

PATENT SPECIFICATION

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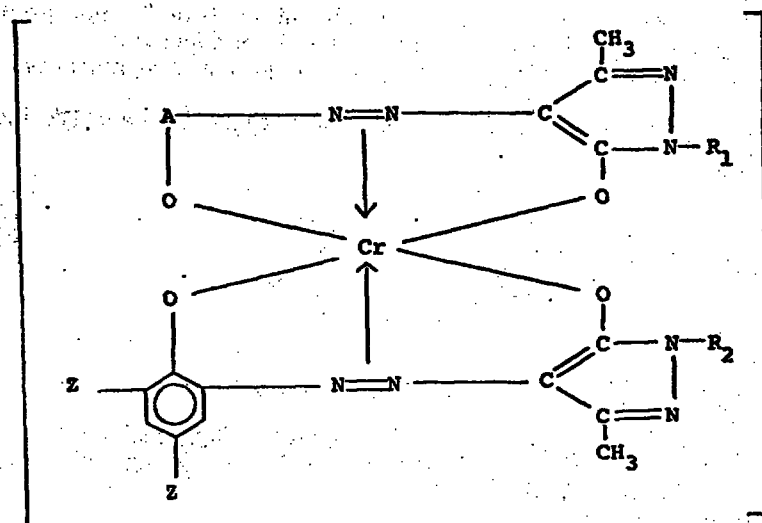


(54) 1:2 CHROMIUM COMPLEXES OF AZO PYRAZOLE DYES

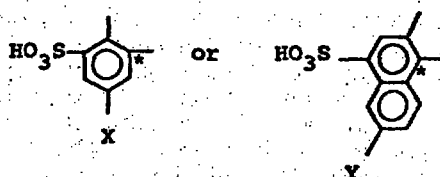
(71) We, SANDOZ LTD., of 35 Lichtstrasse, 4002 Basle, Switzerland, a Swiss Body Corporate, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:-

The present invention relates to asymmetric 1:2 chromium complexes and mixtures thereof, their production and use.

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



in which A is a group of formula (a) or (b)



in which X is halogen, nitro or methyl,

Y is hydrogen or nitro,

* designates the carbon atom bound to the azo group.

Z is halogen or nitro, both substituents being the same.

each or R_1 and R_2 , independently, is unsubstituted phenyl or phenyl substituted by a total of up to three substituents selected from halogen, (C₁₋₆)alkyl, (C₁₋₆) alkoxy, nitro and cyano (maximum of two nitro and/or cyano), and

M is hydrogen or an equivalent of a non-chromophoric cation, with the proviso that the sulpo group is in salt form, and mixtures of such asymmetric 1:2 complexes.

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

Preferably X is X', where X' is halogen or nitro, more preferably X is X'', where X'' is chlorine or nitro, with chlorine being especially preferred.

Preferably Y is hydrogen.

Preferably Z is Z', where Z' is chlorine or nitro, more preferably Z is Z'', where Z'' is chlorine.

Any alkyl substituent on the substituted phenyl as R_1 and/or R_2 is straight chain or branched and preferably contains 1 to 4 carbon atoms, more preferably 1 or 2 carbon atoms with methyl being especially preferred.

Any alkoxy substituent on the substituted phenyl as R_1 and/or R_2 preferably contains 1 to 4, more preferably 1 or 2 carbon atoms.

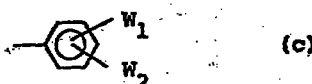
When R_1 and/or R_2 is a trisubstituted phenyl, such phenyl is preferably substituted by three chlorine atoms, preferably in the 2, 4, 6-positions.

When R_1 and/or R_2 is a disubstituted phenyl, the substituents are preferably in the 2,4-, 2,5-, 2,6-, 3,4- or 3,5-positions, with the 2,4-, 2,5- and 3,4-positions being preferred when the two substituents are the same and the 2,5- and 3,4- positions being preferred when the two substituents are different.

When R_1 and/or R_2 are monosubstituted any halogen is preferably in the 3- or 4-, more preferably the 3-position, any alkyl or alkoxy is preferably in the 3- or 4-, most preferably the 4-position, and any cyano or nitro is preferably in the 3- or 4-position.

Monosubstituted or unsubstituted phenyl radicals are the preferred significances for R_1 and R_2 .

Preferably R_1 and R_2 , respectively, are R'_1 and R'_2 , where each of R'_1 and R'_2 , independently, is a group of formula



in which W_1 is hydrogen, chlorine, methyl, methoxy or ethoxy, and W_2 is hydrogen, chlorine or methyl.

More preferably R_1 and R_2 , respectively, are R''_1 and R''_2 , where each of R''_1 and R''_2 , independently, is a group of formula (c) in which W_1 and W_2 are W'_1 and W'_2 , where

W'_1 is hydrogen, chlorine or methyl, and

W'_2 is hydrogen or chlorine.

Even more preferably R_1 and R_2 , respectively, are R'''_1 and R'''_2 , where each of R'''_1 and R'''_2 , independently is a group of formula (c) in which W_1 and W_2 are W''_1 and W''_2 , where W''_1 is hydrogen or chlorine, preferably hydrogen, and W''_2 is hydrogen.

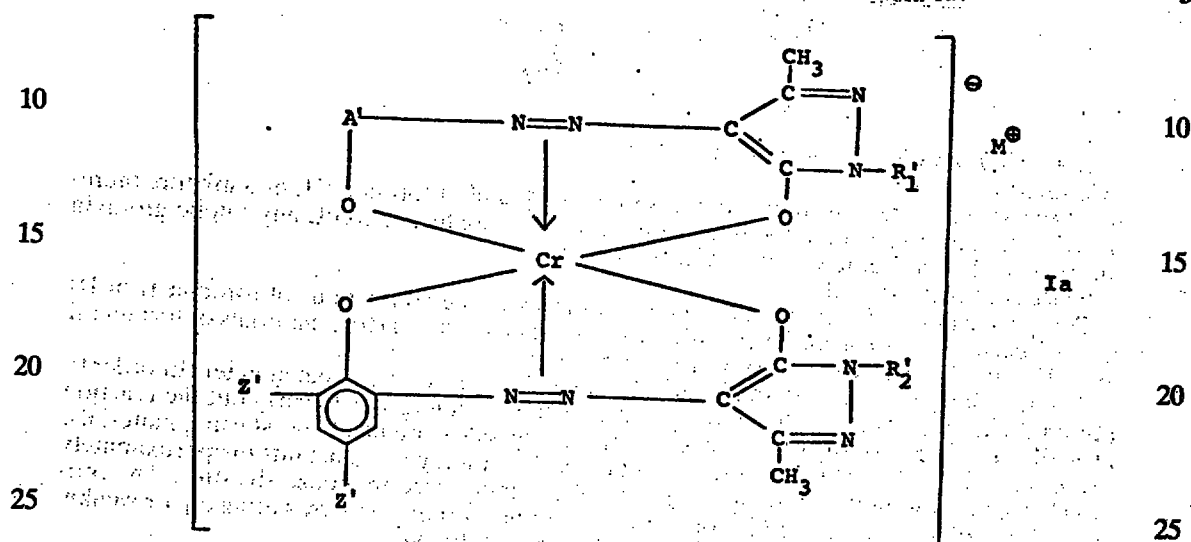
Such substituents W_1 and W_2 are in the preferred positions as given above.

Preferably M is other than hydrogen and signifies an alkali metal cation, an unsubstituted ammonium ion, a lower alkyl (C₁₋₁₄) substituted ammonium ion, a hydroxy-substituted lower-alkyl ammonium ion, a higher (C₅₋₁₂) alkyl substituted ammonium ion, a mono- or di-cycloalkylammonium ion or a cycloimmonium ion. As examples of alkali metal cations, may be given lithium, sodium or potassium. The unsubstituted, lower alkyl substituted and hydroxyalkylsubstituted ammonium may be represented by the formula $N(R)_4$ WHERE EACH R is, independently, hydrogen, (C₁₋₃) alkyl or hydroxy (C₂₋₄) alkyl with the proviso that when one or more of the symbols R signifies hydroxyalkyl at least one R signifies hydrogen, for example, triethylammonium, mono-, di- and triethanolammonium and mono-, di- and tri-isopropanol ammonium.

When M is a higher, e.g. C₅₋₁₂ alkylsubstituted-, mono- or dicyclo- e.g. C₅₋₇ alkylsubstituted-ammonium ion or a cycloimmonium ion the water-solubility of the complexes is reduced such that they are scarcely water-soluble or only soluble in the presence of organic solvents. Examples of such ions include those derived from N-ethyl-N-hexylamine, cyclohexylamine, N,N-dicyclohexyl-amine and morpholine;

More preferably M is an alkali metal cation with sodium being most preferred. The 1:2 complexes in which M is hydrogen, are, in general, scarcely soluble in water. The cation of the sulpho group in salt form may be any one of those given above for M and may be the same as or different from M.

Preferred 1:2 chromium complexes of formula I are those of formula Ia.



in which either A' is a radical of formula (a) wherein X is chlorine or nitro, preferably chlorine,

or A' is a radical of formula (b) wherein Y is hydrogen.

Z' is as defined above, more preferably Z' is Z'', where Z'' is as defined above, and R' and R' are as defined above.

Preferred compounds of formula Ia are those where R' and R' and R' and R', more preferably R' and R', as defined above, with the compounds where R' and R' are phenyl being especially preferred.

Further preferred complexes of formula I are those

(i) wherein Z is Z'' and

A is a radical of formula (a) in which X is chlorine, or a radical of formula (b) in which Y is hydrogen,

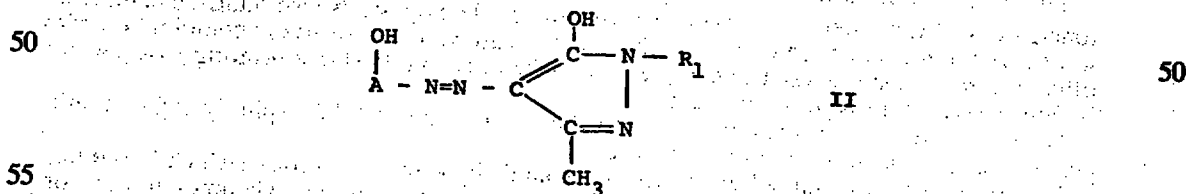
(ii) wherein Z is Z'' and

R' and R', preferably R'', more preferably R'', most preferably phenyl;

(iii) wherein Z is Z'' and

R' is R'', preferably R'', more preferably R'', most preferably phenyl.

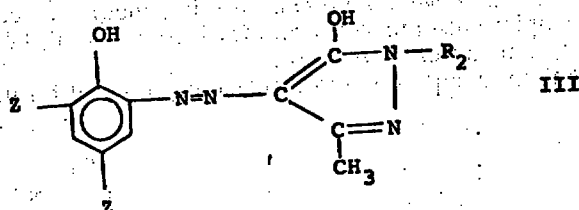
The invention also provides a process for the preparation of complexes of formula I, or mixtures thereof, comprising a) reacting the 1:1 chromium complex of a compound of formula II,



in free acid or salt form,

in which A and R1 are as defined above, or a mixture thereof,

with a metal-free compound of formula III.



in which Z and R₂ are as defined above, or a mixture thereof.

or b) reacting the 1:1 chromium complex of a compound of formula III, or a mixture thereof, with the metal-free compound of formula II, or a mixture thereof, any sulpho group in the free acid form being converted into the salt form.

Process a) is preferred.

The preparation of the 1:1 chromium complexes of the compounds of formula II or III may be carried out in accordance with known methods. The starting materials of formula II and III, may be prepared in conventional manner.

The reaction of process a) and b) may be carried out in conventional manner. In order to obtain the asymmetric 1:2 chromium complexes it is advantageous to carry out the reaction at a pH in the range of 6 to 11 depending on the salt content of the starting materials, preferably at a pH 7 to 9. It is also advantageous to employ the reactants in approximately stoichiometric amounts avoiding an excess of the metal-free monoazo dyestuff. The product obtained may be isolated in conventional manner, for example by salting out or weakly acidifying followed by washing with salt solution and drying.

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 may be 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 from M. When an 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 tertiary amines. It will be appreciated that the cation of the sulpho group may also be replaced at the same time.

The mixtures of the asymmetric 1:2 chromium complexes of formula I, may also be obtained by mere admixture of different asymmetric 1:2 chromium complexes of formula I.

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 complexes of formula I and mixtures thereof are suitable for dyeing from a weakly alkaline, neutral or weakly acid, for example, an acetic acid-containing dyebath.

The dyeings 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 and mixtures thereof are also useful for spin-dyeing synthetic polyamides and acetate rayon in the mass.

The complexes of formula I which are well soluble in water, i.e. those in which M is other than hydrogen, a higher alkylammonium ion, a mono- or dicycloalkylammonium ion or cycloammonium ion are also useful for dyeing metals, especially anodized aluminium.

The compounds of formula I, in which M is a higher alkylammonium ion, a mono- or dicycloalkylammonium ion or cycloammonium ion may also be used in the preparation of printing lacquers 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 prepara-

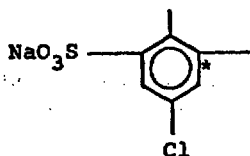
tions may be made, for example, in accordance with the procedure described in German Patent No. 1,619,470 or in German Patent Application No. 2,033,989. Also concentrated stable aqueous preparation which contain the conventional additives may be used.

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.

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

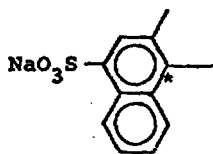
The 1:1-chromium complex which is obtained from 24.5 parts of the azo dyestuff of diazotised 2-amino-4-chloro-1-hydroxybenzene-6-sulphonic acid and 1-phenyl-3-methyl-5-pyrazolone is stirred in 400 parts of water at 80° together with 21 parts of the monoazo dyestuff obtained from diazotised 2-amino-4,6-dichloro-1-hydroxybenzene and 1-phenyl-3-methyl-5-pyrazolone. The suspension is set at a pH value of 7.5 - 8.5 by adding a 20% sodium carbonate solution, and is subsequently stirred at 80-85° UNTIL THE TWO MONOAZO DYESTUFFS ARE NO LONGER DETECTABLE. The uniform complex which is partially in solution is precipitated by adding sodium chloride, isolated by filtration and vacuum dried after washing in a 5% sodium chloride solution. The dyestuff obtained, which after grinding is in the form of a dark-red powder and is well soluble in water, corresponds to formula (I) with A = radical of formula



Z = chlorine, R₁ and R₂ = phenyl and M⁺ = Na⁺. It dyes wool and synthetic polyamides in red shades, and the dyestuff builds-up well tone-in-tone from a neutral bath. The dyeings have very good all-round fastness properties.

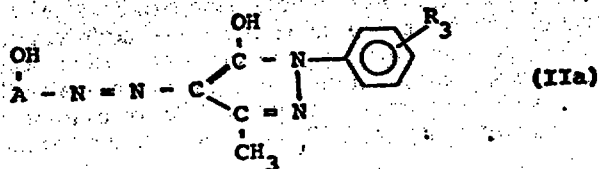
EXAMPLE 2

The 1:1 chromium complex which is obtained from 42.4 parts of the azo dyestuff of diazotised 1-amino-2-hydroxynaphthalene-4-sulphonic acid and 1-phenyl-3-methyl-5-pyrazolone is stirred in 1000 parts of water at 80° together with 38.5 parts of the monoazo dyestuff from diazotised 2-amino-4,6-dichloro-1-hydroxybenzene and 1-(3'-chlorophenyl)-3-methyl-5-pyrazolone. The reaction is continued in accordance with the procedure described in Example 1. The dyestuff obtained corresponds to formula (I) with A = radical of formula

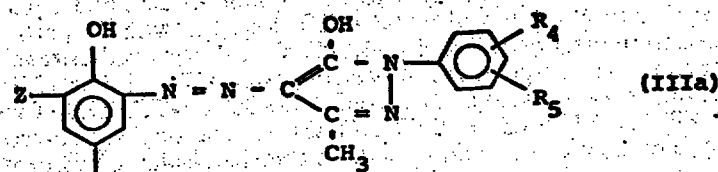


Z = chlorine, R₁ = phenyl, R₂ = and M⁺ = Na⁺.

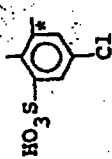
It dyes wool and synthetic polyamide in bluish-red shades and builds-up well, tone-in-tone, from a neutral bath. The dyeings obtained have good all-round fastness properties. In accordance with Examples 1 and 2, further 1:2-chromium complexes may be obtained by reacting the 1:1-chromium complex of a compound of formula

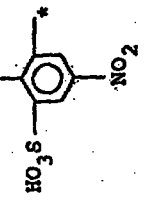
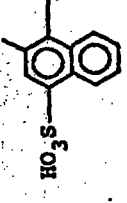


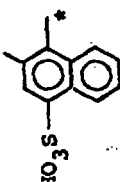
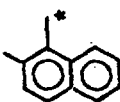
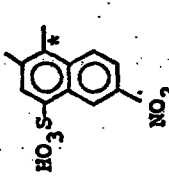
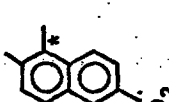
with a compound of formula



The significances of A, R₁, R₂, R₃ and Z as well as the dye-shade on natural ore synthetic polyamide are given in the following Table.

1:1-chromium complex of a compound of formula IIA		Metal-free monoazo dye of Formula IIIa			Dye-shade on polyamide
A	R ₃	Z	R ₄	R ₅	
	H	Cl	Cl (3)	H	red
do.	H	NO ₂	H	H	orange-scarlet
do.	Cl (3)	Cl	Cl (3)	H	bluish-red
do.	Cl (3)	Cl	H	H	do.
do.	H	Cl	CN (3)	H	do.
do.	Cl (3)	NO ₂	Cl (3)	H	scarlet
do.	Cl (2)	NO ₂	Cl (4)	H	do.
do.	H	Cl	Cl (2)	Cl (5)	red
do.	H	Cl	Cl (3)	Cl (4)	do.
do.	Cl (4)	Cl	H	H	do.
do.	H	Cl	CH ₃ (4)	H	do.
do.	H	Cl	Cl (2)	CH ₃ (4)	do.
do.	H	Cl	CH ₃ (3)	CH ₃ (5)	do.
do.	OCH ₃ (4)	Cl	H	H	do.

1:1-chromium complex of a compound of formula Iia	Metal-free monoazo dye of formula IIIa				Dye-shade on polyamide
	R ₃	Z	R ₄	R ₅	
	H	Cl	H	H	orange
	H	Cl	Cl (3)	H	do.
	H	NO ₂	Cl (2)	Cl (5)	do.
	H	Cl	C ₂ H ₅ (2)	H	do.
	Cl (3)	NO ₂	H	H	do.
	C ₂ H ₅ (2)	Cl	H	H	do.
	H	Cl	Cl (4)	H	scarlet
	H	Cl	Cl (3)	Cl (4)	do.
	Cl (4)	Cl	Cl (3)	H	do.
	CH ₃ (4)	Cl	Cl (4)	H	do.
	H	Cl	H	H	bluish-red
	Cl (4)	Cl	H	H	do.

1:1-chromium complex of a compound of formula IIA	Metal-free monoazo dye of formula IIIa				Dye-shade on polyamide
	R ₃	Z	R ₄	R ₅	
 HO ₃ S-  do. do. do. do. do. do. do. do.	H	Cl	Cl (3)	Cl (4)	bluish-red
	H	Cl	C ₂ H ₅ (2)	H	do.
	Cl (3)	Cl	Cl (3)	H	bordeaux
	H	NO ₂	H	H	red
	H	NO ₂	Cl (3)	H	do.
	Cl (3)	NO ₂	Cl (3)	H	do.
	H	NO ₂	Cl (4)	H	do.
	Cl (3)	Cl	H	H	bluish-red
	H	Cl	H	H	brown-red
	Cl (3)	Cl	Cl (3)	H	do.
 HO ₃ S-  do. do.	H	Cl	Cl (3)	H	do.
	Cl (3)	Cl	Cl (3)	H	do.

The dyestuffs of Examples 1 to 39, may also be prepared by reacting the 1:1-chromium complex of the monoazo dyestuff of formula (III) with the metal free monoazo dyestuff of formula (II).

APPLICATION EXAMPLE A

0.1 g of the dyestuff of Example 1 or 2 are dissolved in 300 parts of water, and 0.2 g of ammonium sulphate are added. Subsequently, the moistened material (5 g of wool gabardine or 5 g nylon-satin) is entered into the bath and heated over the course of 30 minutes to boiling temperature. The water which is evaporated during the 30 minutes boiling is replaced and dyeing is completed during the next 30 minutes at the boil. The dyed material is subsequently rinsed. After drying, a red (Example 1) or bluish-red (Example 2) dyeing having good-light- and wet-fastness properties is obtained.

Dyeings may be made in accordance with the above procedure employing any one of the dyestuffs of Examples 3 to 39 or a mixture of any two or more of the dyestuffs of Examples 1 to 39.

APPLICATION EXAMPLE B

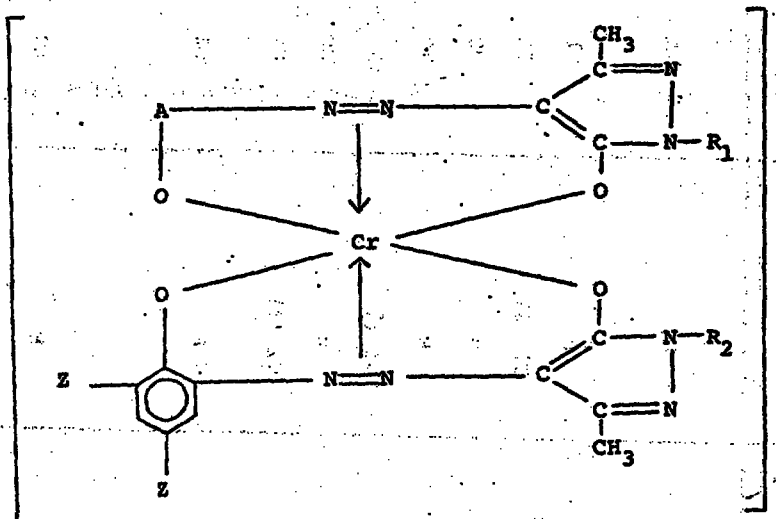
Natural polyamide is printed with a printing paste containing:
30 parts dyestuff of Example 1 or Example 27
50 parts urea
50 parts dissolving agent, for example thiodiethylene glycol,
300 parts water
500 parts suitable thickening agent, for example based on locus bean gum,
60 parts acid acceptor, for example, ammonium tartrate, and
60 parts thiourea

The printed goods are steamed for 40 minutes at 102°C (saturated steam), then rinsed with cold water, washed for 5 minutes at 60°C with a dilute solution of a conventional detergent and then rinsed again. A red (Example 1) or bluish red (Example 27) print having good wet- and light-fastness is obtained.

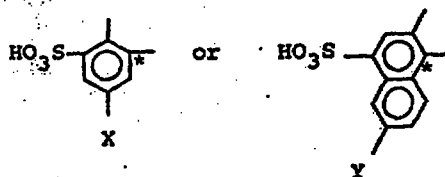
In analogous manner printing pastes may be prepared using any one of the dyestuffs of Examples 2 to 26 or 28 to 39.

WHAT WE CLAIM IS:-

1. An asymmetric 1:2 chromium complex of formula I:



in which A is a group of formula (a) or (b)





The dyestuffs of Examples 1 to 39, may also be prepared by reacting the 1:1-chromium complex of the monoazo dyestuff of formula (III) with the metal free monoazo dyestuff of formula (II).

APPLICATION EXAMPLE A

- 5 0.1 g of the dyestuff of Example 1 or 2 are dissolved in 300 parts of water, and 0.2 g of ammonium sulphate are added. Subsequently, the moistened material (5 g of wool gabardine or 5 g nylon-satin is entered into the bath and heated over the course of 30 minutes to boiling temperature. The water which is evaporated during the 30 minutes boiling is replaced and dyeing is completed during the next 30 minutes at the boil. The dyed material is subsequently rinsed. After drying, a red (Example 1) or bluish-red (Example 2) dyeing having good-light- and wet-fastness properties is obtained.

Dyeings may be made in accordance with the above procedure employing any one of the dyestuffs of Examples 3 to 39 or a mixture of any two or more of the dyestuffs of Examples 1 to 39.

APPLICATION EXAMPLE B

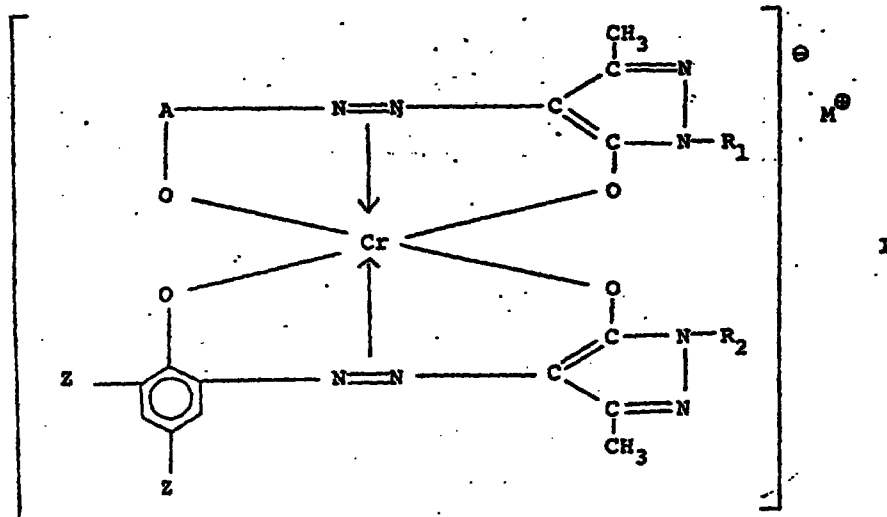
- 15 Natural polyamide is printed with a printing paste containing:
30 parts dyestuff of Example 1 or Example 27
50 parts urea
50 parts dissolving agent, for example thiodiethylene glycol,
20 300 parts water
500 parts suitable thickening agent, for example based on locus bean gum,
60 parts acid acceptor, for example, ammonium tartrate, and
60 parts thiourea

- 25 The printed goods are steamed for 40 minutes at 102°C (saturated steam), then rinsed with cold water, washed for 5 minutes at 60°C with a dilute solution of a conventional detergent and then rinsed again. A red (Example 1) or bluish red (Example 27) print having good wet- and light-fastness is obtained.

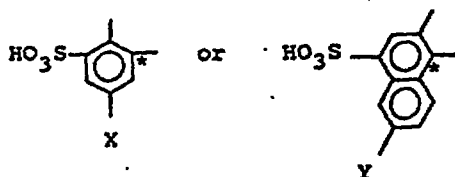
In analogous manner printing pastes may be prepared using any one of the dyestuffs of Examples 2 to 26 or 28 to 39.

WHAT WE CLAIM IS:-

- 30 1. An asymmetric 1:2 chromium complex of formula I.



in which A is a group of formula (a) or (b)





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in which X is halogen, nitro or methyl,

Y is hydrogen or nitro,

* designates the carbon atom bound to be azo group.

Z is halogen or nitro, both substituents being the same,

each of R_1 and R_2 , independently is unsubstituted phenyl or phenyl substituted by a total of up to three substituents selected from halogen, (C1-6), (C1-6) alkoxy, nitro and cyano (maximum of two nitro and/or cyano), and

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

with the proviso that the sulpho group is in salt form, and mixtures of two or such 1:2 asymmetric complexes.

2. A complex or mixture according to Claim 1, in which X is X' , where X' is halogen or nitro.

3. A complex or mixture according to Claim 1 of Claim 2, in which Z is Z' , where Z' is chlorine or nitro.

4. A complex or mixture according to any one of Claims 1 to 3, in which Y is hydrogen.

5. A complex or mixture according to any one of Claims 1 to 4, in which any alkyl or alkoxy substituent on R_1 and/or R_2 contains 1 to 4 carbon atoms.

6. A complex or mixture according to any one of the preceding Claims, in which the alkyl or alkoxy substituent on R_1 and/or R_2 contains 1 or 2 carbon atoms.

7. A complex or mixture according to Claim 6, in which R_1 and R_2 are R'_1 and R'_2 , respectively where each of R'_1 and R'_2 , independently, is a group of formula (c)



(c)

in which W_1 is hydrogen, chlorine, methyl, methoxy or ethoxy, and

W_2 is hydrogen, chlorine or methyl.

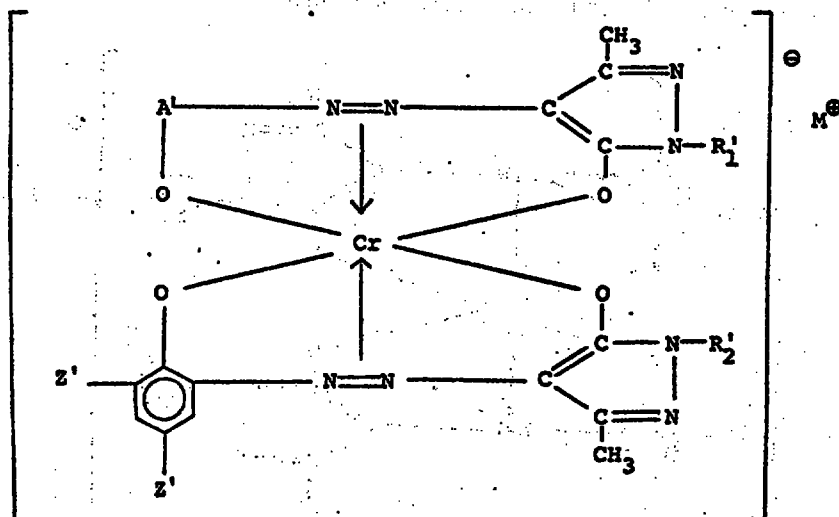
where R_1 and/or R_2 is monosubstituted any chlorine methyl, methoxy or ethoxy is in the 3- or 4-position and where R_1 and/or R_2 is disubstituted the substituents are in the 2, 4-, 2, 5-, 2, 6-, 3, 4- or 3, 5- positions.

8. A complex or mixture according to Claim 7, in which R_1 and R_2 are R''_1 and R''_2 , respectively, where each of R''_1 and R''_2 , independently, is a group of formula (c) in which W_1 and W_2 are W'_1 and W'_2 , where W'_1 is hydrogen, chlorine, or methyl and W'_2 is hydrogen or chlorine.

9. A complex or mixture according to Claim 8, in which R_1 and R_2 are R'''_1 and R'''_2 , where W_1 and W_2 are W''_1 and W''_2 , respectively, where W''_1 is hydrogen or chlorine and W''_2 is hydrogen.

10. A complex or mixture according to claim 9, in which both W_1 and W_2 are hydrogen.

11. A complex or mixture according to Claim 7, of formula Ia



Ia



* C L M S *

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in which either A' is a radical of formula (a) wherein X is chlorine or nitro, or A' is a radical of formula (b) wherein Y is hydrogen, and Z' is chlorine or nitro, R' and R' are as defined in Claim 7, and M is as defined in Claim 1.

12. A complex or mixture according to Claim 11, in which R' and R' are R'' and R'', respectively, where R'' and R'' are as defined in Claim 8.

13. A complex or mixture according to Claim 12, in which R' and R' are R''' and R''', respectively, where R''' and R''' are as defined in Claim 9.

14. A complex or mixture according to Claim 13, in which R' and R' are both unsubstituted phenyl.

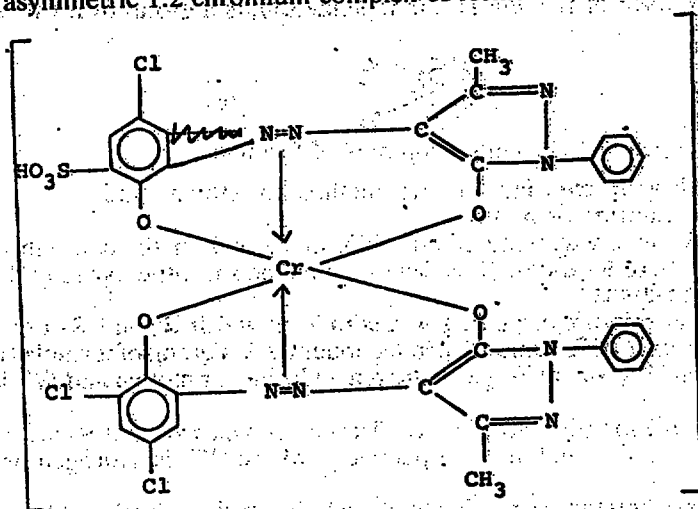
15. A complex or mixture according to any one of Claims 11 to 14, in which Z' is chlorine.

16. A complex or mixture according to Claim 1, in which Z is chlorine and A is either a radical of formula (a) in which X is chlorine or A is a radical of formula (b) in which Y is hydrogen.

17. A complex or mixture according to Claim 1, in which Z is chlorine and R₁ is R', as defined in Claim 7.

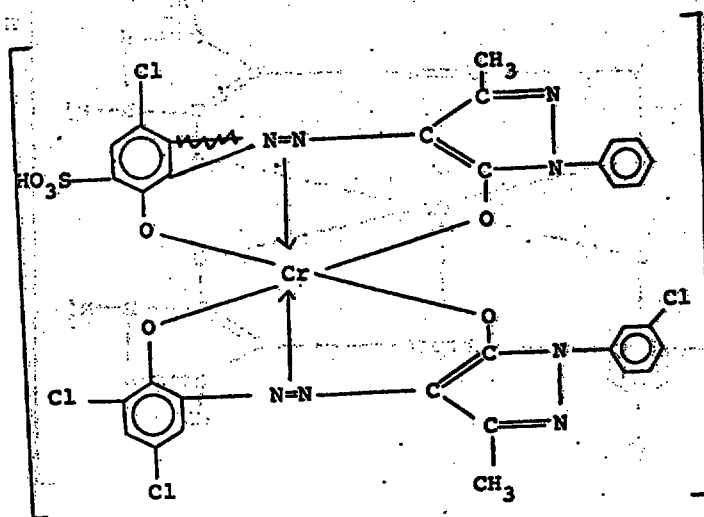
18. A complex or mixture according to Claim 1, in which Z is chlorine and R₁ is R', as defined in Claim 7.

19. An asymmetric 1:2 chromium complex of formula



in which M⁺ is as defined in Claim 1 and the cation of the sulpho group has one of the significances of M and is the same as or different from M.

20. An asymmetric 1:2-chromium complex of formula





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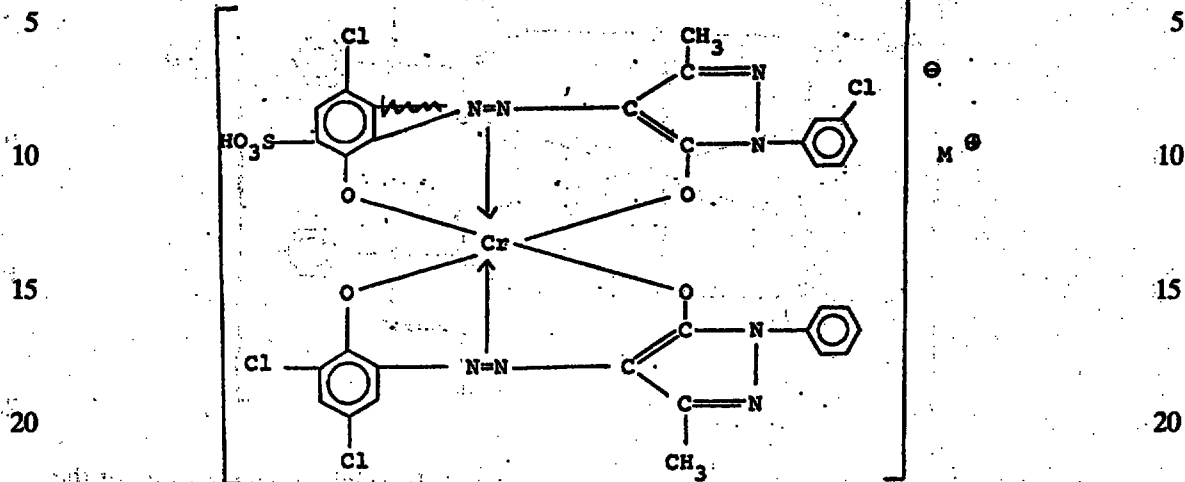
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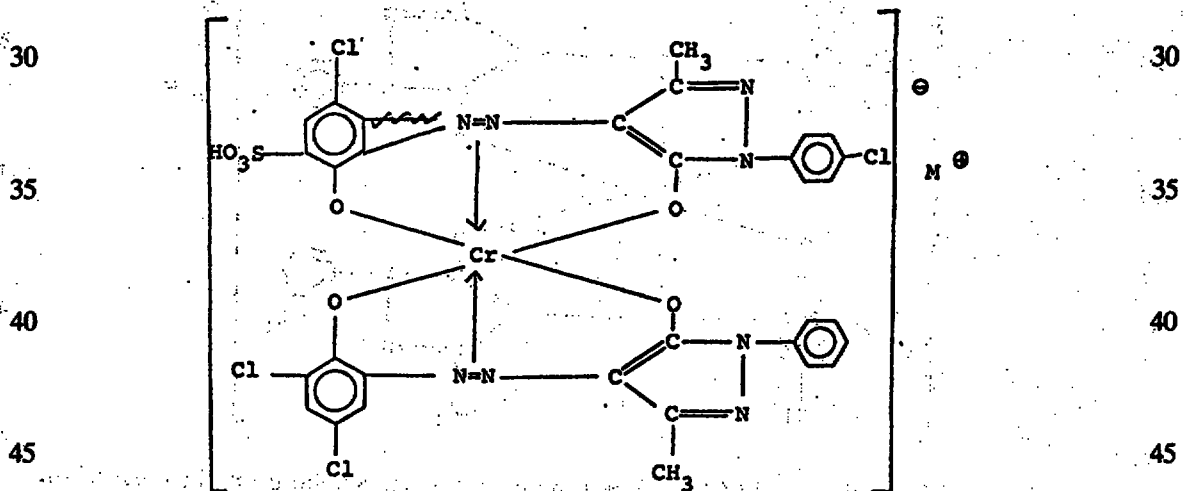
in which $M^{\oplus}$ is as defined in Claim 1 and the cation of the sulpho group has one of the significances of M and is the same as or different from M.

21. An asymmetric 1:2-chromium complex of formula



25 in which $M^{\oplus}$ is as defined in Claim 1 and the cation of the sulpho group has one of the significances of M and is the same as or different from M.

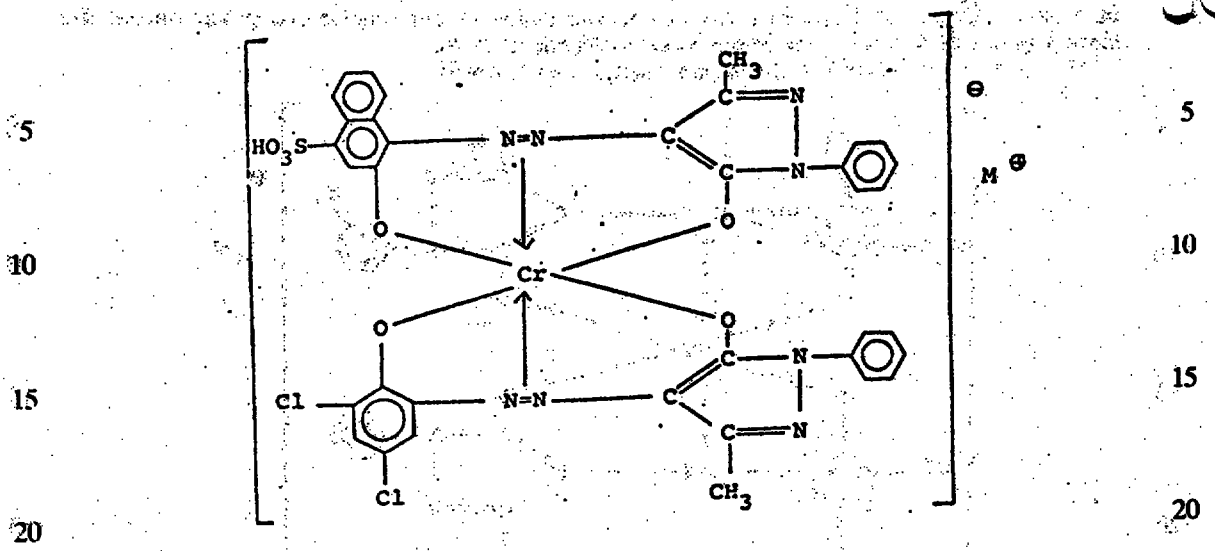
22. An asymmetric 1:2-chromium complex of formula



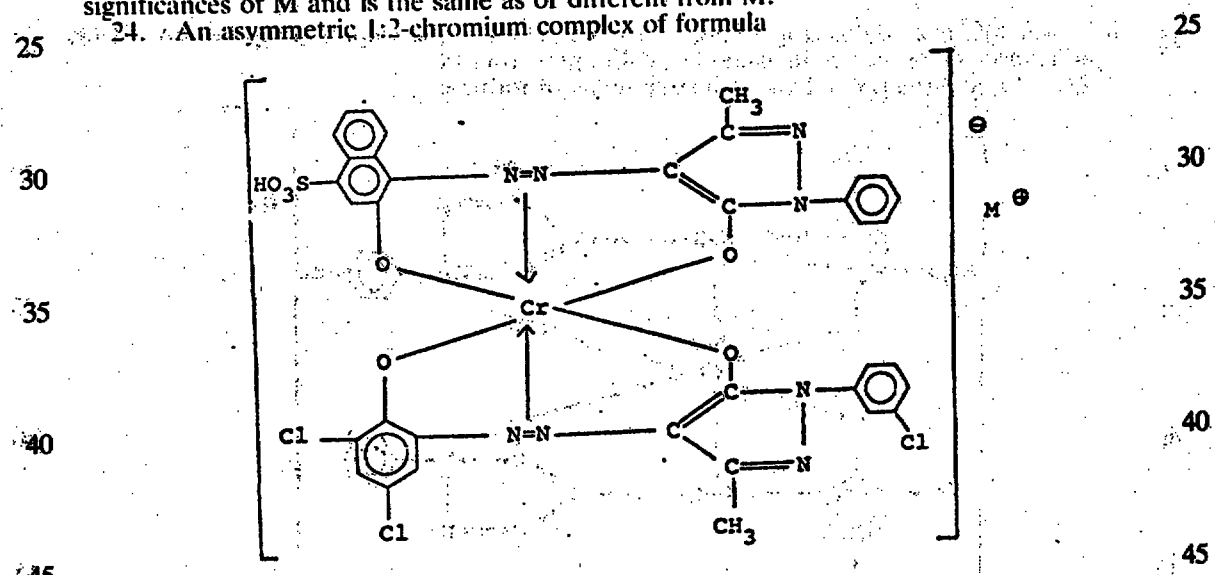
50 in which $M^{\oplus}$ is as defined in Claim 1 and the cation of the sulpho group has one of the significances of M and is the same as or different from M.

23. An asymmetric 1:2-chromium complex of formula

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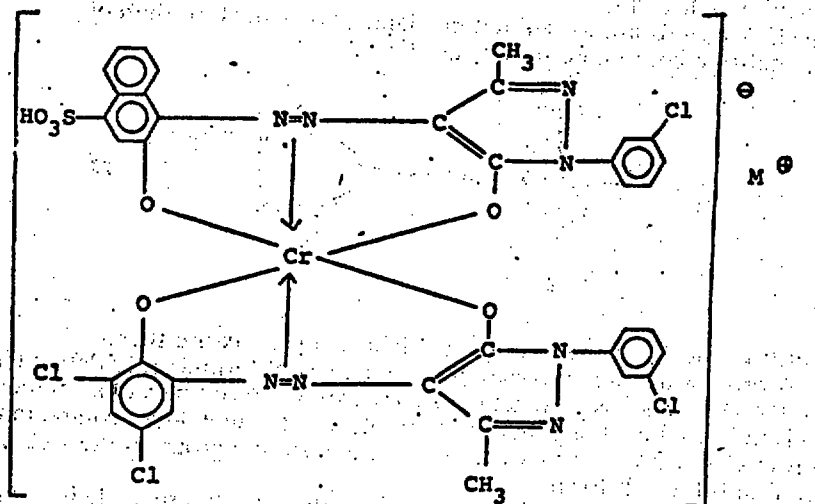


in which $M^{\oplus}$ is as defined in Claim 1 and the cation of the sulpho group has one of the significances of M and is the same as or different from M.



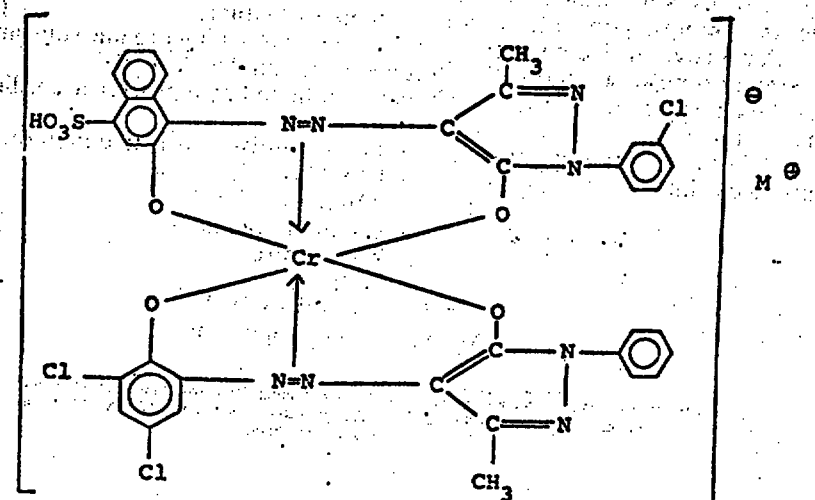
in which $M^{\oplus}$ is as defined in Claim 1 and the cation of the sulpho group has one of the significances of M and is the same as or different from M.

25. An asymmetric 1:2-chromium complex of formula



in which $M^{\oplus}$ is as defined in Claim 1 and the cation of the sulfo group has one of the significances of M and is the same as or different from M.

26. An asymmetric 1:2-chromium complex of formula

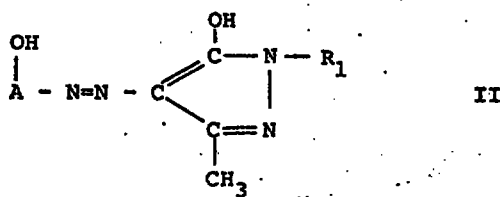


in which $M^{\oplus}$ is as defined in Claim 1 and the cation

27. A complex according to any one of the preceding claims in which the cation of the sulfo group and M are both sodium.

28. A 1:2 complex according to any one of Examples 4, 5, 7 to 11, 13 to 26, 28 to 30, 32 to 35 and 37 to 39.

29. A process for the preparation of a complex of formula I, as defined in Claim 1, or a mixture thereof, comprising reacting the 1:1 chromium complex of a compound of formula II.



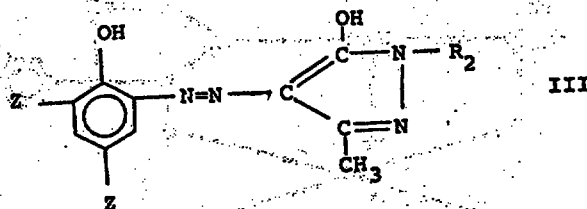
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in free acid or salt form,
in which A and R₁ are as defined in Claim 1, or a mixture thereof,
with a metal-free compound of formula III.



- in which Z and R₂ are as defined in Claim 1, or a mixture thereof.
30. A process for the preparation of a complex of formula I, as defined in Claim 1, or a mixture thereof, comprising reacting the 1:1 chromium complex of a compound of formula III, as given in Claim 29 or a mixture thereof, with the metal-free compound of formula II, as given in Claim 29, or a mixture thereof, any sulpho group in the free acid form being converted into the salt form.
31. A process for the production of a complex or mixture as defined in Claim 1, substantially as hereinbefore described with reference to any one of Examples 1 to 39.
32. An asymmetric 1:2 chromium-complex or mixture whenever obtained by a process according to Claim 29, 30 or 31.
33. A process for dyeing or printing nitrogen-containing organic substances comprising employing a complex or mixture according to any one of Claims 1 to 28 or 32, as dyeing or printing agent.
34. A process according to Claim 33, in which the substrate consists of or comprises natural or synthetic polyamides, polyurethane or leather.
35. A process for dyeing or printing nitrogen-containing organic substances substantially as hereinbefore described with reference to Examples A or B.
36. Dyed or printed substrates whenever obtained by a process according to any one of Claims 33 to 35.
37. A liquid or solid dyestuff preparation comprising as active ingredient a complex or mixture according to any one of Claims 1 to 28 or 32.

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