

PATENT SPECIFICATION

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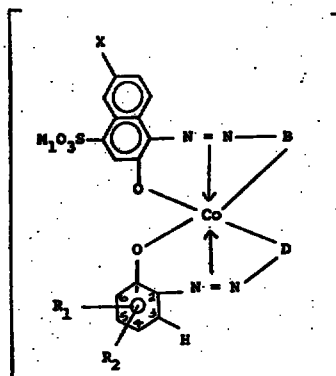


(54) ASYMMETRIC 1:2 COBALT COMPLEXES, THEIR PRODUCTION AND USE

(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:—

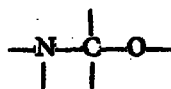
The present invention relates to pure asymmetric 1:2 cobalt complexes and mixtures of such pure asymmetric complexes, their production and use.

More particularly, the present invention provides pure asymmetric 1:2 cobalt complexes of formula I,



- in which
 X is hydrogen or nitro,
 either,
 R₁ and R₂, independently, are hydrogen, (C₁₋₄)alkyl, (C₁₋₄)alkoxy, chlorine, bromine or nitro,
 or
 R₁ is hydrogen, chlorine or nitro, and
 R₂ is —SO₂NR₃R₄, in which case the groups R₁ and R₂ occupy the 4- and 5-positions, either
 R₃ is hydrogen or unsubstituted or substituted (C₁₋₄)alkyl, and
 R₄ is hydrogen, unsubstituted or substituted (C₁₋₄)alkyl, (C₅₋₇)cycloalkyl or phenyl,
 or
 R₃ and R₄, together with the nitrogen atom to which they are bound, form a non-aromatic 5- or 6-membered heterocyclic ring which contains one or two hetero atoms,
 B is a divalent radical of a coupling component of the 1- or 2-hydroxynaphthalene series which is coupled in the 2- or 1-position ortho to the hydroxy group and is bound to the cobalt atom through the oxygen atom,
 D is a divalent radical of a coupling component of the 2-naphthylamine series which is coupled in the 1- position ortho to the amine group, or a divalent radical of the 5-amino pyrazole series which is coupled to the carbon atom next to that carrying the amino group, whereby the divalent radical D is bound to the cobalt atom through the amino group,

M is hydrogen or an equivalent of a non-chromophoric cation, and M_1 is an equivalent of a non-chromophoric cation, with the provisos that the molecule (i) contains a single sulpho group, which sulpho group is in salt form, (ii) contains at maximum a single sulphonamide group which group is in the radical D or is R_2 , and (iii) is free from



groups, and mixtures of such pure asymmetric complexes.

When R_1 and/or R_2 is alkyl, such alkyl is preferably methyl or ethyl, with methyl being especially preferred.

When R_1 and/or R_2 is alkoxy, preferably such alkoxy is methoxy or ethoxy.

When R_3 and/or R_4 is an unsubstituted alkyl group, such alkyl group is straight-chain or branched and preferably contains 1 to 3 carbon atoms, with methyl, ethyl and isopropyl being especially preferred.

When R_3 and/or R_4 is a substituted alkyl group, such alkyl group is straight chain or branched and is substituted by one or more substituents common in the chemistry of anionic azo dyestuffs. Preferably such substituted alkyl groups are substituted by up to two substituents, selected from halogen (preferably chlorine or bromine), hydroxy, cyano, (C_{1-4}) alkoxy (preferably methoxy or ethoxy) and phenyl. Preferred substituents are hydroxy, methoxy and ethoxy. More preferably, any substituted alkyl group as R_3 and/or R_4 is monosubstituted.

When R_4 is substituted cycloalkyl or phenyl such cycloalkyl or phenyl radical is substituted by substituents common in the chemistry of anionic azo dyestuffs.

When R_4 is an unsubstituted or substituted cycloalkyl preferably such cycloalkyl contains 5- or 6-ring carbon atoms, with cyclohexyl being most preferred. Preferred substituted cycloalkyl groups are those which are substituted by up to three methyl groups.

When R_4 is substituted phenyl, preferably such phenyl is substituted by a total of up to three substituents selected from up to three halogen, (C_{1-4}) alkyl, (C_{1-4}) alkoxy and nitro (maximum of two nitro). More preferably, such substituted phenyl is monosubstituted by chlorine, nitro, methyl, methoxy or ethoxy or di-substituted by two methyl, two methoxy or two ethoxy groups. Most preferably any phenyl radical as R_4 is unsubstituted.

When R_3 and R_4 , together with the nitrogen atom to which they are bound, form a heterocyclic ring, such heterocyclic ring is preferably a pyrrolidine, piperidine or morpholine ring.

By halogen is meant chlorine, bromine or fluorine with chlorine and bromine being preferred.

R_3 is preferably R_3' , where R_3' is hydrogen, (C_{1-3}) alkyl or β - or γ -hydroxy (C_{2-3}) alkyl. Most preferably, R_3 is hydrogen.

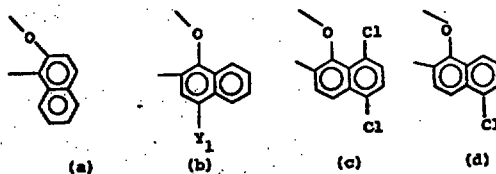
R_4 is preferably R_4' , where R_4' is hydrogen; (C_{1-3}) alkyl; β - or γ -hydroxy (C_{2-3}) alkyl; $R_{11}O-(CH_2)_n-$, where R_{11} is methyl or ethyl and n is 2, 3 or 4, preferably 2 or 3; phenyl; phenyl monosubstituted by chlorine, nitro, methyl, methoxy or ethoxy; or phenyl disubstituted by two methyl, two methoxy or two ethoxy groups. More preferably R_4 is R_4'' , where R_4'' is methyl, ethyl, isopropyl, 2-hydroxyethyl, $-(CH_2)_3-CH(OH)-CH_3$, $-(CH_2)_3-OCH_3$ or phenyl. Even more preferably R_4 is R_4''' , where R_4''' is methyl, $-(CH_2)_3-OCH_3$ or phenyl.

Preferably R_1 is R_1' , where R_1' is hydrogen, methyl, chlorine or nitro. More preferably, R_1 is R_1'' , where R_1'' is hydrogen, chlorine or nitro.

R_2 is preferably R_2' , where R_2' is chlorine, nitro or $-SO_2NHR_4''$ preferably $-SO_2NHR_4'''$, with the proviso that when R_2' is $-SO_2NHR_4''$ or $-SO_2NHR_4'''$, R_1 is hydrogen.

More preferably, R_1 and R_2 , independently, are chlorine or nitro. When one of R_1 and R_2 is hydrogen and the other has a significance other than hydrogen, the substituent is preferably in the 4- or 5- position. When both of R_1 and R_2 have a significance other than hydrogen, the substituents are preferably in the 4- and 6-positions, with the exception that when R_2 is $-SO_2NR_3R_4$, the substituents R_1 and R_2 are in the 4- and 5-positions.

The group B is preferably a group of formula (a), (b), (c) or (d),



in which

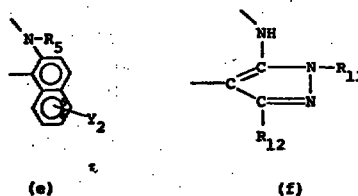
Y_1 is hydrogen, (C_{1-2}) alkyl (preferably methyl), (C_{1-2}) alkoxy (preferably methoxy), chlorine or bromine;

preferably

Y_1 is Y_1' , where Y_1' is hydrogen, methyl or methoxy.

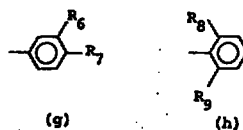
More preferably B is B' , where B' is a group of formula (a), (c), (d), or (b) in which Y_1 is Y_1' .

The group D is preferably a group of formula (e) or (f),



in which

R_5 is hydrogen, (C_{1-4}) alkyl or a group of formula (g) or (h),



in which one of

R_6 and R_7 is hydrogen and the other is hydrogen, chlorine, bromine, (C_{1-2}) alkyl (preferably methyl), (C_{1-2}) alkoxy, (preferably methoxy) or trifluoromethyl,

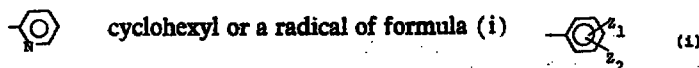
R_8 is hydrogen or methyl, and

R_9 is methyl, chlorine or bromine with the proviso that when R_8 is chlorine or bromine R_9 is hydrogen,

Y_2 is hydrogen or $-\text{SO}_2\text{NHR}_{10}$ in the 5- or 6- position, in which R_{10} is hydrogen, (C_{1-4}) alkyl or hydroxy (C_{2-4}) alkyl,

R_{12} is hydrogen; (C_{1-4}) , preferably (C_{1-2}) alkyl, more preferably methyl; (C_{1-2}) -alkoxy, preferably methoxy; or phenyl,

R_{13} is hydrogen; (C_{1-4}) alkyl, preferably (C_{1-2}) alkyl; phenyl (C_{1-4}) alkyl, preferably phenyl (C_{1-2}) alkyl;



in which either

Z_1 is hydrogen and

Z_2 is hydrogen; fluorine; chlorine, bromine, (C_{1-4}) alkyl, preferably (C_{1-2}) alkyl; (C_{1-2}) alkoxy; nitro; or trifluoromethyl,

or

Z_1 and Z_2 are the same and are both chlorine, bromine, methyl or methoxy, with the provisos that:

when both

Z_1 and Z_2 are chlorine, the chlorine atoms are in the 2,3-, 2,4-, 2,5-, 2,6-, or 3,4-positions,

when both

Z_1 and Z_2 are bromine, the bromine atoms are in the 2,4- or 3,5-positions,

when both

Z_1 and Z_2 are methyl, the methyl groups are in the 2,3-, 2,4-, 2,5-, 2,6- or 3,5-positions,
and when both

Z_1 and Z_2 are methoxy, the methoxy groups are in the 3,4-positions,

or

Z_1 and Z_2 are different and signify 3-chloro-2-methyl, 4-chloro-2-methyl, 5-chloro-2-methyl, 4-bromo-2-methyl or 5-chloro-2-methoxy.

Preferably Z_1 and Z_2 are Z_1' and Z_2' , where Z_1' and Z_2' are, independently, hydrogen, chlorine or methyl.

When R_5 is alkyl it is preferably methyl or ethyl.

When R_5 is a radical of formula (g), preferably one of R_5 and R_7 is hydrogen and the other is hydrogen, chlorine, methyl or methoxy, more preferably hydrogen, chlorine or methyl.

When R_5 is a radical of formula (h), R_5 is preferably R_5' , where R_5' is methyl or chlorine.

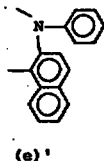
Preferably R_5 is R_5' where R_5' is hydrogen, phenyl, 2-, 3- or 4-chlorophenyl, 2- or 4-methylphenyl or 2,6-dimethylphenyl. More preferably, R_5 is R_5'' where R_5'' is hydrogen or phenyl, with phenyl being especially preferred.

When R_{10} is alkyl, such alkyl is preferably methyl or ethyl, more preferably methyl. When R_{10} is hydroxyalkyl, such hydroxyalkyl is preferably β - or γ -hydroxy(C_{2-3})alkyl with β -hydroxyalkyl being preferred.

Preferably R_{10} is R_{10}' , where R_{10}' is hydrogen, methyl or β -hydroxy(C_{2-3})alkyl.

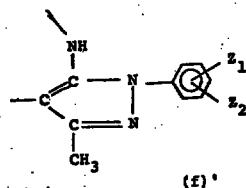
Y_2 is preferably hydrogen or $-\text{SO}_2\text{NHR}_{10}'$, hydrogen being preferred when R_5 is other than hydrogen, and $-\text{SO}_2\text{NHR}_{10}'$ being preferred when R_5 is hydrogen. Most preferably Y_2 is hydrogen.

Preferably, in the radical of formula (e), R_5 is R_5' and Y_2 is hydrogen or $-\text{SO}_2\text{NHR}_{10}'$. Most preferably (e) is a radical of formula (e)',



In the radical of formula (f), R_{12} is preferably methyl and R_{13} is preferably a radical of formula (i).

Preferably (f) is a radical of formula (f)',



wherein

Z_1 and Z_2 are as defined above.

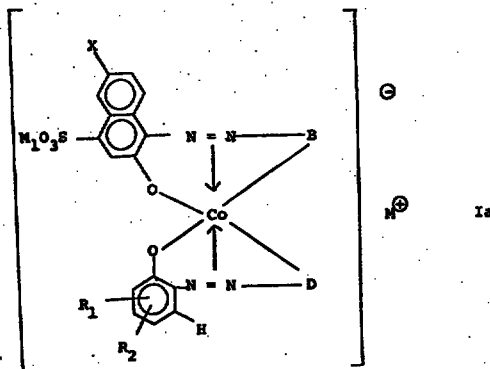
Preferably each of Z_1 and Z_2 are Z_1' and Z_2' .

D is preferably a radical of formula (e), wherein R_5 is R_5' and Y_2 is hydrogen or $-\text{SO}_2\text{NHR}_{10}'$ or a radical of formula (f)'. Most preferably D is a radical of formula (e)'.

Preferably M signifies an alkali metal cation, an unsubstituted or substituted ammonium ion or a quaternary amine. As examples of alkali metal cations may be given sodium, lithium and potassium, with sodium being preferred. Suitable substituted ammonium ions are (C_{1-3})alkyl ammonium and hydroxy (C_{2-4})alkylammonium, for example triethyl ammonium, mono-, di- and triethanol ammonium and mono-, di- and tri-isopropanol ammonium. Suitable quaternized amines include N-ethyl-N-hexylamine, cyclohexylamine, N,N-dicyclohexylamine or cyclic amines such as morpholine in quaternary form. When M is a quaternary amine, the water solubility of the 1:2 complexes is reduced such that they are scarcely soluble or only soluble in the presence of organic solvents.

The 1:2 complexes in which M is hydrogen may, in certain cases, be scarcely soluble in water.

The salt form of the sulpho group M_1 may correspond to any of the above-mentioned cations for M. The salt form cation M_1 may be the same as or different from M. Representative asymmetric 1:2 cobalt complexes of formula I are those of formula

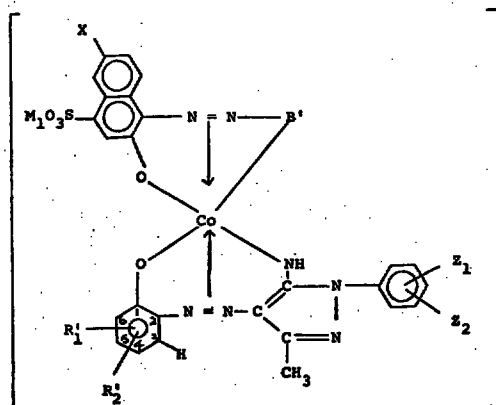
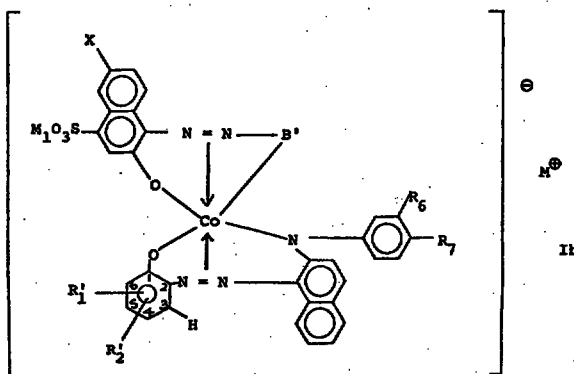


in which

R_1 , R_2 , X, B, D, M_1 and M are as defined above, with the proviso that when D is a radical of formula (e) R_2 is only hydrogen when Y_2 is $-\text{SO}_2\text{NHR}_{10}$ or B is a radical of formula (b), (c) or (d).

Of the complexes of formula Ia, those in which R_2 is R_2' and Y_2 is hydrogen or $-\text{SO}_2\text{NHR}_{10}'$ are preferred.

Preferred complexes of formula I are those of formula Ib and Ic,



in which

R_1' is hydrogen, methyl, chlorine or nitro, with hydrogen, chlorine and nitro being preferred,

R_2' is chlorine, nitro or $-\text{SO}_2\text{NHR}_{10}''$, (preferably $-\text{SO}_2\text{NHR}_{10}'''$), with the proviso that R_2' is only $-\text{SO}_2\text{NHR}_{10}''$ or $-\text{SO}_2\text{NHR}_{10}'''$ when R_1' is hydrogen,

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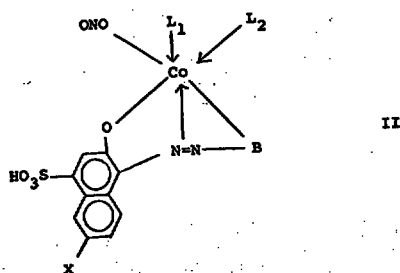
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B is a radical of formula (a), (b), (c) or (d), with the proviso that when B is a radical of formula (b), Y_1 is Y_1' , and X, Z_1 , Z_2 , M, M_1 , R_1 and R_2 are as defined above.

Especially preferred complexes of formula Ib are those wherein one of R_1 and R_2 is hydrogen and the other is hydrogen, chlorine, methyl or methoxy, more preferably hydrogen, chlorine or methyl.

Especially preferred complexes of formula Ic are those in which each of Z_1 and Z_2 are Z_1' and Z_2' .

The present invention also provides a process for the production of complexes or mixtures of complexes of formula I, comprising a) reacting a compound of formula II, in free acid or salt form,

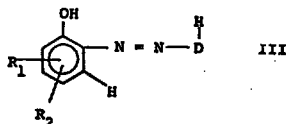


in which

L_1 and L_2 are monodentate ligands and

X and B are as defined above,

or a mixture of compounds of formula II, with a compound of formula III,

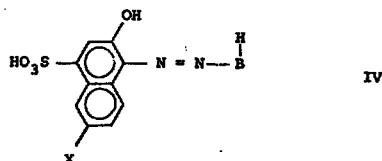


in which

R_1 , R_2 and D are as defined above,

or a mixture of compounds of formula III, or

b) reacting a corresponding nitrite-containing cobalt complex of a compound of formula III, or a mixture thereof, with a compound of formula IV, in free acid or salt form,



in which

X and B are as defined above,

or a mixture thereof, any sulpho in the free acid form being converted into salt form.

The reaction is suitably carried out by employing the reactants in stoichiometric amounts. Suitable monodentate ligands are colourless inorganic or organic molecules which contain an oxygen or nitrogen group with electron-donating properties, in particular water molecules. The reaction may be carried out in aqueous, aqueous/organic or organic medium. Examples of organic solvents include low molecular weight (C_{1-6}) carboxylic acid amides such as formamide or an alkylated derivative thereof, glycols such as ethylene glycol, di- or triethyleneglycol or their derivatives thereof. The reactions are suitably conducted in neutral or alkaline medium and are completed after all the 1:1 complex has been reacted. The product obtained may be isolated in conventional manner, for example by salting out or weakly acidifying, and after washing with a concentrated salt solution may be collected and dried.

Process a) is preferred.

The obtained asymmetric complexes are pure asymmetric complexes, that is, the complexes contain less than 10% of the possible symmetric complexes.

The 1:1 cobalt complex — starting materials may be produced by reacting a compound of formulae III or IV, as the case may be, with a cobalt-donating compound in the form of a cobalt(II) salt in the presence of an inorganic nitrite. Suitably the compound of formula III or IV is reacted with the cobalt-donating compound in a 1:1 molar ratio. Preferably 2 to 6 moles of nitrite per gram atom cobalt are used. The metallization may be conducted in conventional manner.

Depending on the reaction and isolation conditions (e.g. addition of base to obtain an alkaline pH or the salt used to salt-out the product) a complex of formula I is obtained in which M is preferably an alkali metal cation, such as lithium, sodium or potassium, or an ammonium ion and in which the salt form of the sulpho group is the same as or different than M. When a weak acid is used a complex is obtained in which M is hydrogen and the sulpho group is in salt form. The hydrogen ion may be replaced by an alkali metal cation or quaternary ammonium ion by the addition of alkali metal hydroxides or organic amines. It will be appreciated that the cation of the sulpho group may also be replaced at the same time.

The compounds of formula II, III and IV are known or may be prepared in conventional manner from known starting materials.

The complexes of formula I and mixtures thereof are useful for dyeing and printing nitrogen-containing organic substrates. Examples of suitable substrates are those which consist of or comprise natural or synthetic polyamides such as wool, silk or nylon, or polyurethane or leather.

The deyings obtained exhibit notable light and wet fastness. They also exhibit notable rubbing fastness and resistance to carbonization, ironing, wool chlorination and the action of acids and alkalis.

The dyestuffs build up from a neutral medium on polyamide fibres, the build-up being tone-in-tone due to their pure asymmetric character. The dyestuffs also build-up equally on wool and nylon when dyed together. The dyestuffs are suitable for use in combination with other 1:2 metal complexes. The complexes may be formed into stable printing pastes which build-up well on all types of polyamides.

The complexes of formula I which are well soluble in water, i.e. those in which M is other than hydrogen or an amine such as N-ethyl-N-hexylamine, cyclohexylamine, N,N-dicyclohexylamine or cyclic amines such as morpholine in quaternary form are also useful for dyeing metals, especially anodized aluminium.

The compounds of formula I in which M is a quaternary amine as given above may also be used in the preparation of printing laquers and ball-point pen inks.

The dyes according to the invention may be employed as such or in the form of liquid or solid preparations.

Preferably water-soluble organic solvents optionally mixed with water are used for the liquid preparations which are in the form of stable concentrated stock solutions; conventional additives such as dissolving agents (e.g. urea or alkali reacting organic or inorganic substances) may be added thereto. The stock solutions may be diluted with water. Such preparations may be made, for example, in accordance with the procedure described in German Patent No. 1,619,470 or in German Patent Application No. 2,033,989. Also concentrated stable aqueous preparation which contain the conventional additives may be used.

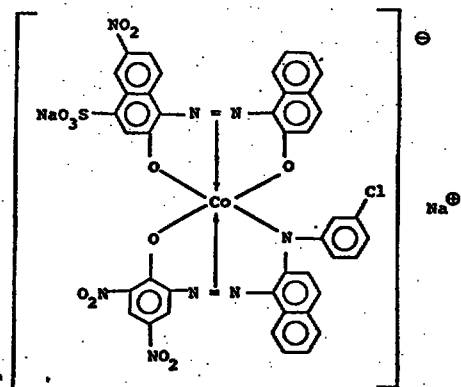
Solid preparations which are in powder or granulate form with an average particle size of at least 20 μ can be used, which preparations contain conventional additives such as standardization agents. Such solid preparations may be made for example in accordance with the procedure described in British Patent 1,370,845. The solid preparations are well soluble in water whereby the exact quantity of dye preparation needed in the dye bath may be added thereto.

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

EXAMPLE 1.

45 Parts of the dyestuff obtained by the acid coupling of diazotised 2 - amino - 1 - hydroxy - 4,6 - dinitrobenzene with 2 - (3' - chlorophenyl) - aminonaphthalene and the paste of the 1:1-cobalt complex obtained from 44 parts of the monoazo dyestuff of 1 - amino - 2 - hydroxy - 6 - nitronaphthalene - 4 - sulphonic acid $\rightarrow$ 2 - hydroxy-naphthalene are stirred into 600 parts of water and 300 parts of ethanol, and this is set at a pH of 11.0—11.5 by adding sodium hydroxide solution. The reaction mixture is heated to 30° and stirred at this temperature for 24 hours. If any starting material remains after this time the temperature is raised to 80°C and stirring is continued until the disappearance of both starting materials. The pH is kept to 11—11.5 during the whole reaction. The chromatograph of the asymmetrical 1:2-cobalt complex thus

formed must show no more or very little traces of the metal-free dyestuff and none of 1:1-cobalt complex. The dyestuff is salted out by adding sodium chloride, it is filtered, washed with a 5% sodium chloride solution and dried. It corresponds to formula



and has a very high degree of purity (in all at most 5% of symmetrical complexes). The dyestuff is well soluble in water and dyes natural and synthetic polyamide fibres such as wool and nylon in a grey or black shade, the dyestuff being absorbed from a neutral bath in an even manner.

The dyeing has good all-round wet fastness and notable light fastness, as well as notable fastness to rubbing. The 1:1-cobalt complex used as the starting material may be produced as follows:

28 parts of cobalt-(II)-sulphate. $7H_2O$ and 28 parts of sodium nitrite are dissolved in a beaker in 500 parts of water. Then, 44 parts of the monoazo dyestuff 1-amino-2-hydroxy-6-nitro-naphthalene-4-sulphonic acid $\rightarrow$ 2-hydroxynaphthalene are entered with good stirring. The pH value is set at 5.5—6.0 during and after addition of the monoazo dyestuff, and is kept in this range for about 20 hours until the initial dyestuff has been completely converted into the 1:1-cobalt complex. During metallisation, the temperature must be maintained at between 20 and 30°. The 1:1-cobalt complex is precipitated by salting out with sodium chloride solution until the filtrate is free from cobalt. The paste of the 1:1-cobalt complex obtained may be used directly for the reaction to form the asymmetrical 1:2-cobalt complex.

In the following Table the structural formulae of further dyestuffs which may be prepared in analogy with the procedure described in Example 1, are given. The dyestuffs in the Table give dyeings on polyamide which have similar properties to the dyeing obtained with the dyestuff of Example 1. The dye shade obtained in each case is indicated by the letters a to i given in column I, whereby

- a is black
- b is reddish black
- c is greenish black
- d is bluish black
- e is brown
- f is red-brown
- g is bordeaux
- h is red-bordeaux, and
- i is rubine

Example No.	Compound of formula IV in the form of 1:1 Co-complex	Compound of formula III in metal free form	I
2	1-amino-2-hydroxy-6-nitro-naphthalene-4-sulphonic acid → 2-hydroxynaphthalene	2-amino-4-chloro-1-hydroxy-6-nitrobenzene → 2-phenylamino-naphthalene	a
3	do.	2-amino-4,6-dinitro-1-hydroxybenzene → 2-aminonaphthalene	a
4	do.	2-amino-4,6-dinitro-1-hydroxybenzene → 2-phenylamino-naphthalene	a
5	do.	2-amino-1-hydroxybenzene → 2-phenylamino-naphthalene	e
6	do.	2-amino-1-hydroxy-4-methyl-6-nitrobenzene → 2-(4'-chlorophenyl)aminonaphthalene	a
7	do.	2-amino-1-hydroxy-4-methoxybenzene → 2-phenylamino-naphthalene	a
8	do.	2-amino-1-hydroxybenzene-4-sulphonic acid amide → 2-(2',6'-dimethylphenyl)aminonaphthalene	b
9	do.	2-amino-1-hydroxybenzene-4-N-(3'-methoxypropyl)sulphonic acid amide → 2-phenylaminonaphthalene	b
10	do.	2-amino-1-hydroxybenzene-4-N-phenyl sulphonic acid amide → 2-phenylaminonaphthalene	b
11	do.	2-amino-1-hydroxybenzene-5-N-methyl sulphonic acid amide → 2-(4'-methylphenyl)aminonaphthalene	a
12	do.	2-amino-1-hydroxybenzene-4-N-(2'-hydroxypropyl)sulphonic acid amide → 2-phenylaminonaphthalene	b
13	do.	2-amino-4-chloro-1-hydroxybenzene-5-sulphonic acid amide → 2-phenylaminonaphthalene	a
14	do.	2-amino-4,6-dinitro-1-hydroxybenzene → 2-aminonaphthalene-6-N-(2'-hydroxypropyl)sulphonic acid amide	a

Example No.	Compound of formula IV in the form of 1:1 Co-complex	Compound of formula III in metal free form	I
15	1-amino-2-hydroxy-6-nitro-naphthalene-4-sulphonic acid $\rightarrow$ 2-hydroxynaphthalene	2-amino-4,6-dinitro-1-hydroxybenzene $\rightarrow$ 2-ethylamino-naphthalene	a
16	do.	2-amino-1-hydroxy-5-nitrobenzene $\rightarrow$ 3-methyl-1-phenyl-5-aminopyrazole	e
17	do.	2-amino-4,6-dinitro-1-hydroxybenzene $\rightarrow$ 3-methyl-1-phenyl-5-aminopyrazole	f
18	1-amino-2-hydroxy-6-nitro-naphthalene-4-sulphonic acid $\rightarrow$ 2-hydroxynaphthalene and 1-amino-2-hydroxynaphthalene-4-sulphonic acid $\rightarrow$ 2-hydroxynaphthalene	2-amino-4,6-dinitro-1-hydroxybenzene $\rightarrow$ 2-(3'-chloro-phenyl)aminonaphthalene	a
19	1-amino-2-hydroxy naphthalene-4-sulphonic acid $\rightarrow$ 2-hydroxy naphthalene	do.	
20	do.	2-amino-4,6-dichloro-1-hydroxybenzene $\rightarrow$ 2-phenylaminonaphthalene and 2-amino-4,6-dichloro-1-hydroxybenzene $\rightarrow$ 2-phenylaminonaphthalene	a
21	do.	2-amino-4,6-dinitro-1-hydroxybenzene $\rightarrow$ 2-aminonaphthalene	d
22	do.	2-amino-4,6-dinitro-1-hydroxybenzene $\rightarrow$ 2-phenylaminonaphthalene	a
23	do.	2-amino-1-hydroxybenzene-4-N-phenylsulphonic acid amide $\rightarrow$ 2-phenylaminonaphthalene	b
24	do.	2-amino-1-hydroxy-5-nitrobenzene $\rightarrow$ 3-methyl-1-(2',5'-dichlorophenyl)-5-aminopyrazole	g
25	do.	2-amino-4,6-dinitro-1-hydroxybenzene $\rightarrow$ 3-methyl-1-phenyl-5-aminopyrazole	i
26	1-amino-2-hydroxy-6-nitro-naphthalene-4-sulphonic acid $\rightarrow$ 1-hydroxy-4-methoxynaphthalene	2-amino-4,6-dinitro-1-hydroxybenzene $\rightarrow$ 2-phenylaminonaphthalene	c
27	1-amino-2-hydroxy-6-nitro-naphthalene-4-sulphonic acid $\rightarrow$ 1-hydroxy-4-methylnaphthalene	2-amino-1-hydroxybenzene-4-sulphonic acid morpholine $\rightarrow$ 2-phenylaminonaphthalene	a

Example No.	Compound of formula IV in the form of 1:1 Co-complex	Compound of formula III in metal free form	I
28	1-amino-2-hydroxy-6-nitro-naphthalene-4-sulphonic acid → 1-hydroxy-4-methyl-naphthalene	2-amino-1-hydroxybenzene-4-N-phenylsulphonic acid amide → 3-methyl-1-phenyl-5-aminopyrazole	a
29	1-amino-2-hydroxynaphthalene-4-sulphonic acid → 1-hydroxy-4-methoxynaphthalene	2-amino-4,6-dinitro-1-hydroxybenzene → 2-phenylaminonaphthalene	a
30	1-amino-3-hydroxynaphthalene-4-sulphonic acid → 1-hydroxy-4-methylnaphthalene	2-amino-6-chloro-4-nitro-1-hydroxybenzene → 2-phenylaminonaphthalene	a
31	1-amino-2-hydroxynaphthalene-4-sulphonic acid → 1-hydroxy-5-chloronaphthalene	2-amino-4,6-dinitro-1-hydroxybenzene → 2-phenylaminonaphthalene	a
32	1-amino-2-hydroxynaphthalene-4-sulphonic acid → 1-hydroxy-5,8-dichloronaphthalene	2-amino-4,6-dinitro-1-hydroxybenzene → 2-ethylaminonaphthalene	a
33	do.	2-amino-1-hydroxybenzene-4-N,N-diethyl sulphonic acid amide → 2-phenylaminonaphthalene	b
34	do.	2-amino-4-chloro-6-nitro-1-hydroxybenzene → 3-methyl-1-(4'-methylphenyl)-5-aminopyrazole	e
35	1-amino-2-hydroxy-6-nitro-naphthalene-4-sulphonic acid → 1-hydroxy-5,8-dichloronaphthalene	2-amino-4,6-dichloro-1-hydroxybenzene → 2-phenylaminonaphthalene	b
36	do.	2-amino-4,6-dinitro-1-hydroxybenzene → 2-(3'-chlorophenyl)aminonaphthalene	a
37	do.	2-amino-4,6-dichloro-1-hydroxybenzene → 3-methyl-1-(3'-chlorophenyl)-5-aminopyrazole	f

APPLICATION EXAMPLE A.

0.03 g (to obtain a grey shade) or 0.15 g (to obtain a black shade) of the dyestuff obtained in Example 1 is dissolved in 300 parts of water, and 0.2 g of ammonium sulphate is added. Subsequently, the moistened material (5 g of wool gabardine or 5 g of nylon satin) is entered into the bath and is heated to boiling temperature over the course of 30 minutes. The water which is evaporated during the 30 minutes boiling is replaced and dyeing is completed at boiling temperature for another 30 minutes, with subsequent rinsing. After drying, a grey or black dyeing with notable wet and light fastness is obtained.

The dyestuffs of Examples 2 to 37 may be used for dyeing in analogous manner to that described above.

APPLICATION EXAMPLE B.

Polyamide is printed with a printing paste containing the following:

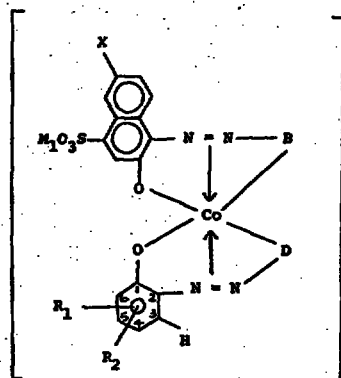
- 50 parts dyestuff of Example 4
 50 parts urea
 50 parts dissolving agent, for example thiodiethylglycol
 300 parts water
 500 parts suitable thickening agent, for example based on locus bean gum
 60 parts acid acceptor for example, ammonium tartrate
 and 60 parts thiourea

The printed goods are steamed for 40 minutes at 102° (saturated steam), then rinsed with cold water, washed for 5 minutes at 60° with a dilute solution of a conventional detergent and then rinsed again. A black print with good wet- and light-fastness is obtained.

In analogous manner printing pastes may be made using the dyestuffs of Examples 1 to 3 and 5 to 37.

WHAT WE CLAIM IS:—

1. A pure asymmetric 1:2 cobalt complex of formula I;



in which

X is hydrogen or nitro,
 either,

R₁ and R₂, independently, are hydrogen, (C₁₋₄)alkyl, (C₁₋₄)alkoxy, chlorine, bromine or nitro

or

R₁ is hydrogen, chlorine or nitro, and

R₂ is —SO₂NR₃R₄, in which the groups R₁ and R₂ occupy the 4- and 5-positions, either

R₃ is hydrogen, unsubstituted or substituted (C₁₋₄)alkyl, and

R₄ is hydrogen, unsubstituted or substituted (C₁₋₄)alkyl, (C₅₋₇)cycloalkyl or phenyl,

or,

R₃ and R₄, together with the nitrogen atom to which they are bound, form a non-aromatic 5- or 6- membered heterocyclic ring which contains one or two hetero atoms,

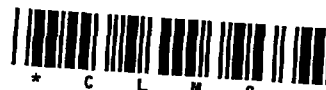
B is a divalent radical of a coupling component of the 1- or 2-hydroxynaphthalene series which is coupled in the 2- or 1- position ortho to the hydroxy group and is bound to the cobalt atom through the oxygen atom,

D is a divalent radical of a coupling component of the 2-naphthylamine series which is coupled in the 1- position ortho to the amine group, or a divalent radical of the 5-amino pyrazole series which is coupled to the carbon atom next to that carrying the amino group, whereby the divalent radical D is bound to the cobalt atom through the amino group,

M is hydrogen or an equivalent of a non-chromophoric cation, and

M₁ is an equivalent of a non-chromophoric cation,

with the provisos that the molecule (i) contains a single sulpho group, which sulpho group is in salt form, (ii) contains at maximum a single sulphonamide group, which group is in radical D or is R₂, and (iii) is free from



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APPLICATION EXAMPLE B.

Polyamide is printed with a printing paste containing the following:

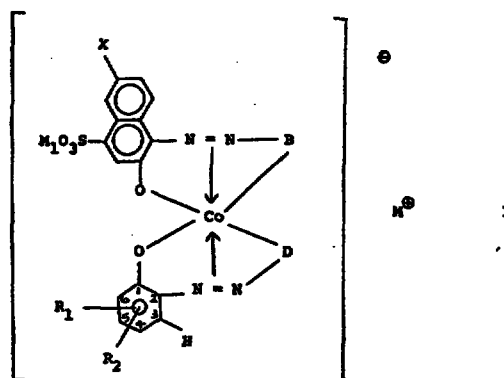
- 50 parts dyestuff of Example 4
- 50 parts urea
- 50 parts dissolving agent, for example thiodiethylglycol
- 300 parts water
- 500 parts suitable thickening agent, for example based on locus bean gum
- 60 parts acid acceptor for example, ammonium tartrate
- and 60 parts thiourea

The printed goods are steamed for 40 minutes at 102° (saturated steam), then rinsed with cold water, washed for 5 minutes at 60° with a dilute solution of a conventional detergent and then rinsed again. A black print with good wet- and light-fastness is obtained.

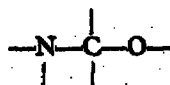
In analogous manner printing pastes may be made using the dyestuffs of Examples 1 to 3 and 5 to 37.

WHAT WE CLAIM IS:—

1. A pure asymmetric 1:2 cobalt complex of formula I,

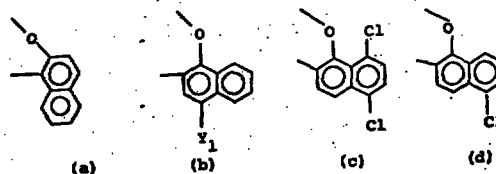


- in which
- X is hydrogen or nitro,
 - either,
 - R₁ and R₂, independently, are hydrogen, (C₁₋₄)alkyl, (C₁₋₄)alkoxy, chlorine, bromine or nitro
 - or
 - R₁ is hydrogen, chlorine or nitro, and
 - R₂ is —SO₂NR₃R₄, in which the groups R₁ and R₂ occupy the 4- and 5-positions,
 - either
 - R₃ is hydrogen, unsubstituted or substituted (C₁₋₄)alkyl, and
 - R₄ is hydrogen, unsubstituted or substituted (C₁₋₄)alkyl, (C₃₋₇)cycloalkyl or phenyl,
 - or,
 - R₃ and R₄, together with the nitrogen atom to which they are bound, form a non-aromatic 5- or 6- membered heterocyclic ring which contains one or two hetero atoms,
 - B is a divalent radical of a coupling component of the 1- or 2-hydroxynaphthalene series which is coupled in the 2- or 1- position ortho to the hydroxy group and is bound to the cobalt atom through the oxygen atom,
 - D is a divalent radical of a coupling component of the 2-naphthylamine series which is coupled in the 1- position ortho to the amine group, or a divalent radical of the 5-amino pyrazole series which is coupled to the carbon atom next to that carrying the amino group, whereby the divalent radical D is bound to the cobalt atom through the amino group,
 - M is hydrogen or an equivalent of a non-chromophoric cation, and
 - M₁ is an equivalent of a non-chromophoric cation,
 - with the provisos that the molecule (i) contains a single sulpo group, which sulpo group is in salt form, (ii) contains at maximum a single sulphonamide group, which group is in radical D or is R₂, and (iii) is free from



groups,
and mixtures of such pure asymmetric complexes.

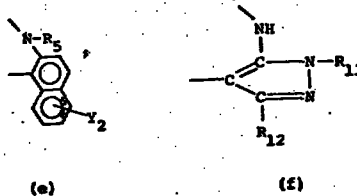
2. A 1:2 cobalt complex or mixture according to Claim 1, in which B is a radical of formula (a), (b), (c) or (d)



in which

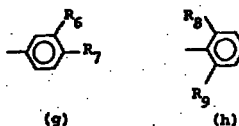
Y₁ is hydrogen, (C₁₋₂)alkyl, (C₁₋₂)alkoxy, chlorine or bromine,
and

D is a group of formula (e) or (f),



in which

R₅ is hydrogen, (C₁₋₄)alkyl or a group of formula (g) or (h),



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R₆ and R₇ is hydrogen and the other is hydrogen, chlorine, bromine, (C₁₋₂)alkyl,
(C₁₋₂)alkoxy, or trifluoromethyl,

R₈ is hydrogen or methyl, and

R₉ is methyl, chlorine or bromine with the proviso that when R₈ is chlorine or bromine
R₉ is hydrogen,

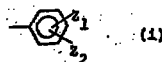
Y₂ is hydrogen or —SO₂NHR₁₀ in the 5- or 6-position, in which R₁₀ is hydrogen
(C₁₋₄)alkyl or hydroxy (C₂₋₄)alkyl,

R₁₂ is hydrogen; (C₁₋₄)alkyl; (C₁₋₂)alkoxy or phenyl,

R₁₃ is hydrogen; (C₁₋₄)alkyl, phenyl(C₁₋₄)alkyl,



cyclohexyl or a radical of formula (i),



in which either

Z₁ is hydrogen and

Z₂ is hydrogen; fluorine; chlorine; bromine; (C₁₋₄)alkyl, (C₁₋₂)alkoxy; nitro; or
trifluoromethyl,

or

Z₁ and Z₂ are the same and are both chlorine; bromine; methyl or methoxy,

with the provisos that:

when both



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Z_1 and Z_2 are chlorine, the chlorine atoms are in the 2,3-, 2,4-, 2,5-, 2,6-, or 3,4-positions,

when both

Z_1 and Z_2 are bromine, the bromine atoms are in the 2,4- or 3,5-positions,

when both

Z_1 and Z_2 are methyl, the methyl groups are in the 2,3-, 2,4-, 2,5-, 2,6- or 3,5-positions,

and when both

Z_1 and Z_2 are methoxy, the methoxy groups are in the 3,4-positions,

or

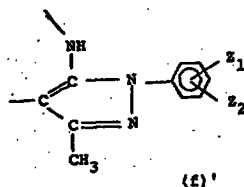
Z_1 and Z_2 are different and signify 3-chloro-2-methyl, 4-chloro-2-methyl, 5-chloro-2-methyl, 4-bromo-2-methyl or 5-chloro-2-methoxy.

3. A 1:2 cobalt complex or mixture according to Claim 1 or Claim 2, in which any substituted alkyl as R_3 and/or R_4 is substituted by up to two substituents selected from halogen, hydroxy, cyano, (C_{1-4}) alkoxy and phenyl, any substituted cycloalkyl is substituted by up to three methyl groups and any substituted phenyl is substituted by up to three substituents selected from up to three halogen, (C_{1-4}) alkyl, (C_{1-4}) alkoxy and nitro (maximum of two nitro).

4. A 1:2 cobalt complex or mixture according to Claim 1, in which R_1 is R_1' , where R_1' is hydrogen, methyl, chlorine or nitro and R_2' is chlorine, nitro or $-\text{SO}_2\text{NHR}_4''$ in which R_4'' is methyl, ethyl, isopropyl, 2-hydroxyethyl, $-\text{CH}_2-\text{CH}(\text{OH})-\text{CH}_3$, $(\text{CH}_2)_3-\text{OOCH}_3$ or phenyl, with the proviso that when R_2' is $-\text{SO}_2\text{NHR}_4''$, R_1' is hydrogen.

5. A 1:2 cobalt complex or mixture according to any one of Claims 1 to 3, in which R_5 is R_5' where R_5' is hydrogen, phenyl, 2-, 3- or 4-chlorophenyl, 2- or 4-methylphenyl or 2,6-dimethylphenyl, and Y_2 is hydrogen or $-\text{SO}_2\text{NHR}_{10}'$ in which R_{10}' is hydrogen, methyl or β -hydroxy (C_{2-3}) alkyl.

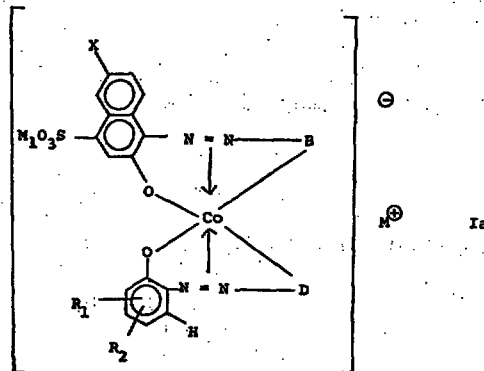
6. A 1:2 cobalt complex or mixture according to Claim 4, in which D is a radical of formula (e) in which R_5 is R_5' and Y_2 is hydrogen or $-\text{SO}_2\text{NHR}_{10}'$, or a radical of formula (f),



wherein

Z_1 and Z_2 are as defined in Claim 2.

7. A 1:2 cobalt complex or mixture according to Claim 2, of formula Ia,



in which

X , M_1 and M are as defined in Claim 1,

either

R_1 and R_2 , independently, are hydrogen, (C_{1-4}) alkyl, (C_{1-4}) alkoxy, chlorine, bromine or nitro,

or



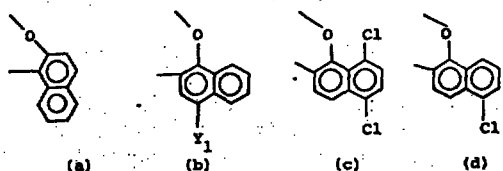
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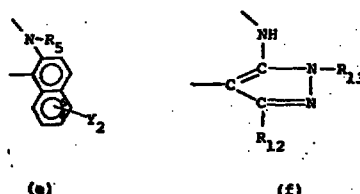
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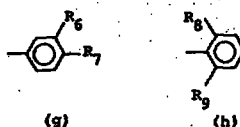
R_1 is hydrogen, chlorine or nitro, and
 R_2 is $-\text{SO}_2\text{NR}_3\text{R}_4$, in which the groups R_1 and R_2 occupy the 4- and 5-positions, either
 R_3 is hydrogen, unsubstituted (C_{1-4}) alkyl or (C_{1-4}) alkyl substituted by up to two substituents selected from halogen, hydroxy, cyano, (C_{1-4}) alkoxy and phenyl, and
 R_4 is hydrogen; unsubstituted (C_{1-4}) alkyl; (C_{1-4}) alkyl substituted by up to two substituents selected from halogen, hydroxy, cyano, (C_{1-4}) alkoxy and phenyl; unsubstituted (C_{5-7}) cycloalkyl; (C_{5-7}) cycloalkyl substituted by up to three methyl groups; unsubstituted phenyl; phenyl substituted by up to three substituents selected from up to three halogen, (C_{1-4}) alkyl, (C_{1-4}) alkoxy groups and nitro (maximum of two nitro), or
 R_3 and R_4 together with the nitrogen atom to which they are bound, form a non-aromatic 5- or 6-membered heterocyclic ring which contains one or two hetero atoms,
 B is a radical of formula (a), (b), (c) or (d)



in which
 Y_1 is hydrogen, (C_{1-2}) alkyl, (C_{1-2}) alkoxy, chlorine or bromine, and
 D is a group of formula (e) or (f),



in which
 R_5 is hydrogen, (C_{1-4}) alkyl or a group of formula (g) or (h),



in which one of
 R_6 and R_7 is hydrogen and the other is hydrogen, chlorine, bromine, (C_{1-2}) alkyl, (C_{1-2}) alkoxy, or trifluoromethyl,
 R_8 is hydrogen or methyl, and
 R_9 is methyl, chlorine or bromine with the proviso that when R_9 is chlorine or bromine
 R_8 is hydrogen,
 Y_2 is hydrogen or $-\text{SO}_2\text{NHR}_{10}$ in the 5- or 6-position, in which R_{10} is hydrogen (C_{1-4}) alkyl or hydroxy (C_{2-4}) alkyl,
 R_{12} is hydrogen; (C_{1-4}) alkyl; (C_{1-2}) alkoxy or phenyl,
 R_{13} is hydrogen; (C_{1-4}) alkyl, phenyl (C_{1-4}) alkyl,



cyclohexyl or a radical of formula (i),





in which either

Z_1 is hydrogen and

Z_2 is hydrogen; fluorine; chlorine; bromine; (C_{1-4}) alkyl, (C_{1-2}) alkoxy; nitro; or trifluoromethyl,

or

Z_1 and Z_2 are the same and are both chlorine; bromine; methyl or methoxy, whereby:

when both

Z_1 and Z_2 are chlorine, the chlorine atoms are in the 2,3-, 2,4-, 2,5-, 2,6-, or 3,4-positions,

when both

Z_1 and Z_2 are bromine, the bromine atoms are in the 2,4- or 3,5-positions,

when both

Z_1 and Z_2 are methyl, the methyl groups are in the 2,3-, 2,4-, 2,5-, 2,6- or 3,5-positions,

and when both

Z_1 and Z_2 are methoxy, the methoxy groups are in the 3,4-positions,

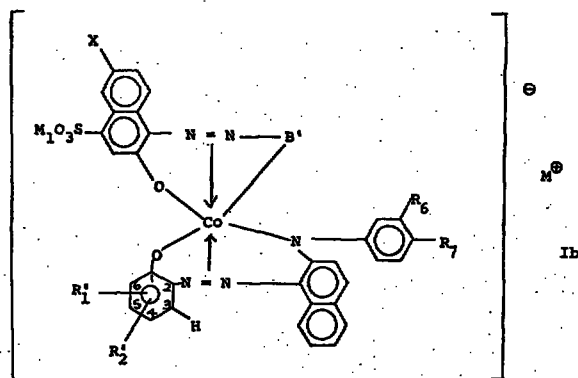
or

Z_1 and Z_2 are different and signify 3-chloro-2-methyl, 4-chloro-2-methyl, 5-chloro-2-methyl, 4-bromo-2-methyl or 5-chloro-2-methoxy,

with the proviso that when D is a radical of formula (e), R_6 is only hydrogen when Y_2 is $-\text{SO}_2\text{NHR}_{10}$ or B is a radical of formula (b), (c) or (d).

8. A 1:2 cobalt complex or a mixture according to Claim 7, in which R_5 is R_5' , where R_5' is hydrogen, phenyl, 2,3-, or 4-chlorophenyl, 2- or 4-methylphenyl or 2,6-dimethylphenyl and Y_2 is hydrogen or $-\text{SO}_2\text{NHR}_{10}'$ in which R_{10}' is hydrogen, methyl or β -hydroxy (C_{2-3}) alkyl.

9. A 1:2 cobalt complex or mixture according to Claim 7, of formula Ib,



in which

R_1' is hydrogen, methyl, chlorine or nitro,

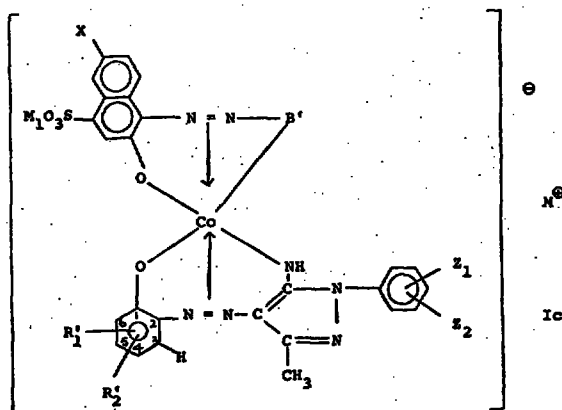
R_2' is chlorine, nitro or $-\text{SO}_2\text{NHR}_4''$, where R_4'' is as defined in Claim 4, with the proviso that R_2' is only $-\text{SO}_2\text{NHR}_4''$ when R_1' is hydrogen,

B' is a radical of formula (a), (b), (c) or (d), with the proviso that when B is a radical of formula (b), Y_1 is Y_1' , and

M , M_1 , R_6 and R_7 are as defined in Claim 7.

10. A 1:2 cobalt complex or mixture according to Claim 9, in which R' is hydrogen, chlorine or nitro and R_2' is chlorine, nitro or $\text{SO}_2\text{NHR}_4'''$, in which R_4''' is methyl, $-(\text{CH}_2)_3-\text{OCH}_3$ or phenyl.

11. A 1:2 cobalt complex or mixture according to Claim 7, of formula Ic,



in which

R_1' is hydrogen, methyl, chlorine or nitro,

R_2' is chlorine, nitro or $-\text{SO}_2\text{NHR}_4''$, where R_4'' is as defined in Claim 4, with the proviso that R_2' is only $-\text{SO}_2\text{NHR}_4''$ or $-\text{SO}_2\text{NHR}_4'''$ when R_1' is hydrogen,

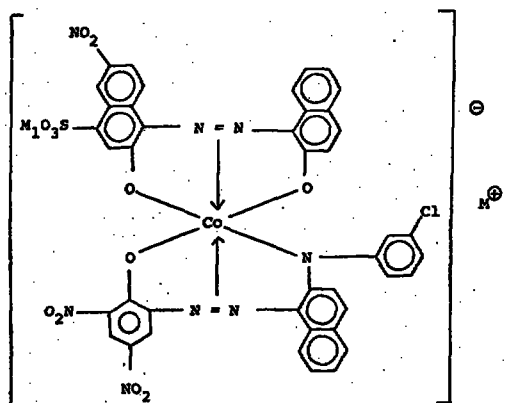
B' is a radical of formula (a), (b), (c) or (d), with the proviso that when B is a radical of formula (6), Y_1 is Y_1' , and X , Z_1 , Z_2 , M_1 and M are as defined in Claim 7.

12. A 1:2 cobalt complex or mixture according to any one of Claims 7 to 10, in which one of R_6 and R_7 is hydrogen and the other is hydrogen, chlorine, methyl or methoxy.

13. A 1:2 cobalt complex or mixture according to Claim 12, in which one of R_6 and R_7 is hydrogen and the other is hydrogen, chlorine or methyl.

14. A 1:2 cobalt complex or mixture according to Claim 7 or Claim 11, in which Z_1 and Z_2 are Z_1' and Z_2' where Z_1' and Z_2' are, independently, hydrogen, chlorine or methyl.

15. A 1:2 cobalt complex of formula



in which

M and M_1 are as defined in Claim 1.

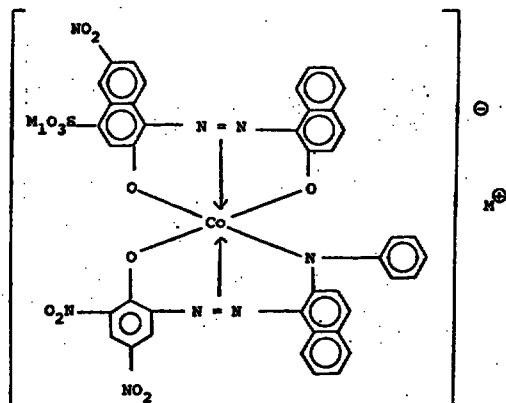
16. A 1:2 cobalt complex of formula



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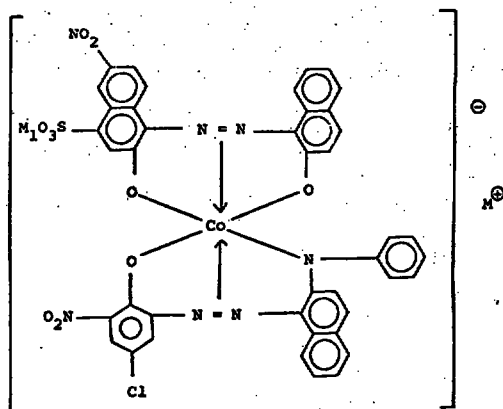
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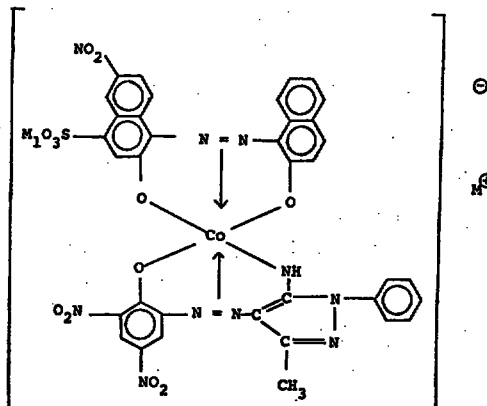
in which
M and M₁ are as defined in Claim 1.

17. A 1:2 cobalt complex of formula



in which
M and M₁ are as defined in Claim 1.

18. A 1:2 cobalt complex of formula



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in which
M and M₁ are as defined in Claim 1.

19. A 1:2 cobalt complex of formula

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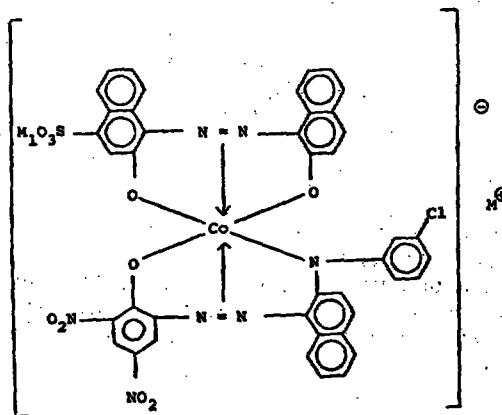


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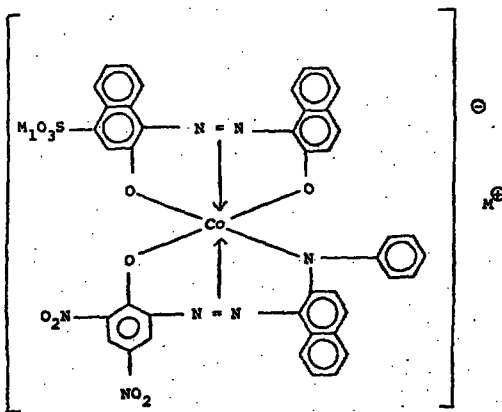
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in which

M and M₁ are as defined in Claim 1.

20. A 1:2 cobalt complex of formula



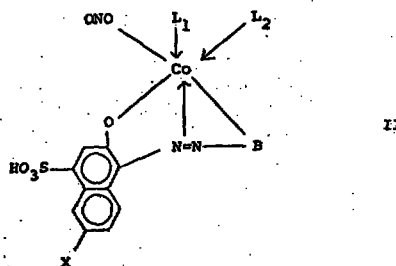
in which

M and M₁ are as defined in Claim 1.

21. A 1:2 cobalt complex according to any one of Examples 3, 5 to 16, 20, 21 and 23 to 37.

22. A mixture of 1:2 cobalt complexes according to Example 18 or 20.

23. A process for the production of a 1:2 cobalt complex of formula I, as defined in Claim 1, or a mixture thereof, comprising reacting a compound of formula II, in free acid form,



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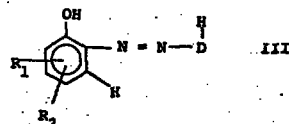
in which

L₁ and L₂ are monodentate ligands and X and B are as defined in Claim 1, or a mixture of compounds of formula II, with a compound of formula III,

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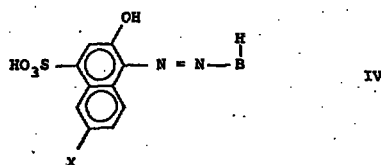
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in which

R₁, R₂ and D are as defined in Claim 1,
or a mixture of compounds of formula III.

24. A process for the production of a 1:2 cobalt coupler of formula I, as defined in Claim 1, or a mixture thereof, comprising reacting a corresponding nitrite-containing cobalt complex of a compound of formula III, or a mixture thereof, with a compound of formula IV,



in which

X and B are as defined in Claim 1,
or a mixture thereof.

25. A process for the production of a 1:2 cobalt complex of formula I, as defined in Claim 1, or a mixture thereof, substantially as hereinbefore described with reference to any one of Examples 1 to 37.

26. A 1:2 cobalt complex or mixture thereof whenever obtained by a process according to Claim 23, 24 or 25.

27. A process for dyeing or printing nitrogen-containing organic substrates comprising employing a complex or mixture according to any one of Claims 1 to 22 or 26, as dyeing or printing agent.

28. A process according to Claim 27, in which the substrate consists of or comprises natural or synthetic polyamides, polyurethane fibres or leather.

29. A process for dyeing or printing nitrogen-containing organic substrates substantially as hereinbefore described with reference to any one of Examples A to C.

30. Dyed or printed substrates whenever obtained by a process according to Claims 26, 27 or 28.

31. A liquid or solid dyestuff preparation comprising as active ingredient a complex or mixture according to any one of Claims 1 to 22 or 26.

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Page 20, line 5, *for coupler read complex*

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