1001840

PATENT SPECIFICATION

NO DRAWINGS

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Int. Cl.:—C 09 b

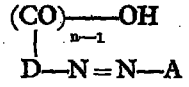
COMPLETE SPECIFICATION

Azo Dyestuffs containing Chromium 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:—

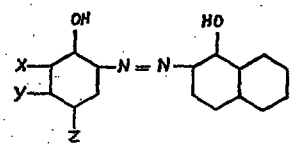
This invention is based on the observation that valuable new chromium-containing azo dyestuffs that contain one chromium atom bound in complex union with two molecules of different monoazo dyestuffs can be obtained when a metallizable monoazo dyestuff that contains a single sulphonic acid group and that corresponds to the formula

(1)



in which D represents the residue of a diazo component bound to the azo bridge in a position vicinal to the —(CO)$_{n-1}$—OH group, preferably a diazo component of the benzene series; A represents the residue of a coupling component which is bound to the azo bridge in a position vicinal to an enolized or enolizable keto group or an amino or hydroxyl group, and n represents 1 or 2, 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 one molecule of a monoazo dyestuff of the formula

(2)



in which one of the symbols, X, Y and Z represents a hydrogen atom and each of the others represents a hydrogen atom or a halogen atom or a nitro group or an alkyl or alkoxy group having 1 to 4 carbon atoms.

The monoazo dyestuffs of formula (1) used in the present process can be obtained in known manner by coupling ortho-carboxydiazo compounds or especially ortho-hydroxydiazo compounds, preferably those of the benzene series, in an acid to alkaline medium with coupling components that couple in a position vicinal to an enolized or enolizable keto group or in a position vicinal to an amino or hydroxyl group. As is evident from the foregoing, the components should contain a single sulphonic acid group. They may also contain a functionally modified sulphonic acid group, that is to say, for example, a sulphonic acid amide group or a sulphonic acid ester group. However, it is generally of advantage to select those components that yield dyestuffs that do not contain any hydroxyl groups in addition to those vicinal to the azo group and that are capable of forming a complex or are part of a complex. In view of these conditions, the components used in the preparation of the monoazo dyestuffs of the formula (1) are, for example, as follows:

The diazo compounds used are those which are derived from ortho-carboxyamines of the benzene series and especially from ortho-hydroxyamines of the benzene series which, in addition to the carboxyl or hydroxyl group and the diazotized amino group, contain further substituents such as nitro groups, halogen atoms (for example, chlorine), alkyl groups (for example, methyl) or alkoxy groups (for example, methoxy), especially those with only a few carbon atoms, that is to say, at most 4 carbon atoms. Specially advantageous are those 1-hydroxy- or 1-carboxy-2-amino-benzene derivatives that contain a substituent, advantageously a nitro group, in 4-position.

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As examples there may be mentioned:
2-aminobenzoic acid,
5-nitro-2-aminobenzoic acid,
5-chloro-2-aminobenzoic acid,
4- or 5-chloro-2-amino-1-hydroxybenzene,
4:6-dichloro-2-amino-1-hydroxybenzene,
3:4:6 - trichloro - 2 - amino - 1 - hydroxybenzene,
4-chloro-5- or -6-nitro-2-amino-1-hydroxybenzene,
6 - nitro - 4 - methyl - 2 - amino - 1-hydroxybenzene,
6 - nitro - 4 - acetylamino - 2 - amino - 1-hydroxybenzene,
4:6 - dinitro - 2 - amino - 1 - hydroxybenzene and especially
4- or 5-nitro-2-amino-1-hydroxybenzene,
4 - nitro - 6 - chloro - 2 - amino - 1-hydroxybenzene and
4 - nitro - 6 - acetylamino - 2 - amino-1-hydroxybenzene, and also compounds containing sulphonic acid groups, for example, 2-aminobenzoic acid-4- or -5-sulphonic acid, 2-aminophenol-4- or -5-sulphonic acid, which are to be coupled only with coupling components that are free from sulphonic acid groups.

As coupling components there are used keto compounds that can be coupled in a position vicinal to their enolized or enolizable keto group, especially those derivatives of the barbituric acid, pyrazolone and β-keto-carboxylic acid amide or ester series, and also naphthols and naphthylamines. As examples of coupling components that may be used there may be mentioned:

barbituric acid, acetoacetic acid ethyl ester, acetoacetic acid phenyl ester, acetoacetic acid cyclohexyl ester, acetoacetic acid para-chloro- or -para-methyl-phenyl ester, and also the corresponding benzoyl-, 4-chloro-benzoyl-, 4-methylbenzoyl-, 4-methoxybenzoyl- or naphthoyl acetic acid esters, acetoacetic acid amide, acetoacetic acid-N-methyl-, -N-ethyl-, -N-isopropyl-, -N-butyl-, -N-dimethyl-, -N-diethyl-, -N-dibutyl-, -N-hydroxyethylamide, acetoacetic acid-N-methyl- or -ethylanilide, acetoacetylaminocyclohexane, acetoacetylaminobenzene, 1-acetoacetylamino-2-methylbenzene, 1 - acetoacetylamino - 2:5 - dimethylbenzene, 1 - acetoacetylamino - 2- or -4-ethylbenzene, 1-acetoacetylamino-2:5-dichlorobenzene, 1 - acetoacetylamino - 4-methyl- or -4-methoxybenzene, benzoylacetylaminocyclohexane, benzoylacetylaminobenzene, 1-benzoylacetylamino-2-, 3- or 4-chlorobenzene, 1 - (4^1 - methylbenzoylacetylamino) - 4 - methylbenzene, 1 - (4^1-methoxy-benzoylacetylamino) - 4 - chlorobenzene and 1-acetoacetylamino-2-, 3- or 4-chlorobenzene; 5-pyrazolones that are substituted or unsubstituted in 1-position and that contain a methyl group or a —CO— group in 3-position, for example, 3-methyl-5-pyrazolone, 1-alkyl-3-methyl-5-pyrazolones, such as 1-methyl-, 1-*n*-propyl-, 1-isopropyl-, 1-*n*-butyl-, 1-*n*-hexyl- or 1-*n*-octyl-3-methyl-5-pyrazolone, and also 1-cyclohexyl- or 1-aryl-3-methyl-5-pyrazolones, such as 1-α-naphthyl-3-methyl-5-pyrazolone, but preferably 1 - phenyl - 3 - methyl - 5 - pyrazolone, 1-(2^1-, 3^1- or 4^1-chlorophenyl)-3-methyl-5-pyrazolone, 1-(2^1-, 3^1- or 4^1-methylphenyl)-3-methyl-5-pyrazolone, 1-(3^1- or 4-nitrophenyl) - 3 - methyl - 5 - pyrazolone, 1-(4^1-tertiary - amylphenyl) - 3 - methyl - 5-pyrazolone, 1 - (2^1:5^1 - dichlorophenyl)-3 - methyl - 5 - pyrazolone, 1 - (2^1:5^1-dibromophenyl) - 3 - methyl - 5 - pyrazolone, 1 - (2^1 - methyl - 6^1 - chlorophenyl) - 3-methyl - 5 - pyrazolone, 5 - pyrazolone - 3-carboxylic acid amides that may be substituted or unsubstituted in 1-position, for example, 5-pyrazolone-3-carboxylic acid anilide, 5-pyrazolone - 3 - carboxylic acid - para-chloroanilide, 5 - pyrazolone - 3 - carboxylic acid-methyl-, ethyl-, isopropyl-, *n*-butyl- or cyclohexylamide, 5-pyrazolone-3-carboxylic acid-N-dimethyl- or diethylamide, 1-phenyl-5-pyrazolone-3-carboxylic acid amide or the corresponding methyl-, ethyl-, isopropyl-, *n*-butyl- or dimethyl-amide, 1-(4^1-chloro)-phenyl - 5 - pyrazolone - 3 - carboxylic acid amide, β - naphthyl - amine, 1 - acylamino-7-hydroxynaphthalenes (for example, 1-acetyl-, 1-benzoyl-, 1-methanesulphonyl-, 1-dimethylaminosulphonyl-, 1-butyrylamino-7-hydroxynaphthalene- or 1-carbethoxyamino- or 1 - carbomethoxyamino - 7 - hydroxynaphthalene), β-naphthol and coupling components containing sulphonic acid groups which are to be coupled only with diazo compounds free from sulpho groups, for example, 1-phenyl - 3 - methyl - 5 - pyrazolone-sulphonic acids, 1 - naphthyl - 3 - methyl-5-pyrazolone sulphonic acids, 2-aminonaphthalene-6-sulphonic acid and naphthol sulphonic acids that couple in a position vicinal to the hydroxyl group.

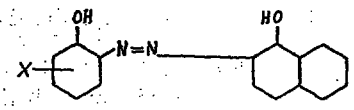
The monoazo dyestuffs of formula (2) can likewise be prepared in a similar manner by coupling a diazo compound of one of the above-mentioned ortho-hydroxyaminobenzenes free from sulphonic acid groups with 1-hydroxynaphthalene-4-sulphonic acid and removing the sulphonic acid group from the monoazo dyestuff sulphonic acid thus obtained.

The conversion of these dyestuffs into the 1:1-chromium complexes is effected by known methods, for example, by treating them at boiling temperature or, if desired or required, at a temperature above 100° C in an acid medium 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 metallization in known manner, for example, in the presence of an organic solvent such as

alcohol or formamide, but more especially ethyleneglycol.

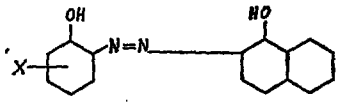
As is known, the 1:1-metal complexes of ortho:ortho¹-dihydroxy-monoazo dyestuffs can be prepared not only from the ortho:ortho¹-dihydroxy-monoazo dyestuffs themselves, but also from the corresponding ortho-alkoxy-ortho¹-hydroxymonoazo dyestuffs. Accordingly, the corresponding ortho-alkoxydiazo compound, especially the methoxy compound, can also be used for the preparation of the chromium-containing dyestuffs used as starting materials in the present process instead of the ortho-hydroxydiazo compound. The desulphonation to form dyestuffs of the formula (2) is likewise carried out by known methods during the preparation of the complexes.

Complex chromium compounds which may be used as starting materials are for example the 1:1-chromium complex compounds of monoazo dyestuffs of the formula



in which X represents a chlorine atom or a nitro group.

Of particular interest are the chromium complex compounds obtained according to the invention in which the dyestuff free from sulphonic acid groups corresponds to the formula



in which X represents a chlorine atom or a nitro group.

It is generally of advantage not to dry the starting materials used in the present process after they have been prepared and separated, but to use them in the form of a moist paste during the further processing. The 1:1-chromium complexes so obtained are advantageously reacted with the dyestuffs free from metal 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. The addition of solvents, for example, alcohol or formamide can assist the reaction in some cases. It is generally of advantage to use the chromium-containing 1:1-complex and the metal-free dyestuff as near as possible in equivalent proportions, 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. An 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.

A modification of the present process consists in starting from a 1:1-chromium complex compound of a dyestuff of the formula (1) instead of a dyestuff of the formula (2) and reacting the said chromium compound with a dyestuff of the formula (2) free from heavy metal to form a mixed complex.

The new chromium-containing mixed complexes obtainable by the above process and by the modification thereof are suitable for dyeing and printing a very wide variety of materials, but more especially for dyeing animal materials such as silk, leather and especially wool. However, they are also suitable for dyeing and printing synthetic fibres made of polyamides, polyurethanes and polyacrylonitrile. They are mainly suitable for application from a slightly alkaline, neutral or slightly acid bath, for example, an acetic acid bath. The dyeings so obtained are uniform and possess a good fastness to washing, to light, to milling, to decatizing and to carbonizing.

The following Examples illustrate the invention. Unless otherwise stated, the parts and percentages are by weight.

EXAMPLE 1.

9.70 Parts of a monoazo dyestuff prepared from diazotized 1-hydroxy-2-amino-5-nitrobenzene and 1-hydroxynaphthalene-4-sulphonic acid were introduced into a solution of 7.30 parts of chromic chloride hexahydrate in 100 parts of anhydrous ethylene glycol heated to 100° C. The reaction mixture, which was initially viscous, was stirred for 3 to 4 hours at 130 to 135° C whereby a clear, greenish blue solution was formed. After cooling the solution to 50° C, it was diluted with 500 parts of water and the chromium-containing dyestuff precipitated by the addition of 50 parts of sodium chloride. The dyestuff was filtered and then thoroughly washed with a dilute sodium chloride solution. The chromium complex so obtained contained 1 atom of metal per molecule of monoazo dyestuff and was essentially free from sulphonic acid groups. It was added in the form of a filter paste, while stirring, to a solution of 9.43 parts of a metal-free monoazo dyestuff prepared from diazotized 1-hydroxy-2-amino-4-chlorobenzene and 1-hydroxynaphthalene-5-sulphonic acid in 300 parts of water and 50 parts of a 1N sodium hydroxide solution, the said solution having been heated to 80 to 85° C. The reaction mixture was stirred at 85 to 95° C until the two dyestuffs used as starting materials were no longer detectable.

The resulting blue-violet mixed complex was isolated by the addition of sodium chloride to the solution and subsequent filtration. A blue-black powder was obtained after

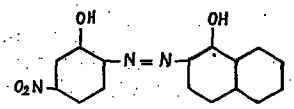
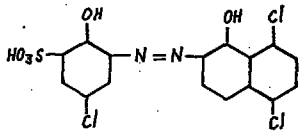
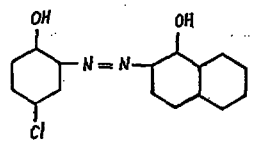
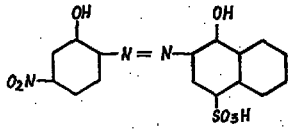
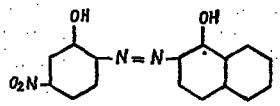
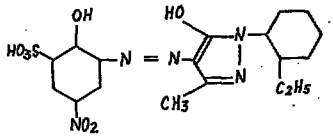
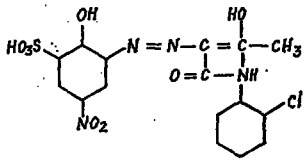
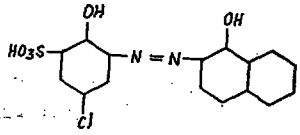
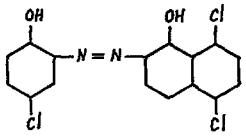
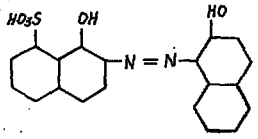
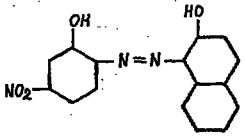
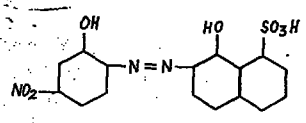
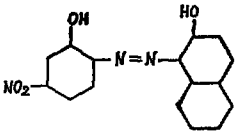
drying and grinding; it dyed wool full, navy-blue tints possessing good properties of fastness when applied from a bath containing ammonium sulphate.

When the chromium complex free from sulphonic groups prepared in ethylene glycol was not isolated by precipitating with a sodium chloride solution as described above, but was used directly in the form of the glycol solution in the reaction with the afore-said metal-free monoazo dyestuff in aqueous solution, the same mixed complex dyestuff was obtained.

EXAMPLE 2.

4.50 Parts of crystallized cupric chloride were dissolved in 100 parts of anhydrous ethylene glycol while stirring. The blue solution was heated to 100° C and then 9.70 parts of the monoazo dyestuff prepared from diazotized 1 - hydroxy - 2 - amino - 5-nitrobenzene and 1 - hydroxynaphthalene-4-sulphonic acid were added. The reaction mixture was then stirred for 3 to 4 hours at 130 to 135° C. The clear, deep violet solution of the resulting copper complex was cooled to 80° C and then introduced into a mixture comprising 500 parts of water and 100 parts of concentrated hydrochloric acid. The brown-red suspension was heated to the boil for 30 minutes and then cooled. The almost completely precipitated monoazo dyestuff which was free from metal was filtered and washed thoroughly, first with a mixture comprising dilute hydrochloric acid and sodium chloride solution, and then with a dilute sodium chloride solution only. The resulting dyestuff was free from sulphonic acid groups; it dissolved in a sodium carbonate solution to a pure blue solution, and in concentrated sulphuric acid to a dull, red-violet solution. It was introduced as a filter paste, while stirring, into a solution of 9.70 parts of the metal-containing monoazo dyestuff prepared from diazotized 1 - hydroxy - 2 - amino - 5-nitrobenzene and 1 - hydroxynaphthalene-4-sulphonic acid, in the form of a chromium complex containing one atom of chromium per molecule of monoazo dyestuff, and 50 parts of N sodium hydroxide solution, the said solution having been heated to 80 to 85° C. The reaction mixture was stirred at 85 to 95° C until the two dyestuffs used as starting materials were no longer detectable. The blue homogeneous mixed complex was precipitated by the addition of sodium chloride and isolated by filtration. When dry, the dyestuff was a dark powder readily soluble in water to form a reddish blue solution. It dyed wool fast, blue tints when applied from a bath containing ammonium sulphate.

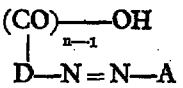
In Column I of the following Table are listed further Examples of dyestuffs whose 1:1-chromium complex compounds yield further mixed complexes after reaction with metal-free monoazo dyestuffs given in Column II by the process described above. The tints obtained on wool are listed in Column III.

I	II	III
		Blue
		Navy blue
		Brown
"		Olive-green
		Navy blue
		Blue
		Blue-grey

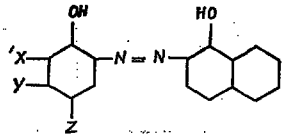
Specification No. 765,355 describes and claims metal compounds which contain one atom of chromium or cobalt bound in complex union with two molecules of different ortho-ortho¹-dioxy-, ortho-carboxy-ortho¹-oxy- or ortho-oxy-ortho¹-aminomonoazo-dyestuffs, of which both are free from carboxylic acid groups 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 preparation of a metal-containing azo dyestuff which contains one atom of chromium bound in complex union with two molecules of different monoazo dyestuffs, wherein a metallizable monoazo dyestuff free from carboxylic acid groups not in a position vicinal to the azo group and which contains a single sulphonic acid group, which dyestuff corresponds to the formula



in which D represents the residue of a diazo component bound to the azo bridge in a position vicinal to the $-(CO)_{n-1}-OH-$ group, A represents the residue of a coupling component which is bound to the azo bridge in a position vicinal to an enolized or enolizable keto group or an amino or hydroxyl group, and n represents a positive integer 1 or 2, is reacted in a molar ratio of about 1:1 with a complex chromium compound which contains one chromium atom bound in complex union with a molecule of a monoazo dyestuff of the formula

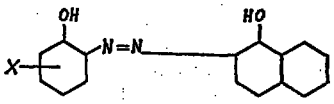


in which one of the symbols X, Y and Z represents a hydrogen atom and each of the others represents a hydrogen atom or a halogen atom or a nitro group or an alkyl or alkoxy group having 1 to 4 carbon atoms.

2. A process as claimed in claim 1 wherein D in the given formula represents the residue of a diazo component of the benzene series.

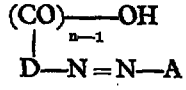
3. A process as claimed in claim 1 or 2, wherein the starting material used is a metal-free monoazo dyestuff prepared from a diazotized chloro- or nitro-aminophenol or from a diazotized anthranilic acid.

4. A process as claimed in any one of claims 1—3, wherein the starting material used is a 1:1-chromium complex of a monoazo dyestuff of the formula

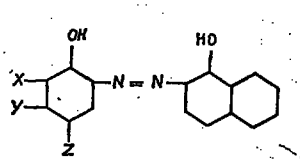


in which X represents a chlorine atom or a nitro group.

5. A modification of the process claimed in any one of the claims 1 to 4, wherein a 1:1-chromium complex compound of a metallizable monoazo dyestuff free from carboxylic acid groups not in a position vicinal to the azo group and which contains a single sulphonic acid group, which dyestuff corresponds to the formula



in which D represents the residue of a diazo component bound to the azo bridge in a position vicinal to the $-(CO)_{n-1}-OH-$ group, A represents the residue of a coupling component which is bound to the azo bridge in a position vicinal to an enolized or enolizable keto group or an amino or hydroxyl group, and n represents a positive integer 1 or 2, is reacted in a molar ratio of about 1:1 with a monoazo dyestuff of the formula



in which one of the symbols X, Y and Z represents a hydrogen atom and each of the others represents a hydrogen atom or a halogen atom or a nitro group or an alkyl or alkoxy group of low molecular weight.

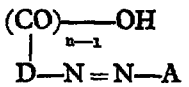
6. A process as claimed in claim 5 wherein D in the given formula represents the residue of a diazo component of the benzene series.

7. A process for the manufacture of azo dyestuffs containing chromium as claimed in claim 1 or 5 conducted substantially as described in either of the Examples or with reference to the Table herein.

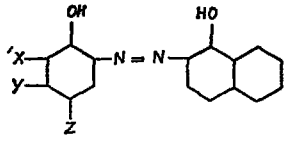
Specification No. 765,355 describes and claims metal compounds which contain one atom of chromium or cobalt bound in complex union with two molecules of different ortho-ortho¹-dioxy-, ortho-carboxy-ortho¹-oxy- or ortho-oxy-ortho¹-aminomonoazo-dyestuffs, of which both are free from carboxylic acid groups 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 preparation of a metal-containing azo dyestuff which contains one atom of chromium bound in complex union with two molecules of different monoazo dyestuffs, wherein a metallizable monoazo dyestuff free from carboxylic acid groups not in a position vicinal to the azo group and which contains a single sulphonic acid group, which dyestuff corresponds to the formula



in which D represents the residue of a diazo component bound to the azo bridge in a position vicinal to the $-(CO)_{n-1}-OH-$ group, A represents the residue of a coupling component which is bound to the azo bridge in a position vicinal to an enolized or enolizable keto group or an amino or hydroxyl group, and n represents a positive integer 1 or 2, is reacted in a molar ratio of about 1:1 with a complex chromium compound which contains one chromium atom bound in complex union with a molecule of a monoazo dyestuff of the formula

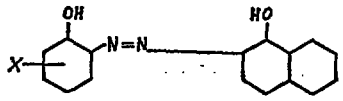


in which one of the symbols X, Y and Z represents a hydrogen atom and each of the others represents a hydrogen atom or a halogen atom or a nitro group or an alkyl or alkoxy group having 1 to 4 carbon atoms.

2. A process as claimed in claim 1 wherein D in the given formula represents the residue of a diazo component of the benzene series.

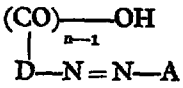
3. A process as claimed in claim 1 or 2, wherein the starting material used is a metal-free monoazo dyestuff prepared from a diazotized chloro- or nitro-aminophenol or from a diazotized anthranilic acid.

4. A process as claimed in any one of claims 1—3, wherein the starting material used is a 1:1-chromium complex of a monoazo dyestuff of the formula

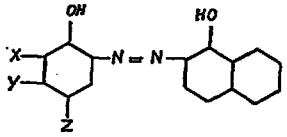


in which X represents a chlorine atom or a nitro group.

5. A modification of the process claimed in any one of the claims 1 to 4, wherein a 1:1-chromium complex compound of a metallizable monoazo dyestuff free from carboxylic acid groups not in a position vicinal to the azo group and which contains a single sulphonic acid group, which dyestuff corresponds to the formula



in which D represents the residue of a diazo component bound to the azo bridge in a position vicinal to the $-(CO)_{n-1}-OH-$ group, A represents the residue of a coupling component which is bound to the azo bridge in a position vicinal to an enolized or enolizable keto group or an amino or hydroxyl group, and n represents a positive integer 1 or 2, is reacted in a molar ratio of about 1:1 with a monoazo dyestuff of the formula

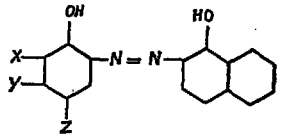


in which one of the symbols X, Y and Z represents a hydrogen atom and each of the others represents a hydrogen atom or a halogen atom or a nitro group or an alkyl or alkoxy group of low molecular weight.

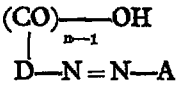
6. A process as claimed in claim 5 wherein D in the given formula represents the residue of a diazo component of the benzene series.

7. A process for the manufacture of azo dyestuffs containing chromium as claimed in claim 1 or 5 conducted substantially as described in either of the Examples or with reference to the Table herein.

8. 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



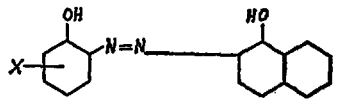
in which one of the symbols X, Y and Z represents a hydrogen atom and each of the others represents a hydrogen atom or a halogen atom or a nitro group or an alkyl or alkoxy group having 1 to 4 carbon atoms, and the other corresponds to the formula



in which D represents the residue of a diazo compound bound to the azo bridge in a position vicinal to the $-(CO)_{n-1}-OH-$ group, A represents the residue of a coupling component which is bound to the azo bridge in a positional vicinal to an enolized or enolizable keto group or an amino or hydroxyl group, and n represents a positive integer 1 or 2, and one of the residues D and A contains a sulphonic acid group.

9. Metal compounds as claimed in claim 8 wherein the residue D in the given formula represents the residue of a diazo compound of the benzene series.

10. Complex chromium compounds as claimed in claim 8 or 9 in which the dyestuff free from sulphonic acid groups corresponds to the formula



in which X represents a chlorine atom or a nitro group.

11. Complex chromium compounds as claimed in any one of claims 8—10, in which the dyestuff that contains the sulphonic acid group contains the residue of a chloro- or nitro-phenol as the residue of the diazo component.

12. Complex chromium compounds as claimed in any one of the claims 8—11, in which the dyestuff that contains the sulphonic acid group is also a dyestuff of the benzene-azo-naphthol series.

13. Any one of the azo dyestuffs containing chromium obtainable as end products in the Examples or with reference to the Table herein.

14. Any one of the azo dyestuffs containing chromium obtained as an end product as described herein.

15. A dyeing or printing process wherein a complex chromium compound claimed in any one of the claims 8 to 14, is used.

16. A dyeing process as claimed in claim 15, in which nitrogenous fibres are dyed in a weakly alkaline, neutral or weakly acid bath with the complex chromium compounds.

17. A process as claimed in claim 16 wherein the fibres to be dyed consist of wool, silk or fibres of polyamides or polyurethanes.

18. Nitrogenous fibrous materials dyed or printed by a process claimed in any one of claims 15—17.

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