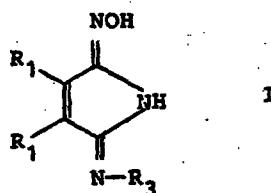


SPECIFICATION

Oximino-imino-isoidindoline metal complexes useful as pigments

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The present invention relates to oxime compounds, their preparation and use. More particularly, the present invention provides compounds of formula I



and metal complexes thereof, in which both

R_1 's are hydrogen or halogen or form a condensed optionally substituted ring of the benzene series, or $-\text{S}-\text{CH}_2\text{CH}_2-\text{S}-$, and

R_3 is hydrogen, a mono- or dicyclic-aromatic group or is a divalent radical of the phenylene or naphthalene series linking one further compound of formula I, wherein R_3 is a direct bond and the R_1 groups are the same as or different from the R_1 groups of the first compound of formula I, which metal complexes are either 1:1 metal complexes when R_3 is a divalent linking radical, or 1:2 metal complexes of monomeric compounds of formula I such 1:2 complexes being symmetric or asymmetric and the metal is a divalent transition metal.

When the R_1 's form a condensed ring of the benzene series, such a ring is preferably an unsubstituted condensed benzene ring or a condensed benzene which is substituted by a total of up to 4 substituents selected from chlorine and bromine atoms or is monosubstituted by a nitro group.

When R_3 is a mono- or dicyclic-aromatic group it is preferably a group of the phenyl, naphthyl, triazolyl or thiazolyl series. More preferably any such aromatic group as R_3 is phenyl optionally substituted by up to three substituents selected from the group consisting of chlorine, bromine, methyl and methoxy or phenyl monosubstituted by benzoylamino or N-phthalimido; triazolyl; or thiazolyl. Preferably any such substituted phenyl is substituted by up to two substituents selected from chlorine and methyl or by a single substituent selected from methoxy, benzoylamino or N-phthalimido.

Preferred divalent radicals of the phenylene series are 1,3- and 1,4-phenylene optionally substituted by a total of up to two substituents selected from chlorine, bromine, methyl, methoxy and nitro, more preferably any divalent phenylene is unsubstituted 1,3- or 1,4-phenylene.

The preferred divalent radicals of the naphthalene series are unsubstituted 1,4- and 2,6-naphthalenes.

The complex forming metals may be any divalent transition metal preferably the metal is divalent nickel cobalt or copper.

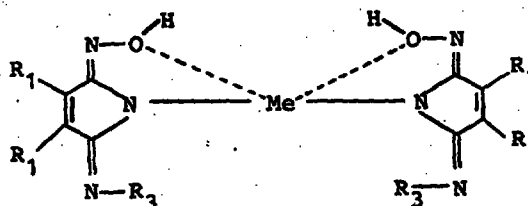
Preferably both R_1 groups are R_1' , where both R_1' groups are hydrogen or halogen or together they form a condensed benzene ring optionally substituted by up to 4 substituents selected from chlorine and bromine atoms or is monosubstituted by a nitro group or they form $-\text{SCH}_2\text{CH}_2\text{S}-$. More preferably both R_1 groups are R_1'' , where both R_1'' groups together form a condensed benzene ring optionally substituted by two or four chlorine atoms.

In the compounds of formula I, when R_3 is a divalent linking radical preferably all the R_1 's are the same.

R_3 is preferably R_3' , where R_3' is hydrogen; phenyl optionally substituted by up to two substituents selected from chlorine and methyl or monosubstituted by methoxy, benzoylamino or N-phthalimido; triazolyl; or thiazolyl; or R_3' is 1,3- or 1,4-phenylene. More preferably R_3 is hydrogen.

The preferred 1:2 complexes of formula I are the symmetrical complexes i.e. those where the R_1 's and the R_3 's are the same. The metal complexes of the invention may be mono or mixed metal complexes.

It is believed that the metal complexes of the compounds of formula I are of formula



in which the R_1 's are the same or different and,

each R_3 , independently, is hydrogen or mono- or dicyclic-aromatic group,

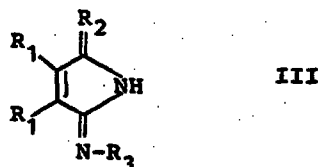
or, one R_3 is a divalent radical of the phenylene or naphthalene series and the other R_3 is a direct bond.

Preferred compounds of formula I are those in which R_1 is R_1' and R_3 is R_3' and all R_1 groups are the same. More preferred compounds are those where R_1 is R_1'' and R_3 is hydrogen.

Preferred nickel, cobalt and copper complex of the compounds of formula I are those in which all R_1 groups are R_1' and R_3 is R_3'' where each R_3'' is hydrogen; phenyl optionally substituted by up to two substituents selected from chlorine, methyl or monosubstituted by methoxy, benzoylamino or N-phthalimido; triazolyl; or thiazolyl; or one R_3'' is 1,3- or 1,4-phenylene and the other is a direct bond. More preferred complexes are those where each R_3 is hydrogen and all R_1 groups are R_1'' .

The present invention also provides a process for the production of compounds of formula I and the metal complexes thereof which comprises

a) condensing a compound of formula III



in which R_2 is $=NH$ or $=(OC_{1-4}alkyl)_2$ with a hydroxylammonium salt, to obtain a compound of formula I,

b) metallizing a compound of formula I or a mixture thereof, with a salt of a divalent transition metal or a mixture of metal salts.

The metallization is effected in accordance with known methods. The condensation of the compound of formula III may be effected in analogy with known methods. Condensation is preferably carried out in the presence of a solvent in which the compound of formula III is at least partially soluble, for example water or preferably dimethylformamide. The condensation is generally effected at temperatures in the range of from 20 to 100°C.

The compounds of formula III are known or may be prepared by known methods from available starting materials.

The metal complexes according to the invention are useful as pigments for the mass pigmenting of synthetic plastics and resins free from or containing solvents, e.g. viscose, cellulose acetate, polyethylene, polystyrene, polyvinyl chloride, synthetic rubber and synthetic leather; of surface coatings, such as paints, whether oil or water-based, lacquers and inks. They may also be used for pigment printing, textile coating and for pigmenting paper in the mass. Such application pigmenting is carried out in accordance with known methods. The pigmented products have good light fastness, weather fastness, resistance to chemicals, migration fastness, resistance to bleeding, fastness to overlacquering and solvents. The pigments give intense dyeings and have good application properties e.g. resistance to flocculation, crystallization and dispersion and have good covering power.

The properties of the pigments can often be improved by treating the raw pigment in organic solvents at elevated temperatures e.g. 110° to 200°C. Suitable organic solvents are those in which the pigment itself is not dissolved e.g. chlorobenzenes (mixtures), nitrobenzene, dimethylformamide, glacial acetic acid, ethylene glycol and quinoline.

The following Examples further serve to illustrate the present invention. In the Examples all parts are by weight and all temperatures are in degrees Centigrade.

Example 1

29 Parts, 1,3-diimino-isoindoline are dissolved in 100 parts dimethylformamide and are stirred with 14 parts hydroxylammoniumchloride for 1 hour at 80°. The reaction mixture is poured onto 500 parts ice water, the precipitate is filtered off and washed salt-free with water. After drying 22 parts 1-oximino-3-imino-isoindoline pale yellow crystals (m.pt. 210—214° with decomposition) are obtained.

For the complex formation 11.3 parts of the product are dissolved in 200 parts dimethylformamide at 80°. 7 Parts anhydrous sodium acetate and then 35 parts of a 2-N-aqueous nickel chloride solution are added. The orange complex forms immediately; after stirring for 1 hour at 80° the dyestuff is suction filtered, washed with hot water and dried. The pigment obtained gives brown-orange dyeings in plastics and lacquers which dyeings have good migration fastness and fastness to overlacquering as well as good light fastness.

Example 2

28.3 Parts 1,3-diimino-4,5,6,7-tetrachloro-isoindoline and 8.5 parts hydroxyl-ammonium sulphate are stirred in 150 parts dimethylformamide for 1 hour at 80°. After cooling the product can be filtered and washed with dimethylformamide and water to obtain pure 1-oximino-3-imino-4,5,6,7-tetrachloroisoindoline in the form of colourless crystals which up to 300° only darken but do not melt.

To form the metal complex the suspension (without intermediate isolation) is taken and 100 parts dimethylformamide are added thereto and subsequently reacted with 10 parts anhydrous sodium acetate as well as a solution of 13 parts nickelchloride ($NiCl_2 \cdot 6 H_2O$) in 30 parts water. The complex forms immediately; after stirring for 1 hour at 80° the product is suction filtered and washed with

dimethylformamide and water. 32 Parts of a bordeaux-red pigment is obtained which is suitable for dyeing plastics and lacquers to give dyeings having good light-, heat- and migration fastness and fastness to overlacquering.

Example 3

- 5 44 Parts 1-imino-3,3-diethoxy-isoindoline with 33 parts 2,5-dichloroaniline and 2 parts glacial acetic acid in 200 parts methanol are stirred at 65° under reflux for 5 hours. The precipitated sulphur-yellow 1-imino-3-(2',5'-dichlorophenylimino)-isoindoline is suction filtered at room temperature, washed with methanol and dried in vacuo at 80°. 29 Parts of this product are stirred with 7 parts hydroxylammoniumchloride in 150 parts dimethylformamide for 3 hours at 80°. After pouring onto 10 300 parts ice water the precipitated product is suction filtered, washed salt-free with cold water and dried in vacuo at 60°. The product 1-oximino-3-(2',5'-dichlorophenylimino)-isoindoline is in the form of pale yellow crystals which melt at 233—238° with gas formation. 15.3 Parts of this product are stirred in 250 parts dimethylformamide at 80°. After the addition of 13 parts nickel acetate the red complex forms immediately. After stirring for 1 hour at 80° followed by cooling to room temperature, 15 the product is filtered and washed salt-free with water. 14 Parts of pigment which gives dyeings in plastics and lacquers of red shades having good migration- and light fastness as well as fastness to overlacquering are obtained.

Further metal complex pigments which may be prepared in analogy with the procedures of the foregoing Examples are given in the following Table.

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Ex. No.	Metal-free Compounds	metal complex	Shade on PVC
4		Ni	scarlet
5		Ni	red
6		Ni	red
7		Ni	scarlet
8		Ni	red
9		Ni	brown-violet
10		Cu	yellow-brown
11	do.	Co	do.

Table (cont).

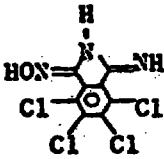
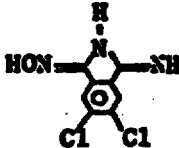
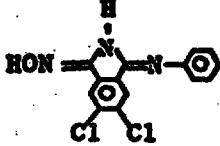
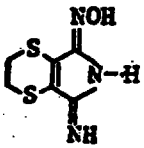
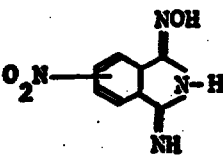
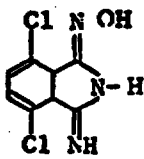
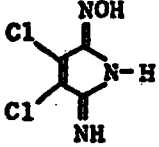
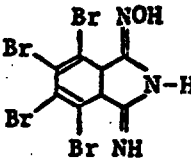
Ex. No.	Metal-free Compounds	metal complex	Shade on PVC
12		Co	do.
13	do.	Cu	yellow
14	do.	Ni/Cu 1:1	brown
15		Ni	orange
16		Ni	red
17		Ni	bluish-red
18		Ni	do
19		Ni	red
20		Ni	violet
21		Ni	bluish-red

Table (cont).

Ex. No.	Metal-free Compounds	metal complex	Shade on PVC
22		Ni	yellow
23		Ni	orange

Application Example

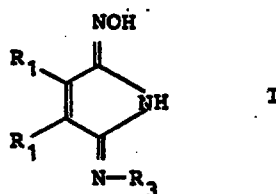
05. Parts pigment of Example 2 and 5 parts titanium dioxide are added to a basic mixture containing:

- 63 parts polyvinylchloride-emulsion
- 32 parts dioctylphthalate
- 3 parts conventional epoxy softener
- 1.5 parts stabiliser (conventional barium-cadmium-stearate mixture) and
- 0.5 parts conventional chelator

and the whole is mixed to homogeneity. The mixture is rolled on a mixing roller apparatus heated to 160° having friction roller (one roller with 20 rotations and the other with 25 rotations per minute) for 8 minutes, the foils of 0.3 mm which have a bluish-red shade are taken-off the rollers.

Claims

1. A compound of formula I



or a metal complex thereof in which both

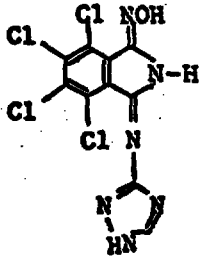
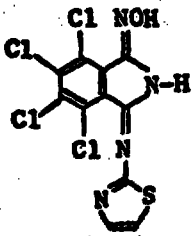
R_1 's are hydrogen or halogen or form a condensed optionally substituted ring of the benzene series, or $-S-CH_2CH_2-S-$, and

R_3 is hydrogen, a mono- or dicyclic-aromatic group or is a divalent radical of the phenylene or naphthalene series linking one further compound of formula I, wherein R_3 is a direct bond and the R_1 groups are the same as or different from the R_1 groups of the first compound of formula I, which metal complex is either a 1:1 metal complex when R_3 is a divalent linking radical, or a 1:2 metal complex of monomeric compounds of formula I, such 1:2 complex being symmetric or asymmetric and the metal is a divalent transition metal.

2. A complex according to Claim 1, in which when both R_1 groups form a condensed ring of the



Table (cont).

Ex. No.	Metal-free Compounds	metal complex	Shade on PVC
22		Ni	yellow
23		Ni	orange

Application Example

05. Parts pigment of Example 2 and 5 parts titanium dioxide are added to a basic mixture containing:

63 parts polyvinylchloride-emulsion

32 parts dioctylphthalate

3 parts conventional epoxy softener

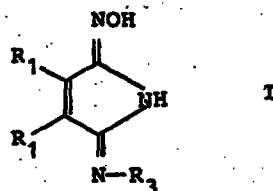
1.5 parts stabiliser (conventional barium-cadmium-stearate mixture) and

0.5 parts conventional chelator

and the whole is mixed to homogeneity. The mixture is rolled on a mixing roller apparatus heated to 160° having friction roller (one roller with 20 rotations and the other with 25 rotations per minute) for 8 minutes, the foils of 0.3 mm which have a bluish-red shade are taken-off the rollers.

Claims

1. A compound of formula I



or a metal complex thereof in which both

R_1 's are hydrogen or halogen or form a condensed optionally substituted ring of the benzene series, or $-S-CH_2CH_2-S-$, and

R_2 is hydrogen, a mono- or dicyclic-aromatic group or is a divalent radical of the phenylene or naphthalene series linking one further compound of formula I, wherein R_3 is a direct bond and the R_1 groups are the same as or different from the R_1 groups of the first compound of formula I, which metal complex is either a 1:1 metal complex when R_3 is a divalent linking radical, or a 1:2 metal complex of monomeric compounds of formula I, such 1:2 complex being symmetric or asymmetric and the metal is a divalent transition metal.

2. A complex according to Claim 1, in which when both R_1 groups form a condensed ring of the



benzene series it is unsubstituted or substituted by a total of up to 4 substituents selected from chlorine and bromine atoms or is monosubstituted by a nitro group.

3. A complex according to Claim 1 or Claim 2, in which any mono- or dicyclic aromatic group as R_3 is phenyl optionally substituted by up to three substituents selected from the group consisting of chlorine, bromine, methyl and methoxy or phenyl monosubstituted by benzoylamino or N-phthalimido; triazolyl; or thiazolyl.

4. A complex according to any one of Claims 1 to 3, in which both R_1 are R_1' , where both R_1' are hydrogen or halogen or together form a condensed benzene ring optionally substituted by up to 4 substituents selected from chlorine and bromine atoms or is monosubstituted by a nitro group or they form $-\text{SCH}_2\text{CH}_2\text{S}-$.

5. A complex according to any one of Claims 1 to 5, in which R_3 is R_3' , where R_3' is hydrogen; phenyl optionally substituted by up to two substituents selected from chlorine and methyl or monosubstituted by methoxy, benzoylamino or N-phthalimido; triazolyl; or thiazolyl; or R_3' is 1,3- or 1,4-phenylene.

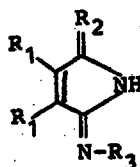
6. A complex according to any one of the preceding claims in which when R_3 is a divalent radical all the R_1 groups are identical.

7. A complex according to any one of the preceding claims in which both R_1 groups form a condensed benzene ring optionally substituted by two or four chlorine atoms.

8. A complex according to any one of the preceding claims, in which R_3 is hydrogen.

9. A complex according to any one of the preceding claims, in which the metal is divalent nickel, cobalt or copper.

10. A process for the production of a compound of formula I as defined in Claim 1, comprising condensing a compound of formula III



III

- 25 in which R_1 and R_2 are as defined in Claim 1, and

R_3 is $=\text{NH}$ or $=(\text{OC}_{1-4}\text{alkyl})_2$, with a hydroxyl-ammonium salt.

11. A process for the production of a metal complex as defined in Claim 1 comprising metallising a compound of formula I or a mixture thereof with a salt of a divalent transition metal.

12. A process for the production of a compound of formula I or a complex thereof, as defined in

- Claim 1, substantially as hereinbefore described with reference to any one of the Examples.

13. A compound of formula I or a complex thereof, whenever obtained by a process according to any one of Claims 10 to 12.

14. A process for mass pigmenting of synthetic plastic and resins, surface coatings, lacquers and inks comprising employing a complex according to any one of Claims 1 to 9 or 13, as pigmenting agent.

15. A process according to Claim 14, substantially as hereinbefore described with reference to the Application Example.

16. Mass pigmented materials whenever obtained by a process according to Claim 14 or Claim 15.