

PATENT SPECIFICATION

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 (72) Inventor HANSPETER UEHLINGER

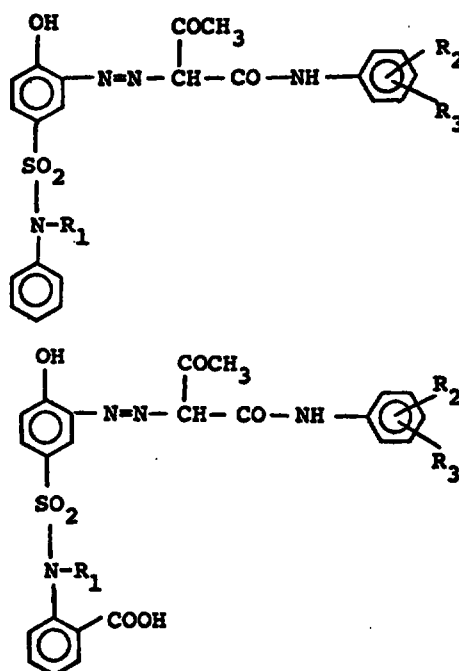


(54) MIXTURES OF 1:2 COBALT COMPLEXES OF AZO DYES,

(71) We, SANDOZ LTD., of Lichtstrasse 35, 4002 Basle, Switzerland, a Swiss Body Corporate, do hereby declared 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 metal complex mixtures, their production and use.

Accordingly, the present invention provides a mixture of symmetrical and asymmetrical 1:2 cobalt complexes of a compound of formula I and a compound of formula II,



in which compounds, each R_1 , independently, is hydrogen or (C_{1-4}) alkyl, and each R_2 and R_3 , independently, is hydrogen, halogen, (C_{1-4}) alkyl or (C_{1-4}) alkoxy, which complexes are optionally in salt form.

Preferably the mixture contains the compounds of formula I and II in a molar ratio range of from 80:20 to 20:80, more preferably 30:70 to 70:30, even more preferably 40:60 to 60:40 with a ratio of 1:1 being most preferred.

Where any of R_1 , R_2 and/or R_3 is (C_{1-4}) alkyl, such alkyl may be straight chain or branched and is preferably methyl or ethyl, with methyl being especially preferred.

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Where any R_2 and/or R_3 is (C_{1-4}) alkoxy such alkoxy is preferably methoxy or ethoxy.

By halogen is meant fluorine, chlorine or bromine. The preferred halogen is chlorine.

Preferably the radicals R_1 are R'_1 , where each R'_1 , independently, is hydrogen or methyl. More preferably R_1 is hydrogen.

Preferably the radicals R_2 are R'_2 , where each R'_2 , independently, is hydrogen, chlorine, methyl, methoxy or ethoxy. More preferably the radicals R_2 are R''_2 , where each R''_2 , independently, is hydrogen, methyl, methoxy or chlorine. Most preferably each R_2 is hydrogen.

The radicals R_3 are preferably R'_3 , where each R'_3 , independently, has one of the significances of R'_2 . More preferably the radicals R_3 are R''_3 , where each R''_3 , independently, has one of the significances of R''_2 . Most preferably each R_3 is hydrogen.

Where the R_2/R_3 bearing phenyl ring is monosubstituted, the substituent is preferably chlorine, methyl, methoxy or ethoxy. Where the phenyl ring is disubstituted, each substituent R_2 and R_3 , independently, is preferably chlorine, methyl or methoxy. The substituents are preferably in the 2,4-, 2,5-, 2,6- or 3,4-, with the positions 2,5- and 2,6- being most preferred.

Preferred complex mixtures are those in which, in the compounds of formulae I and II, the radicals R_1 are R'_1 , the radicals R_2 are R'_2 and the radicals R_3 are R'_3 . More preferred mixtures are those in which, in the compounds of formulae I and II, the radicals R_2 are R''_2 , more preferably hydrogen and the radicals R_3 are R''_3 , of these mixtures, those in which each R_1 is hydrogen are especially preferred. Most preferred mixtures are those in which R_2 is identical with R_3 and the radicals R_2 are R'_2 , more preferably R''_2 , especially hydrogen.

The present invention also provides a process for the production of a mixture of symmetrical and asymmetrical 1:2 cobalt complexes of the compounds of formulae I and II, comprising reacting a mixture of the compounds of formulae I and II with a cobalt donating compound.

The metallisation of the mixture of monoazo compounds of formulae I and II may be carried out in accordance with conventional methods. It is preferred that the molar ratio of the mixture of compounds I and II to cobalt donating compound is 2:1. Suitable cobalt donating compounds are cobalt(II)-sulphate, -acetate, -formate and -chloride.

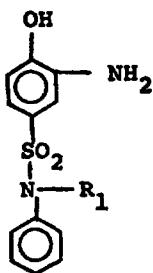
It is preferred to employ the compounds of formula I and formula II in a 1:1 molar ratio.

The mixture of 1:2 cobalt complexes obtained may be isolated in accordance with known methods, for example, the product may be salted out with an alkali metal salt or a weak acid, filtered, washed with an alkali metal salt solution and dried. The product obtained contains symmetrical and asymmetrical complexes in a statistical relationship dependent upon the ratio of the compound of formula I to that of the compound of formula II employed.

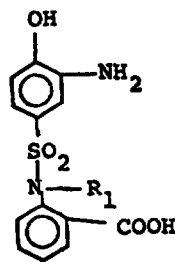
Depending on the reaction and isolation conditions the mixture of 1:2 cobalt complexes may be obtained in the salt form. The complex anion-neutralising cation may be any non-chromophoric cation for example, an alkali metal cation, such as lithium, sodium or potassium (preferably sodium); an unsubstituted, lower alkyl substituted or hydroxyalkyl substituted ammonium ion represented by the formula

$N(R_5)_4$, where each R_5 is, independently, hydrogen, (C_{1-3}) alkyl or β -, γ - or δ -hydroxy (C_{2-4}) alkyl. It will be appreciated that groups which would cause steric or stability problems for example, tetra-alkanol ammonium would not be present in the complex mixtures. As examples of substituted ammonium ions may be given, mono-, di-, tri- and tetramethylammonium, and mono-, di- and triethanolammonium. Similarly, the cation of the carboxy group may be any one of those indicated above for the complex anion-neutralizing cation and may be the same as or different therefrom. Preferably, the cation of the carboxylic acid group and the complex anion-neutralizing cation are the same, most preferably they are both sodium.

The monoazo compounds of formula I and II are known or may be prepared in analogy with known methods from available starting materials. Preferably the mixture of compounds of formula I and II are prepared by diazotizing a mixture of amines of formulae III and IV.

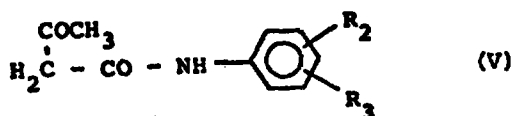


III



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in the desired ratio and coupling the diazonium mixture with a compound of formula V,



(V)

5 or a mixture thereof, under alkaline conditions.

The product obtained may be directly metallized.

10 The mixtures of 1:2 cobalt complexes according to the present invention are well soluble in water and are useful for dyeing or printing substrates dyeable with anionic dyes. Suitable substrates are natural and synthetic polyamides such as wool, silk and nylon; synthetic polyamides in the mass; polyurethanes; basic modified polyolefins; leather and metals such as anodically oxidised aluminium. The dyes are also useful for cross wound bobbin dyeing (cheese dyeing).

15 The mixtures according to the present invention may be employed for dyeing as such or may be made up into liquid or solid preparations.

20 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 preparations which contain conventional additives may be used.

25 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.

30 Further, the mixtures according to the present invention may be made up into preparations which are dispersible in cold water. For the preparation of such dispersions the dye mixture may be ground wet or dry to a particle size of less than 20 μ , preferably 1—5 μ , in the presence of one or more conventional anionic dispersing agents and optionally in the presence of a non-ionic dispersing agent, with or without subsequent spray drying. The preparations so obtained are finely dispersed in cold water and are thus easy to handle.

35 The dyestuff mixtures according to the invention give dyeings which have notable light-fastness, wet-fastness (wash, water, sea-water-, acid, and alkali-sweat- and milling-fastness), ironing-fastness, fastness to solvents, wet and dry rubbing fastness, fastness to chloride, carbonization fastness and fastness to decatizing. The dyestuffs are not adversely affected by electrolytes or chalk.

40 The dyestuff mixtures according to the invention exhaust from a neutral bath and build-up well on polyamide fibres. They have generally a good build-up power and build-up equally on natural and synthetic polyamides when dyed in the same dye bath. They are also suitable for dyeing in combination with other asymmetric or symmetric 1:2 metal complex dyestuffs, for example dyes C.I. Acid Brown 363, C.I. Acid Blue 296 and C.I. Acid Green 106. The dyeings obtained with such combinations exhibit notable light-fastness.

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

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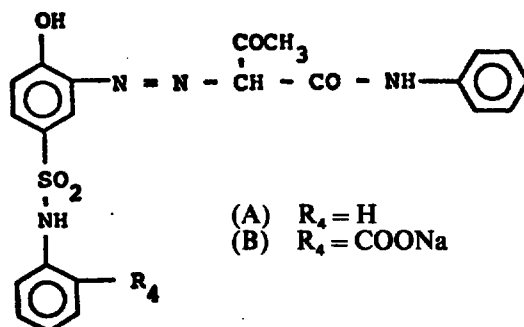
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Example 1

39.6 parts of 2-amino-1-hydroxybenzene - 4-sulphonic acid - N - phenylamide and 46.2 parts of 2-amino - 1-hydroxy - benzene - 4 - sulphonic acid - N - phenylamide^{2'} - carboxylic acid are dissolved at 65° in 700 parts water with the addition of a 30% sodium hydroxide solution and are reacted with 20.7 parts sodium nitrite. The solution cooled to 0—5° is added dropwise over a period of 1 hour to 115 parts of a 30% hydrochloric acid and 80 parts of ice, the temperature being maintained at 0—5° by the addition of further ice.

53.1 parts of acetoacetanilide are stirred to a fine suspension in 200 parts of a 20% sodium carbonate solution and are added to the diazo suspension over a period of 15 minutes. After 1½ hours coupling is completed and the monoazo dyestuff mixture is filtered.

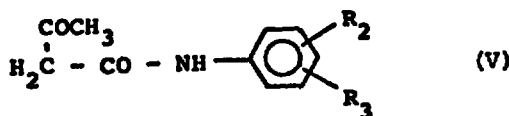
For metallisation the paste of the monoazo dyestuffs is stirred in 1500 parts of water and adjusted to a pH value of 10 with 50 parts of a 30% sodium hydroxide solution. At a temperature of 50—60°, a solution of 42.2 parts cobalt(II)sulphate in 150 parts water is added dropwise thereto, the pH being maintained at a value of 10 by the addition of further sodium hydroxide. After metallisation the 1:2 cobalt complex mixture is salted out with sodium chloride, isolated by filtering, dried and ground. The dyestuff mixture obtained in the form of the sodium salt contains the two monoazo dyes of compounds (A) and (B) of general formula



in a 1:1 molar ratio. The mixture contains two symmetrical 1:2 cobalt complexes (a 1:2 complex of (A)/(A) and a 1:2 complex of (B)/(B) and an asymmetrical 1:2 cobalt complex of the compounds (A) and (B).

The dyestuff mixture is well soluble in water and dyes natural and synthetic polyamide fibres in yellow shades. The dyeings have notable wet- and light-fastness.

In accordance with the procedure described in Example 1, further dyestuff 1:2 cobalt complex mixtures may be prepared which contain monoazo dyes having the diazo components of compounds (A) and (B) of Example 1 and both having the same coupling component of formula V,



in a 1:1 ratio. The significances of R_2 and R_3 and the positions of the substituents are given in the following Table 1. The dyestuffs give dyeings of yellow shades on natural and synthetic polyamide fibres which dyeings possess wet- and light-fastness comparable with that of the dyeings of the dyestuff mixture of Example 1.

TABLE 1

Example No.	R ₂ (position)	R ₃ (position)
2	H	Cl (2)
3	H	Cl (3)
4	H	Cl (4)
5	H	CH ₃ (3)
6	Cl (2)	Cl (5)
7	Cl (2)	CH ₃ (6)
8	H	OCH ₃ (2)
9	H	OC ₂ H ₅ (4)
10	H	C ₂ H ₅ (2)
11	OCH ₃ (2)	OCH ₃ (5)
12	OCH ₃ (2)	CH ₃ (5)
13	CH ₃ (2)	CH ₃ (6)

In analogous manner to the procedure described in Example 1, further 1:2 cobalt complex mixtures containing the two monoazo dyestuffs of formula (A) and (B) of Examples 1 to 13 in varying ratios 30:70, 70:30, 40:60, 60:40 may be prepared. The dyestuff mixtures are also water soluble and give similar dyeings to the mixtures of Examples 1 to 13. Further 1:2 cobalt complex mixtures containing compounds (A) and (B), as indicated in Table 2, may be prepared in analogy with the procedure described in Example 1. The dyestuffs are in the form of sodium salts and have good water solubility. They also give dyeings of yellow shades on natural and synthetic polyamides having notable wet- and light-fastness.

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TABLE 2

Example No.	Monoazo Compounds (A)			Monoazo Compounds (B)			Ratio (I) : (II)
	R ₁	R ₂ (position)	R ₃ (position)	R ₁	R ₂ (position)	R ₃ (position)	
14 15 16 17 18	CH ₃	H	Cl (2)	H	H	Cl (2)	{ 50:50 40:60 60:40 30:70 70:30
19 20 21 22 23	H	H	H	H	H	Cl (2)	{ 50:50 45:55 55:45 25:75 75:25
24 25 26	CH ₃	H	H	H	H	Cl (2)	{ 40:60 50:50 60:40
27 28 29 30	H	H	OCH ₃ (2)	H	H	H	{ 50:50 35:65 65:35 20:80
31 32 33	CH ₃	H	OCH ₃ (2)	H	H	OCH ₃ (2)	{ 50:50 40:60 60:40
34 35 36 37 38	H	H	H	H	OCH ₃ (2)	CH ₃ (5)	{ 50:50 40:60 60:40 35:65 65:35

TABLE 2 (Continued)

Example No.	Monoazo Compounds (A)			Monoazo Compounds (B)			Ratio (I) : (II)
	R ₁	R ₂ (position)	R ₃ (position)	R ₁	R ₂ (position)	R ₃ (position)	
39 40 41	CH ₃	OCH ₃ (2)	OCH ₃ (5)	H	OCH ₃ (2)	OCH ₃ (5)	$\left\{ \begin{array}{l} 50:50 \\ 25:75 \\ 75:25 \end{array} \right\}$
42 43 44 45 46	H	H	Cl (2)	H	H	Cl (4)	$\left\{ \begin{array}{l} 50:50 \\ 40:60 \\ 30:70 \\ 60:40 \\ 70:30 \end{array} \right\}$
47 48 49	H	H	Cl (2)	CH ₃	H	Cl (2)	$\left\{ \begin{array}{l} 50:50 \\ 30:70 \\ 70:30 \end{array} \right\}$
50 51 52	H	H	Cl (2)	H	H	OCH ₃ (2)	$\left\{ \begin{array}{l} 50:50 \\ 40:60 \\ 60:40 \end{array} \right\}$
53 54 55 56	H	H	H	H	Cl (2)	Cl (5)	$\left\{ \begin{array}{l} 50:50 \\ 65:35 \\ 35:65 \\ 30:70 \end{array} \right\}$

Application Example A

1 Part of the 1:2 cobalt complex mixture of Example 1 is dissolved in 3000 parts water and 2 parts ammonium sulphate are added thereto. Subsequently, pre-moistened material (50 parts wool gaberdine or 50 parts nylon satin) is put in the bath which is heated over a period of 30 minutes to boiling temperature. The material is dyed for a further 30 minutes, any evaporated water being replaced. Subsequently, the dyed material is rinsed and after drying, a yellow dyeing having notable wet- and light-fastness is obtained. The dyestuff mixtures of Examples 2—56 may be employed for dyeing in analogous manner.

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Application Example B

0.5 Parts of the 1:2 cobalt complex mixture of Example 1 and 0.5 parts of dyestuff C.I. Acid Brown 363 are dissolved in 3000 parts of water and 2 parts amino-sulphate are added thereto. Subsequently pre-moistened material (50 parts wool gaberdine or 50 parts nylon satin) are put in the bath which is heated over a period of 30 minutes to boiling temperature. The further dyeing is carried out as described in Example A. After drying, a yellow brown dyeing having notable light- and wet-fastness is obtained.

The dyestuff mixtures of Examples 2 to 56 may be employed for combination dyeings in accordance with the same procedure.

Application Example C

Polyamide fabric is printed with a printing paste containing:

30 parts dyestuff complex mixture of Example 1,

50 parts urea

50 parts dissolving agent (e.g. thiodiethylene glycol),

300 parts water,

500 parts thickening agent (e.g. based on locus bean gum),

60 parts acid donating agent (ammonium tartrate),

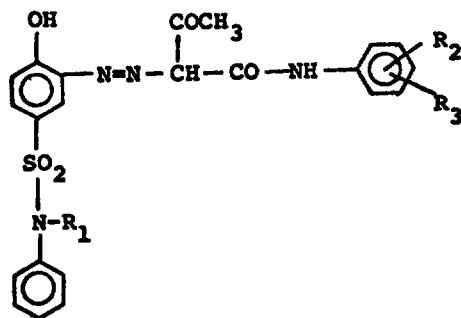
and 60 parts thiourea.

The printed textile 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 conventional detergent and rinsed again. A yellow print having notable wet- and light-fastness is obtained.

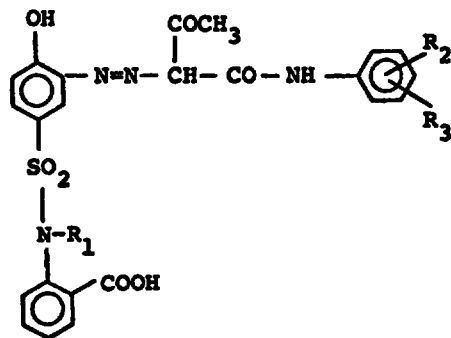
In analogous manner printing paste may be prepared using any one of the dyestuff mixtures of Examples 2 to 56.

WHAT WE CLAIM IS:—

1. A mixture of symmetrical and asymmetrical 1:2 cobalt complexes of a compound of formula I and a compound of formula II,



I



II

in which compounds, each R_1 , independently, is hydrogen or (C_{1-4}) alkyl, and each R_2 and R_3 , independently, is hydrogen, halogen, (C_{1-4}) alkyl or (C_{1-4}) alkoxy, which complexes are optionally in salt form.

2. A mixture according to Claim 1, which comprises the compounds of formulae I and II in a molar ratio range of from 80:20 to 20:80.

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Application Example B

5 0.5 Parts of the 1:2 cobalt complex mixture of Example 1 and 0.5 parts of dyestuff C.I. Acid Brown 363 are dissolved in 3000 parts of water and 2 parts amino-sulphate are added thereto. Subsequently pre-moistened material (50 parts wool gaberdine or 50 parts nylon satin) are put in the bath which is heated over a period of 30 minutes to boiling temperature. The further dyeing is carried out as described in Example A. After drying, a yellow brown dyeing having notable light- and wet-fastness is obtained.

10 The dyestuff mixtures of Examples 2 to 56 may be employed for combination dyeings in accordance with the same procedure.

Application Example C

Polyamide fabric is printed with a printing paste containing:

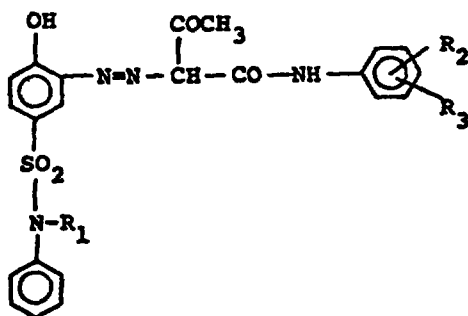
15 30 parts dyestuff complex mixture of Example 1,
50 parts urea
50 parts dissolving agent (e.g. thiodiethylene glycol),
300 parts water,
500 parts thickening agent (e.g. based on locus bean gum),
60 parts acid donating agent (ammonium tartrate),
and 60 parts thiourea.

20 The printed textile 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 conventional detergent and rinsed again. A yellow print having notable wet- and light-fastness is obtained.

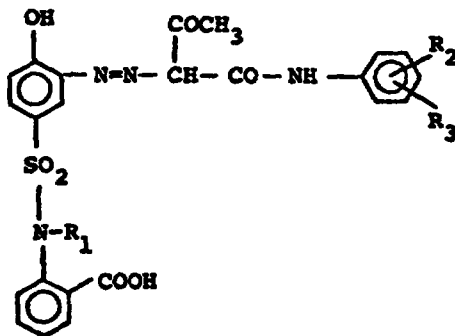
25 In analogous manner printing paste may be prepared using any one of the dyestuff mixtures of Examples 2 to 56.

WHAT WE CLAIM IS:—

1, A mixture of symmetrical and asymmetrical 1:2 cobalt complexes of a compound of formula I and a compound of formula II,



I



II

in which compounds,
each R_1 , independently, is hydrogen or (C_{1-4}) alkyl, and
each R_2 and R_3 , independently, is hydrogen, halogen, (C_{1-4}) alkyl or (C_{1-4}) alkoxy,
which complexes are optionally in salt form.

2. A mixture according to Claim 1, which comprises the compounds of formulae I and II in a molar ratio range of from 80:20 to 20:80.



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3. A mixture according to Claim 2, in which the molar ratio range is from 30:70 to 70:30.

4. A mixture according to Claim 3, in which the molar ratio range is from 40:60 to 60:40.

5. A mixture according to Claim 1, which comprises the compounds of formulae I and II in a 1:1 molar ratio.

6. A mixture according to any one of the preceding claims, in which the radicals R_1 are R'_1 , where each R'_1 , independently is hydrogen or methyl.

7. A mixture according to any one of the preceding claims, in which the radicals R_2 are R'_2 , where each R'_2 , independently, is hydrogen, chlorine, methyl, methoxy or ethoxy.

8. A mixture according to any one of the preceding claims, in which the radicals R_3 are R'_3 , where each R'_3 , independently, has one of the significances of R'_2 .

9. A mixture according to any one of the preceding claims, in which, in the compounds of formulae I and II, the radicals R_1 are R'_1 as defined in Claim 6, the radicals R_2 are R'_2 , as defined in Claim 7, and the radicals R_3 are R'_3 , as defined in Claim 8.

10. A mixture according to any one of Claims 1 to 8, in which the radicals R_2 are R'_2 , where each R'_2 , independently, is hydrogen, methyl, methoxy or chlorine.

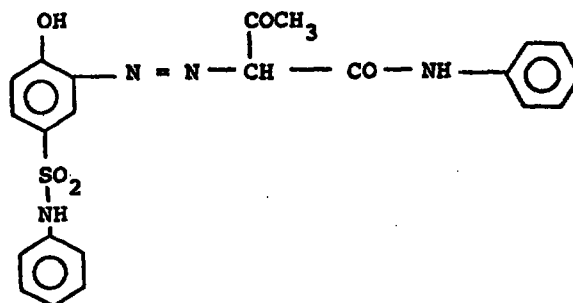
11. A mixture according to any one of Claims 1 to 8 or 10, in which the radicals R_3 are R'_3 , where each R'_3 , has one of the significances of R'_2 , as defined in Claim 10.

12. A mixture according to any one of the preceding claims, in which the radicals R_2 are hydrogen and the radicals R_3 are R'_3 .

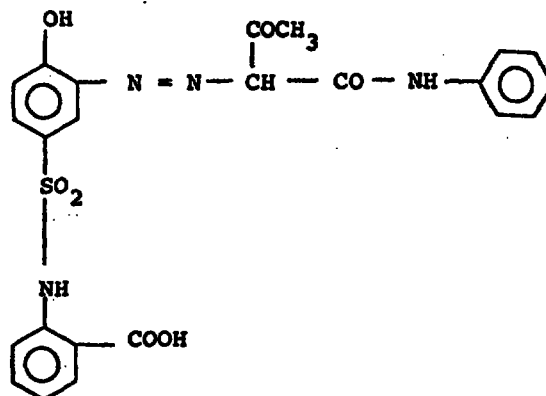
13. A mixture according to any one of the preceding claims, in which the radicals R_1 are hydrogen.

14. A mixture according to any one of the preceding claims, in which the radicals R_2 and R_3 are identical.

15. A mixture of symmetrical and asymmetrical 1:2 cobalt complexes of the compounds of formulae



and



which compounds are present in a 1:1 molar ratio, and which complexes are optionally in salt form.

16. A mixture of symmetrical or asymmetrical 1:2 cobalt complexes of the compounds of formulae

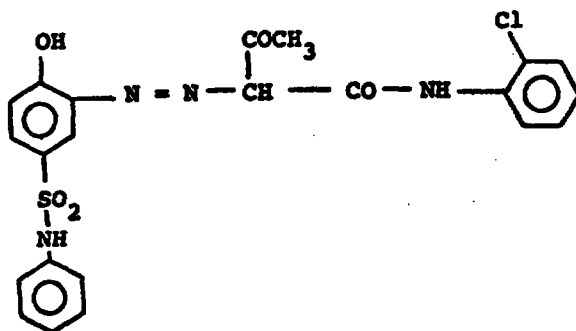
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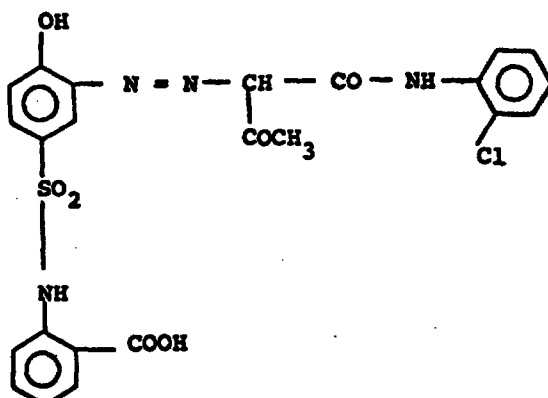
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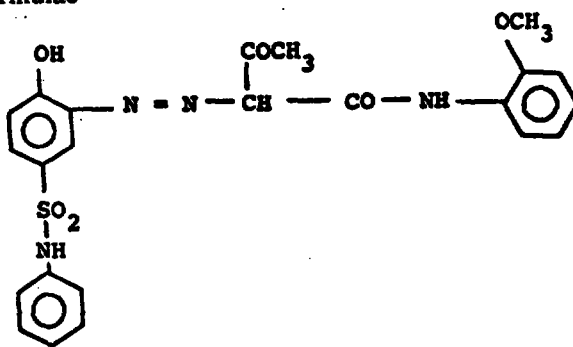


which compounds are present in a 1:1 molar ratio, and which complexes are optionally in salt form.

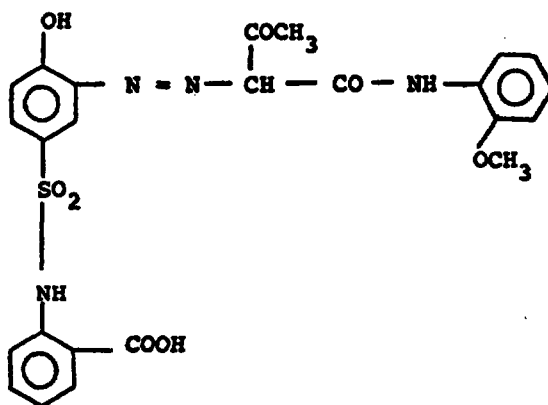
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17. A mixture of symmetrical and asymmetrical 1:2 cobalt complexes of the compounds of formulae



and



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which compounds are present in a 1:1 molar ratio, and which complexes are optionally in salt form.



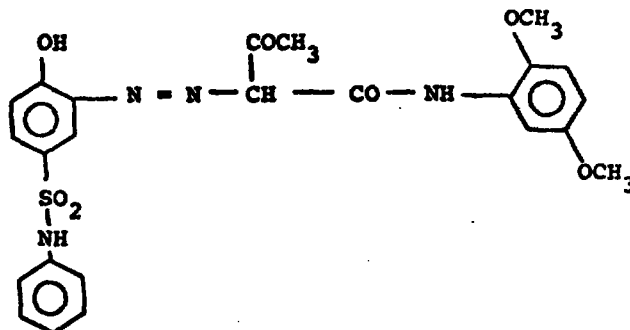
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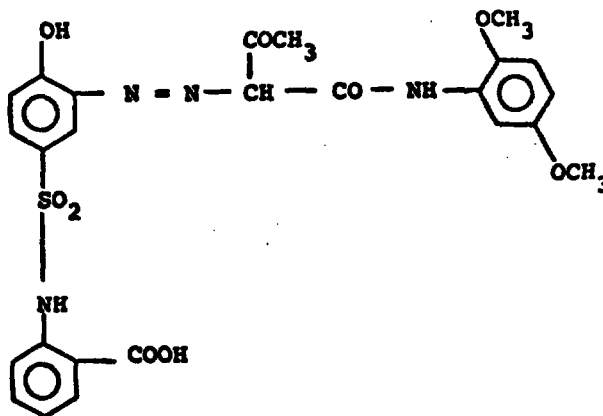
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18. A mixture of symmetrical and asymmetrical 1:2 cobalt complexes of the compounds of formulae



and

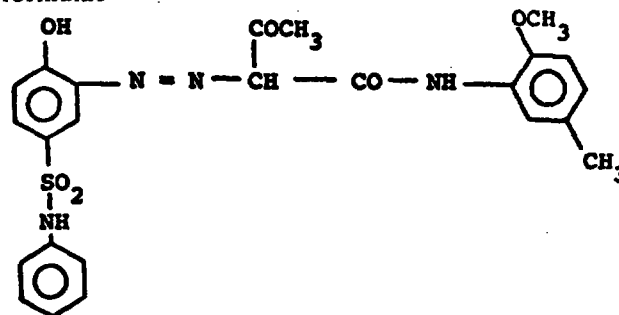


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which compounds are present in a 1:1 molar ratio, and which complexes are optionally in salt form.

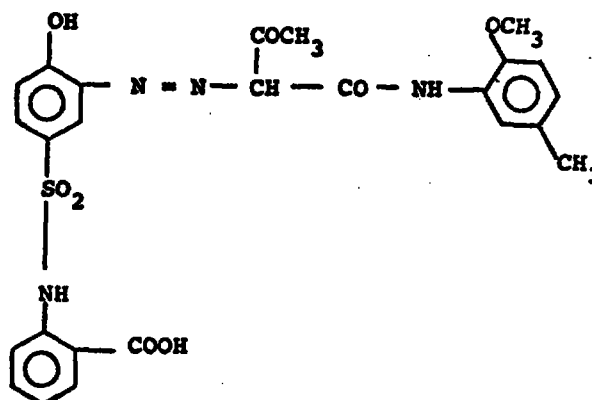
19. A mixture of symmetrical or asymmetrical 1:2 cobalt complexes of the compounds of formulae



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and



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which compounds are present in a 1:1 molar ratio, and which complexes are optionally in salt form.

20. A mixture according to any one of the preceding claims in which the complexes are in the sodium salt form.

5 21. A process for the production of a mixture of symmetrical and asymmetrical 1:2 cobalt complexes of the compounds of formulae I and II as defined in Claim 1, comprising reacting a mixture of compounds of formulae I and II with a cobalt donating compound.

10 22. A process for the production of a mixture of symmetrical and asymmetrical 1:2 cobalt complexes of the compounds of formulae I and II, substantially as hereinbefore described with reference to any one of Examples 1 to 56.

23. A mixture whenever obtained by a process according to Claim 21 or Claim 22.

15 24. A process for dyeing or printing substrates dyeable with anionic dyes comprising employing a mixture according to any one of Claims 1 to 20 or 23 as dyeing or printing agent.

25. A process according to Claim 24 in which the substrate consists of natural or synthetic polyamides, polyurethanes, basic modified polyolefins, leather and anodically oxidised aluminium.

20 26. A process according to Claim 24 or 25, for dyeing or printing substantially as hereinbefore described with reference to any one of Examples A to C.

27. Dyed or printed substrates whenever obtained by a process according to any one of Claims 24 to 26.

B. A. YORKE & CO.,
Chartered Patent Agents,
98, The Centre, Feltham,
Middlesex, TW 13 4EP.
Agents for the Applicants.

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