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PATENT SPECIFICATION

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 (54) Inventor HANSPETER UEHLINGER

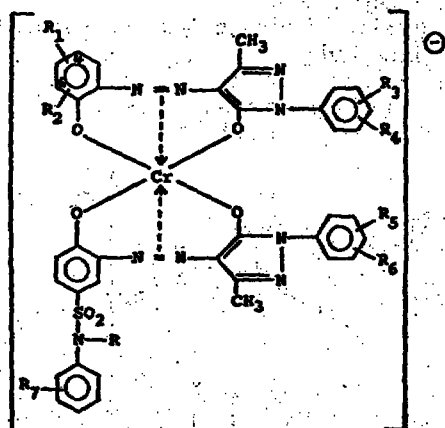


(54) SULPHONATED ASYMMETRIC 1:2 CHROMIUM COMPLEXES

(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.

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



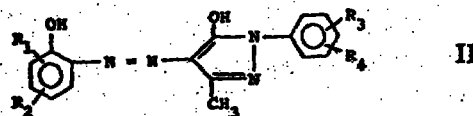
in which

- 15 R_1 signifies a hydrogen or halogen atom or a nitro group,
 R_2 signifies a hydrogen or halogen atom, a nitro or sulpho group,
 R_3 signifies a hydrogen or halogen atom, or a lower alkyl radical,
 20 R_4 signifies a hydrogen or halogen atom, a lower alkyl radical or a sulpho group,
 each of R_5 , R_6 and R_7 , independently, signifies a hydrogen or halogen atom or a lower alkyl radical,
 25 R signifies a hydrogen atom or a lower alkyl radical, and
 M signifies a non-chromophoric cation, with the provisos
 30 (i) the radicals R_1 and R_2 occupy the 4- and 6-positions,

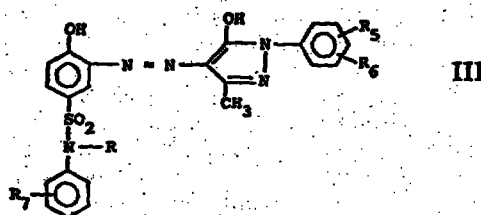
(ii) where R_1 signifies a sulpho group one of the radicals R_1 and R_2 signifies a halogen atom or a nitro group in the 4-position, and

(iii) the compounds contain a single sulpho group which is in free acid or salt form.

The present invention also provides a process for the production of compounds of formula I, characterized by reacting the 1:1 chromium complex of a compound of formula II,



in which R_1 , R_2 , R_3 and R_4 are as defined above, with a compound of formula III,



in which R_5 , R_6 , R_7 and R are as defined above.

The reaction of the compounds of formula II with the compounds of formula III may be carried out in a known manner, for example by the method described in German Auslegeschrift 1,644,390 or U.S. Patent No. 2,806,760. Preferably, the 1:1 chromium complex of the compound of formula II is reacted with stoichiometric amounts of the compound of formula III. The reaction is preferably carried out in an aqueous or aqueous-organic medium. Preferably weakly alkaline to strongly alkaline conditions are employed, more preferably at a constant pH. Preferred reaction temperatures are in the range of from 20° to 100°C. On completion of the reaction, i.e. when all the 1:1 chromium complex has been

reacted, the product may be salted out and dried.

In the compounds of formula I, any halogen atom is preferably chlorine, bromine or fluorine, more preferably chlorine.

Any lower alkyl radical in the compounds of formula I may be straight chain or branched and preferably contains 1 to 4, more preferably 1 or 2, carbon atoms, with methyl being especially preferred.

Preferred cations for M include lithium, sodium, potassium, ammonium, mono-, di-, tri- or tetra-(C₁₋₂)alkylammonium or mono-, di-, tri or tetra-(C₁₋₂)alkanolammonium, with lithium, sodium, potassium, ammonium and tetra-(C₁₋₂)alkylammonium being more preferred and sodium being the most preferred cation. However, any cation conventional in the art may be employed, whether mono-, di- or polyvalent.

Preferably R₁ signifies chlorine or nitro and R₂ signifies a sulfo group. More preferably R₁ signifies nitro and is in the 4-position and R₂ signifies a sulfo group in the 6-position.

Where R₂ has a significance other than sulfo, R₄ signifies a sulfo group and is preferably in the 3-, 4- or 5-position.

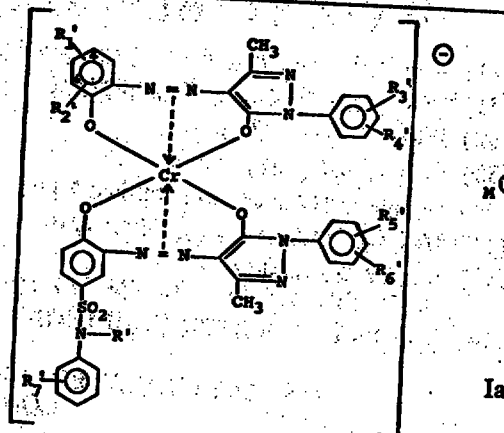
Preferably, each of R₃ and R₄, independently, signifies a hydrogen or chlorine atom or a methyl radical. Where both of R₃ and R₄ have a significance other than hydrogen, preferably such substituents are in the 2,5-, 2,6- or 3,4-positions. More preferably, one of R₃ and R₄ signifies a hydrogen atom and the other signifies a chlorine atom. Even more preferably, both of R₃ and R₄ signify hydrogen.

Preferably, each of R₅ and R₆, independently, signifies a hydrogen or chlorine atom or a methyl radical. Where both of R₅ and R₆ have a significance other than hydrogen, preferably such substituents are in the 2,5-, 2,6- or 3,4-positions. More preferably, one of R₅ and R₆ signifies hydrogen and the other signifies a chlorine atom. Even more preferably, both of R₅ and R₆ signify hydrogen.

Preferably R₇ signifies a hydrogen or chlorine atom or a methyl radical; the preferred positions for such chlorine or methyl substituent are the 2- and 4-positions. More preferably R₇ signifies hydrogen.

R preferably signifies hydrogen or methyl, with hydrogen being more preferred.

Preferred compounds of formula I include those of formula Ia,



in which

R₁ signifies a chlorine atom or a nitro group,

R₂ signifies a chlorine atom, a nitro or sulfo group,

R₃ signifies a hydrogen or chlorine atom or a methyl radical,

R₄ signifies a hydrogen or chlorine atom or a sulfo group,

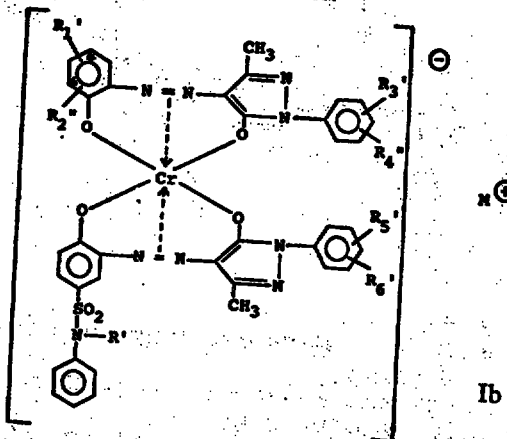
R₅ signifies a hydrogen or chlorine atom or a methyl radical,

R₆ signifies a hydrogen or chlorine atom, R₇ signifies a hydrogen or chlorine atom or a methyl radical,

R' signifies a hydrogen atom or a methyl radical, and

M is as defined above.

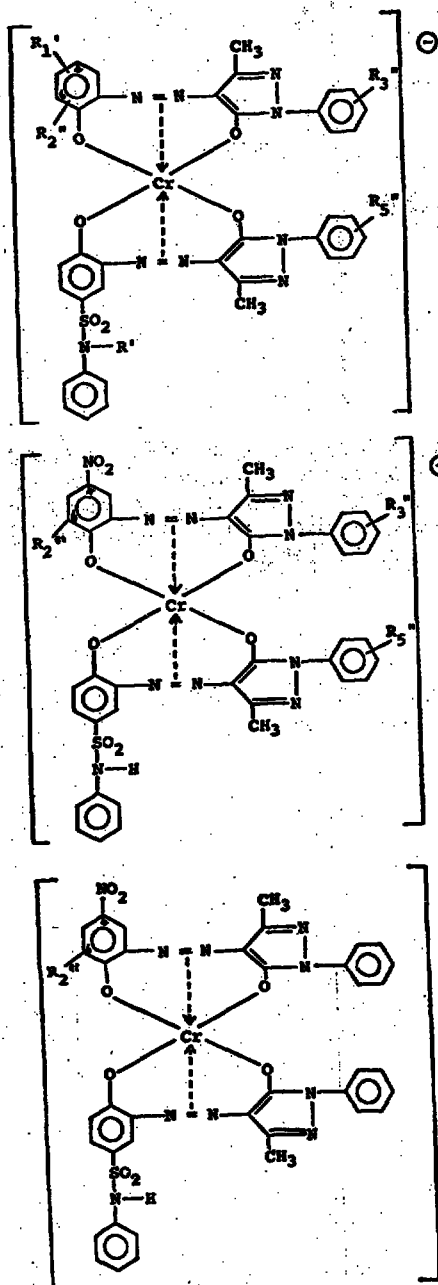
More preferred compounds of formula I include those of formula Ib,



in which

R₁, R₂, R₃, R₄, R₅, R₆, R' and M are as defined above,

R_2'' signifies a sulpho group, and R_4'' signifies a hydrogen or chlorine atom. Even more preferred compounds of formula I include those of formulae Ic, Id and Ie,



in which

R_1' , R_2'' , R' and M are as defined above, and

each of R_3'' and R_5'' , independently, signifies a hydrogen or chlorine atom.

As will be appreciated the sulpho group present in the compounds of formula I may be present in the free acid or salt form, more preferably the latter.

The cation of the salt form of the sulpho group may, for example, be any of those in-

dicated above for M . Depending on the reaction conditions employed in the preparation of or working up of the 1:2 chromium complexes of formula I, the cation of the salt form of the sulpho group may be the same as or different from the cation M , preferably conditions are so chosen that they are the same.

The 1:1 chromium complex of the compounds of formula II, as defined above, may be prepared by known methods, for example in accordance with the method described in U.S. Patent No. 2,806,760.

The compounds of formula III are known or may be prepared by known methods.

The compounds of formula I are indicated for use as dyes for dyeing or printing natural and synthetic organic substrates. Examples of substrates which can be dyed or printed with the compounds of formula I include natural or synthetic polyamides e.g. wool, nylon and silk, polyurethane and basic modified polyolefins. Such substrates may be in loose fibre, yarn or fabric form. The compounds of formula I are also useful for dyeing synthetic polyamides in the mass and for dyeing leather and metals, especially anodized aluminium.

Conventional dyeing and printing methods may be employed.

The compounds of formula I may be employed alone or in combination with other asymmetric or symmetric 1:2 metal complex dyes.

The compounds of formula I have marked solubility in water and show notable light fastness, wet fastness (fastness to washing, water, seawater, acid and alkaline perspiration and milling) and fastness to ironing, solvents, rubbing, chlorine, carbonizing and decatizing.

The compounds of formula I build up from a neutral bath on polyamide fibres in even shades.

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

EXAMPLE 1.

The 1:1 chromium complex produced by known methods from 46.9 parts of the mono-azo dye produced by coupling diazotised 4-nitro-2-aminophenol-6-sulphonic acid with 1-phenyl-3-methyl-5-pyrazolone, is stirred together with 44.9 parts of the monoazo dye produced by coupling diazotised 2-amino-1-hydroxybenzene-4-sulphonic acid-phenylamide with 1-phenyl-3-methyl-5-pyrazolone and with water to give a volume of 500 parts, and is dissolved at 80° at a pH of 10.0 after the addition of a 30% sodium hydroxide solution. In order to form the asymmetric 1:2-chromium complex, the pH value of the reaction solution is kept at 10.0 by adding a 30% sodium hydroxide solution dropwise. On completion of the reaction, the solution is cooled and the pH is adjusted to 6.5 by

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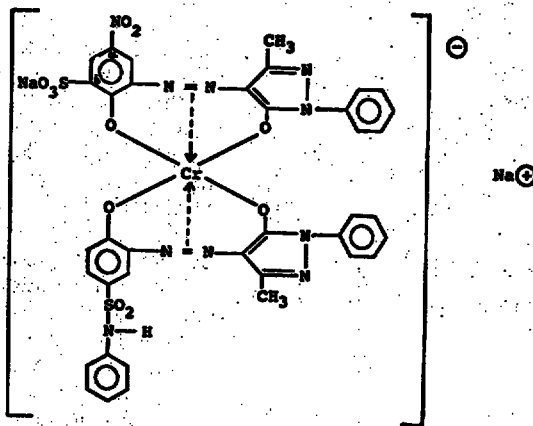
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the dropwise addition of 30% hydrochloric acid. The precipitated 1:2 chromium complex is filtered off, washed and dried.

The resulting dyestuff complex which agrees with the formula

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is soluble in water and dyes natural and synthetic polyamide fibres in orange shades. Dyeings obtained have notable wet fastness and fastness to light.
10 In the following Table further dyes are in-

dicated which may be produced in accordance with the procedure of Example 1. The significances of the radicals R_1 to R_7 and R in the starting materials of formulae II and III 15 are given in the Table.

TABLE

Example	Compound of Formula II					Compound of Formula III				Shade on nylon
	R ₁	R ₂	R ₃	R ₄	R ₅	R ₆	R ₇	R		
2	4-NO ₂	6-SO ₃ H	3'-Cl	H	H	H	H	H	orange	
3	4-NO ₂	6-SO ₃ H	2'-Cl	5'-Cl	H	H	H	H	do.	
4	4-NO ₂	6-SO ₃ H	H	H	3'-Cl	H	H	H	do.	
5	4-NO ₂	6-SO ₃ H	H	H	2'-Cl	5'-Cl	H	H	do.	
6	6-NO ₂	4-SO ₃ H	2'-CH ₃	6'-Cl	4'-Cl	H	H	H	do.	
7	4-Cl	H	H	4'-SO ₃ H	2'-CH ₃	H	H	H	do.	
8	4-Cl	6-SO ₃ H	H	H	H	H	H	-CH ₃	do.	
9	H	4-SO ₃ H	2'-C ₂ H ₅	H	2'-Cl	6'-CH ₃	H	H	do.	
10	4-NO ₂	6-SO ₃ H	3'-Cl	H	2'-Cl	H	4'-Cl	H	do.	
11	4-NO ₂	6-SO ₃ H	2'-Cl	5'-Cl	H	H	4'-CH ₃	H	do.	
12	4-NO ₂	6-SO ₃ H	2'-CH ₃	H	H	H	H	-CH ₃	do.	
12	6-NO ₂	4-SO ₃ H	H	H	H	H	H	H	do.	
14	4-Cl	6-SO ₃ H	H	H	H	H	H	H	do.	
15	6-Cl	4-SO ₃ H	H	H	H	H	H	H	do.	
16	4-NO ₂	6-SO ₃ H	2'-Cl	H	H	H	H	H	do.	
17	4-NO ₂	6-SO ₃ H	4'-Cl	H	H	H	H	H	do.	

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12
12

TABLE (cont.)

Example	Compound of Formula II				Compound of Formula III				Shade on nylon
	R ₁	R ₂	R ₃	R ₄	R ₅	R ₆	R ₇	R	
18	6-NO ₂	4-SO ₃ H	2'-Cl	H	H	H	H	H	orange
19	6-NO ₂	4-SO ₃ H	3'-Cl	H	H	H	H	H	do.
20	6-NO ₂	4-SO ₃ H	4'-Cl	H	H	H	H	H	do.
21	4-Cl	6-SO ₃ H	2'-Cl	H	H	H	H	H	do.
22	4-Cl	6-SO ₃ H	3'-Cl	H	H	H	H	H	do.
23	4-Cl	6-SO ₃ H	4'-Cl	H	H	H	H	H	do.
24	6-Cl	4-SO ₃ H	2'-Cl	H	H	H	H	H	do.
25	6-Cl	4-SO ₃ H	3'-Cl	H	H	H	H	H	do.
26	6-Cl	4-SO ₃ H	4'-Cl	H	H	H	H	H	do.
27	6-Cl	4-SO ₃ H	H	H	4'-CH ₃	H	H	H	do.
28	4-NO ₂	6-SO ₃ H	H	H	4'-C ₂ H ₅	H	H	H	do.
29	4-NO ₂	6-SO ₃ H	H	H	4'-isopropyl	H	H	H	do.
30	4-NO ₂	6-SO ₃ H	H	H	4'-n-butyl	H	H	H	do.
31	6-NO ₂	4-SO ₃ H	2'-Cl	H	H	H	H	-CH ₃	do.
32	4-NO ₂	6-SO ₃ H	4'-Br	H	H	H	H	H	do.
33	4-NO ₂	6-SO ₃ H	H	H	4'-Br	H	H	H	do.

TABLE (cont.)

Example	Compound of Formula II				Compound of Formula III				Shade on nylon
	R ₁	R ₂	R ₃	R ₄	R ₅	R ₆	R ₇	R	
34	4-NO ₂	6-SO ₃ H	4'-Br	H	4'-Br	H	H	H	orange
35	4-Cl	6-SO ₃ H	4'-CH ₃	H	H	H	4'-Cl	H	do.
36	4-Cl	6-SO ₃ H	4'-C ₂ H ₅	H	H	H	H	-CH ₃	do.
37	4-NO ₂	H	H	4'-SO ₃ H	2'-Cl	H	H	H	do.
38	4-NO ₂	H	2'-Cl	5'-SO ₃ H	4'-Cl	H	H	H	do.
39	4-NO ₂	6-SO ₃ H	2'-Cl	H	2'-Cl	H	H	H	do.
40	4-NO ₂	6-SO ₃ H	3'-Cl	H	4'-Cl	H	H	H	do.
41	4-NO ₂	H	H	3'-SO ₃ H	3'-Cl	H	H	H	do.
42	4-Cl	H	H	3'-SO ₃ H	2'-Cl	H	H	-CH ₃	do.
43	4-NO ₂	6-SO ₃ H	H	H	2'-Cl	H	H	H	do.
44	4-NO ₂	6-SO ₃ H	H	H	4'-Cl	H	H	H	do.
45	4-NO ₂	6-SO ₃ H	2'-CH ₃	6'-CH ₃	H	H	H	H	do.
46	4-Cl	6-SO ₃ H	2'-Cl	H	H	H	2'-CH ₃	H	do.
47	6-Cl	4-SO ₃ H	2'-CH ₃	6'-Cl	H	H	2'-Cl	H	do.
48	6-Cl	4-SO ₃ H	2'-Cl	5'-Cl	H	H	2'-CH ₃	H	do.
49	4-NO ₂	6-SO ₃ H	4'-Br	H	4'-Br	H	H	H	do.

TABLE (cont.)

Example	Compound of Formula II							Compound of Formula III				Shade on nylon
	R ₁	R ₂	R ₃	R ₄	R ₅	R ₆	R ₇	R				
50	4-NO ₂	6-SO ₃ H	H	H	2'-Cl	6'-CH ₃	H	H	orange			
51	4-NO ₂	6-SO ₃ H	3'-Cl	4'-Cl	H	H	H	H	do.			
52	4-NO ₂	6-SO ₃ H	H	H	3'-Cl	4'-Cl	H	H	do.			
53	H	4-SO ₃ H	3'-Cl	H	4'-Cl	H	H	H	do.			
54	4-NO ₂	6-Cl	H	4'-SO ₃ H	2'-Cl	H	H	H	do.			
55	4-Cl	6-NO ₂	H	4'-SO ₃ H	2'-CH ₃	H	H	H	do.			
56	4-Cl	6-Cl	H	3'-SO ₃ H	2'-Cl	5'-Cl	H	H	do.			
57	4-NO ₂	6-NO ₂	H	3'-SO ₃ H	2'-Cl	6'-CH ₃	H	H	do.			

APPLICATION EXAMPLE A.

0.1 g of the dyestuff obtained in accordance with Example 1 are dissolved in 300 parts of water and 0.2 g of ammonium sulphate are added thereto. A previously moistened material (5 g of wool gabardine or 5 g of nylon satin) is subsequently introduced into the bath which is heated to boiling temperature over the course of 30 minutes. The water evaporated

during the 30 minutes is replaced and dyeing is completed over the course of a further 30 minutes at boiling temperature. The dyed material is then rinsed. After drying, an orange dyeing with notable light and wet fastnesses is obtained.

The dyestuffs of Examples 2 to 57 of the Table may be employed in the same manner.



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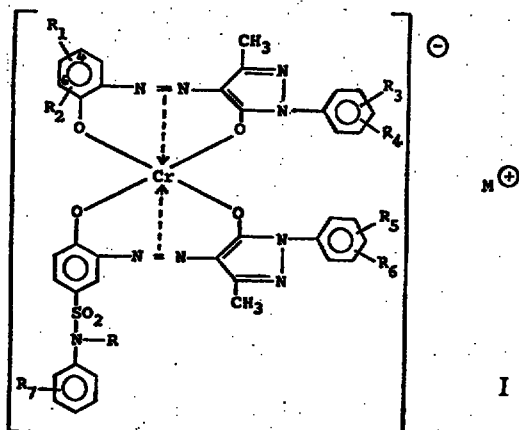
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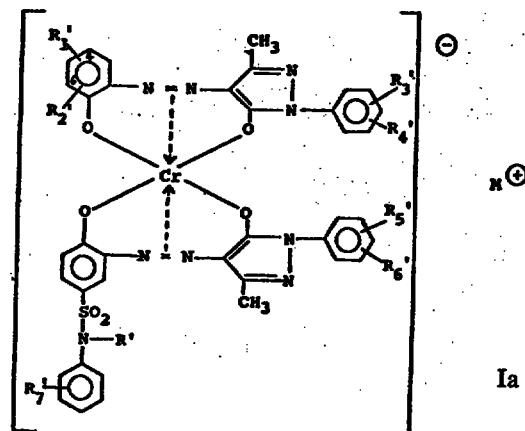
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WHAT WE CLAIM IS:—

1. A 1:2 chromium complex compound of formula I,



I



Ia

in which

R₁' signifies a chlorine atom or a nitro group,

R₂' signifies a chlorine atom, a nitro or sulfo group,

R₃' signifies a hydrogen or chlorine atom or a methyl radical,

R₄' signifies a hydrogen or chlorine atom or a sulfo group,

R₅' signifies a hydrogen or chlorine atom, or a methyl radical,

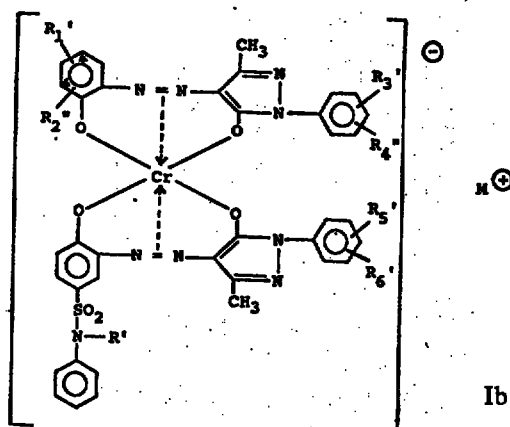
R₆' signifies a hydrogen or chlorine atom,

R₇' signifies a hydrogen or chlorine atom or a methyl radical,

R' signifies a hydrogen atom or a methyl radical, and

M is as defined in Claim 1.

4. A compound according to Claim 3, of formula Ib,



Ib

5 in which

R₁ signifies a hydrogen or halogen atom or a nitro group,

R₂ signifies a hydrogen or halogen atom, a nitro or sulfo group,

R₃ signifies a hydrogen or halogen atom, or a lower alkyl radical,

R₄ signifies a hydrogen or halogen atom, a lower alkyl radical or a sulfo group,

each of R₅, R₆ and R₇, independently, signifies a hydrogen or halogen atom or a lower alkyl radical,

R signifies a hydrogen atom or a lower alkyl radical, and

M signifies a non-chromophoric cation,

with the provisos

(i) that the radicals R₁ and R₂ occupy the 4- and 6-positions,

(ii) where R₁ signifies a sulfo group one of the radicals R₁ and R₂ signifies a halogen atom or a nitro group in the 4-position, and

(iii) the compounds contain a single sulfo group which is in free acid or salt form.

2. A compound according to Claim 1, in which any lower alkyl radical contains 1 to 4 carbon atoms and any halogen atom is chlorine, bromine or fluorine.

3. A compound according to Claim 2, of formula Ia,

in which

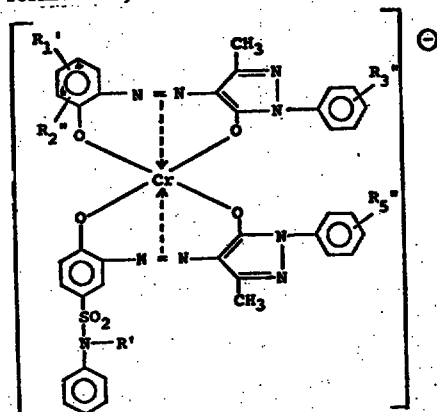
R_1' , R_2' , R_3' , R_4' and R' are as defined in Claim 3,

R_5'' signifies a sulpho group,

5 R_4'' signifies a hydrogen or a chlorine atom, and

M is as defined in Claim 1.

5. A compound according to Claim 4, of formula Ic,



Ic

in which

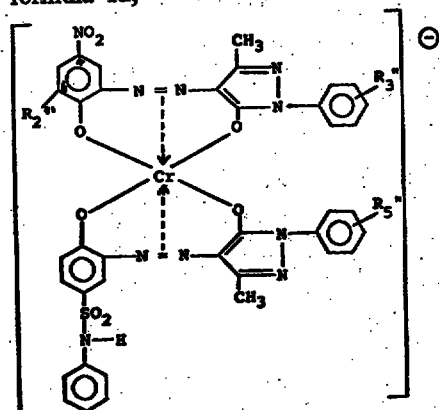
R_1' and R' are as defined in Claim 3,

R_2'' is as defined in Claim 4,

15 each of R_3'' and R_5'' , independently, signifies a hydrogen or chlorine atom, and

M is as defined in Claim 1.

6. A compound according to Claim 5, of formula Id,



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in which

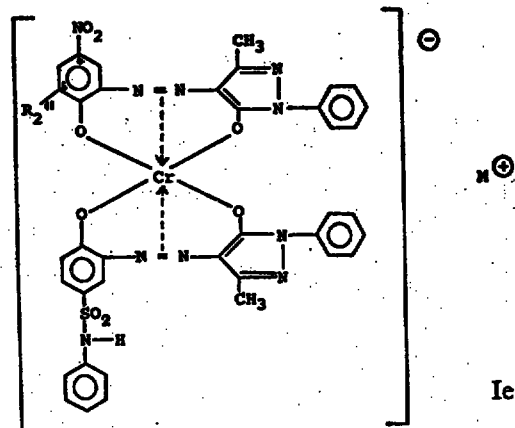
R_2'' is as defined in Claim 4,

R_3'' and R_5'' are as defined in Claim 5,

and

M is as defined in Claim 1.

7. A compound according to Claim 6, of formula Ie,



Ie

in which

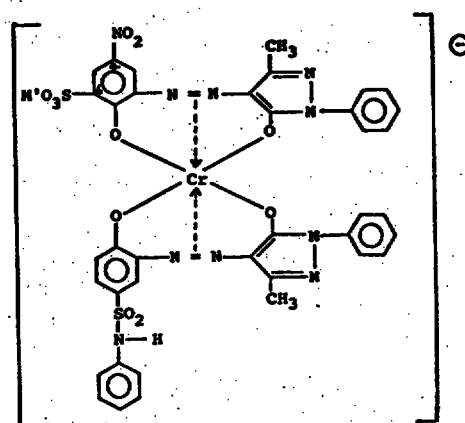
R_3'' is as defined in Claim 4, and

M is as defined in Claim 1.

8. A compound according to any one of the preceding Claims, in which each of M and the cation of the sulpho group when in salt form, independently, is lithium, sodium, potassium, ammonium or tetra-(C_{1-2})alkylammonium.

9. A compound according to Claim 8 in which each of M and the cation of the sulpho group when in salt form, independently, is sodium or potassium.

10. A compound of formula



in which each of M and M' , independently, signifies a non-chromophoric cation.



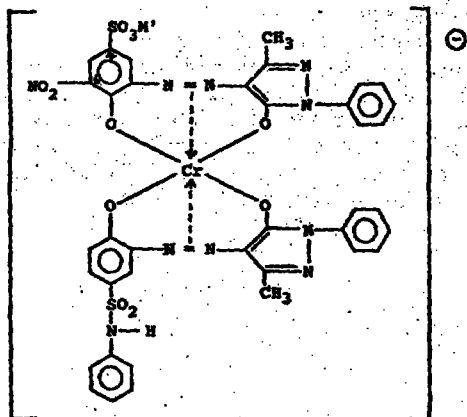
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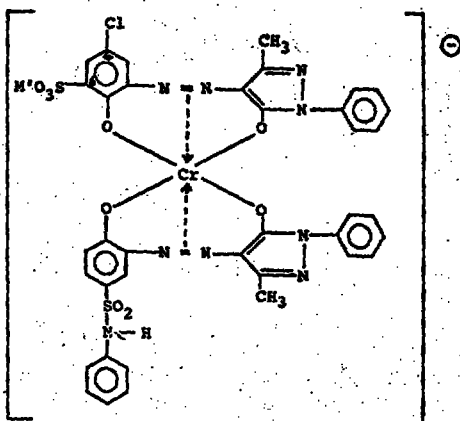
11. A compound of formula



in which each of M and M', independently, signifies a non-chromophoric cation.

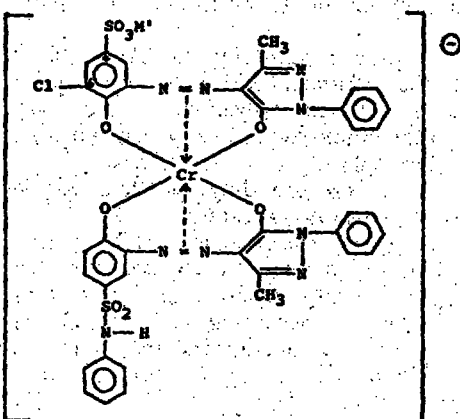
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12. A compound of formula



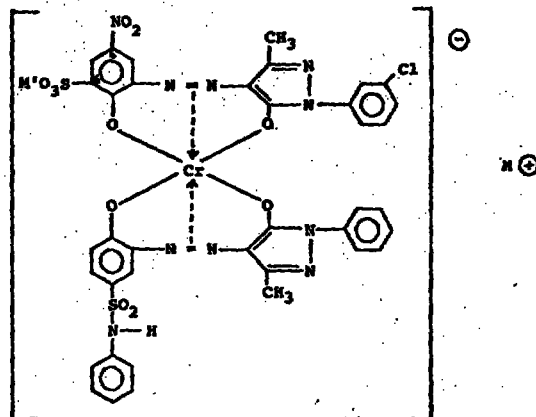
in which each of M and M', independently, signifies a non-chromophoric cation.

13. A compound of formula



in which each of M and M', independently, signifies a non-chromophoric cation.

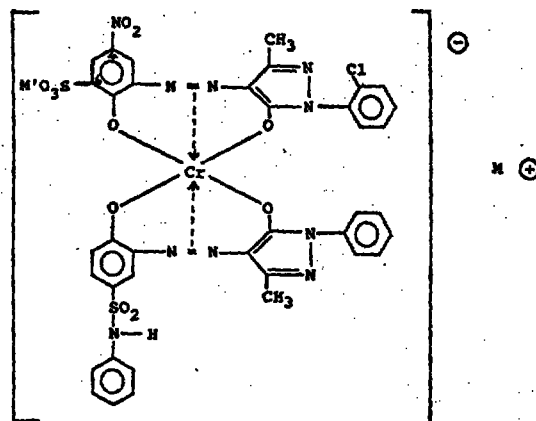
14. A compound of formula



in which each of M and M', independently, signifies a non-chromophoric cation.

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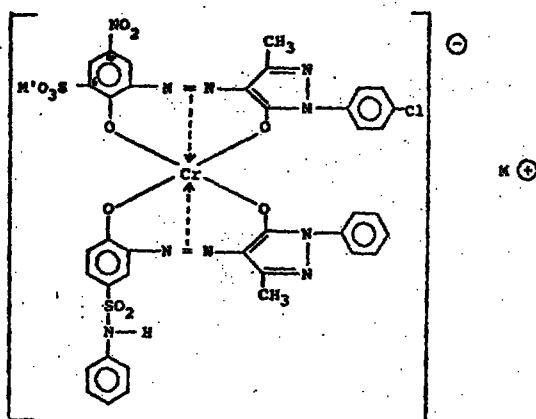
15. A compound of formula



in which each of M and M', independently, signifies a non-chromophoric cation.

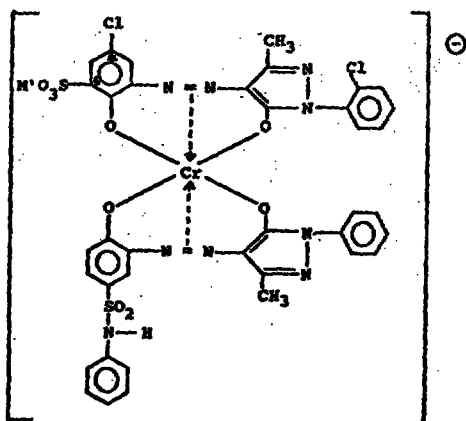
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16. A compound of formula



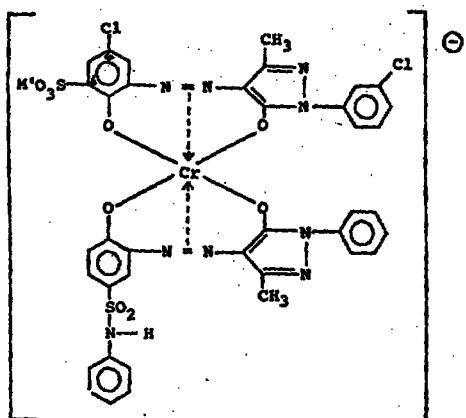
in which each of M and M', independently, signifies a non-chromophoric cation.

17. A compound of formula



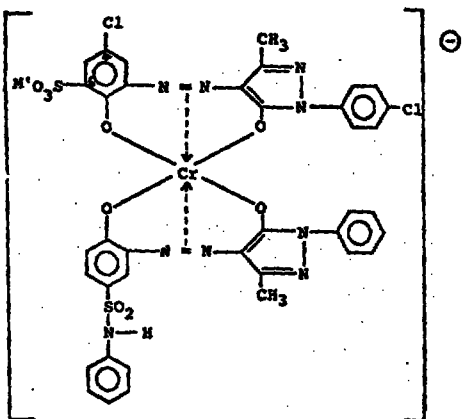
in which each of M and M', independently, signifies a non-chromophoric cation.

18. A compound of formula



in which each of M and M', independently, signifies a non-chromophoric cation.

19. A compound of formula

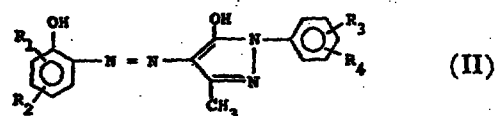


in which each of M and M', independently, signifies a non-chromophoric cation.

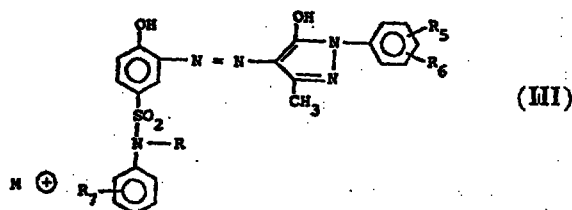
20. A compound according to any one of Claims 10 to 19, in which M and M' are the same and signify sodium.

21. A compound according to any one of Claims 11 to 19, in which M and M' are the same and signify potassium.

22. A process for the production of a compound of formula I, as defined in Claim 1, characterized by reacting the 1:1 chromium complex of the compound of formula II,



in which R₁, R₂, R₃ and R₄ are as defined in Claim 1, with a compound of formula III,



in which R₅, R₆, R₇ and R are as defined in Claim 1.

24. A process for the production of a compound of formula I, as defined in Claim 1, substantially as hereinbefore described with reference to any one of Examples 1 to 57.

25. A compound of formula I, whenever prepared by a process according to Claim 23 or 24.

26. A process for dyeing or printing natural or synthetic organic substrates, characterized by employing a compound of formula I, as defined in Claim 1, as dyeing or printing agent.

27. A process according to Claim 26, in which the substrate consists of or comprises natural or synthetic polyamides, polyurethane or basic modified polyolefins, which substrates are in loose fibre, yarn or fabric form.

28. A process according to Claim 26, in which the substrate is leather.

29. A process for dyeing metals, characterized by employing a compound of formula I, as defined in Claim 1, as dyeing agent.

30. A process according to Claim 29, in which the metal is anodized aluminium.

31. A process for dyeing or printing organic substrates, substantially as hereinbefore described with reference to Example A.

32. Dyed or printed substrates, whenever obtained by a process according to any one of Claims 26 to 31.



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B. A. YORKE & CO.,
Chartered Patent Agents,
98, The Centre,
Feltham,
Middlesex, TW13 4EP.
Agents for the Applicants.

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