981,349

PATENT SPECIFICATION

NO DRAWINGS

981,349

Date of Application and filing Complete Specification: April 8, 1963.

No. 13940/63.

Application made in Switzerland (No. 4228) on April 6, 1962.

Complete Specification Published: Jan. 27, 1965.

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Index at acceptance:—C4 P(8A1A, 8A1B, 8B1, 8C3)

Int. Cl.:—C 09 b

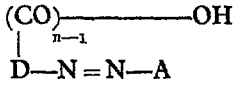
COMPLETE SPECIFICATION

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:—

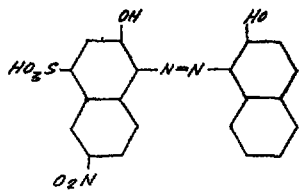
The present invention is based on the observation that valuable new chromiferous azo dyestuffs which contain two molecules of different monoazo dyestuffs to which one atomic proportion of chromium is bound in complex union are obtained when a metallisable monoazo dyestuff of the formula

(1)



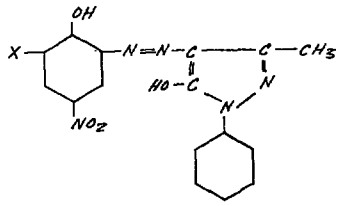
which is free from carboxyl groups not in ortho-position relatively to the azo bridge and is free from sulphonic acid groups—in which formula D stands for the residue of a diazo component of the benzene series which is bound to the azo bridge in vicinal position to the —(CO)$_{n-1}$—OH; A stands for the residue of a coupling component capable of coupling in vicinal position to an enolised or enolisable keto group, and n = 1 or 2—is reacted in the molecular ratio of approximately 1 : 1 with a complex chromium compound which contains one atomic proportion of chromium linked in complex union to one molecule of the monoazo dyestuff of the formula

(2)

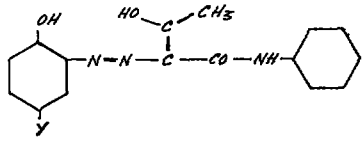


Especially valuable are complex chromium compounds wherein the benzene-azo dyestuff corresponds to the formula D_1—N=N—A_2— where D_1 stands for an unsubstituted or substituted orthocarboxyphenyl residue or for an ortho-hydroxyphenyl residue containing a nitro group and possibly a further substituent, and A_2 stands for the residue of a coupling component of the pyrazolone or acetoacetylanilide series, preferably complex chromium compounds wherein the benzene-azo dyestuff corresponds to the formula

[*Price 4s. 6d.*]

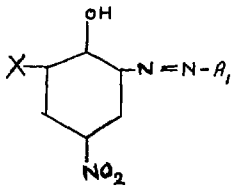


where X stands for a hydrogen or chlorine atom or for a nitro or acylamino group, and complex chromium compounds wherein the benzene azo dyestuff corresponds to the formula



where Y stands for a hydrogen or chlorine atom or for a nitro group.

The monoazo dyestuffs of the formula (1) required for the performance of the present process can be prepared in known manner by coupling in a weakly acidic to alkaline medium an ortho-carboxy or more especially ortho-oxydiazo compound of the benzene series with a coupling component capable of coupling in ortho-position to an enolised or enolisable keto group. As can be seen from the foregoing statements, the components must not contain any sulphonic acid groups nor any free carboxyl groups except, however, those which may be in ortho-position to the diazotisable amino group of the diazo components. Advantageously, the parent compounds are also free from functionally converted sulphonic acid groups, that is to say, for example, from sulphonamide or sulphonic acid ester groups. It is further of advantage to select components that give rise to dyestuffs which contain no hydroxyl groups other than those capable of participating in the complex formation and are in ortho-position relatively to the azo bridge, e.g. a process is particularly valuable, wherein the starting material used is a metal-free monoazo dyestuff from a diazotised nitroaminophenol or from a diazotised anthranilic acid and a ketomethylene compound which is free from substituents containing sulphur or wherein the starting material used is a metal-free monoazo dyestuff of the formula



where X stands for a hydrogen or chlorine atom or for a nitro or acylamino group and A_1 for a 1-phenyl-3-methyl-5-pyrazolone residue bound to the azo bridge in position 4 or for an acetoacetylamide residue bound to the azo bridge in β-position. Having in mind these conditions, there are suitable, for example, for the synthesis of the monoazo dyestuffs of the formula (1) by the present process the following components:

As diazo compounds those which are derived from ortho-carboxyamines of the benzene series, above all from ortho-hydroxyamines of the benzene series that may contain in addition to the carboxy or hydroxyl group and the amino group further substituents, such as nitro groups, halogen (for example chlorine) atoms, alkyl groups (for example methyl), alkoxy groups (for example methoxy) or acylamino groups more especially those acylamino groups which contain at most 4 carbon atoms (for example acetylamino). Especially suitable are 1-hydroxy-2-aminobenzene or 1-carboxy-2-aminobenzene derivatives that contain in position 4 a substituent, preferably a nitro group.

As relevant 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 more 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.

Suitable coupling components are keto compounds that can be coupled in vicinal position to their enolised or enolisable keto group, more especially derivatives of the barbituric acid, pyrazolone and *β*-ketocarboxylic acid amide or ester series that are free from substituents containing sulphur. As examples of suitable coupling components there may be mentioned: barbituric acid, acetoacetic acid ethyl ester, acetoacetic acid phenyl ester, acetoacetic acid cyclohexyl ester, acetoacetic acid-para-chlorophenyl or -para-methylphenyl ester, and the corresponding benzoyl-, 4-chlorobenzoyl-, 4-methylbenzoyl-, 4-methoxybenzoyl, or naphthoyl-acetic acid esters, acetoacetamide, acetoacetic acid - N - isopropylamide, - N - butylamide, - N - dimethylamide, - N - diethylamide, - N - dibutylamide, - N - methoxypropylamide, acetoacetic acid - N - methylanilide or - N - ethylanilide, acetoacetylamino-cyclohexane, acetoacetylaminobenzene, 1-acetoacetylamino - 2:5 - dimethylbenzene, 1 - acetoacetylamino - 2 - or - 4 - ethylbenzene, 1 - acetoacetylamino - 2:5 - dichlorobenzene, 1 - acetoacetylamino - 4 - methylbenzene or - 4 - methoxybenzene, benzoylacetylamino - cyclohexane, benzoylacetylaminobenzene, 1 - benzoylacetylamino - 2 -, -3- or -4-chlorobenzene, 1 - (4^1 - methyl - benzoylacetylamino) - 4 - methylbenzene, 1 - (4^1 -methoxybenzoylacetylamino) - 4 - chlorobenzene; 5 - pyrazolones that are substituted or unsubstituted in 1-position and carry in 3-position a methyl or —CO— group, such, for example, as 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; furthermore 1-cyclohexyl- or 1-aryl-3-methyl-5-pyrazolones such as 1-*α*-naphthyl-3-methyl-5-pyrazolone, or 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 4^1-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, such as 5-pyrazolone-3-carboxylic acid anilide, 5-pyrazolone-3-carboxylic acid-para-chloranilide, 5-pyrazolone-3-carboxylic acid-methylamide, -ethylamide, -isopropylamide, -*n*-butylamide or -cyclohexylamide, 5-pyrazolone-3-carboxylic acid-N-dimethylamide or -N-diethylamide, 1-phenyl-5-pyrazolone-3-carboxylic acid amide or the corresponding methylamide, ethylamide, isopropylamide, *n*-butylamide or dimethylamide, and 1-(4^1-chlorophenyl)-5-pyrazolone-3-carboxylic acid amide.

The monoazo dyestuff of the formula (2) is likewise accessible by coupling performed in known manner. Its conversion into the 1:1-chromium complex is performed by a conventional method, for example by reacting it in an acid medium with an excess of a salt of trivalent chromium such as chromium formate, chromic sulphate or chromic fluoride, at the boil or, if required, at a temperature above 100°C. In this process it is generally advantageous to carry out the metallisation in known manner, for example in the presence of an organic solvent, such as alcohol or formamide.

In general, it is found advantageous when the parent materials required for the performance of the present process are not dried after having been manufactured and separated but are further worked up in the form of a moist paste.

The reaction of the 1:1-chromium complex with the metal free dyestuffs is advantageously carried out in an aqueous neutral to weakly alkaline medium, under atmospheric or super-atmospheric pressure, at room temperature or with heating, preferably at a temperature ranging from 50 to 120°C. The addition of a solvent, for example alcohol or formamide, may promote the reaction. In general, it is of advantage to use

for the reaction as far as possible equimolecular proportions of the chromiferous 1:1-complex and of the metal-free dyestuff; the molecular ratio between metal-free dyestuff and 1:1-complex is advantageously at least 0.85:1 and at most 1:0.85, and as a rule an excess of metalliferous dyestuff has a less harmful effect than an excess of metal-free dyestuff. The closer the selected ratio is to 1:1, the more favourable is as a rule the result obtained.

The new chromiferous mixed complexes obtained by the present process are suitable for dyeing and printing a very wide variety of materials and above all for dyeing animal materials, such as silk, leather and more especially wool. Furthermore, they are suitable for dyeing and printing synthetic fibres from polyamides, polyurethanes or polyacrylonitrile. They are particularly suitable for dyeing from a neutral or weakly acidic (for example acetic acid) bath. The dyeings obtained in this manner are level and have good properties of fastness to light, washing, perspiration, fulling, decatising and carbonising. In this respect they may replace the so-called chroming dyestuffs or one-bath after-chroming dyestuffs and offer advantages over the latter by virtue of the much simpler and shorter dyeing method which they require.

It is a special advantage of the present dyestuffs that they yield very strong tints, since a relatively small amount of dyestuff will produce valuable, covered shades in the range from brown to olive.

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

EXAMPLE 1.

49.1 Parts of the 1:1-chromium complex of the dyestuff from diazotized 6-nitro-1-amino-2-hydroxynaphthalene-4-sulphonic acid and 2-hydroxynaphthalene, and 38.4 parts of the dyestuff from diazotized 4:6-dinitro-2-aminophenol and 1-phenyl-3-methyl-5-pyrazolone are stirred in 2000 parts of hot water, and the mixture is then neutralised. 4.0 Parts of sodium hydroxide are added, and the whole is stirred for 24 hours at 95 to 98°C. On completion of the reaction the dyestuff is salted out from the resulting solution with sodium chloride, filtered off and dried. It forms a brown powder which gives in water a brown solution and in concentrated sulphuric acid a blue-green solution and dyes wool from a weakly acidic bath brown shades having good properties of fastness.

EXAMPLE 2.

49.1 Parts of the 1:1-chromium complex of the dyestuff from diazotized 6-nitro-1-amino-2-hydroxynaphthalene-4-sulphonic acid and 2-hydroxynaphthalene, and 32.5 parts of the dyestuff from diazotized 2-aminobenzoic acid acetoacetylanilide are stirred in 2000 parts of hot water and the resulting mixture is neutralised. 4.0 Parts of sodium hydroxide and 6.2 parts of sodium acetate are added, and the mixture is stirred for 6 hours at 95—98°C, then filtered, and the dyestuff is salted out from the filtrate with sodium chloride, filtered off and dried. It forms a brown powder which gives in water a brown-olive solution and in concentrated sulphuric acid a blue-green solution and dyes wool from a weakly acidic bath olive-green shades having good properties of fastness.

In the following Table there are listed a few further chromiferous dyestuffs (1:2-complexes) which are obtained by reacting at a molecular ratio of 1:1 a chromium-free dyestuff shown in Column I with the 1:1-chromium complex of the monoazo dyestuff from diazotized 6-nitro-1-amino-2-hydroxynaphthalene-4-sulphonic acid and 2-hydroxynaphthalene. The shades obtained on wool with the dyestuffs listed are shown in column II.

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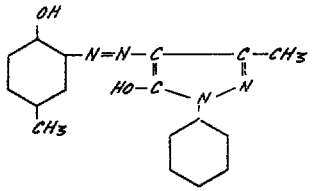
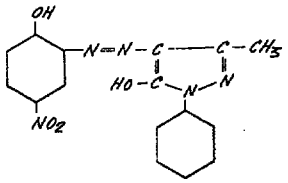
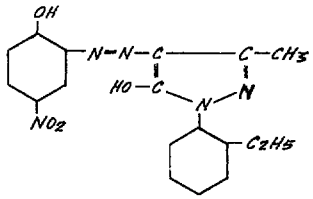
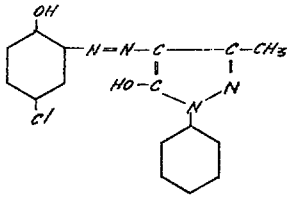
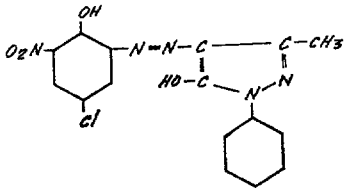
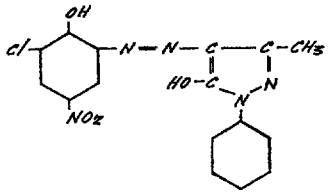
1		grey
2		brown
3		brown
4		violet-brown
5		violet-brown
6		brown

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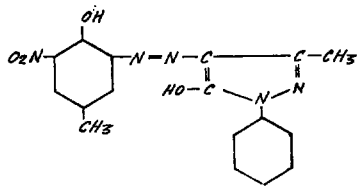
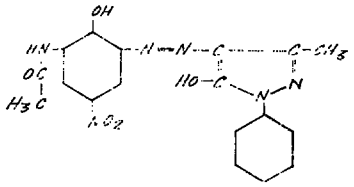
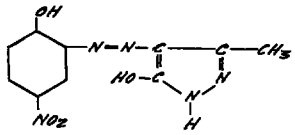
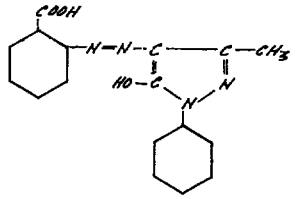
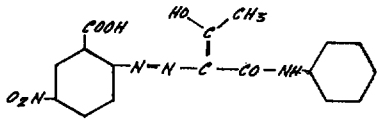
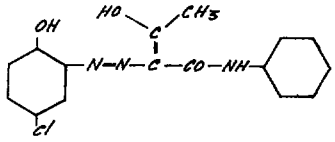
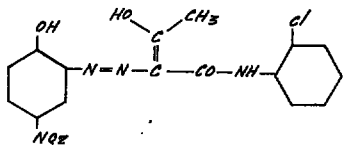
7		violet-brown
8		brown
9		brown
10		brown-olive
11		olive
12		olive-brown
13		brown-olive

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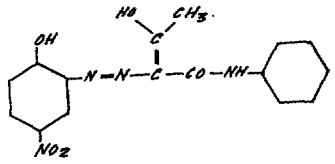
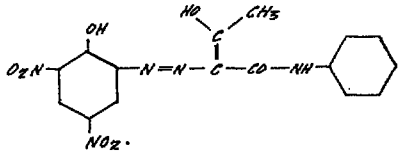
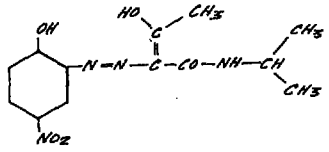
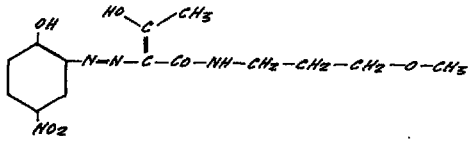
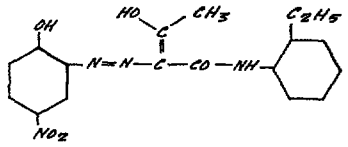
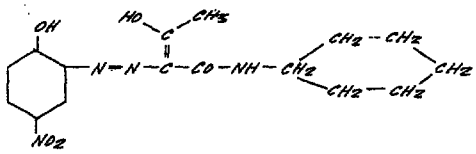
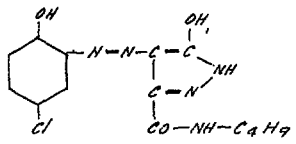
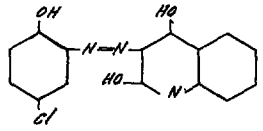
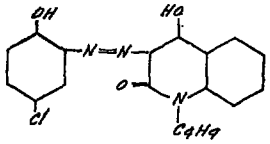
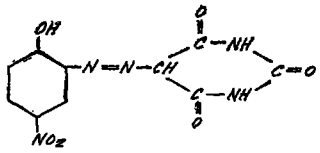
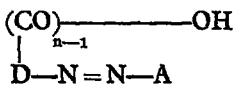
14		brown-olive
15		grey-brown
16		olive
17		olive
18		olive
19		olive
20		violet-brown

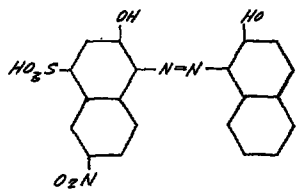
	I	II
21		violet-brown
22		violet-brown
23		brown

WHAT WE CLAIM IS:—

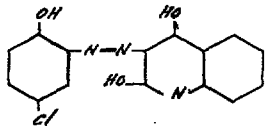
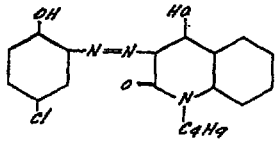
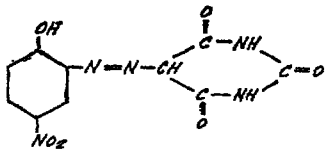
1. Process for the manufacture of metalliferous azo dyestuffs that contain one atomic proportion of chromium bound in complex union to two molecules of different monoazo dyestuffs, wherein a metallisable monoazo dyestuff of the formula



which is free from carboxyl groups not in ortho-position to the azo bridge and is free from sulphonic acid groups—where D stands for the residue of a diazo component of the benzene series bound to the azo bridge in vicinal position to the —(CO)$_{n-1}$—OH group; A represents the residue of a coupling component capable of coupling in vicinal position to an enolised or enolisable keto group, and n = 1 or 2—is reacted in molecular ratio of approximately 1:1 with a complex chromium compound which contains one atomic proportion of chromium bound in complex union to one molecular proportion of the monoazo dyestuff of the formula

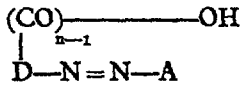


2. Process as claimed in Claim 1, wherein the starting material used is a metal-free monoazo dyestuff from a diazotised nitroaminophenol or from a diazotised anthranilic acid and a ketomethylene compound which is free from substituents containing sulphur.

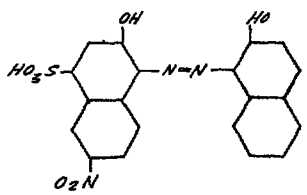
	I	II
21		violet-brown
22		violet-brown
23		brown

WHAT WE CLAIM IS:—

1. Process for the manufacture of metalliferous azo dyestuffs that contain one atomic proportion of chromium bound in complex union to two molecules of different monoazo dyestuffs, wherein a metallisable monoazo dyestuff of the formula

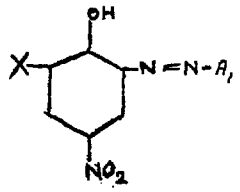


which is free from carboxyl groups not in ortho-position to the azo bridge and is free from sulphonic acid groups—where D stands for the residue of a diazo component of the benzene series bound to the azo bridge in vicinal position to the —(CO)$_{n-1}$—OH group; A represents the residue of a coupling component capable of coupling in vicinal position to an enolised or enolisable keto group, and n = 1 or 2—is reacted in molecular ratio of approximately 1:1 with a complex chromium compound which contains one atomic proportion of chromium bound in complex union to one molecular proportion of the monoazo dyestuff of the formula



2. Process as claimed in Claim 1, wherein the starting material used is a metal-free monoazo dyestuff from a diazotised nitroaminophenol or from a diazotised anthranilic acid and a ketomethylene compound which is free from substituents containing sulphur.

3. Process as claimed in Claim 1 or 2, wherein the starting material used is a metal-free monoazo dyestuff of the formula

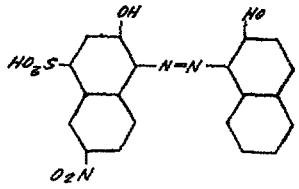


where X stands for a hydrogen or chlorine atom or for a nitro or acylamino group and A_1 for a 1-phenyl-3-methyl-5-pyrazolone residue bound to the azo bridge in position 4 or for an acetoacetylamide residue bound to the azo bridge in β-position.

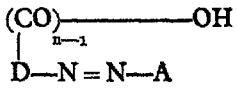
4. Process as claimed in Claim 1, 2 or 3, wherein the reaction is performed in an aqueous medium, preferably at an elevated temperature ranging, for example, from 50 to 120°C.

5. Process as claimed in Claim 1, which is conducted substantially as described in Example 1 or 2 or with reference to the Table herein.

6. Metal compounds containing one atomic proportion of chromium bound in complex union to two molecular proportions of different monoazo dyestuffs, of which one corresponds to the formula



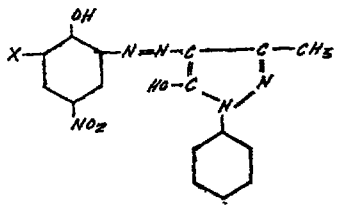
and the other to the formula



which is free from carboxyl groups not in ortho-position to the azo bridge and is free from sulphonic acid groups in which D represents the residue of a diazo component of the benzene series linked with the azo bridge in vicinal position relatively to the $-(CO)_{n-1}-OH$ group; A represents the residue of a coupling component capable of coupling in vicinal position to an enolised or enolisable keto group and n = 1 or 2.

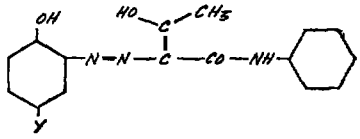
7. Complex chromium compounds as claimed in Claim 6, wherein the benzene-azo dyestuff corresponds to the formula $D_1-N=N-A_2-$ where D_1 stands for an unsubstituted or substituted ortho-carboxyphenyl residue or for an ortho-hydroxyphenyl residue containing a nitro group and possibly a further substituent, and A_2 stands for the residue of a coupling component of the pyrazolone or acetoacetylanilide series.

8. Complex chromium compounds as claimed in Claim 6 or 7, wherein the benzene-azo dyestuff corresponds to the formula



where X stands for a hydrogen or chlorine atom or for a nitro or acylamino group.

9. Complex chromium compounds as claimed in Claim 6 or 7, wherein the benzene-azo dyestuff corresponds to the formula



where Y stands for a hydrogen or chlorine atom or for a nitro group.

10. Any one of the complex chromium compounds in accordance with Claim 6 and which is described in the Examples and with reference to the Table herein.

11. A dyeing or printing method, wherein a complex chromium compound as claimed in any one of Claims 6 to 10 is used.

12. A dyeing method as claimed in Claim 11, wherein nitrogenous fibres, more especially wool, silk or leather, or polyamide or polyurethane fibres are dyed with the complex chromium compounds from a weakly alkaline, neutral or weakly acidic bath.

13. Nitrogenous textile material whenever dyed or printed as claimed in Claim 11 or 12.

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Leamington Spa: Printed for Her Majesty's Stationery Office, by the Courier Press (Leamington) Ltd.—1965. Published by The Patent Office, 25 Southampton Buildings, London, W.C.2, from which copies may be obtained.