1,001,717

PATENT SPECIFICATION

NO DRAWINGS

1,001,717

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Application made in Switzerland (No. 11875) on Oct. 10, 1962.
Application made in Switzerland (No. 10927) on Sept. 4, 1963.
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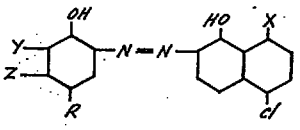
Index at acceptance:—C4 P(8A1B, 8B1, 8C3)
Int. Cl.:—C 09 b

COMPLETE SPECIFICATION

Chromium-Containing Azo Dyestuffs and process for their manufacture

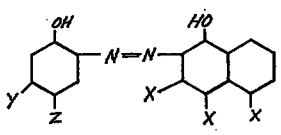
We, CIBA LIMITED, a body corporate organised according to the laws of Switzerland of Basle, Switzerland, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention is based on the observation that valuable new chromium-containing azo dyestuffs that contain one atom of chromium bound in complex union with two molecules of different monoazo dyestuffs are obtained when a monoazo dyestuff of the formula



(1)

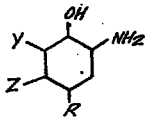
in which R, Y and Z each represents a hydrogen atom or a chlorine atom or a nitro group, but at most R and Y simultaneously represent a nitro group, and R may also represent a low-molecular alkyl or alkoxy group containing up to 5 carbon atoms, and X represents a hydrogen atom or a chlorine atom, is 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 a monoazo dyestuff of the formula



(2)

in which one X represents a sulphonic acid group and the other two X's represent hydrogen atoms, Y represents a hydrogen atom or a nitro group, and Z represents a hydrogen atom or a chlorine atom or a nitro group or a low-molecular alkyl or alkoxy group containing up to 5 carbon atoms, and in which Y and Z must be different from each other.

The monoazo dyestuffs of the formula (1) used in the present process can be prepared in known manner by coupling 5-chloro- or 5 : 8-dichloro-1-hydroxynaphthalene with orthohydroxy-diazo compounds prepared from amines of the formula



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

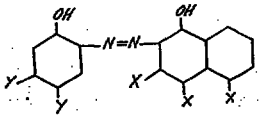
As examples of such amines there may be mentioned
2-amino-1-hydroxybenzene,
4 - methyl - or 4 - methoxy - 2 - amino - 1 - hydroxybenzene,
5-chloro-2-amino-1-hydroxybenzene,
4:6-dichloro-2-amino-1-hydroxybenzene
4 - chloro - 5 - or - 6 - nitro - 2 - amino - 1-hydroxybenzene,
6-nitro-4-methyl-2-amino-1-hydroxybenzene,
5 - chloro - 4 - methoxy - 2 - amino - 1 - hydroxybenzene,
4-nitro-6-chloro-2-amino-1-hydroxybenzene,
4:6 - dinitro - 2 - amino - 1 - hydroxybenzene especially
4- or 5-nitro-2-amino-1-hydroxybenzene and 4-chloro-2-amino-1-hydroxybenzene.

The monazo dyestuffs of formula (1) prepared from diazotised nitro- or chloro- aminophenols are of particular interest.

[Price 4s. 6d.]

The monazo dyestuffs of the formula (2) can likewise be prepared in known manner by coupling 1 - hydroxynaphthalene-3-, -4- or -5-sulphonic acid with diazo compounds prepared, for example, from 4-chloro-, 4-methyl-, 4-methoxy- or 4-nitro- 2-aminophenol, 5-nitro-2-aminophenol or 4-chloro-, 4-methyl- or 4-methoxy-5-nitro-2-aminophenol. Their conversion into 1:1-chromium complexes may be performed by conventional known 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 of advantage to carry out the metallisation in known manner in an aqueous medium, if necessary, in the presence of an organic solvent, for example, ethanol or formamide.

Of special interest are chromium-containing monoazo dyestuffs of the formula



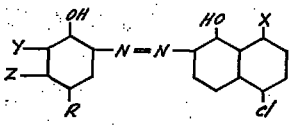
in which one Y represents a hydrogen atom and the other Y represents a nitro group, one X represents a sulphonic acid group and the other two X's represent hydrogen atoms.

As is known, the 1:1-metal complexes of ortho:ortho¹-dihydroxy-monoazo dyestuffs can be prepared not only from the ortho:ortho¹-dihydroxy-monoazo dyestuffs themselves, but also from the corresponding ortho-alkoxy-ortho¹-hydroxy-monoazo dyestuffs. Accordingly, for the preparation of the chromium-containing dyestuffs used as starting materials in the present process there can be used, instead of the ortho-hydroxydiazo compound of the formula (2), the corresponding ortho-alkoxy-diazo compound, especially the methoxy compound.

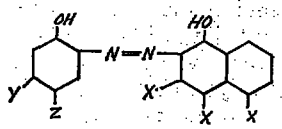
In the present process it is generally of advantage not to dry the starting dyestuffs after their preparation and precipitation, but to use them in the form of a moist paste for further processing.

The reaction of the 1:1-chromium complexes with the metal-free dyestuffs is advantageously carried out in a neutral to to slightly alkaline aqueous 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. The addition of solvents, for example, ethanol or formamide, can assist the reaction in some cases. It is generally of advantage to react equivalent proportions of chromium-containing 1:1-complexes and metal-free dyestuffs, the molar ratio between metal-free dyestuffs and 1:1-complex advantageously being at least 0.85:1 and 1:0.85; an excess of metal-containing dyestuff is generally less disadvantageous than an excess of metal-free dyestuff. The closer this ratio is to 1:1, the more advantageous is the result.

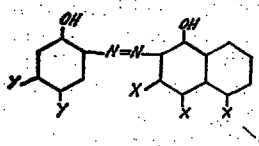
Metal compounds that contain one atom of chromium bound in complex union with two molecules of different monoazo dyestuffs, one of which corresponds to the formula



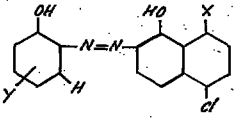
in which R, Y and Z each represents a hydrogen atom or a chlorine atom or a nitro group, but at most R and Y simultaneously represent a nitro group, and R may also represent a low-molecular alkyl or alkoxy group containing up to 5 carbon atoms, and X represents a hydrogen atom or a chlorine atom, and the other corresponds to the formula



in which one X represents a sulphonic acid group and the other two X's represent hydrogen atoms, Y represents a hydrogen atom or a nitro group, and Z represents a hydrogen atom or a chlorine atom or a nitro group or a low-molecular alkoxy or alkyl group containing up to 5 carbon atoms, and in which Y and Z must be different from each other are of special value and in particular complex chromium compounds that contain a dyestuff of the formula



in which one Y represents a hydrogen atom and the other Y represents a nitro group, one X represents a sulphonic acid group and the other two X's represent hydrogen atoms and complex chromium compounds which contain a dyestuff of the formula



in which X represents a hydrogen atom or a chlorine atom and Y represents a chlorine atom or a nitro group are preferred.

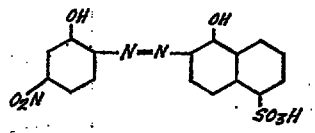
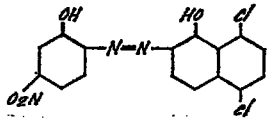
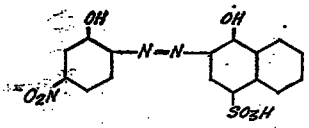
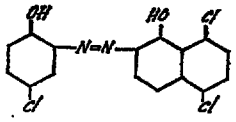
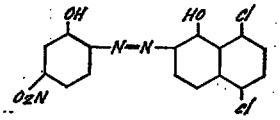
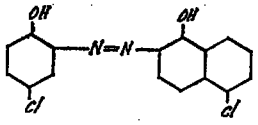
The new chromium-containing mixed complexes obtainable by the present process are suitable for dyeing and printing a very wide variety of materials, but more especially for dyeing animal materials for example, silk, leather and more especially wool. They are also suitable for dyeing and printing synthetic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

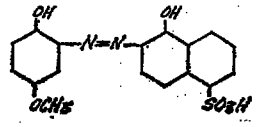
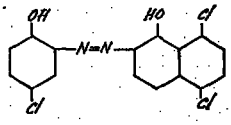
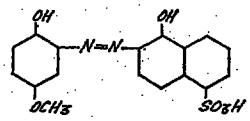
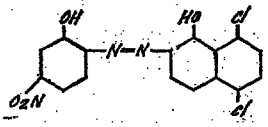
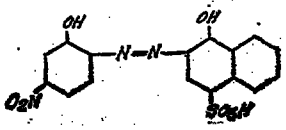
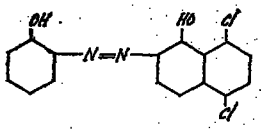
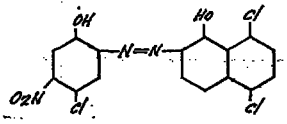
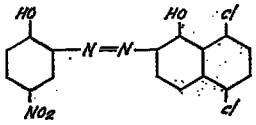
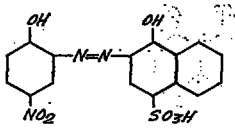
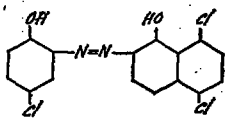
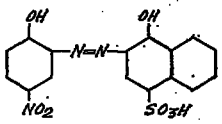
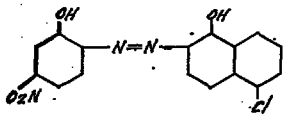
The following Example illustrates the invention. Unless otherwise stated, the parts and percentages are by weight.

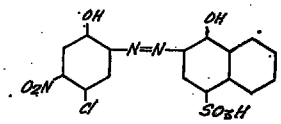
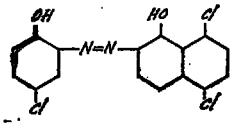
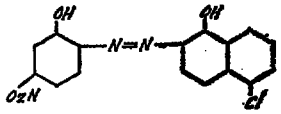
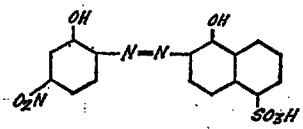
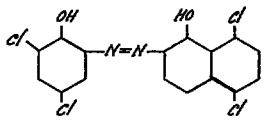
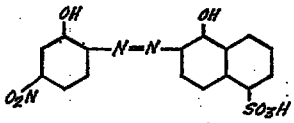
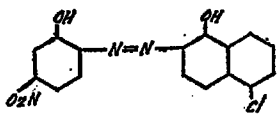
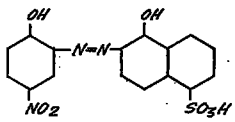
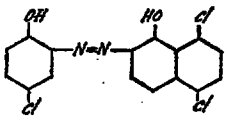
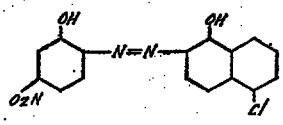
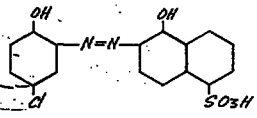
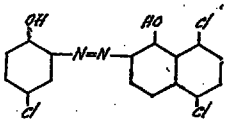
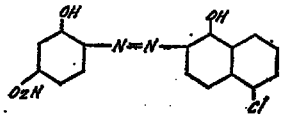
EXAMPLE

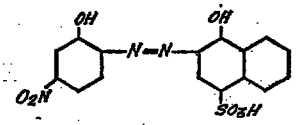
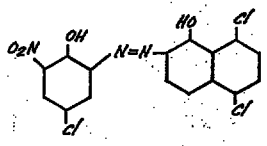
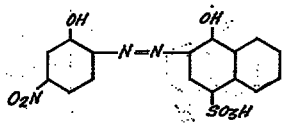
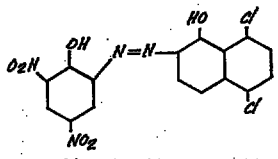
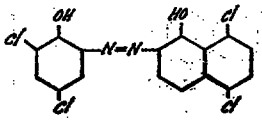
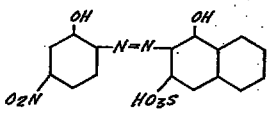
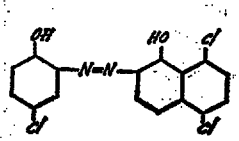
44.1 parts of the 1:1-chromium complex of a dyestuff prepared from diazotised 5-nitro-2-amino-1-hydroxybenzene and 1-hydroxy napthalene-5-sulphonic acid and 36.75 parts of a dyestuff prepared from diazotised 4-chloro-2-amino-1-hydroxybenzene and 5:8-dichloro-1-hydroxynaphthalene are stirred in 5000 parts of hot water and the mixture is then neutralised. 6.0 parts of sodium hydroxide are added, and the mixture is stirred at 95 to 98°C until both starting dyestuffs have practically disappeared. The dyestuff is then precipitated out of the resulting blue-black solution by the addition of sodium chloride, filtered off and dried. It constitutes a blue-black powder that dissolves in water to give a blue solution and in concentrated sulphuric acid to give a violet-grey solution. It dyes wool dark blue tints possessing good properties of fastness when applied from a weakly acid bath.

In the following Table there are listed a number of other chromium-containing dyestuffs (1:2-complexes) that are obtained when the chromium-free dyestuffs listed in Column II are reacted with the 1:1-chromium complex compounds of the corresponding monoazo dyestuffs listed in Column I in a molar ratio of 1:1. Column III indicates the tints obtained on wool with the dyestuffs listed.

I	II	III
		dark blue
		dark blue
"		dark blue
"		dark blue

I	II	III
		reddish blue
		blue
		blue
"		blue
"		bluish grey
		dull violet
		grey-violet

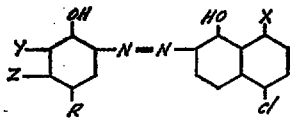
I	II	III
		reddish blue
"		dark blue
		blue
		blue
		grey-violet
"		reddish grey
		blue-violet
"		blue-violet

I	II	III
		blue-grey
		grey
"		dark-blue
		blue

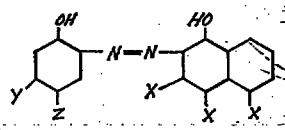
Specification No. 765,355 describes and claims metal compounds which contain one atom of chromium or cobalt bound in complex union with two molecules of different ortho-ortho[1]-dioxy-, ortho-carboxy-ortho[1]-oxy- or ortho-oxy-ortho[1]-amino-monoazo-dyestuffs, of which both are free from carboxylic acid 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.

WHAT WE CLAIM IS:—

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

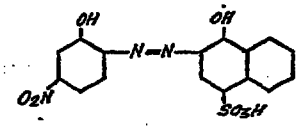
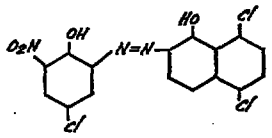
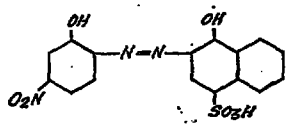
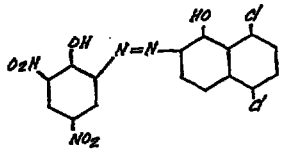
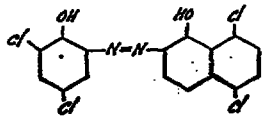
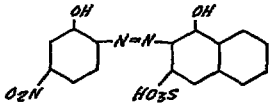
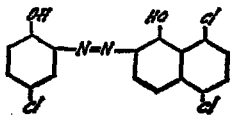


in which R, Y and Z each represents a hydrogen atom or a chlorine atom or a nitro group, but at most R and Y simultaneously represent a nitro group, and R may also represent a low molecular alkyl or alkoxy group containing up to 5 carbon atoms, and X represents a hydrogen atom or a chlorine atom, is 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 a monoazo dyestuff of the formula



in which one X represents a sulphonic acid group and the other two X's represent hydrogen atoms, Y represents a hydrogen atom or a nitro group and Z represents a hydrogen atom or a chlorine atom or a nitro group or a low-molecular alkyl or alkoxy group containing up to 5 carbon atoms, and in which Y and Z must be different from each other.

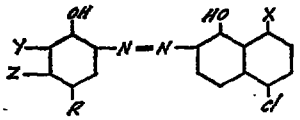
2. A process as claimed in claim 1, wherein the monoazo dyestuff prepared from a diazotised nitro- or chloro-amino-phenol is used as metal-free starting material.

I	II	III
		blue-grey
		grey
"		dark-blue
		blue

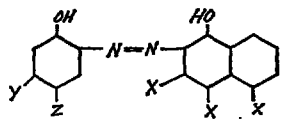
Specification No. 765,355 describes and claims metal compounds which contain one atom of chromium or cobalt bound in complex union with two molecules of different ortho-ortho¹-dioxy-, ortho-carboxy-ortho¹-oxy- or ortho-oxy-ortho¹-amino-monoazo-dyestuffs, of which both are free from carboxylic acid groups 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.

WHAT WE CLAIM IS:—

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



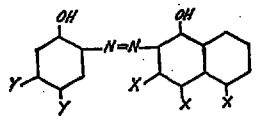
in which R, Y and Z each represents a hydrogen atom or a chlorine atom or a nitro group, but at most R and Y simultaneously represent a nitro group, and R may also represent a low molecular alkyl or alkoxy group containing up to 5 carbon atoms, and X represents a hydrogen atom or a chlorine atom, is 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 a monoazo dyestuff of the formula



in which one X represents a sulphonic acid group and the other two X's represent hydrogen atoms, Y represents a hydrogen atom or a nitro group and Z represents a hydrogen atom or a chlorine atom or a nitro group or a low-molecular alkyl or alkoxy group containing up to 5 carbon atoms, and in which Y and Z must be different from each other.

2. A process as claimed in claim 1, wherein the monoazo dyestuff prepared from a diazotised nitro- or chloro-amino-phenol is used as metal-free starting material.

3. A process as claimed in claim 1 or claim 2, wherein a chromium-containing monoazo dyestuff of the formula



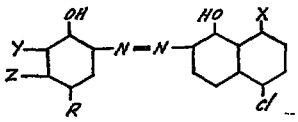
in which one Y represents a hydrogen atom and the other Y represents a nitro group, one X represents a sulphonic acid group and the other two X's represent hydrogen atoms, is used as starting material.

4. A process as claimed in any one of claims 1 to 3, wherein the reaction is carried out in aqueous medium.

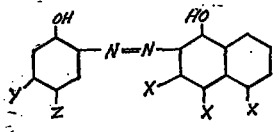
5. A process as claimed in any one of claims 1 to 4, wherein the reaction is carried out at a temperature in the range of 50 to 120°C.

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

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

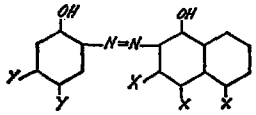


in which R, Y and Z each represents a hydrogen atom or a chlorine atom or a nitro group, but at most R and Y simultaneously represent a nitro group, and R may also represent a low-molecular alkyl or alkoxy group containing up to 5 carbon atoms, and X represents a hydrogen atom or a chlorine atom, and the other corresponds to the formula



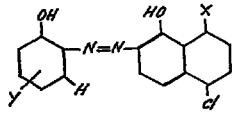
in which one X represents a sulphonic acid group and the other two X's represent hydrogen atoms, Y represents a hydrogen atom or a nitro group, and Z represents a hydrogen atom or a chlorine atom or a nitro group or a low-molecular alkoxy or alkyl group containing up to 5 carbon atoms, and in which Y and Z must be different from each other.

8. Complex chromium compounds as claimed in claim 7, that contain a dyestuff of the formula



in which one Y represents a hydrogen atom and the other Y represents a nitro group, one X represents a sulphonic acid group and the other two X's represent hydrogen atoms.

9. Complex chromium compounds as claimed in claim 7 or claim 8, which contain a dyestuff of the formula



in which X represents a hydrogen atom or a chlorine atom and Y represents a chlorine atom or a nitro group.

10. Any one of the complex chromium compounds as claimed in claim 7, and which is described in the Example and Table herein.

11. A dyeing or printing process in which there is used a complex chromium compound as claimed in any one of claims 7 to 10.

12. A dyeing process as claimed in claim 11, wherein fibres containing nitrogen, especially wool, silk, leather or polyamide or polyurethane fibres are dyed with the complex chromium compounds in a weakly alkaline, neutral or weakly acid bath.

13. Nitrogenous textile material which has been dyed or printed by the process claimed in claim 11 or claim 12.

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