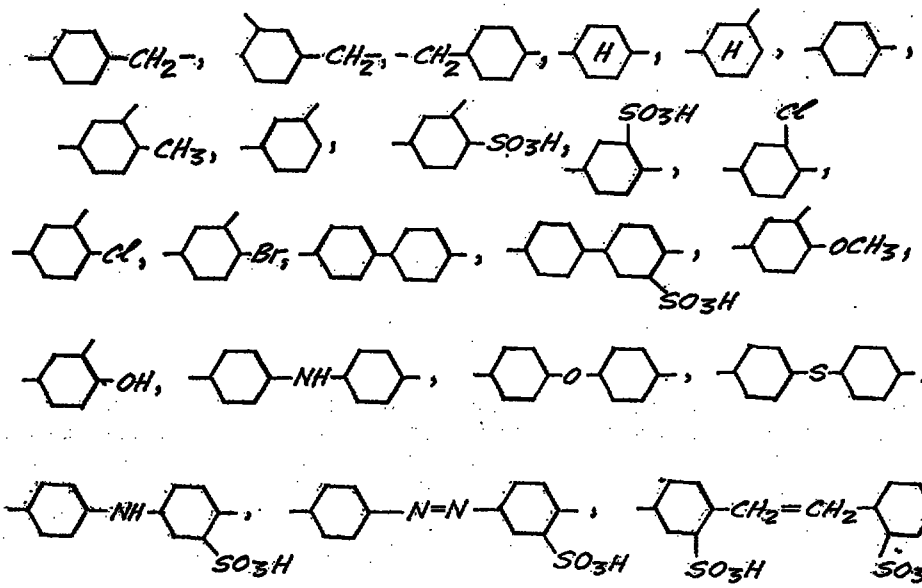
(III)

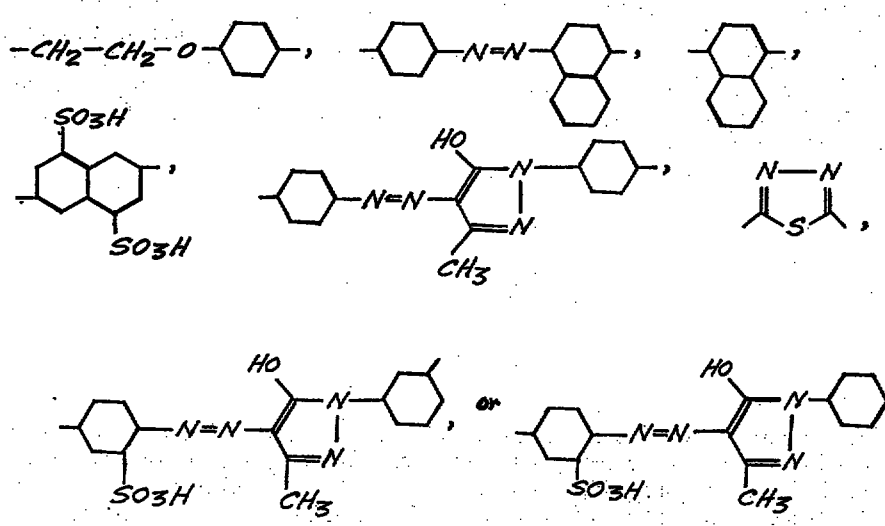
where Hal represents chlorine or bromine and v the radical, which may be further substituted, of a primary or secondary aliphatic, alicyclic, aromatic or heterocyclic amine, of an aliphatic, alicyclic, aromatic or heterocyclic hydroxyl or thiol compound in particular the radical of aniline, its alkyl, sulphonic acid or carboxylic acid derivatives, or the radical of a lower mono- or di-alkylamine or of ammonia.

Each of the radicals R_3, R_4 and R_5 may represent hydrogen or a substituted or unsubstituted alkyl radical, preferably a lower hydroxyalkyl or aralkyl radical or an unsubstituted lower alkyl radical, e.g. methyl, ethyl, propyl, isopropyl, butyl, isobutyl, n-amyl, hydroxymethyl, 2-hydroxyethyl, 2- or 3-hydroxypropyl, 2-, 3- or 4-hydroxy-n-butyl, benzyl, phenylethyl or p-methylbenzyl.

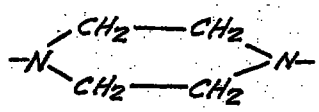
The bridge member A may be any desired divalent radical of the aliphatic (preferably with 2 to 6 carbon atoms), cycloaliphatic, aromatic (preferably mono- or dinuclear) or heterocyclic series, provided that it contains at least two carbon atoms, e.g. one of the radicals of the following formulae:







If R_3 and R_4 are conjoined to form a bridge member, A is preferably aliphatic and the radical $-N(R_3)-A-N(R_4)-$ represents the divalent radical of a heterocyclic ring containing two nitrogen atoms, e.g.

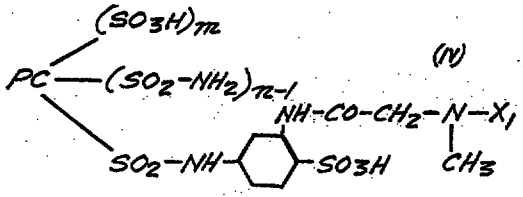


It is of advantage for A to be a divalent aromatic radical, preferably a benzene radical which bears a substituent, in particular a sulphonic acid group, in ortho-position to the $>NR_4$ group.

R_1 and R_2 may each be, besides a hydrogen atom, a hydrocarbon radical, those of lower molecular weight being preferred, e.g. an optionally substituted alkyl radical, such as a methyl, ethyl, propyl, iso-propyl, hydroxyethyl, β- or γ-hydroxypropyl or β-hydroxybutyl radical.

The phthalocyanine radical PC may contain or may be free from metal, though it is preferably metal-containing, cobalt-, copper- and nickel-containing phthalocyanine radicals being of special interest.

Compounds of formula (I) of notably high quality are those of formula



(IV)

where PC represents the radical of a nickel or preferably copper phthalocyanine and X_1 the radical of a polyhalogenopyrimidine, where halogen means fluorine, chlorine or bromine but is preferably fluorine or chlorine. The reaction of the compound of formula (II) with the reactive component can be conveniently effected in aqueous medium. To introduce the acyl radical of a heterocyclic acid or of a heterocyclic-substituted aliphatic acid, which acid contains at least one fibre-reactive halogen atom, it is best to employ the halide of the acid, which can be used as it is, or which can be dissolved in two to five times its weight of benzene, chlorobenzene, methylbenzene, dimethylbenzene or acetone. It is also best to work with a well cooled medium set with an agent which binds acid, such as sodium carbonate, sodium hydroxide, barium hydroxide, calcium hydroxide or sodium acetate. With carboxylic or sulphonic acid

halides of the halogen-containing heterocyclic compounds, the temperature may range from 0° to 100° C., e.g. from 0° to 50° C. or preferably 0—25° C. for the 2, 4-dihalogenopyrimidine-5-carboxylic acid halides, from about 10° to 50° C. or preferably 20—30° C. for the 3- or 4-(4′, 5′-dichloro-6′-pyridazonyl-1′)-benzoic acid chlorides and β-(4′,-5′-dichloro-6′-pyridazonyl-1′)-propionic acid chlorides, and from about 20° to 90° C. for the halogenoquinoxaline-, phthalazine-, -benzoxazole- or -benzothiazole-carboxylic acid chlorides or -sulphonic acid chlorides, preferably from about 30° to 70° C. for the 2, 3-dichloroquinoxaline-6-carboxylic acid chloride or -6-sulphonic acid chloride. The reaction is preferably allowed to proceed at a weakly alkaline, neutral to weakly acid reaction, preferably in the pH region of 7 to 3, e.g. at pH 6 to 4.

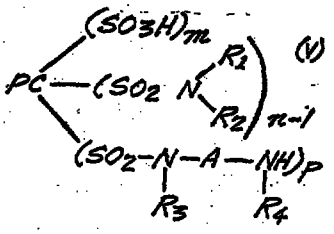
The reaction with a polyhalogenopyrimidine, polyhalogenotriazine or halogenoalkyl-mono- or -polyhalogenopyrimidine is likewise preferably effected in aqueous medium, the polyhalogenopyrimidine, polyhalogenotriazine or halogenoalkyl-mono- or -polyhalogenopyrimidine being employed either as it occurs in concentrated form or in solution in an organic solvent. Acetone, chloroform, benzene, chlorobenzene and toluene are highly suitable solvents for this purpose.

The reaction temperature is preferably adjusted to the reactivity of the starting products and may vary from 0° to 100° C. It lies in the region of 0° to 20° C. for cyanuric chloride and cyanuric bromide, 0° to 30° C. for tri- and tetra-fluoropyrimidines, 30° to 50° C. for the compounds of formula (III) (for example the products which contain two easily replaceable halogen atoms which can be produced by monocondensation of cyanuric chloride or bromide with ammonia, with a primary or secondary amine, or with an alcohol, thioalcohol, phenol or thiophenol), and 20° to 100° C. for polyhalogenopyrimidines bearing 2, 3 or 4 chlorine and/or bromine atoms. If temperatures higher than about 40° C. are necessary it is advisable to react in a vessel fitted with a reflux condenser in view of the volatility in water vapour of the halogenopyrimidines. The reaction can be conducted in a weakly alkaline, neutral to weakly acid medium at a pH from 9 to 4, a value in the region of pH 8 to 5 being preferable.

In order to maintain the pH constant in the course of the reaction of the amino compound of formula (II) with the acylating agent or the polyhalogenopyrimidine, polyhalogenotriazine or halogenoalkylmono- or polyhalogenopyrimidine, an agent which binds acid, for example sodium acetate, can be added to the solution at the commencement of the reaction, or alternatively small amounts of sodium or potassium carbonate or bicarbonate in solid, pulverized form or in concentrated aqueous solution can be added during the reaction. Other suitable neutralizing agents are aqueous solutions of sodium or potassium hydroxide. The rate of reaction can be accelerated by adding small amounts of a wetting or emulsifying agent.

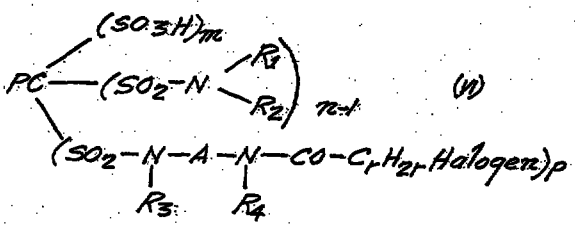
The phthalocyanine dyes of formula (I) thus formed can be precipitated from their aqueous solutions by the addition of salt, after which they may be filtered off, washed if necessary and dried.

The compounds of formula (II) can be produced by reaction of 1 mole of a compound of formula



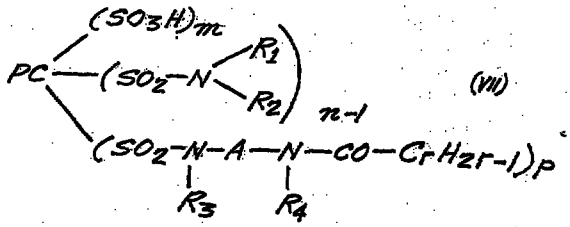
(V)

with p moles of a halide or anhydride of a halogenated carboxylic acid of formula Halogen—C_rH_{2r}—COOH, or of an unsaturated carboxylic acid of formula C_rH_{2r-1}—COOH, followed by reaction of the resulting compound of formula



(VI)

or



(VII)

with p moles of an amine of formula R_5NH_2 (VIII).

Examples of carboxylic acid derivatives which are suitable for reaction with compounds of formula (V) are the anhydrides and halides of α-, β- or γ-halogenated aliphatic acids and or α,β- or β,γ-unsaturated aliphatic acids. These include chloroacetic acid chloride, bromoacetic acid bromide, α-chloropropionic acid chloride, β-chloropropionic acid chloride, acrylic acid chloride and α-methacrylic acid chloride.

The reaction of a compound of formula (V) with a halide or anhydride of an acid of formula Halogen—C_rH_{2r}—COOH or C_rH_{2r-1}—COOH is preferably effected in aqueous, neutral to basic, preferably sodium carbonate solution, at a temperature in the range of 0° to 50° C., preferably 0—20° C., and at a pH value of 6.5 to 12, preferably at pH 8 to 10.

The addition of R_5—NH_2 followed by several hours' stirring and final heating yields the compound of formula (II).

The range of suitable compounds of formula (VIII) includes ammonia and primary aliphatic amines of low molecular weight which may be substituted, for example methyl-, ethyl-, propyl- and iso-propyl-amine, 2-hydroxyethylamine, 2- and 3-hydroxypropylamine and 2-hydroxybutylamine.

The phthalocyanine dyes of formula (I) are suitable for dyeing leather and for the exhaustion dyeing, pad dyeing and printing of wool, silk, synthetic polyamide fibres, natural and regenerated cellulosic fibres such as cotton, linen, hemp, viscose and cuprammonium rayon, and of blends and other forms of these fibres. They are especially suitable for the exhaustion dyeing of natural and regenerated cellulosic fibres.

In dyeing, padding and printing methods of application the commonly used wetting, levelling, thickening and other textile and leather auxiliary agents can be employed as required. During or subsequent to dyeing, padding or printing, the goods are preferably submitted to a heat treatment in the presence of an agent which binds acid. With wool, silk and synthetic polyamide fibres it is advisable to use an acid-binding agent which adjusts the pH to a value between 5 to 8, e.g. an acetate or phosphate buffer, hexamethylene tetramine, or, especially when acetic acid is used for dyeing, sodium carbonate or bicarbonate. Suitable acid-binding agents for cellulosic fibres are sodium carbonate and bicarbonate, sodium metasilicate and hydroxide, trisodium phosphate, and the corresponding potassium compounds.

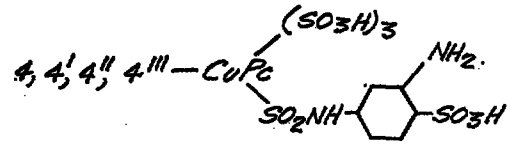
On natural and regenerated cellulosic fibres the dyes of this invention give dyeings and prints of very good fastness to wet treatments (washing at 95° C., water and perspiration), together with good fastness to rubbing, stoving and dry cleaning.

The new dyes reserve acetate, triacetate, polyacrylonitrile and polyester fibres.

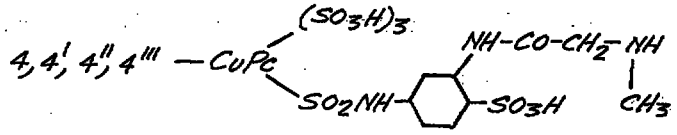
In the following Examples the parts and percentages are by weight and the temperatures are expressed in degrees centigrade.

Example 1

106 Parts of the compound of formula



are added to 1200 parts of water to form a neutral solution. To this 16 parts of sodium carbonate are added, then 17 parts of chloroacetyl chloride are dropped in slowly at 5°, after which 100 parts of a 40% methylamine solution are allowed to flow in. The mixture is stirred for 12 hours. After this time the temperature is increased to 80° and the reaction mixture neutralized with hydrochloric acid. Sodium chloride and further hydrochloric acid are added to precipitate the intermediate of formula



The intermediate is filtered off and the filter cake washed well with a hydrochloric-acid solution of sodium chloride, stirred into 1200 parts of water and brought into solution by the addition of sodium hydroxide solution in an amount sufficient to adjust the pH to the neutral point. Then 10 parts of sodium bicarbonate are added and in the course of 2 hours 20 parts of 5-chloro-2,4,6-trifluoropyrimidine are dropped in at 10°. Stirring is continued for 12 hours without further cooling and subsequently the temperature is raised to 40°. The dye is precipitated by the addition of sodium chloride, filtered off and vacuum dried at 40°.

Printing Method

A mercerized cotton fabric is printed with a paste of the following composition:

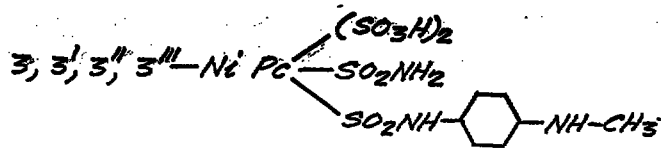
30 parts of the dye obtained as in Example 1;
100 parts of urea,
395 parts of water,
450 parts of a 3% sodium alginate thickening agent,
10 parts of sodium 1-nitrobenzene-3-sulphonate and
15 parts of sodium bicarbonate

1000 parts

The fabric is dried, steamed for 10—15 minutes at 102—104°, rinsed with cold and warm water, soaped at the boil, rinsed again and dried. A print of greenish turquoise shade is obtained which has very good light and wet fastness properties. The unprinted areas of the pattern are left a clear white.

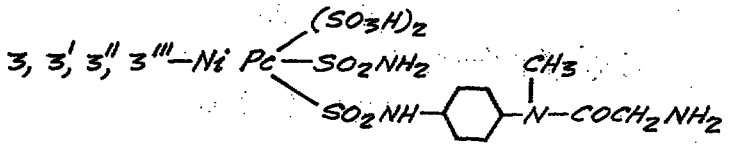
Example 2

A neutral solution of 99 parts of the compound of formula



in 1800 parts of water is prepared. The mode of operation of Example 1 is followed, the compound being condensed with chloroacetyl chloride with the subsequent addition of 150 parts of 25% ammonia solution. The mixture is then stirred for 12 hours,

raised to 80° and neutralized with hydrochloric acid, on which the intermediate of formula



is precipitated by the addition of sodium chloride. It is filtered off, the filter cake washed well with sodium chloride solution and dissolved in 1500 parts of water at 70°. 22 Parts of 2,4,5,6-tetrachloropyrimidine are added and the mixture is stirred vigorously at 70°, the pH being maintained at 5—7 by the gradual addition of 10% sodium hydroxide solution. As soon as no further alkali is consumed the dye is precipitated with sodium chloride, filtered off and dried at 70—80° with vacuum.

Printing Method

A mercerized cotton fabric is printed with a paste of the following composition:

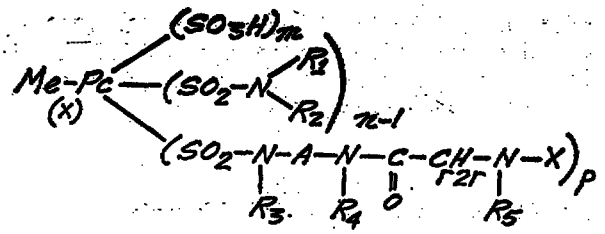
30	parts of the dye obtained as in Example 2,
100	parts of urea
395	parts of water,
450	parts of a 3% sodium alginate thickening agent,
10	parts of sodium 1-nitrobenzene-3-sulphonate and
15	parts of sodium carbonate
1000	parts.

The fabric is dried, steamed for 10—15 minutes at 102—104°, rinsed with cold and warm water, soaped at the boil, rinsed again and dried. A turquoise blue print is obtained which has very good light and wet fastness properties. The unprinted parts of the fabric show a clear, unstained white.

Pad Dyeing Method

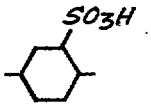
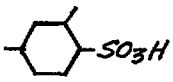
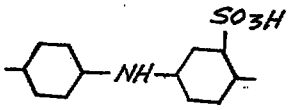
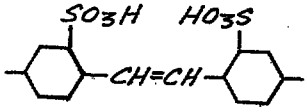
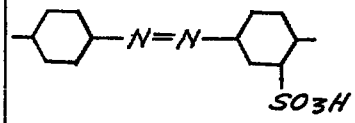
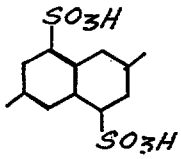
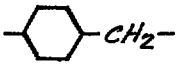
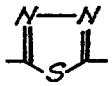
A mercerized cotton fabric is padded with a solution of 30 parts of the dye of Example 1 in 1000 parts of water; expressed to retain 90% of its weight of the solution and then treated for 30 minutes at 70° in a bath containing 30 parts of calcined sodium sulphate and 10 parts of calcined sodium carbonate in 1000 parts of water. The fixed dyeing is washed off by the normal method. The brilliant turquoise dyeing thus produced has excellent light and wet fastness properties.

The following table gives details of further compounds of formula (I) which have the specific formula

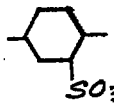
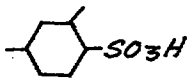
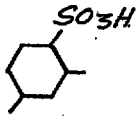
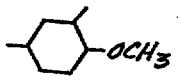
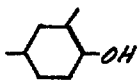
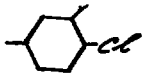
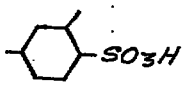


where x denotes the position of the substituent in the phthalocyanine nucleus. The last column of the table gives the shade of these dyes in prints on mercerized cotton fabric.

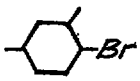
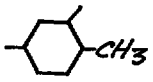
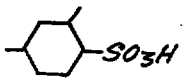
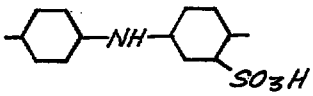
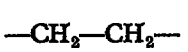
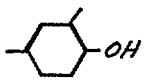
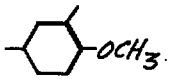
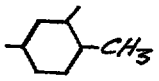
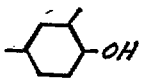
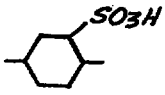
Ex. No.	Me	x	m	n	p	R_1	R_2	R_3	R_4
3	Ni	3	3	1	1	—	—	$-CH_2$ ——	CH_2-
4	Cu	3	2	2	1	CH_3	CH_3	H	H
5	Ni	3	2	2	1	H	H	CH_3	H
6	Ni	4	1	2	1	CH_2CH_2- $-OH$	CH_2CH_2- $-OH$	H	H
7	Cu	4	2	2	1	H	H	H	H
8	Ni	3	3	1	1	—	—	H	H
9	Ni	3	1	3	1	H	H	H	H
10	Ni	4	2	2	1	C_2H_5	C_2H_5	H	H
11	Cu	3	2	2	1	H	H	H	H
12	Cu	4	2	2	1	H	H	CH_2CH_2- $-OH$	CH_2CH_2- $-OH$
13	Cu	3	2	2	1	CH_2CH_2- $-OH$	H	H	H

A	$-C_rH_{2r}-$	R_5	X	Shade
$-CH_2-CH_2-$	$-CH_2-$	$-H$	2,4,6-Trichloro-pyrimidyl-5-methylene	turquoise
	$-CH_2CH_2-$	H	2,4,5-Trifluoro-pyrimidyl-6	do
	$-CH_2-$	$-CH_3$	2,4-Dichloro-5-bromopyrimidyl-6	do
	do	$-C_2H_5$	do	do
	do	$-CH_3$	2,4-Dibromo-1,3,5,-triazinyl-6	do
	do	do	2,4-Dichloropyrimidyl-5-carbonyl	green
	do	H	2,4,5-Trifluor-pyrimidyl-6	turquoise
	do	CH_3	2,4-Dichloro-1,3,-5-triazinyl-6	do
	do	do	2,4,5-Trichloro-pyrimidyl-6	do
$-CH_2-CH_2-$	do	do	2,3-Dichloroquinoxalyl-6-carbonyl	do
$-CH_2-CH_2-$	$-CH_2-$	CH_2CH_2- —OH	2-Chloro-4-amino-1,3,5-triazinyl-6	turquoise

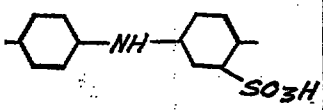
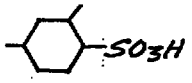
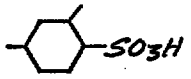
Ex. No.	Me	x	m	n	p	R_1	R_2	R^1	R_4
14	Ni	3	2	1	1	—	—	H	H
15	Ni	3	3	1	1	—	—	H	H
16	Ni	4	3	1	1	—	—	H	H
17	Ni	3	3	1	1	—	—	H	H
18	Cu	4	2	2	1	CH_3	CH_3	H	H
19	Ni	3	3	1	1	—	—	H	H
20	Cu	4	3	1	1	—	—	H	H
21	Ni	4	3	1	1	—	—	H	H
22	Ni	3	3	1	1	—	—	H	H
23	Ni	3	1	2	2	H	H	CH_3	CH_3

A	$-C_rH_{2r}-$	R_5	X	Shade
	$-CH_2-$	$-CH_3$	2-Chloro-4-amino-1,3,5-triazinyl-6	turquoise
	do	do	2-Chloro-4-methyl-amino-1,3,5-triazinyl-6	do
do	do	do	2-Chloro-4-(3'-sulphophenylamino)-1,-3,5-triazinyl-6	do
	do	$-C_2H_5$	2-Chloro-4-methoxy-1,3,5-triazinyl-6	do
	do	CH_3	2-Chloro-4-hydroxyethylamino-1,3,5-triazinyl-6	do
	do	do	2-Chloro-4-di-(hydroxyethyl)-amino-1,3,5-triazinyl-6	do
	do	H	2,4-Dichloro-5-methylpyrimidyl-6	do
	do	H	2,4-Dibromo-pyrimidyl-5-methylene	do
	$-CH_2CH_2-$ CH_2-CH_2-	H	2,4-Dichloro-6-methylpyrimidyl-5-methylene	turquoise
	$-CH_2$	H	2,4-Dichloropyrimidyl-6	turquoise

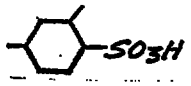
Ex. No.	Me	x	m	n	p	R_1	R_2	R_3	R_4
24	Cu	4	2	2	1	H	H	H	H
25	Cu	4	2	2	1	H	H	H	H
26	Cu	4	2	2	1	H	H	H	H
27	2H	3	3	1	1	—	—	H	H
28	Cu	4	3	1	1	—	—	$-CH_2$	CH_2-
29	Cu	4	2	2	1	n-C_3H_7	n-C_3H_7	H	H
30	Cu	4	2	2	1	$-CH_3$	$-CH_3$	H	H
31	Cu	3	1	3	1	H	H	CH_3	CH_3
32	Ni	4	2	2	1	$CH_2CHCH_2CH_3$ (OH)	H	H	H
33	Cu	3	2	2	1	H	H	H	H

A	—C_rH_{2r}—	R_5	X	Shade
	—CH_2	CH_3	2,4-Dichloropyrimidyl-6	turquoise
	do	do	2,4-Dibromo-5-methoxycarbonylpyrimidyl-6	turquoise
	—CH_2CH_2—	H	2,4-Dichloro-5-ethoxycarbonylpyrimidyl-6	do
	—CH_2—	H	2,4-Dichloro-5-bromopyrimidyl-6	do
	—CH_2—	CH_3	2,3-Dibromoquinoxalyl-5-sulphonyl	turquoise
	do	do	1,4-Dichlorophthalazyl-6-carbonyl	do
	do	do	2-Chlorobenzothiazolyl-5-carbonyl	do
	do	H	2-Chlorobenzothiazolyl-5-carbonyl	do
	do	H	2-Chlorobenzothiazol-5-sulphonyl	do
	do	H	3-(4',5'-Dichloro 6'-pyridazonyl-1')-benzoyl	do

Ex. No.	Mt	x	m	n	p	R_1	R_2	R_3	R_4
34	Cu	3	2	2	1	H	H	C_2H_5	H
35	Cu	3	3	1	1	—	—	H	H
36	Cu	4	3	1	1	—	—	H	H
37	Cu	4	2	2	1	H	H	H	H
38	Cu	4	2	2	1	H	H	H	H
39	Cu	4	1	3	1	H	H	H	H
40	Cu	4	1	3	1	H	H	H	H
41	Cu	3	2	2	1	H	H	H	H
42	Cu	3	2	2	1	H	H	H	H
43	Cu	3	3	1	1	—	—	H	H
44	Cu	3	3	1	1	—	—	H	H
45	Cu	3	3	1	1	—	—	H	H
46	Cu	3	3	1	1	—	—	H	H

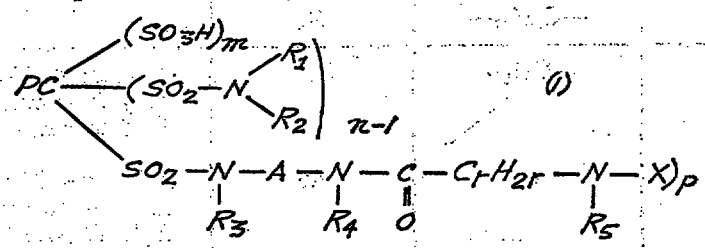
A	C_rH_{2r}—	R_5	X	Shade
	—CH_2—	CH_3	β-(4',5'-Dichloro-6'-pyridazonyl-1')-propionyl	turquoise
	do	do	2,4-Difluoro-5-chloropyrimidyl-6	do
	do	do	2,4,5-Trichloro-pyrimidyl-6	do
do	do	do	2,4-Difluoro-5-chloropyrimidyl-6	do
do	do	do	2,4,5-Trichloro-pyrimidyl-6	do
do	do	do	2,4-Difluoro-5-chloropyrimidyl-6	do
	—CH_2—	CH_3	2,4,5-Trichloro-pyrimidyl-6	tur-quoise
do	do	do	2,4-Difluoro-5-chloropyrimidyl-6	do
do	do	do	2,4,5-Trichloro-pyrimidyl-6	do
do	do	do	2-Chloro-4-ethyl-amino-1,3,5-tri-azinyl-6	do
do	do	do	2-Chloro-4-ethyl-thylamino-1,3,5-triazinyl-6	do
do	do	do	2-Chloro-4-(2'-hy-droxypropylamino)-1,3,5-triazinyl-6	do
do	do	do	2-Chloro-4-(3'-me-thoxypropylamino)-1,3,5-triazinyl-6	do

Ex. No.	Me	x	m	n	p	R_1	R_2	R_3	R_4
47	Cu	3	3	1	1	—	—	H	H
48	Cu	3	3	1	1	—	—	H	H
49	Cu	3	3	1	1	—	—	H	H
50	Cu	3	3	1	1	—	—	H	H
51	Cu	4	3	1	1	—	—	H	H
52	Cu	4	3	1	1	—	—	H	H
53	Cu	4	3	1	1	—	—	H	H
54	Cu	4	3	1	1	—	—	H	H
55	Cu	3	3	1	1	—	—	H	H

A	—C_rH_{2r}—	R_5	X	Shade
	—CH_2—	CH_3	2-Chloro-4-(2′-carboxyethylamino)-1,3,5-triazinyl-6	turquoise
do	do	do	2-Chloro-4-N-methyl-N-carboxymethylamino-1,3,5-triazinyl-6	do
do	do	do	2-Chloro-4-morpholino-1,3,5-triazinyl-6	do
do	do	do	2-Chloro-4-(2′-sulphethylamino)-1,3,5-triazinyl-6	do
do	do	do	2-Chloro-4-(4′-carboxyphenylamino)-1,3,5-triazinyl-6	do
do	do	do	2-Chloro-4-N-methyl-N-phenylamino-1,3,5-triazinyl-6	do
do	do	do	2-Chloro-4-phenylamino-1,3,5-triazinyl-6	do
do	do	do	2-Chloro-4-benzylamino-1,3,5-triazinyl-6	do
do	do	do	2-Chloro-4-cyclohexylamino-1,3,5-triazinyl-6	do

WHAT WE CLAIM IS:—

1. Reactive phthalocyanine compounds of formula



(I)

where

PC stands for the radical of a phthalocyanine,

A for a divalent bridge member containing at least two carbon atoms,

R_1 and R_2 each for a hydrogen atom or a hydrocarbon radical, or R_1 and R_2 together with the adjacent nitrogen atom form a heterocyclic ring,

R_3 and R_4 each for a hydrogen atom or a lower alkyl radical which may be substituted, or R_3 and R_4 together with the adjacent nitrogen atoms and the bridge member A form a heterocyclic ring,

R_5 for a hydrogen atom or a lower alkyl radical which may be substituted,

X for a halogenopyrimidyl, halogenotriazinyl or halogenopyrimidylalkylene radical, or for an acyl radical of a heterocyclic acid or of a heterocyclic-substituted aliphatic acid, which acid contains at least one fibre-reactive halogen atom,

m for 1 to 3,

n for 1 to 3,

p for 1 or 2, and

r for 1 to 5, where the sum of m, n and p is 4 or 5.

2. Reactive phthalocyanine compounds of formula (I) according to claim 1, where

PC stands for a copper or nickel phthalocyanine,

R_1, R_2, R_3 and R_4 each stands for hydrogen, methyl, ethyl or hydroxyethyl,

R_5 for hydrogen or methyl,

A for a benzene radical substituted in ortho-position to the $-NR_4-$ group,

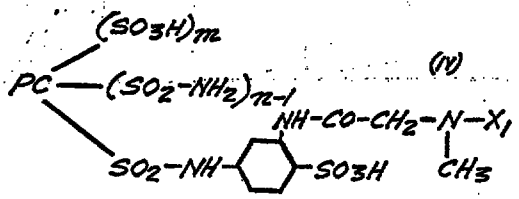
X for a halogenopyrimidyl, halogenotriazinyl, halogenopyrimidylalkylene or halogenopyrimidylcarbonyl group,

m for 1 to 3,

n for 1 to 3, and

p for 1, where the sum of m, n and p is 4 or 5.

3. Reactive phthalocyanine compounds according to claim 1 and of formula



(IV)

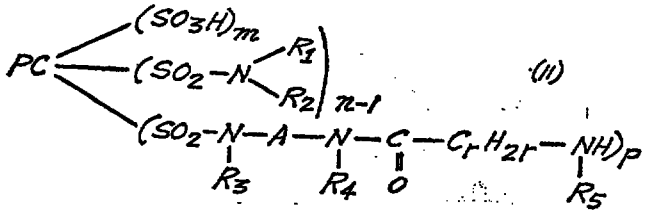
where

PC stands for the radical of copper or nickel phthalocyanine,

X_1 for the radical of a polyhalogenopyrimidine and halogen for fluorine, chlorine or bromine.

4. A reactive phthalocyanine compound of formula (I) as identified in any one of Examples 1 to 55.

5. A process for the production of a reactive phthalocyanine compounds of formula (I) according to claim 1, which comprises reacting 1 mole of a compound of formula



(II)

* C L M S *

with p moles of a polyhalogenopyrimidine, polyhalogenotriazine or halogenalkyl-monohalogeno- or -polyhalogeno-pyrimidine or of an acylating agent capable of introducing an acyl radical of a heterocyclic acid or of a heterocyclic-substituted aliphatic acid, which acid contains at least one fibre-reactive halogen atom.

6. A process according to claim 5, in which PC represents a copper- or nickel-containing phthalocyanine radical.

7. A process according to claim 5, in which 1 mole of a compound of formula (II) is reacted with p moles of a polyhalogenopyrimidine.

8. A process according to claim 7, in which 1 mole of a compound of formula (II) is reacted with p moles of a trifluoro-5-chloropyrimidine.

9. A process according to claim 5, in which 1 mole of a compound of formula (II) is reacted with p moles of a polyhalogeno-1, 3, 5-triazine.

10. A process according to claim 5, in which A in formula (II) represents a divalent aromatic radical which is substituted in the ortho-position to the —NR_4— group.

11. A process according to claim 5, in which A in formula (II) represents a divalent benzene radical which bears a sulphonic acid group in ortho-position to the —NR_4— group.

12. A process for the production of a dye of formula (I) according to claim 1 substantially as hereinbefore described, with reference to Example 1 or Example 2.

13. Phthalocyanine compounds of formula (I), whenever prepared by a process according to any one of claims 5 to 12.

14. An exhaustion dyeing, pad dyeing or printing process in which natural or synthetic polyamide fibres or natural or regenerated cellulosic fibres are exhaustion dyed, pad dyed or printed with a reactive phthalocyanine compound of formula (I) according to claim 1.

15. Printing process substantially as herein described, with reference to Example 1 or Example 2.

16. Padding process substantially as herein described and exemplified.

17. Natural and synthetic polyamide fibres and natural and regenerated cellulosic fibres whenever exhaustion dyed pad dyed or printed by a process according to any one of claims 14 to 16.

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* C L M S *