986.655

PATENT SPECIFICATION

NO DRAWINGS

986.655

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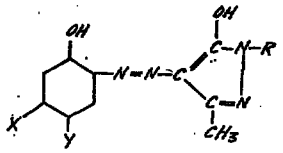
Int. Cl.:—C 09 b

COMPLETE SPECIFICATION

Chromium-containing Azo Dyestuffs and Process for their manufacture

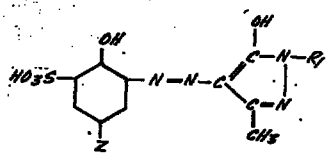
We, CIBA LIMITED, a body corporate organised according to the laws of Switzerland, of Basle, Switzerland, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention is based on the observation that valuable new chromium-containing azo dyestuffs that contain one chromium atom bound in complex union with two molecules of different monoazo dyestuffs are obtained when a metallisable monoazo dyestuff free from carboxylic acid groups and sulphonic acid groups that corresponds to the formula



(1)

in which X represents a hydrogen atom or a chlorine atom or a nitro group, Y represents a hydrogen atom or a chlorine atom or a nitro group or a methyl group, and in which X and Y are different from each other, and R represents a benzene residue that advantageously is unsubstituted or halogenated, is reacted in a molar ratio of about 1:1 with a complex chromium compound that contains one chromium atom bound in complex union with a molecule of the monoazo dyestuff of the formula



(2)

in which Z represents a chlorine atom or a nitro group and R_1 represents a benzene residue that advantageously is unsubstituted or halogenated.

More especially the present invention provides a process as formulated above, wherein X represents a hydrogen atom or a nitro group, Y represents a hydrogen atom or nitro group, Z represents a chlorine atom or a nitro group, R represents an unsubstituted phenyl residue and R_1 represents an unsubstituted phenyl residue or a chlorophenyl residue or a dichlorophenyl residue. Advantageously X represents a nitro group and Y represents a hydrogen atom or a chlorine atom. The dyestuffs obtained by the above described process are metal compounds that contain one chromium atom bound in complex union with two molecules of different monoazo dyestuffs, which correspond to the above defined formulæ.

The monoazo dyestuffs of the formula (1) used in the process of the invention can be prepared in known manner by coupling in a weakly acid to alkaline medium, in which process the diazo compounds used are, for example, those that are derived form the following amines:

4- or 5-chloro-2-amino-1-hydroxybenzene,
4-methyl-2-amino-1-hydroxybenzene,
4 - chloro - 5 - nitro - 2 - amino - 1 - hydroxybenzene and
4- or 5-nitro-2-amino-1-hydroxybenzene.

As coupling components there may be used, for example,
1-(2^1-ethyl-phenyl)-3-methyl-5-pyrazolone,
1-(4^1-bromophenyl)-3-methyl-5-pyrazolone,
1 - (2^1 - chloro - 6^1 1 methylphenyl) - 3-methyl - 5 - pyrazolone,
1 - (3^1 - nitrophenyl) - 3 - methyl - 5-pyrazolone, and especially
1-phenyl-3-methyl-5-pyrazolone,
1-(2^1-, 3-, or 4^1-chlorophenyl)-3-methyl-5-pyrazolone,
1-(2^1-, 5^1- or 3^1:4^1-dichlorophenyl)-3-methyl-5-pyrazolone,

[*Price 4s. 6d.*]

1 - (2:5¹ - dibromophenyl) - 3 - methyl - 5-pyrazolone, and
1 - (2¹:4¹:6¹ - trichlorophenyl) - 3 - methyl-5 - pyrazolone.

The monoazo ~~dyestuffs~~ of the formula (2) can likewise be prepared in known manner from 1-hydroxy-2-amino-4-chloro (or nitro)-6-sulphonic acid and one of the above-mentioned coupling components by coupling.

Its conversion into a 1:1-chromium complex can be effected by conventional known methods, for example, by reacting it in an acid medium with an excess of a salt of trivalent chromium, for example, chromium formate, chromium sulphate or chromium fluoride, at boiling temperature or, if desired or required, at a temperature above 100°C. It is generally of advantage to carry out the metallisation in known manner, for example, in aqueous solution, if necessary, in the presence of an organic solvent, for example, ethanol or formamide.

As is known, the 1:1 metal complexes of ortho:ortho¹-dihydroxymonoazo dyestuffs can be prepared not only from the ortho:ortho¹-dihydroxymonoazo dyestuffs themselves, but also from the corresponding ortho-alkoxy-ortho¹-hydroxymonoazo dyestuffs. Accordingly, for the manufacture of the chromium-containing ~~dyestuffs~~ of the formula (2) used as starting material there could be used the corresponding ortho - alkoxy - diazo compounds, especially the methoxy compound, instead of the ortho-hydroxy diazo compounds.

It is generally of advantage not to dry the starting materials used in the present process after they have been prepared and precipitated, but to use them in the form of a moist paste in the subsequent processing.

The reaction of the 1:1-chromium complex with the metal-free dyestuffs is advantageously carried out in an aqueous, neutral or weakly alkaline medium in an open or closed vessel at room temperature or at a raised temperature, for example, at a temperature between 50 and 120°C. The addition of a solvent, for example, ethanol or formamide, can assist the reaction in some cases. It is generally of advantage if the proportions of the chromium-containing 1:1 complex and the metal-free dyestuff used are as close to being equivalent proportions as possible, the molar ratio between the metal-free dyestuff and the 1:1 complex advantageously being at least 0.85:1 and at most 1:0.85; and excess of metal-containing dyestuff is generally less disadvantageous than an excess of metal-free dyestuff. The closer the ratio is to 1:1, the more advantageous is the result.

The new chromium-containing mixed complexes obtainable by the present process are suitable for dyeing and printing a very wide variety of materials, especially animal materials such as silk, leather and especially wool, but they are also suitable for dyeing and printing synthetic fibres made of polyamides, polyurethanes and polyacrylonitrile, and also fibre mixtures, for example, wool/polyamide mixtures. They are mainly suitable for dyeing from a neutral or weakly acid bath, for example, an acetic acid bath. The dyeings so obtained are uniform and possess a good fastness to washing, to milling, to decatising, to rubbing and to carbonising, as well as a surprisingly good fastness to light.

The following Example illustrates the invention. Unless otherwise stated, the parts and percentages are by weight:

Example

9.55 parts of a monoazo dyestuff, prepared from diazotised 1-hydroxy-2-amino-4-chlorobenzene-6-sulphonic acid and 1-(2¹:5¹-dichlorophenyl)-3-methyl-5-pyrazolone, in the form of a chromium complex containing 1 atom of chromium per molecule of monoazo dyestuff and 6.78 parts of a metal-free monoazo dyestuff prepared from diazotised 4-nitro-2-amino-1-hydroxy-benzene and 1-phenyl-3-methyl-5-pyrazolone are stirred in 300 parts of water at 40°C. 4.2 parts of sodium bicarbonate are added and the suspension is heated to 90 to 95°C, while stirring, in which process a clear, red solution is formed. As soon as the two dyestuffs used as starting materials are no longer detectable, the resulting homogeneous mixed complex is precipitated by the addition of sodium chloride to the reaction solution and isolated by filtration, whereupon it is washed with a dilute sodium chloride solution and dried. The new dyestuff constitutes a red-brown powder that dyes wool yarn full, orange-red tints possessing good properties of fastness when applied from a bath containing ammonium sulphate.

Instead of sodium bicarbonate, a corresponding proportion of another alkali, for example, a dilute sodium carbonate or sodium hydroxide solution, can be used.

Further homogeneous mixed complexes are obtained by reacting the 1:1-chromium complexes of the monoazo dyestuffs listed in Column I of the following Table with the metal-free monoazo dyestuffs listed in Column II by the above process. The tints obtained on wool fibres are listed in Column III.

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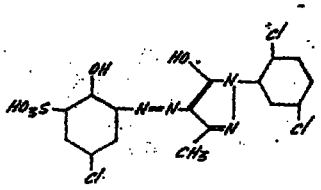
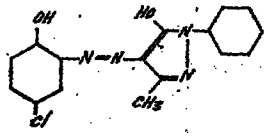
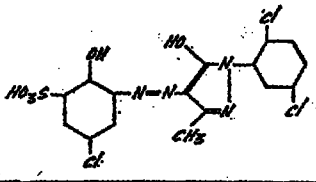
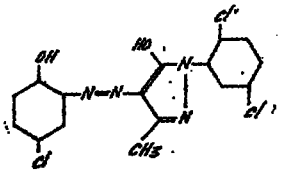
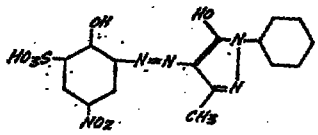
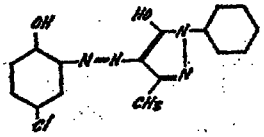
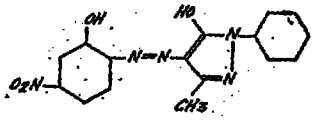
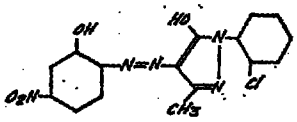
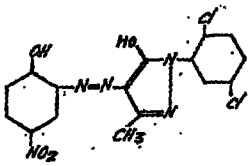
1			Red
2			Red
3			Orange
4	"		Red
5	"		Red
6	"		Orange

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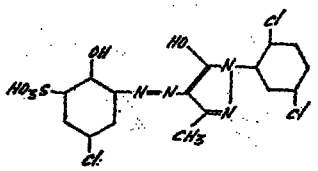
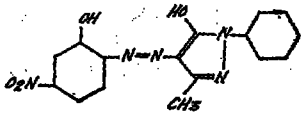
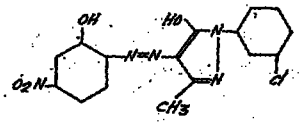
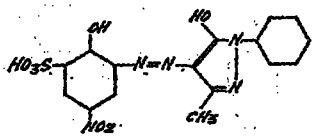
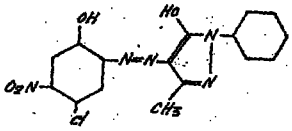
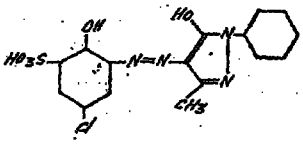
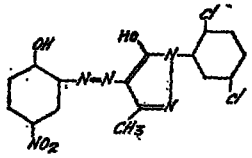
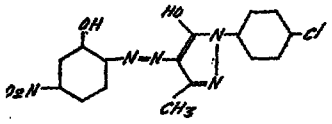
7			Bluish Red
8	〃		Bluish Red
9			Red
10			Orange-Red
11	〃		Bluish Red

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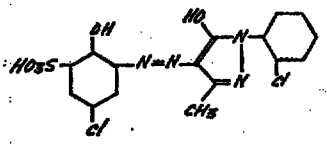
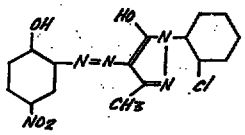
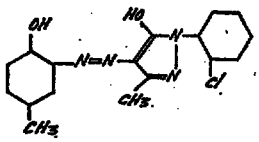
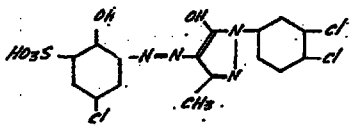
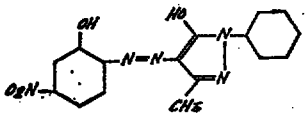
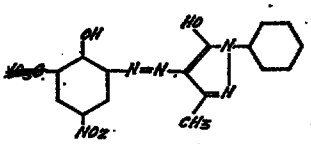
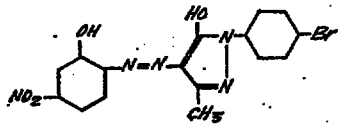
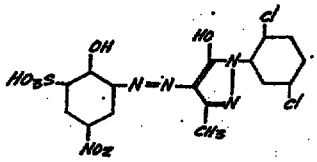
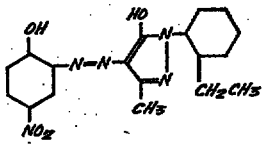
12			Orange-Red
13	"		Orange-Red
14			Bluish Red
15			Red
16			Orange

PATENT OFFICE

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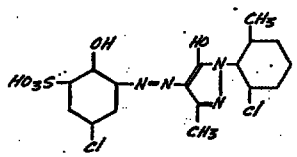
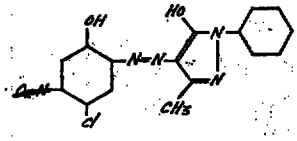
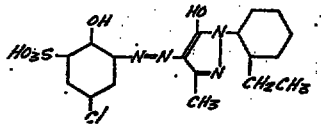
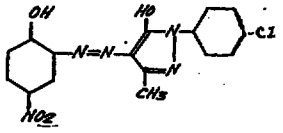
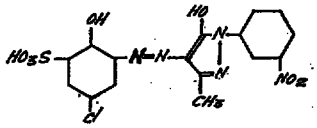
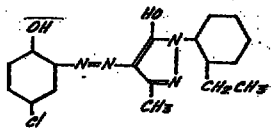
17			Bluish Red
18			Red
19			Red

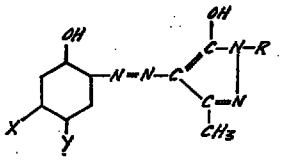
Dyeing Prescription

100 parts of woollen knitting yarn are entered at 50°C into a dyebath that contains 2 parts of the dyestuff described in the first paragraph of the preceding Example and 4 parts of ammonium sulphate. The liquor is brought to the boil in the course of 45 minutes and is kept at that temperature for a further 45 minutes. The yarn is then removed from the dyebath, thoroughly rinsed with cold water and dried.

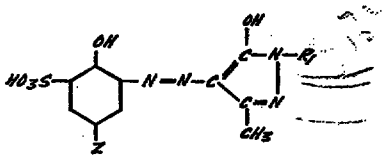
Specification No. 765,355 describes and claims metal compounds which contain one atom of chromium or cobalt bound in complex union with two molecules of different ortho-ortho[1]-dioxy-, ortho - carboxy - ortho[1]-oxy- or ortho - oxy - ortho[1] - amino - monoazo - dyestuffs, of which both are free from carboxylic acid groups other than in ortho-position to the azo linkage and from functionally converted sulphonic acid groups (that is to say, sulphonic acid ester, sulphonic acid amide and sulphone groups), and of which one contains a free sulphonic acid group and the other is free from sulphonic acid groups, the said chromium or cobalt compounds being free from substantial amounts of metal compounds which contain one atom of metal per molecule of dyestuff or one atom of metal bound in complex union to two molecules of the same dyestuff and processes for their manufacture.

WHAT WE CLAIM IS:—

1. A process for the manufacture of metal-containing azo dyestuffs that contain one chromium atom bound in complex union with two molecules of different monoazo dyestuffs, wherein a metallisable monoazo dyestuff of the formula



in which X represents a hydrogen atom or a chlorine atom or a nitro group, Y represents a hydrogen atom or a chlorine atom or a nitro group or a methyl group, and in which X and Y are different from each other, and R represents a benzene residue, is reacted in a molar ratio of about 1:1 with a complex chromium compound that contains one atom or chromium bound in complex union with a molecule of the monoazo dyestuff of the formula



in which Z represents a chlorine atom or a nitro group, and R_1 represents a benzene residue.

2. A process as claimed in claim 1, wherein the benzene residue R is unsubstituted or halogenated and the benzene residue R_1 is unsubstituted or halogenated.

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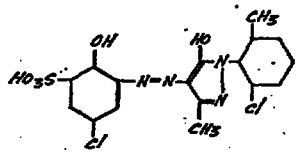
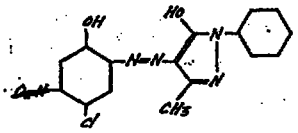
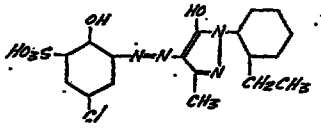
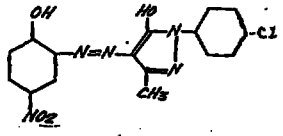
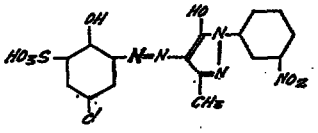
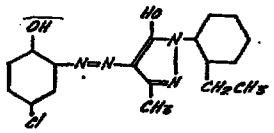
17			Bluish Red
18			Red
19			Red

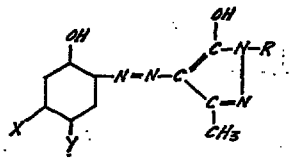
Dyeing Prescription

100 parts of woollen knitting yarn are entered at 50°C into a dyebath that contains 2 parts of the dyestuff described in the first paragraph of the preceding Example and 4 parts of ammonium sulphate. The liquor is brought to the boil in the course of 45 minutes and is kept at that temperature for a further 45 minutes. The yarn is then removed from the dyebath, thoroughly rinsed with cold water and dried.

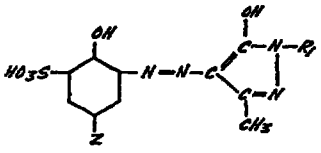
Specification No. 765,355 describes and claims metal compounds which contain one atom of chromium or cobalt bound in complex union with two molecules of different ortho-ortho¹-dioxy-, ortho - carboxy - ortho¹-oxy- or ortho - oxy - ortho¹ - amino - monoazo - dyestuffs, of which both are free from carboxylic acid groups other than in ortho-position to the azo linkage and from functionally converted sulphonic acid groups (that is to say, sulphonic acid ester, sulphonic acid amide and sulphone groups), and of which one contains a free sulphonic acid group and the other is free from sulphonic acid groups, the said chromium or cobalt compounds being free from substantial amounts of metal compounds which contain one atom of metal per molecule of dyestuff or one atom of metal bound in complex union to two molecules of the same dyestuff and processes for their manufacture.

WHAT WE CLAIM IS:—

1. A process for the manufacture of metal-containing azo dyestuffs that contain one chromium atom bound in complex union with two molecules of different monoazo dyestuffs, wherein a metallisable monoazo dyestuff of the formula



in which X represents a hydrogen atom or a chlorine atom or a nitro group, Y represents a hydrogen atom or a chlorine atom or a nitro group or a methyl group, and in which X and Y are different from each other, and R represents a benzene residue, is reacted in a molar ratio of about 1:1 with a complex chromium compound that contains one atom or chromium bound in complex union with a molecule of the monoazo dyestuff of the formula



in which Z represents a chlorine atom or a nitro group, and R_1 represents a benzene residue.

2. A process as claimed in claim 1, wherein the benzene residue R is unsubstituted or halogenated and the benzene residue R_1 is unsubstituted or halogenated.

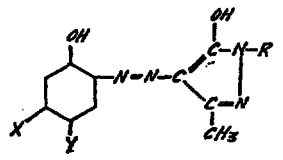
3. A process as claimed in claim 1 or claim 2, wherein X represents a hydrogen atom or a nitro group, Y represents a hydrogen atom or nitro group, Z represents a chlorine atom or a nitro group, R represents an unsubstituted phenyl residue and R_1 represents an unsubstituted phenyl residue or a chlorophenyl residue or a dichlorophenyl residue.

4. A process as claimed in claim 1 or claim 2, wherein X represents a nitro group and Y represents a hydrogen atom or a chlorine atom.

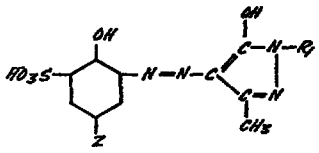
5. A process as claimed in any one of claims 1 to 4, wherein the reaction is carried out in aqueous medium, advantageously at a raised temperature, for example, at a temperature within the range 50 to 120°C.

6. A process as claimed in claim 1, conducted substantially as described in the Example herein.

7. Metal compounds that contain one chromium atom bound in complex union with two molecules of different monoazo dyestuffs, one of which corresponds to the formula



and the other corresponds to the formula



in which formulæ X represents a hydrogen atom or a chlorine atom or a nitro group, Y represents a hydrogen atom or a chlorine atom or a nitro group or a methyl group, and in which X and Y are different from each other, R and R_1 each represents a benzene residue and Z represents a chlorine atom or a nitro group.

8. Complex chromium compounds as claimed in claim 7, wherein R represents an unsubstituted or halogenated benzene residue and R_1 represents an unsubstituted or halogenated benzene residue.

9. Complex chromium compounds as claimed in claim 7 or claim 8, wherein X represents a hydrogen atom or a nitro group, Y represents a hydrogen atom or a nitro group, Z represents a chlorine atom or a nitro group, R represents an unsubstituted phenyl residue and R_1 represents an unsubstituted phenyl residue or a chlorophenyl residue or a dichlorophenyl residue.

10. Complex chromium compounds as claimed in claim 7 or claim 8, wherein X represents a nitro group and Y represents a hydrogen atom or a chlorine atom.

11. Any one of the complex chromium compounds as claimed in claim 1 and which is described in the Example and Table herein.

12. A dyeing or printing process in which a complex chromium compound as claimed in any one of claims 7 to 11 is used.

13. A dyeing process as claimed in claim 12, wherein nitrogen containing fibres, especially wool, silk, leather or polyamide or polyurethane fibres are dyed in a neutral or weakly acid bath with the complex chromium compound.

14. Nitrogenous textile material dyed or printed by a process claimed in Claim 12 or 13.

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