

PATENT SPECIFICATION

(11) 1 413 510

(21) Application No. 59607/72 (22) Filed 27 Dec. 1972

(31) Convention Application No. 19258/71

(32) Filed 31 Dec. 1971

(31) Convention Application No. 1317/72

(32) Filed 28 Jan 1972 in

(33) Switzerland (CH)

(44) Complete Specification published 12 Nov. 1975

(51) INT CL² C09B 57/00

(52) Index at acceptance C4P 104 110 112 D1X1 D1X

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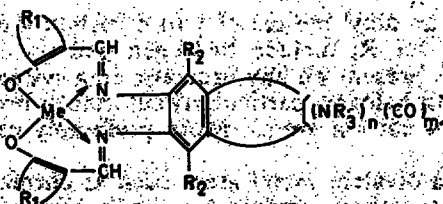


(54) HETEROCYCLIC METALLIZED PIGMENTS

(71) We SANDOZ LTD., of 35 Lichtstrasse, 4002 Basle, Switzerland, a Swiss Body Corporate, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to metal containing heterocyclic compounds which are free from water-solubilising groups.

More particularly, this invention provides compounds of formula I,

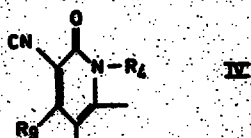


in which the radicals R_1 , which may be the same or different, together with the carbon atoms to which they are attached, signify a carbocyclic or heterocyclic ring system of aromatic character, the radicals R_2 , which may be the same or different, each signify a hydrogen atom or a substituent, R_3 signifies a hydrogen atom or an alkyl or phenyl radical which may be substituted, Me signifies a divalent metal atom, m signifies 1 or 2, and n signifies 1 or 2

provided that the sum of n and m is at least 3 and that the compounds contain no carboxylic or sulphonic acid groups.

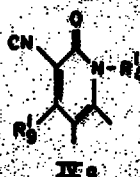
When R_1 , together with the carbon atoms to which it is attached, signifies an aromatic carbocyclic ring, it preferably signifies 1,2-phenylene, or 1,2 or 2,3-naphthalene. When R_1 , together with the carbon atoms to which it is attached signifies a heterocyclic ring of aromatic character, it may contain one or two oxygen, nitrogen or sulphur atoms. These aromatic rings may for example bear 1, 2, 3 or 4 substituents. Suitable such substituents include halogen, in particular chlorine or bromine, alkyl of 1 to 8, preferably 1 to 4 carbon atoms, trifluoromethyl, alkoxy of 1 to 8, preferably 1 to 4 carbon atoms, cyano, nitro, hydroxylamino, alkylamino or dialkylamino in which the alkyl group(s) contain 1 to 8, preferably 1 to 4 carbon atoms, or acyl. Preferred acyl groups are of formula $R-Y$ or $R'-Z$, in which R signifies a hydrocarbon radical which may be substituted, for example by any of the above mentioned substituents and may contain hetero atoms, e.g. oxygen, nitrogen or sulphur atoms, but is preferably an alkyl radical of 1 to 8, preferably 1 to 4 carbon atoms, or the phenyl radical, Y signifies $-O-CO-$, $-SO_2-$ or $-O-SO_2-$, R' signifies hydrogen or R, Z signifies $-CO-$, $-NR''-CO-$ or $-NR''SO_2-$, in which R'' signifies hydrogen or R. Preferred acyl radicals include alkoxycarbonyl and alkanoyl radicals of 2 to 5 carbon atoms, alkylsulphonyl or alkoxysulphonyl radicals of 1 to 4 carbon atoms, phenylsulphonyl, benzoyl, phenoxycarbonyl, phenoxysulphonyl and alkylaminocarbonyl and dialkylaminocarbonyl, in which the alkyl radical(s) contain 1 to 4 carbon atoms.

Particularly, preferred heterocyclic radicals for R_1 , together with the carbon atom to which it is attached, include those of formula IV,



in which R_4 signifies hydrogen or an alkyl radical of 1 to 8 carbon atoms or a phenyl radical which may be substituted and R_9 signifies an alkyl radical of 1 to 8 carbon atoms.

R_{10} , together with the carbon atoms to which it is attached, more preferably signifies a radical of formula II, III or IVa.

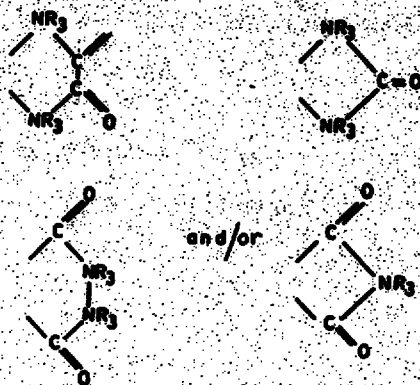


in which R_7 and R_8 , which may be the same or different, each signifies a hydrogen or halogen atom, or an alkyl or alkoxy radical of 1 to 4 carbon atoms, R_7' signifies a hydrogen atom, an alkyl radical of 1 to 4 carbon atoms, or the phenyl radical, and R_9' signifies an alkyl radical of 1 to 4 carbon atoms.

Suitable significances for R_7 include hydrogen and the above mentioned substituents which may be present on any aromatic ring system as R_1 . Suitably, each R_2 signifies hydrogen or halogen, particularly chlorine or bromine, or an alkyl or alkoxy radical of 1 to 4 carbon atoms. More preferably each R_2 signifies a hydrogen atom.

Me suitably signifies a divalent metal atom such as chromium, manganese, iron, copper, zinc, nickel or cobalt, preferably copper, zinc, nickel or cobalt.

The formula $>[(NR_3)_2(CO)]_n$ suitably signifies the following radicals



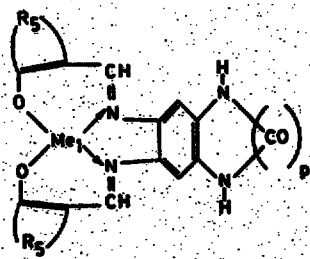
When R_3 signifies an alkyl radical, it preferably contains 1 to 8, more preferably 1 to 4 carbon atoms. Suitable substituents on such alkyl radicals, and on any other alkyl radicals present in the molecule include halogen, in particular chlorine or bromine, cyano, alkoxy of 1 to 8, preferably 1 to 4 carbon atoms, phenyl, phenoxy, acyl, acyloxy and acylamino. Suitable such acyl radicals are those mentioned above. When R_3 signifies phenyl it may suitably bear as substituents any of those mentioned above in connection with R_1 . Preferably, however, R_3 signifies hydrogen, unsubstituted alkyl of 1 to 4 carbon atoms or phenyl, more preferably hydrogen.

The preferred compounds of formula I are those of formula Ia,

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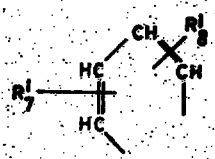
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I

in which Me, signifies nickel, cobalt, copper or zinc, P signifies 1 or 2, and R₅ signifies a radical of formula V,

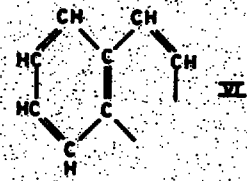


V

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in which R₁ and R₂, which may be the same or different, each signifies hydrogen, chlorine or methoxy; a radical of formula VI,

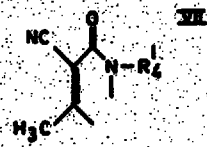
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VI

or a radical of formula VII,

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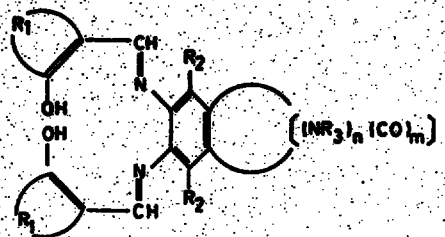


VII

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in which R₄ is as defined above.

The invention also provides a process for the production of compounds of formula I, characterised by metallising a compound of formula X,



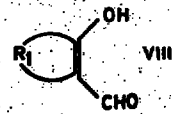
X

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in which R₁, R₂, R₃, n and m are as defined above, with a salt of the divalent metal Me.

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The compounds of formula X are novel and may be produced by reacting a compound or mixture of compounds of formula VIII,

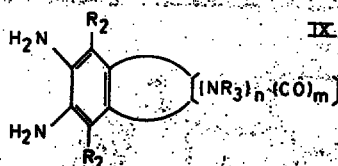


VIII

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in which R₁ is as defined above, with a compound of formula IX,

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in which R_2 , R_3 , n and m are as defined above, or an acid addition salt thereof.

As will be appreciated, where the radicals R , in the desired final product or compound X differ, then a mixture of compounds of formula VIII is employed.

As will also be appreciated, the metallisation of the compounds of formula X may be effected simultaneously with or subsequent to the reaction of the compound(s) VII and the compound IX.

The condensation of the compound(s) VIII and compound IX is suitably effected in an aqueous medium or in an organic solvent which is miscible with water, e.g. an alkanol of 1 to 4 carbon atoms, dimethyl formamide, dimethyl acetamide, a glycol or glycol ether, dioxane or N-methylpyrrolidone. Suitably, the condensation is effected at a temperature of from room temperature to 250°C, preferably 30° to 150°C. Suitable salts of the compound of formula IX include the hydrochloride or sulphate. As indicated, the reaction with the divalent metal salt may be effected simultaneously with the condensation. Alternatively, it may be effected subsequently in conventional manner. Suitable salts of the divalent metal include the chloride, formate and acetate.

The resulting compounds of formula I may be isolated and purified using conventional techniques.

The compounds of the invention are useful as pigments, particularly after conditioning by the normal methods for pigments. They are thus suitable for the pigmentation of synthetic polymeric materials in the mass. By this is to be understood synthetic polymers and resins containing or free from solvents, including surface coatings of an oil or water base, lacquers and enamels of various compositions and spinning solutions. The pigments are particularly useful in the pigmenting of viscose rayon and cellulose acetate, polyethylene, polystyrene, polyvinyl chloride, rubber and poromerics (synthetic leather). The pigments are also suitable for use in printing inks, for dyeing paper in the stock, and for pigment printing or coating of textiles.

Standard methods of application of the pigments may be employed.

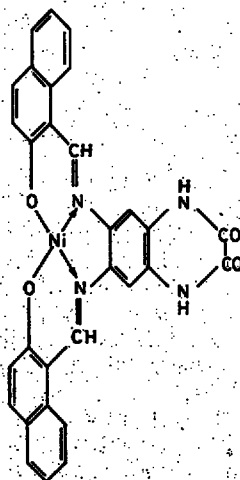
The compounds of formula X also have the pigmentary properties described above but, in general, these are somewhat less satisfactory than those possessed by the metallised compounds of formula I.

The following Examples, in which parts are by weight and temperatures in °C, illustrate the invention.

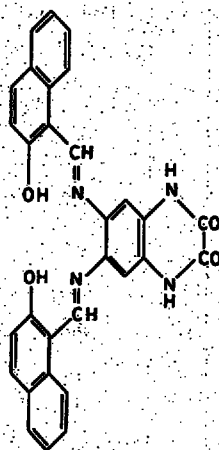
EXAMPLE 1.

A solution of 34.4 parts of 2-hydroxy-1-naphthaldehyde and 30 parts of 6,7-diamino-2,3-dihydroxyquinoxaline-dihydrochloride dihydrate in 3000 parts of dimethyl formamide is reacted for 2 hours at 140° with stirring. A solution of 12 parts of nickel chloride in 1000 parts of dimethyl formamide are added, after which the temperature is maintained at 140°C for a further 2 hours with stirring. On cooling, yellowish red crystals settle out. The crystals are isolated by filtration, washed with dimethyl formamide and then with water, and dried, which frees the product from impurities and solvent. The pigment of formula

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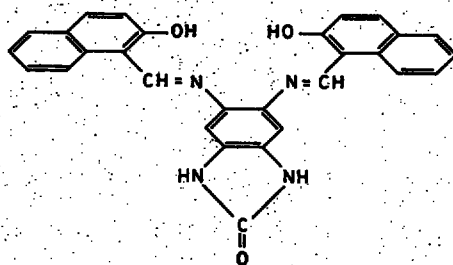
thus obtained (via the corresponding intermediate of formula X), pigments polyvinyl chloride in yellowish red shades with satisfactory fastness properties. The above Example proceeds through the intermediate of formula



which, whilst not isolated, may be isolated in analogous manner to the corresponding intermediate in the following Example 2.

EXAMPLE 2.

A solution of 47.4 parts of 5,6-diamino-2-(3H)-benzimidazolone dihydrochloride in 400 parts of water is gradually combined over 30 minutes with a solution of 68.8 parts of 2-hydroxy-1-naphthaldehyde in 1000 parts of 2-methoxyethanol, at room temperature, with stirring. Stirring is continued for 1 hour at room temperature, and the solution is reacted further for 1 hour at 60° to 70° with continued stirring. The crystalline orange product of formula



is filtered at room temperature, washed with methanol and dried.

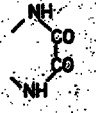
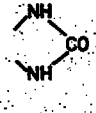
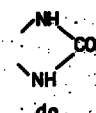
47.2 parts of this compound are suspended in 1500 parts of dimethyl formamide. A solution of 12 parts of nickel chloride in 1500 parts of dimethyl formamide is stirred into the suspension and the metallising reaction carried out

for 2 hours at 125°, with stirring. On cooling to room temperature, the orange-red crystalline precipitate is filtered, washed with dimethyl formamide and then with water, and dried. The pigment thus formed which is the nickel derivative of the above compound pigments polyvinyl chloride in intense orange shades which show satisfactory fastness properties.

The same pigment can also be produced as follows. A mixture of 24.6 parts of 5,6 diamino-2-(3H)-benzimidazolone and 51.6 parts of 2-hydroxy-1-naphthaldehyde in 750 parts of dimethyl formamide is reacted for 1 hour at 23° and then for 1 hour at 60° with constant stirring. A clear solution of orange colour is formed which is cooled to 25° and set with 35.5 parts of nickel chloride hexahydrate, added with continued stirring. The reaction mixture is raised to 125° and held at this temperature for 2 hours with stirring. The orange-red pigment is filtered from the hot medium, washed with dimethyl formamide, then with water and finally with ethanol, and dried.

The pigments specified in the table below may be produced in analogy with the procedures of Example 1 or 2 and are identified in the table by the significance of the symbols in formula I and by their shades in polyvinyl chloride.

TABLE

Exa- mple Nr.	R ₁	R ₂	(NR ₃) _n (CO) _m	Me	Shade in Polyvinyl chloride
3		H		Ni	yellow- orange
4	do.	H	do.	Co	brown
5		H	do.	Ni	brown
6	do.	H	do.	Cu	yellow.
7		H	do.	Cu	orange
8	do.	H		Zn	yellow- orange
9	do.	H	do.	Cu	brown- orange
10		H	do.	Cu	brown- yellow
11	do.	H	do.	Co	yellow- orange
12		H		Zn	yellow
13		H	do.	Cu	yellow
14		H	do.	Ni	orange
15	do.	H	do.	Zn	yellow
16		H	do.	Cu	yellow- orange
17	do.	H	do.	Ni	orange

Exa- mple Nr.	R ₁	R ₂	$[(NR_3)_n(CO)_m]$	Me	Shade in Polyvinyl chloride
18	do.	H	do.	Zn	yellow
19		H	do.	Zn	do.
20		H	do.	Ni	red- orange
21		H	do.	Zn	do.
22		H	do.	Cu	brown- orange

APPLICATION EXAMPLE.

0.2 parts of the pigment obtained according to Example 1
and

5 parts of titanium dioxide are added to a starting mixture of

63 parts of polyvinyl chloride emulsion,

32 parts of dioctyl phthalate,

3 parts of a commercial epoxy softener,

1.5 parts of a commercial stabiliser (a barium-cadmium complex) and

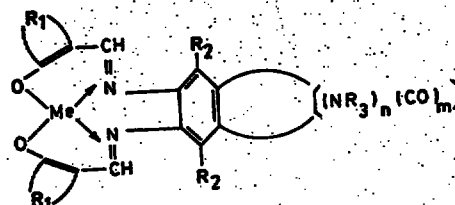
0.5 parts of a commercial chelator.

with stirring for intimate mixing. The mixture is worked on a roller mill between
two rolls heated to 160° and set to rotate at 20 and 25 r.p.m. respectively to exert
frictional force for improved pigment distribution. The mixture is extruded as film
of 0.3 mm thickness, which is pigmented in a yellowish red shade showing
satisfactory light and migration fastness and heat stability.

Similar results may be obtained with the pigments of any of the other
foregoing Examples.

WHAT WE CLAIM IS:—

I. A process for the production of a compound of formula I,



in which the radicals R₁, which may be the same or different, together with the
carbon atoms to which they are attached, signify a carboxylic or
heterocyclic ring system of aromatic character, the radicals R₂, which
may be the same or different, each signify a hydrogen atom or a
substituent,

R₃ signifies a hydrogen atom or an alkyl or phenyl radical which may be
substituted,

Me signifies a divalent metal atom,

m signifies 1 or 2,

and n signifies 1 or 2

provided that the sum of n and m is at least 3 and that the compounds contain no
carboxylic or sulphonic acid groups, characterised by metallising a compound of
formula X



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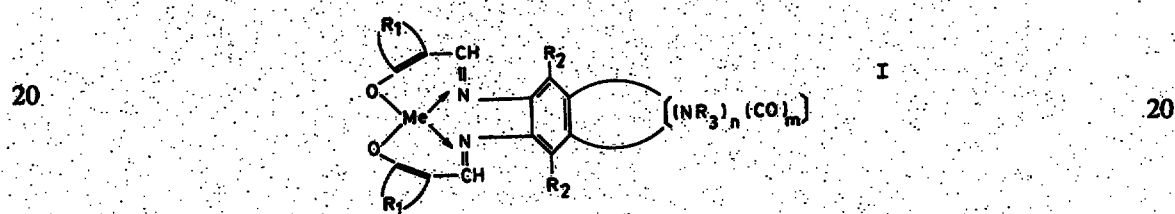
Exa- mple Nr.	R ₁	R ₂	$[(NR_3)_n(CO)_m]$	Me	Shade in Polyvinyl chloride
18	do.	H	do.	Zn	yellow
19		H	do.	Zn	do.
20		H	do.	Ni	red- orange
21		H	do.	Zn	do.
22		H	do.	Cu	brown- orange

APPLICATION EXAMPLE.

- 0.2 parts of the pigment obtained according to Example 1 and
- 5 5 parts of titanium dioxide are added to a starting mixture of
- 63 parts of polyvinyl chloride emulsion,
- 32 parts of dioctyl phthalate,
- 3 parts of a commercial epoxy softener,
- 10 1.5 parts of a commercial stabiliser (a barium-cadmium complex) and
- 0.5 parts of a commercial chelator
- with stirring for intimate mixing. The mixture is worked on a roller mill between two rolls heated to 160° and set to rotate at 20 and 25 r.p.m. respectively to exert frictional force for improved pigment distribution. The mixture is extruded as film of 0.3 mm thickness, which is pigmented in a yellowish red shade showing satisfactory light and migration fastness and heat stability.
- 15 Similar results may be obtained with the pigments of any of the other foregoing Examples.

WHAT WE CLAIM IS:—

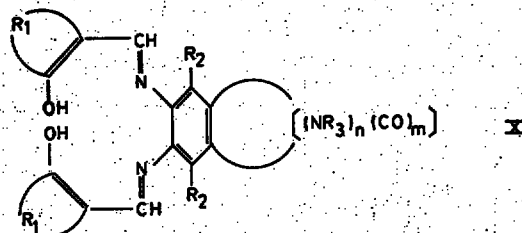
I. A process for the production of a compound of formula I,



- in which the radicals R₁, which may be the same or different, together with the carbon atoms to which they are attached, signify a carboxylic or heterocyclic ring system of aromatic character, the radicals R₂, which may be the same or different, each signify a hydrogen atom or a substituent,
- 25 R₃ signifies a hydrogen atom or an alkyl or phenyl radical which may be substituted,
- Me signifies a divalent metal atom,
- m signifies 1 or 2,
- 30 and n signifies 1 or 2
- provided that the sum of n and m is at least 3 and that the compounds contain no carboxylic or sulphonic acid groups, characterised by metallising a compound of formula X

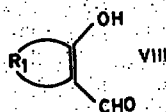


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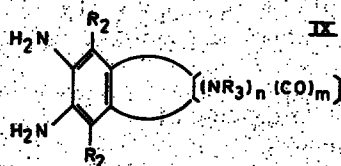


in which R_1 , R_2 , R_3 , n and m are as defined above, with a salt of the divalent metal Me.

2. A process according to claim 1, in which the compound of formula X is produced by reacting a compound or mixture of compounds of formula VIII,



in which R_1 is as defined in claim 1, with a compound of formula IX,



in which R_2 , R_3 , n and m are defined in claim 1, or an acid addition salt thereof.

3. A process for the production of a compound of formula I, stated in claim 1, substantially as herein described with reference to any one of the Examples.

4. A process for the production of a compound of formula X, stated in claim 1, characterised by reacting a compound or mixture of compounds of formula VIII, stated in claim 2, with a compound of formula IX, stated in claim 2.

5. A process for the production of a compound of formula X, stated in claim 1, substantially as herein described with reference to any one of the Examples.

6. A compound of formula I, stated in claim 1, whenever produced by a process according to claim 1, 2 or 3.

7. A compound of formula I, stated in claim 1.

8. A compound according to claim 7, in which the radicals R_1 are the same.

9. A compound according to claim 7, in which the radicals R_1 , together with the carbon atoms to which they are attached, each signifies a 1,2-phenylene, 1,2-naphthalene or 2,3-naphthalene radical or an aromatic heterocyclic ring containing 1 or 2 oxygen, nitrogen and/or sulphur atoms, which radicals are either unsubstituted or substituted by 1, 2, 3 or 4 halogen atoms, alkyl or alkoxy groups of 1 to 8 carbon atoms, trifluoromethyl, cyano, nitro, hydroxylamino, alkylamino or dialkylamino groups, in which the alkyl radical(s) contain 1 to 8 carbon atoms or acyl.

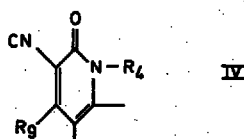
10. A compound according to claim 9, in which the substituents are chlorine, bromine, alkyl or alkoxy of 1 to 4 carbon atoms, trifluoromethyl, cyano, nitro, hydroxylamino, alkyl or dialkylamino, in which the alkyl radical(s) contain 1 to 4 carbon atoms, alkoxycarbonyl and alkanoyl in which the alkyl radical contains 1 to 4 carbon atoms, alkylsulphonyl or alkoxysulphonyl of 1 to 4 carbon atoms, phenylsulphonyl, benzoyl, phenoxycarbonyl, phenoxysulphonyl and alkylaminocarbonyl and dialkylaminocarbonyl in which the alkyl radical(s) contain 1 to 4 carbon atoms.

11. A compound according to claim 7 or 8, in which the radicals R_1 , together with the carbon atoms to which they are attached, each signifies a radical of formula IV,



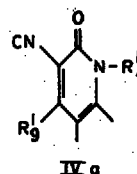
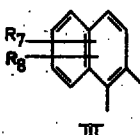
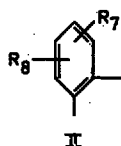
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in which R_4 signifies hydrogen or an alkyl radical of 1 to 8 carbon atoms or a phenyl radical which may be substituted, and R_9 signifies an alkyl radical of 1 to 8 carbon atoms.

- 5 12. A compound according to claim 7 or 8, in which the radicals R_1 , together with the carbon atoms to which they are attached, each signify a radical of formula II, III, IV,



10 in which R_7 and R_8 , which may be the same or different, each signifies a hydrogen or halogen atom, or an alkyl or alkoxy radical of 1 to 4 carbon atoms, R_4 signifies a hydrogen atom, or an alkyl radical of 1 to 4 carbon atoms, or the phenyl radical, and R_9 signifies an alkyl radical of 1 to 4 carbon atoms.

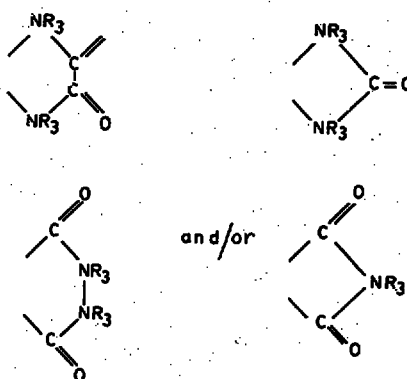
- 15 13. A compound according to any one of claims 7 to 12, in which each R_2 is hydrogen, halogen, or alkyl or alkoxy of 1 to 4 carbon atoms.

14. A compound according to any one of claims 7 to 13, in which each R_2 is hydrogen.

15. A compound according to any one of claims 7 to 14, in which Me signifies chromium, manganese, iron, copper, zinc, nickel or cobalt.

- 20 16. A compound according to any one of claims 7 to 15, in which Me signifies copper, zinc, nickel or cobalt.

17. A compound according to any one of claims 7 to 16, in which the radical $>[(NR_3)_n(CO)_m]$ signifies a radical



25 in which R_3 is as defined in claim 1.

18. A compound according to any one of claims 7 to 17, in which R_3 signifies an alkyl radical of 1 to 8 carbon atoms which is unsubstituted or substituted by halogen, cyano, alkoxy of 1 to 8 carbon atoms, phenyl, phenoxy, acyl, acylamino or acyloxy; or a phenyl radical which is unsubstituted or substituted by 1, 2 or 3 of the substituents listed in claim 9.

19. A compound according to any one of claims 7 to 18, in which R_3 signifies hydrogen, unsubstituted alkyl of 1 to 4 carbon atoms, or unsubstituted phenyl.

20. A compound according to any one of claims 7 to 19, in which R_3 signifies hydrogen.

- 35 21. A compound of formula Ia,

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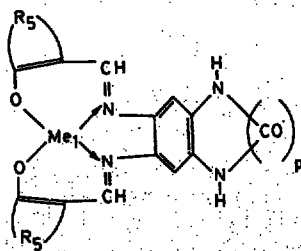


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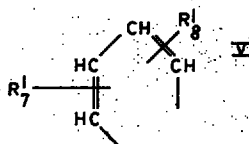
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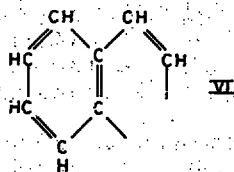
in which Me, signifies nickel, cobalt, copper or zinc, P signifies 1 or 2, and R₅ signifies a radical of formula V,



V

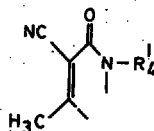
5 in which R₇ and R₈, which may be the same or different, each signifies hydrogen, chlorine or methoxy; a radical of formula VI,

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VI

or a radical of formula VII,

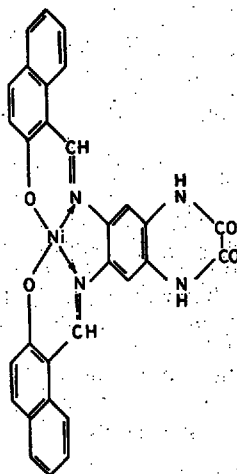


VII

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in which R₄ is as defined in claim 12.
22. A compound of formula



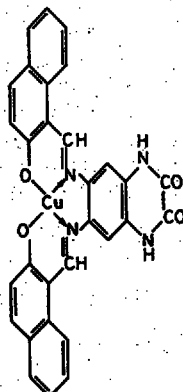
23. A compound of formula



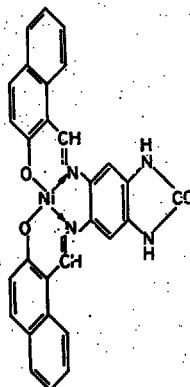
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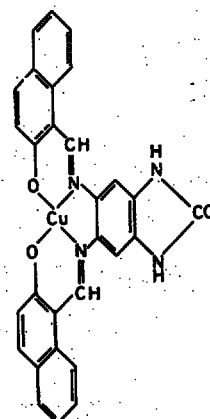
(50)



24. A compound of formula



25. A compound of formula



26. A compound of formula I, stated in claim 1, as described in any one of the foregoing Examples 1 to 7.

27. A compound of formula I, stated in claim 1, as described in any one of the foregoing Examples 8 to 22.

28. A method for the pigmentation of synthetic polymeric materials, which comprises incorporating therein a compound according to any one of claims 7 to 27.

29. Synthetic polymeric materials whenever pigmented by a process according to claim 28.

30. A method of dyeing paper in the stock, which comprises incorporating



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therein a compound according to any one of claims 7 to 27.

31. A method according to claim 30, substantially as herein described with reference to any one of the Application Examples.

32. Paper whenever dyed by a method according to claim 30 or 31.

33. A method for pigment printing or coating textile materials which comprise applying a compound according to any one of claims 7 to 27.

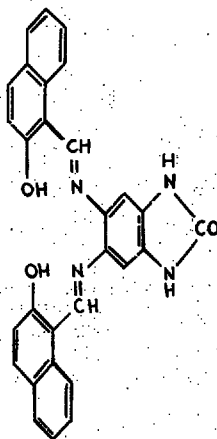
34. Textile materials whenever pigment printed or coated by method according to claim 33.

35. A printing ink comprising a compound according to any one of claims 7 to 27.

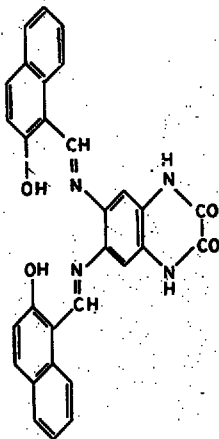
36. A compound of formula X, stated in claim 1, whenever produced by a process according to claim 4 or 5.

37. A compound of formula X, stated in claim 1.

38. A compound of formula



39. A compound of formula



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