1,040,557

PATENT SPECIFICATION

NO DRAWINGS

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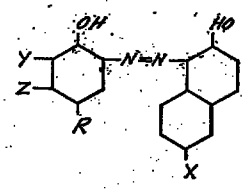
Int. Cl.:—C 09 b 45/48

COMPLETE SPECIFICATION

Azo Dye 2:1-Chromium Complex Compounds containing different Azo Dyestuff Residues and process for their manufacture

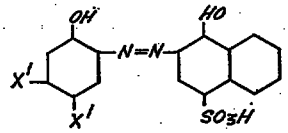
We, CIBA LIMITED, a body corporate organized according to the laws of Switzerland, of Basle, Switzerland, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention is based on the observation that valuable new-chromium-containing azo dyestuffs in which 1 chromium atom is bound in complex union to 2 molecules of different monoazo dyestuffs are obtained when a monoazo dyestuff of the formula



(1)

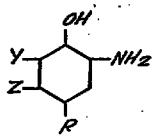
in which the symbols R, Y and Z each represent a hydrogen or chlorine atom or a nitro group, but in which at most R and Y may simultaneously represent a nitro group, Y may also represent an acylamino group containing at most five carbon atoms and R may also represent an alkyl or alkoxy group containing at most five carbon atoms, and X represents a hydrogen or bromine atom or an alkoxy group containing at most five carbon atoms, is reacted in a molar ratio of about 1:1 with a complex chromium compound which contains one atom of chromium bound in complex union to one molecule of a ~~monaze~~ monoazo dyestuff of the formula



(2)

in which one X′ represents a hydrogen atom and the other X′ represents a nitro group.

The monoazo dyestuffs of the formula (1) required in the present process may be obtained according to known methods by coupling 6-bromo- or 6-methoxy-2-hydroxynaphthalene, but more especially β-naphthol with ortho-hydroxy-diazo compounds obtained from amines of the formula



in which Y, Z and R have the meanings ascribed to them in formula (1), in a slightly acid to slightly alkaline medium.

Examples of amines of the kind defined are as follows:

2-amino-1-hydroxybenzene,
4-methyl- or 4-methoxy-2-amino-1-hydroxybenzene,
5-chloro-2-amino-1-hydroxybenzene,
4:6-dichloro-2-amino-1-hydroxybenzene,
5:4:6-trichloro-2-amino-1-hydroxybenzene,
4-chloro-5- or -6-nitro-2-amino-1-hydroxybenzene,
6-nitro-4-methyl-2-amino-1-hydroxybenzene,

4 - nitro - 6 - methylsulphonylamino - 2-amino-1-hydroxybenzene,
5 - chloro - 4 - methoxy - 2 - amino - 1-hydroxybenzene,
4 - nitro - 6 - acetylamino - 2 - amino - 1-hydroxybenzene,
4:6 - dinitro - 2 - amino - 1 - hydroxybenzene and especially
4 - or 5 - nitro - 2 - amino - 1 - hydroxybenzene and
4-chloro-2-amino-1-hydroxybenzene.

The monoazo dyestuffs of the formula (2) can likewise be prepared by known methods by coupling 1-hydroxynaphthalene-4-sulphonic acid with diazo compounds prepared from 4-nitro-2-amino-phenol, or 5-nitro-2-amino-phenol. Their conversion into 1:1 chromium complexes is effected by customary methods, for example, by reacting them in an acid medium at boiling temperature or, if necessary, at a temperature above 100°C, with an excess of a salt of trivalent chromium, for example, chromium formate, chromium sulphate or chromium fluoride. It is generally advantageous to carry out the metallization process in known manner in an aqueous medium, if necessary, in the presence of an organic solvent, for example, alcohol or formamide.

It is known that the 1:1 metal complexes of ortho:ortho'-dihydroxymonoazo dyestuffs can be prepared not only from the ortho:ortho-dihydroxymonoazo dyestuffs themselves, but also from the corresponding ortho-alkoxy-ortho'-hydroxymonoazo dyestuffs. Accordingly, preparation of the chromium-containing starting dyestuffs used in the process of the invention can be effected with the monoazo dyestuffs obtained from the corresponding ortho-alkoxydiazo compound, especially the methoxy compound, instead of the ortho-hydroxydiazo compound as above described.

In general, it has been found advantageous not to dry the starting dyestuffs used in the present process after their preparation and precipitation, but to use them in the form of a moist paste in the subsequent treatments.

The reaction between the 1:1 chromium complexes and the metal-free dyestuffs is advantageously carried out in an aqueous, neutral to slightly alkaline medium in an open or closed vessel at room temperature or at an elevated temperature, for example at a temperature between 50 and 120°C. In some cases, the addition of a solvent, for example, alcohol or formamide, assists the reaction. It is generally of advantage if the amounts of chromium-containing 1:1 complex and metal-free dyestuff used in the reaction are as close to equivalent amounts as possible, the molecular ratio between metal-free deystuff and 1:1 complex advantageously being between 0.85:1 and 1:0.85; an execess of metal-containing dyestuff is generally less deleterious than an excess of metal-free dyestuff. As a rule, the closer the ratio is to 1:1, the better are the results.

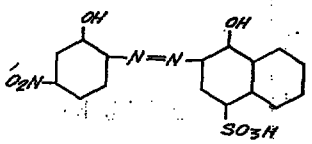
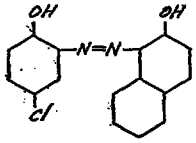
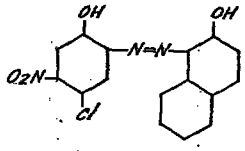
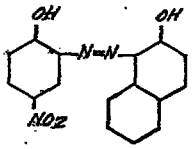
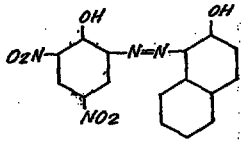
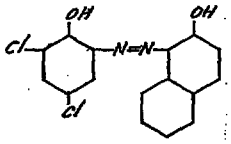
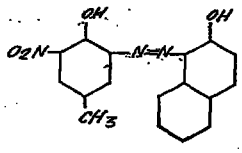
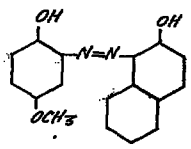
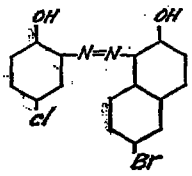
The new chromium-containing mixed complexes obtainable by the process described above are suitable for dyeing and printing a very wide variety of materials. In particular, they are suitable for dyeing animal substances, i.e. nitrogen-containing fibres such as silk, leather and especially wool, but they are also suitable for dyeing and printing synthetic fibres made from polyamides, polyurethanes and polyacrylonitrile. Above all, they are suitable for application from a slightly alkaline, neutral or slightly acid bath, for example, from a bath containing acetic acid. The dyeings thus obtained are level and display a good fastness to light, to washing, to milling, to decatizing and to carbonizing. They are also distinguished by their attractive appearance in artificial light.

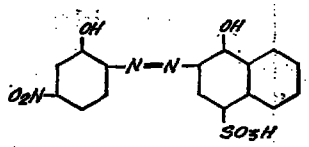
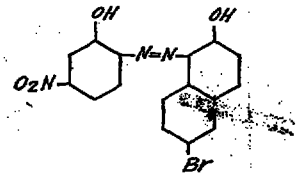
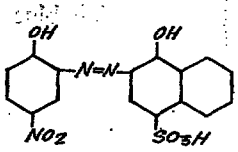
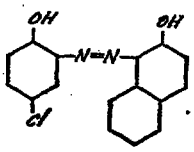
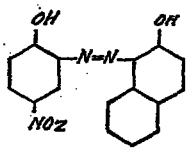
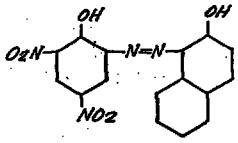
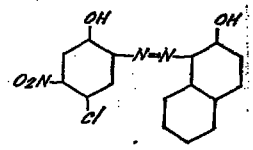
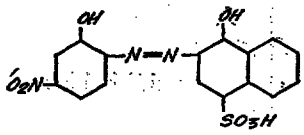
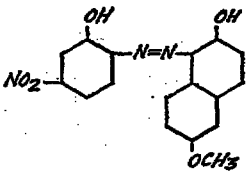
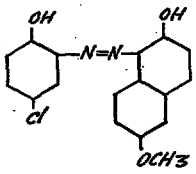
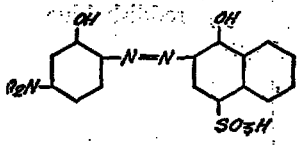
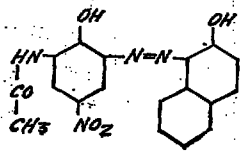
The following Example illustrates the invention. Unless otherwise stated, the parts and percentages are by weight.

EXAMPLE

44.1 Parts of the 1:1 chromium complex of a dyestuff prepared from diazotized 5-nitro - 2 - amino - 1 - hydroxybenzene and 1-hydroxynaphthalene-4-sulphonic acid and 30.9 parts of a dyestuff prepared from diazotized 5-nitro-2-amino-1-hydroxybenzene and 2-hydroxynaphthalene were stirred in 5,000 parts of hot water and the mixture then neutralized. 6.0 Parts of sodium hydroxide were added and the mixture stirred at 95 to 98°C until the two starting dyestuffs had practically disappeared. The 1:2 complex thus formed was precipitated from the blue-black solution by the addition of sodium chloride, isolated by filtration and dried. It was a blue-black powder that dissolved in water to give a blue solution and in concentrated sulphuric acid to give a violet solution. It dyed wool dark blue tints possessing good properties of fastness when applied from a silghtly acid bath.

Further chromium - containing dyestuffs (1:2 complexes) are listed in the following Table. They were obtained by reacting in a molar ratio of 1:1 the chromium-free dyestuffs listed in Column II with the 1:1 chromium-complex compounds of the corresponding monoazo dyestuffs listed in Column I. The tints obtained on wool with the corresponding dyestuffs are listed in Column III.

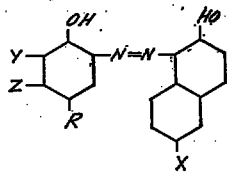
I	II	III
		blue violet
〃		dull blue
〃		reddish grey
〃		grey
〃		reddish blue
〃		reddish blue
〃		blue
〃		reddish blue

I	II	III
		reddish blue
		red violet
〃		brown violet
〃		brown violet
〃		red violet
		blue-grey
〃		reddish blue
		reddish black

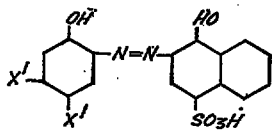
* C L M S *

WHAT WE CLAIM IS:—

1. Metal compounds containing one chromium atom bound in complex union to two molecules of different monoazo dyestuffs, one of which corresponds to the formula

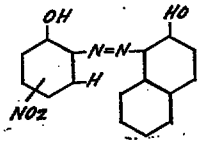


in which the symbols R, Y and Z each represents a hydrogen or chlorine atom or a nitro group, but in which at most R and Y may simultaneously represent a nitro group, Y may also represent an acylamino group containing at most five carbon atoms and R may also represent an alkyl or alkoxy group containing at most five carbon atoms and X represents a hydrogen or bromine atom or an alkoxy group containing at most five carbon atoms, and the other corresponds to the formula



in which one X′ represents a hydrogen atom and the other X′ represents a nitro group.

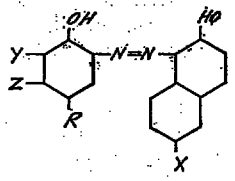
2. Complex chromium compounds as claimed in claim 1 that contain a dyestuff of the formula



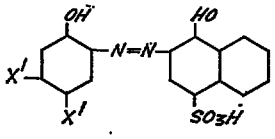
3. Any one of the complex metal compounds as claimed in claim 1 obtained as described in the Example and with reference to the Table therein.

4. Complex chromium compounds as claimed in claim 1 obtained from any of the monoazo azo dyes described and specified herein.

5. A process for the manufacture of metal-containing azo dyestuffs in which one atom of chromium is bound in complex union to two molecules of different monoazo dyestuffs, wherein a monoazo dyestuff of the formula



in which the symbols R, Y and Z each represent a hydrogen or chlorine atom or a nitro group, but in which at most R and Y may simultaneously represent a nitro group, Y may also represent an acylamino group containing at most five carbon atoms and R may also represent an alkyl or alkoxy group containing at most five carbon atoms, and X represents a hydrogen or bromine atom or an alkoxy group containing at most five carbon atoms, is reacted in a molar ratio of about 1:1 with a complex chromium compound which contains one atom of chromium bound in complex union to a molecule of a monoazo dyestuff of the formula



in which one X′ represents a hydrogen atom and the other X′ represents a nitro group.

6. A process as claimed in claim 5, wherein a monoazo dyestuff prepared from a diazotized 4,5- or 6-nitro-2-aminophenol is used as metal-free starting material.

7. A process as claimed in claim 5 or 6, wherein the reaction is carried out in an aqueous medium.

8. A process as claimed in claim 7 which is carried out at an elevated temperature.

9. A process as claimed in claim 7 or 8 which is carried out at a temperature between 50° and 120°C.

10. A process as claimed in any one of claims 5 to 9, wherein the amounts of chromium-containing 1:1 complex and metal-free dyestuff are used in a molecular ratio of between 0.85:1 and 1:0.85.

11. A process for the manufacture of chromium-containing azo dyestuffs as claimed in claim 1 conducted substantially as described in the Example and with reference to the Table herein.

12. A dyeing or printing process wherein a dyestuff claimed in any one of claims 1 to 4 is used.

* C L M S *

13. A dyeing process as claimed in claim 12, wherein nitrogen-containing fibres are dyed in a slightly alkaline, neutral or slightly acid bath.

14. A process as claimed in claim 13, wherein materials made of or containing wool, silk, leather, polyamide, polyurethane or polyacrylonitrile are dyed.

15. Material dyed or printed by a process claimed in any one of claims 12 to 14.

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