Patented Mar. 5, 1935 1,993,462

UNITED STATES PATENT OFFICE

1,993,462

CHROMIFEROUS AZO-DYESTUFF AND PROCESS OF MAKING SAME

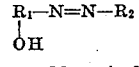
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No Drawing. Application January 10, 1934, Serial No. 706,148. In Switzerland January 25, 1933

14 Claims. (Cl. 260—12)

The present invention relates to chromiferous azo-dyestuffs. It comprises the process of making these dyestuffs as well as the new dyestuffs themselves.

It has been found that chromiferous azo-dyestuffs are obtained by causing azo-dyestuffs of the general formula



wherein R_1 means a sulfonated naphthalene radical and R_2 a naphthol radical, and wherein the hydroxyl group of the naphthalene radical R_1 stands in ortho-position to the azo-bridge, to react with agents yielding chromium in such quantities that less than 1 atom of chromium devolves upon each chromable group of the dyestuff molecule, the reaction being conducted in presence of soluble salts of organic acids.

Azo-dyestuffs of the above general formula may be obtained from different diazotized ortho-hydroxyaminonaphthalene sulfonic acids by coupling with different naphthols. Diazo compounds of suitable ortho-hydroxyaminonaphthalene sulfonic acids are, for example, the diazo compounds of 1-amino-2-hydroxynaphthalene-4-sulfonic acid, 1-hydroxy-2-aminonaphthalene-4-sulfonic acid, 1-amino-2-hydroxynaphthalene-6-sulfonic acid, 1-amino-2-hydroxynaphthalene-6-chloro-4-sulfonic acid, 1-amino-2-hydroxynaphthalene-6-bromo-4-sulfonic acid; further there may also be used as diazo components for example the nitrated 1-diazo-2-hydroxynaphthalene-4-sulfonic acid and the nitrated 1-diazo-2-hydroxynaphthalene-6-sulfonic acid. Suitable coupling components are α- and β-naphthol, as well as their substitution products, such as for example 8-chloro-α-naphthol and 5:8-dichloro-α-naphthol.

The treatment with the agents yielding chromium may take place in an open vessel or under pressure, in the presence or absence of further additions, such as, for example, inorganic salts, organic or inorganic acids, or in neutral or acid medium.

As agents yielding chromium there may be used chromium salts, such as, for example, chromium chloride, chromium fluoride, chromium sulfate, chromium sulfite, chromium acetate, chromium formate, chromium oxalate, the chromium salt of benzene-sulfonic acid, or mixtures of such chroming agents.

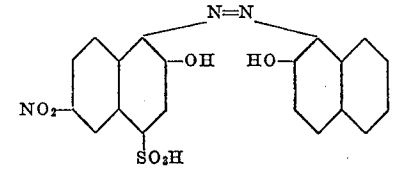
As soluble salts of organic acids in whose presence the treatment with agents yielding chromium must be carried out in accordance with the present process, there come into consideration, for example, soluble salts of sulfonic acids and carboxylic acids of the aliphatic, aromatic and hydroaromatic series. Such salts are, for example, the alkali metal salts, such as the sodium, potassium and ammonium salts of formic acid, acetic acid, propionic acid, oxalic acid, succinic acid, malonic acid, hexahydrobenzoic acid and hexahydrophthalic acid, or salts of the amino acids, hydroxy acids, aminohydroxy acids, halogenated acids, nitrated acids, so-called exo-acids, such as ω-benzylsulfonic acids, sulfamic acids, ω-methanesulfonic acids, oxamic acids, amino-, mono- and polysulfonic acids of the benzene, naphthalene and anthracene series, the homologues, analogues and substitution products thereof, naphthylamine-sulfonic acids, aminonaphtholsulfonic acids, arylcarboxylic acids such as benzoic acids, hydroxybenzoic acids, phthalic acids and the sulfonic acids thereof, such as sulfo-salicylic acids, sulfo-amino-salicylic acids or sulfo-phthalic acids; particularly valuable results, however, being obtained with the alkali metal salts of aliphatic acids.

The chromiferous azo-dyestuffs obtainable according to the present process dye animal fibers, such as, for example, wool and silk, blue to black tints. They are considerably superior, with regard to the fastness properties, to the dyestuffs obtained from the same azo-dyestuffs by treatment with the same quantities of the same chroming agent, but in the absence of soluble salts of organic acids. Dyeing with the dyestuffs obtainable according to the present process can be carried out in the usual manner from a sulfuric acid bath or from dye baths which, besides inorganic acids, contain aromatic acids, or advantageously according to the process described in Patent No. 1,903,884.

The following examples illustrate the invention, the parts being by weight:—

Example 1

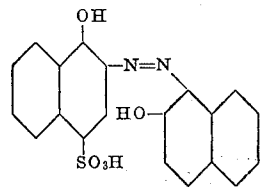
46,1 parts of the azo dyestuff from nitrated 1-diazo-2-hydroxynaphthalene-4-sulfonic acid and 2-hydroxynaphthalene of the formula



are stirred in 1000 parts of water. There are then added 4 parts of caustic soda solution of 30 per cent. strength, 12 parts of sodium formate and a chromium fluoride solution corresponding with 5,32 parts of Cr_2O_3. The whole is thereupon boiled for 5 hours in a reflux apparatus, and the black-violet solution thus obtained evaporated to dryness on the water bath in a vacuum. The chromiferous dyestuff obtained dyes wool in a bath containing organic acid and sulfuric acid black tints of excellent fastness.

Example 2

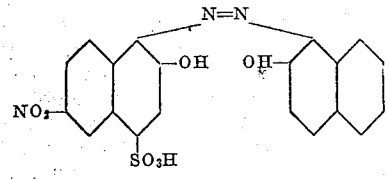
4,16 parts of the azo-dyestuff from diazotized 2-amino-1-hydroxynaphthalene-4-sulfonic acid and 2-hydroxynaphthalene of the formula



are dissolved in 100 parts of water containing 0,6 part of caustic soda solution of 30 per cent. strength. A chromium formate solution corresponding with 0,45 part of Cr_2O_3, and 3 parts of crystallized sodium acetate are added to this solution and the whole is boiled in a reflux apparatus for a long time. The blue solution thus obtained is filtered from small quantities of insoluble impurities, and after concentrating the solution with addition of common salt, the dyestuff is precipiated. The new chromium compound is obtained after drying in the form of a violet-black powder which is easily soluble in water to a reddish-blue solution. In soda solution of 10 per cent. strength, and in dilute caustic soda solution, as well as in concentrated sulfuric acid it dissolves to a greenish blue solution. It dyes wool from a bath containing organic acid and sulfuric acid fast navy blue tints.

Example 3

46,1 parts of the azo-dyestuff from nitrated 1-diazo-2-hydroxynaphthalene-4-sulfonic acid and 2-hydroxynaphthalene of the formula



are suspended in 1000 parts of water. After stirring with 4 parts of caustic soda solution of 30 per cent. strength, there is added a chromium fluoride solution containing 6 parts of Cr_2O_3, as well as 22,4 parts of sodium lactate and the whole is heated to boiling for a long time in a reflux apparatus. The filtered, brown-violet solution is evaporated to dryness in a vacuum. There is obtained a black powder which is easily soluble in water and dyes wool in a bath containing organic acid and sulfuric acid black tints of excellent fastness properties.

Example 4

46,1 parts of the azo-dyestuff from nitrated 1-diazo-2-hydroxynaphthalene-4-sulfonic acid and 2-hydroxynaphthalene are suspended in 1000 parts of water. After stirring with 4 parts of caustic soda solution of 30 per cent. strength there is added a chromium fluoride solution corresponding with 5,5 parts of Cr_2O_3, as well as 36 parts of the sodium salt of benzene-sulfonic acid, and the whole is boiled in a reflux apparatus until unchromed dyestuff can no longer be detected. The filtered, violet-black solution is evaporated to dryness in a vacuum. There is obtained a powder which is easily soluble in water and dyes wool in a bath containing organic acid and sulfuric acid black tints of excellent fastness properties.

Example 5

46,1 parts of the azo-dyestuff from nitrated 1-diazo-2-hydroxynaphthalene-4-sulfonic acid and 2-hydroxynaphthalene are suspended in 1200 parts of water. After stirring with 4 parts of caustic soda solution of 30 per cent. strength there is added a chromium fluoride solution containing 5,4 parts of Cr_2O_3, and 46 parts of the sodium salt of naphthalene-1-sulfonic acid, and the whole boiled for 6 to 8 hours in a reflux apparatus. After filtering off small amounts of impurities the solution is evaporated to dryness in a vacuum. The chromiferous dyestuff is obtained as a black powder which is easily soluble in water and dyes wool in a bath containing organic acid and sulfuric acid black tints of excellent fastness properties.

Example 6

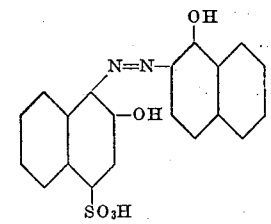
46,1 parts of the azo-dyestuff from nitrated 1-diazo-2-hydroxynaphthalene-4-sulfonic acid and 2-hydroxynaphthalene are suspended in 1200 parts of water which contains 4 parts by volume of caustic soda solution of 30 per cent. strength. To this solution there is added a chromium fluoride solution containing 5,6 parts of Cr_2O_3, as well as 46 parts of the sodium salt of naphthalene-2-sulfonic acid and the whole boiled for 6 to 8 hours in a reflux apparatus. After filtering off small amounts of impurities the solution is evaporated to dryness in a vacuum. The chromium compound which easily dissolves in water to a brown-violet black solution dyes wool in a bath containing organic acid and sulfuric acid black tints of excellent fastness properties.

Example 7

Into 1500 parts of water which contain 3 parts by volume of caustic soda solution of 30 per cent. strength there are introduced, while stirring, 46,1 parts of the azo-dyestuff from nitrated 1-diazo-2-hydroxynaphthalene-4- sulfonic acid and 2-hydroxynaphthalene. To this solution there are added 50 parts of the sodium salt of 1-aminonaphthalene-5-sulfonic acid and chromium fluoride solution corresponding to 5,8 parts of Cr_2O_3. The whole is boiled for 6 to 8 hours in a reflux apparatus. The brown-violet black solution thus obtained is then somewhat concentrated, filtered from mineral salts that have precipitated, and evaporated to dryness. The new chromium compound dyes wool in a bath containing organic acid and sulfuric acid black tints of very good fastness properties.

Example 8

41,6 parts of the azo-dyestuff from diazotized 1-amino-2-hydroxynaphthalene-4-sulfonic acid and 1-hydroxynaphthalene of the formula



are dissolved in 800 parts of water containing 5 parts by volume of caustic soda solution of 30 per cent. strength. To this solution there is added a chromium formate solution containing 5,4 parts of Cr_2O_3, as well as 21 parts of the sodium salt of phthalic acid, and the whole boiled

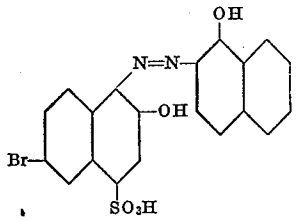
for 6 to 8 hours in a reflux apparatus. After filtering off small amounts of impurities and evaporating to dryness in a vacuum the chromium compound formed is obtained in the form of a violet black powder. It dissolves freely in water, soda solution of 10 per cent. strength and caustic soda solution of 10 per cent. strength to a blue solution, and in concentrated sulfuric acid to a blue-green solution. The new chromiferous dyestuff dyes wool in a bath containing organic acid and sulfuric acid blue tints of good fastness properties.

Example 9

41,6 parts of the azo-dyestuff from diazotized 1-amino-2-hydroxynaphthalene-4-sulfonic acid and 1-hydroxynaphthalene are dissolved in 900 parts of water containing 5 parts by volume of caustic soda solution of 30 per cent. strength. To this solution there is added a chromium lactate solution containing 5,3 parts of Cr_2O_3, as well as 22 parts of the disodium salt of the 1-amino-4-sulfobenzene-2-carboxylic acid. The whole is boiled for about 6 hours in a reflux apparatus and after filtering off small amounts of impurities the chromium compound formed is isolated by evaporation to dryness in a vacuum. It represents a violet-black powder and dissolves freely in water, soda solution of 10 per cent. strength and caustic soda solution of 10 per cent. strength to a blue solution. In concentrated sulfuric acid it dissolves to a blue-green solution and dyes wool in a bath containing organic acid and sulfuric acid blue tints of good fastness properties.

Example 10

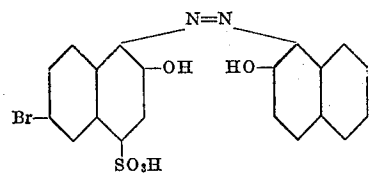
49,5 parts of the azo-dyestuff from brominated 1-diazo-2-hydroxynaphthalene-4-sulfonic acid and 1-hydroxynaphthalene of the formula



are dissolved in 700 parts of water containing 5 parts by volume of caustic soda solution of 30 per cent. strength. To this solution there is added a solution of the chromium salt of benzene sulfonic acid of about 3 per cent. strength containing 5,5 parts of Cr_2O_3, as well as 18 parts of sodium formate, and the whole is boiled for 6 to 8 hours in a reflux apparatus. The solution is then evaporated to dryness in a vacuum. The chromium compound which is freely soluble in water to a blue solution dyes wool in a bath containing organic acid and sulfuric acid blue tints of excellent fastness properties.

Example 11

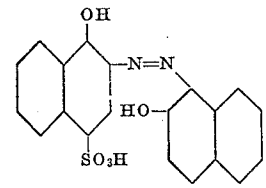
49,5 parts of the azo-dyestuff from brominated 1-diazo-2-hydroxynaphthalene-4-sulfonic acid and 2-hydroxynaphthalene of the formula



are dissolved in 1000 parts of water containing 6 parts by volume of caustic soda solution of 30 per cent. strength. To this solution there are added 40,8 parts of sodium acetate, as well as a chromium solution containing 4,5 parts of Cr_2O_3, 2 parts of hydrofluoric acid, and 5 parts of formic acid of 85 per cent. strength, and the whole is heated for 3–4 hours to 120° C. After filtering off small amounts of impurities the blue solution obtained is concentrated and the chromiferous dyestuff precipitated by addition of common salt. The chromium compound which is freely soluble in water dyes wool in a bath containing organic acid and sulfuric acid blue tints of excellent fastness properties.

Example 12

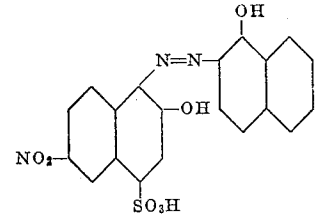
4,16 parts of the azo-dyestuff from diazotized 2-amino-1-hydroxynaphthalene-4-sulfonic acid and 2-hydroxynaphthalene of the formula



are dissolved in 100 parts of water and 2 parts of caustic soda solution of 10 per cent. strength. To this solution there are added chromium formate corresponding with 0,42 part of Cr_2O_3 as well as 4 parts of the disodium salt of 1-hydroxy-4-sulfobenzene-2-carboxylic acid. The whole is boiled for a long time in a reflux apparatus. The blue solution which has formed is concentrated, if necessary after filtering off small amounts of impurities, and the dyestuff precipitated by addition of common salt. There is obtained a violet-black powder which dissolves in water to a reddish blue solution and dyes wool in a bath containing organic acid and sulfuric acid navy blue tints of good fastness properties.

Example 13

46,1 parts of the azo-dyestuff from nitrated 1-diazo-2-hydroxynaphthalene-4-sulfonic acid and 1-hydroxynaphthalene of the formula



are dissolved in 1000 parts of water with addition of 5 parts by volume of caustic solution of 30 per cent. strength. To this solution there is added a solution of chromium formate containing 5,3 parts of Cr_2O_3, as well as 20 parts of sodium formate, and the whole is boiled for 6 to 8 hours in a reflux apparatus. The violet-black solution of the chromium compound which has formed is evaporated to dryness in a vacuum, if necessary after filtering off small amounts of impurities. There is obtained a black powder which dissolves in water to a violet-black solution, and in soda solution of 10 per cent. strength and caustic soda solution of 10 per cent. strength to a brown-violet black solution. The new dyestuff dissolves in concentrated sulfuric acid to a green black solution. It dyes wool and silk in a bath containing organic

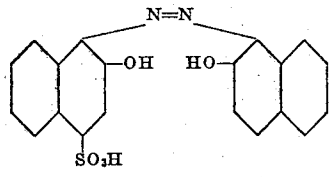
acid and sulfuric acid black tints of good fastness properties.

Example 14

41,6 parts of the azo-dyestuff from diazotized 1-amino-2-hydroxynaphthalene-4-sulfonic acid and 1-hydroxynaphthalene are dissolved in 7 parts by volume of caustic soda solution of 30 per cent. strength and 1000 parts of water. To this solution there is added a chromium fluoride solution containing 5,4 parts of Cr_2O_3, as well as 20 parts of sodium formate, and the whole is boiled for 6 hours in a reflux apparatus. The blackish-blue solution which has formed is evaporated to dryness in a vacuum, if necessary after filtering off small quantities of impurities. There is obtained a violet-black powder which freely dissolves in water, soda solution of 10 per cent. strength and caustic soda solution of 10 per cent. strength to a blue solution, and in concentrated sulfuric acid to a blackish blue-green solution. The new chromiferous dyestuff dyes wool in a bath containing organic acid and sulfuric acid blue to navy blue tints of very good fastness properties.

Example 15

83,2 parts of the azo-dyestuff from diazotized 1-amino-2-hydroxynaphthalene-4-sulfonic acid and 2-hydroxynaphthalene of the formula



are suspended in a pressure vessel in 1200 parts of water. To this suspension there are added 10 parts by volume of caustic soda solution of 30 per cent. strength, 30 parts of sodium formate, as well as a chromium formate solution corresponding with 8 parts of Cr_2O_3, and the whole is heated to 120 to 130° C. for 3 to 4 hours. After cooling, small amounts of impurities are filtered off and the blackish blue solution is evaporated to dryness in a vacuum, a violet-black powder being obtained. The chromium compound which is freely soluble in water to a reddish blue, red dichroic solution dissolves also in soda solution of 10 per cent. strength and in caustic soda solution of 10 per cent. strength to a reddish blue solution, whereas in concentrated sulfuric acid it dissolves to a greenish blue solution. The new dyestuff dyes wool in a bath containing organic acid and sulfuric acid fast navy blue tints.

What we claim is:—

1. Process for the manufacture of chromiferous azo-dyestuffs, consisting in causing azo-dyestuffs of the general formula



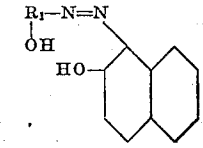
wherein R_1 means a sulfonated naphthalene radical and R_2 a naphthol radical, and wherein the hydroxyl group of the naphthalene radical R_1 stands in ortho-position to the azo-bridge, to react with agents yielding chromium in such a proportion as to provide less than one atom of chromium to each chromable group of the dyestuff molecule, the reaction being conducted in presence of soluble salts of organic acids.

2. Process for the manufacture of chromiferous azo-dyestuffs, consisting in causing azo-dyestuffs of the general formula



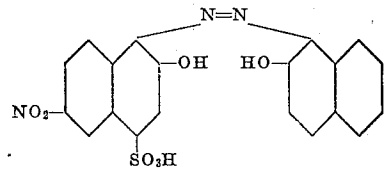
wherein R_1 means a sulfonated naphthalene radical and R_2 a naphthol radical, and wherein the hydroxyl group of the naphthalene radical R_1 stands in ortho-position to the azo-bridge, to react with agents yielding chromium in such a proportion as to provide less than one atom of chromium to each chromable group of the dyestuff molecule, the reaction being conducted in presence of alkali metal salts of aliphatic acids.

3. Process for the manufacture of chromiferous azo-dyestuffs, consisting in causing the azo-dyestuff of the general formula



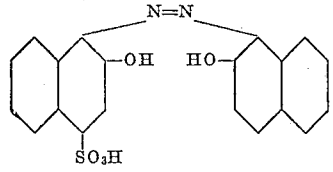
wherein R_1 means a sulfonated naphthalene radical and the hydroxyl group of the naphthalene radical R_1 stands in ortho-position to the azo-bridge, to react with agents yielding chromium in such a proportion as to provide less than one atom of chromium to each chromable group of the dyestuff molecule, the reaction being conducted in presence of alkali metal salts of aliphatic acids.

4. Process for the manufacture of chromiferous azo-dyestuffs, consisting in causing the azo-dyestuff of the formula



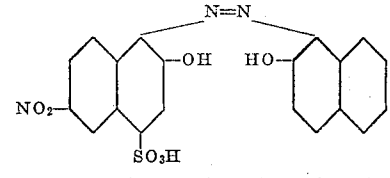
to react with agents yielding chromium in such a proportion as to provide less than one atom of chromium to each chromable group of the dyestuff molecule, the reaction being conducted in presence of alkali metal salts of aliphatic acids.

5. Process for the manufacture of chromiferous azo-dyestuffs, consisting in causing the azo-dyestuff of the formula



to react with agents yielding chromium in such a proportion as to provide less than one atom of chromium to each chromable group of the dyestuff molecule, the reaction being conducted in presence of alkali metal salts of aliphatic acids.

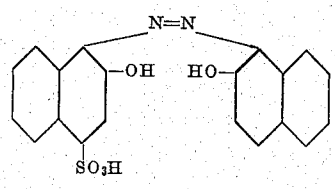
6. Process for the manufacture of a chromiferous azo-dyestuff, consisting in causing the azo-dyestuff of the formula



to react with agents yielding chromium in such a

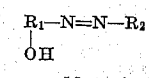
proportion as to provide less than one atom of chromium to each chromable group of the dyestuff molecule, the reaction being conducted in presence of sodium formate.

7. Process for the manufacture of a chromiferous azo-dyestuff, consisting in causing the azo-dyestuff of the formula



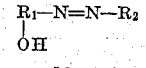
to react with agents yielding chromium in such a proportion as to provide less than one atom of chromium to each chromable group of the dyestuff molecule, the reaction being conducted in presence of sodium formate.

8. Chromiferous azo-dyestuffs obtained by causing azo-dyestuffs of the general formula



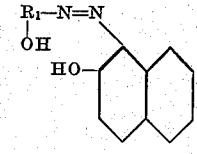
wherein R_1 means a sulfonated naphthalene radical and R_2 a naphthol radical, and wherein the hydroxyl group of the naphthalene radical R_1 stands in ortho-position to the azo-bridge, to react with agents yielding chromium in such a proportion as to provide less than one atom of chromium to each chromable group of the dyestuff molecule, the reaction being conducted in presence of soluble salts of organic acids which products represent black powders dissolving in water to blue to black solutions and dyeing animal fibers fast blue to black tints.

9. Chromiferous azo-dyestuffs obtained by causing azo-dyestuffs of the general formula



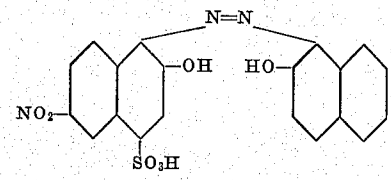
wherein R_1 means a sulfonated naphthalene radical and R_2 a naphthol radical, and wherein the hydroxyl group of the naphthalene radical R_1 stands in ortho-position to the azo-bridge, to react with agents yielding chromium in such a proportion as to provide less than one atom of chromium to each chromable group of the dyestuff molecule, the reaction being conducted in presence of alkali metal salts of aliphatic acids which products represent black powders dissolving in water to blue to black solutions and dyeing animal fibers fast blue to black tints.

10. Chromiferous azo-dyestuffs obtained by causing azo-dyestuffs of the general formula



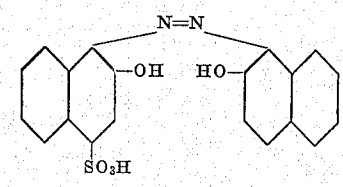
wherein R_1 means a sulfonated naphthalene radical and the hydroxyl group of the naphthalene radical R_1 stands in ortho-position to the azo-bridge, to react with agents yielding chromium in such a proportion as to provide less than one atom of chromium to each chromable group of the dyestuff molecule, the reaction being conducted in presence of alkali metal salts of aliphatic acids, which products represent black powders dissolving in water to blue to black solutions and dyeing animal fibers fast blue to black tints.

11. Chromiferous azo-dyestuffs obtained by causing the azo-dyestuff of the general formula



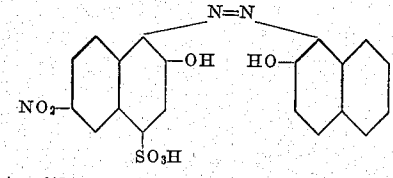
to react with agents yielding chromium in such a proportion as to provide less than one atom of chromium to each chromable group of the dyestuff molecule, the reaction being conducted in presence of alkali metal salts of aliphatic acids, which products represent black powders dissolving in water to black solutions and dyeing wool fast black tints.

12. Chromiferous azo-dyestuffs obtained by causing the azo-dyestuff of the formula



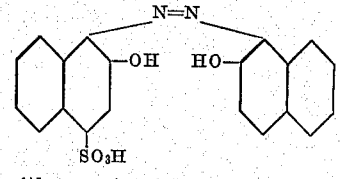
to react with agents yielding chromium in such a proportion as to provide less than one atom of chromium to each chromable group of the dyestuff molecule, the reaction being conducted in presence of alkali metal salts of aliphatic acids, which products represent black powders dissolving in water to blue solutions and dyeing wool fast blue to navy blue tints.

13. A chromiferous azo-dyestuff obtained by causing the azo-dyestuff of the formula



to react with agents yielding chromium in such a proportion as to provide less than one atom of chromium to each chromable group of the dyestuff molecule, the reaction being conducted in presence of sodium formate, which product represents a black powder dissolving in water to a black solution and dyeing wool fast black tints.

14. A chromiferous azo-dyestuff obtained by causing the azo-dyestuff of the formula



to react with agents yielding chromium in such a proportion as to provide less than one atom of chromium to each chromable group of the dyestuff molecule, the reaction being conducted in presence of sodium formate, which product represents a black powder, dissolving in water to a blue solution and dyeing wool fast blue to navy blue tints.

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