

UNITED STATES PATENT OFFICE

2,428,866

CHROMABLE DYESTUFFS AND A PROCESS
OF MAKING SAME

Achille Conzetti and Guido Schetty, Basel, and
Otto Schmid, Muttetz, Switzerland, assignors
to J. R. Geigy, Basel, Switzerland, a Swiss firm

No Drawing. Application May 1, 1944, Serial No.
533,660. In Switzerland June 4, 1943

15 Claims. (Cl. 260—149)

1

It is well known to transform dyestuffs, which are capable of being chromed and contain sulfonic acid groups, into the corresponding chromium complex compounds by heating the said dyestuffs with chromium compounds in the presence of water or of other solvents.

We have now found that it is possible to produce new, valuable, chromium-containing dyestuffs in substance by using chromium complex compounds of o-hydroxy carboxylic acids of the benzene series for the purpose of chroming chromable dyestuffs containing sulfonic acids.

As starting materials for the chromium complex compounds in accordance with the invention use may be made of o-hydroxybenzoic acid, its homologues and substitution products, such as for instance 2-hydroxy-3-, -4- or 5-methylbenzoic acid, 2-hydroxy-5-chlorobenzoic acid, 2-hydroxy-1-benzoic acid-5-sulfonic acid, their derivatives like for example 2-hydroxy-1-benzoic acid-5-sulfethyl anilide, 2-hydroxy-1-benzoic acid-5-sulfonic acid-phenyl- or -o-tolyl ester; moreover, 4-p-toluene sulfamino-salicylic acid, 2-hydroxy-5-phenoxybenzoic acid, etc., may also be used. The preparation of the chromium complex compounds is carried out according to usual methods, cf. e. g. Barbieri, R. A. L. (5) 24.1.608.

When chroming with the chromium complex compounds of o-hydroxy carboxylic acid of the benzene series there has surprisingly been observed that in many cases the chroming takes place in a much more rapid and smoother manner than when working according to the chroming methods known hitherto, i. e. by means of chromium salts, chromites, chromium compounds with auxiliary agents like for instance oxalic acid, salicylic acid, sulfosalicylic acid and so on. In many cases dyestuff complex compounds can be produced within a short time according to the invention, whereas the known chroming methods require incomparably longer reaction periods or the working under pressure at temperatures above 100° C. Since the chroming in accordance with the invention can be carried out in a neutral reaction medium, this method allows in general the chroming of dyestuffs containing groups which are sensitive to alkalis or acids, without changing these groups which, according to the constitution of the dyestuff to be chromed, are of decisive importance for the fastness properties or the levelling power of the complex dyestuff. Of course, in the literature also chroming agents have become known which react only slightly acid or even neutral, so that the same leave intact such sensitive groups. Thus, for example,

2

the chroming with chromium oxide hydrate pastes or with chromium salts of weak organic carboxylic acids like chromium acetate may be mentioned. It is a known fact, that, when working with the said chromium compounds, generally the chroming according to usual methods is not successful with o:o'-dihydroxy- or o-hydroxy-o'-carboxy azo dyestuffs containing only one solubilising group. In such cases it is mostly necessary to use diluents in a disproportionate ratio in order to guarantee the chromation, whereby this method of working becomes uneconomic.

It is known that chromium-containing wool dyestuffs may be dyed in an optimal manner from relatively weakly acid baths and preferably from organic acid baths (compare Ender and Müller, Melland's Textilberichte 1938, pages 65, 81 and 272). However, apart from some exceptions, such dyeings obtained with the chromium-containing dyestuffs known hitherto are worthless, since their shades are not yet completely developed and they give uneven dyeings on fabrics, so that the same have a skittery appearance. Only from a mineral acid bath (there has been proposed to add 8-10% sulfuric acid calculated with reference to the dyeing goods) the known chromium complex dyestuffs yield as a rule practically useful, beautiful and even dyeings which have been developed only by the strong acid dyeing. Moreover, the dyeings obtainable from an organic acid bath often possess inferior fastness properties than the dyeings resulting from a mineral acid bath. In contradistinction thereto the chromium complex dyestuffs of the present invention have the surprising and remarkable properties that they dye wool from a slightly mineral acid bath, e. g. from a 1% sulfuric acid bath, or more preferably from an organic acid bath, e. g. from a 2-4% formic acid bath, in full and even shades of excellent fastness properties without change of shades, whereas dyestuffs chromed according to hitherto known methods only obtain their full coloring properties on dyeing or developing respectively with a relatively high percentage of mineral acid.

These important properties of the new chromium-containing dyestuffs consisting in that they yield from an organic acid dyeing bath satisfactory dyeings create for the dyestuff chromium complex compounds new possibilities of application, which were not accessible hitherto for most of the known metallised dyestuffs in view of the high acid concentration required for dyeing. As such possibilities may be mentioned for instance: the semi-wool dyeing or the dyeing of

loose wool whose quality is decreased on dyeing with great quantities of mineral acid. The application of the dyestuff chromium compounds prepared according to this invention is not limited only to wool dyeing and printing. They can also successfully be dyed and printed on natural silk and on wool-like artificial fibres as well as on leather.

The present invention is illustrated, but not limited by the following examples, wherein the parts are by weight.

Example 1

61 parts of the sodium salt of the dyestuff from diazotised 4-chloro-5-nitroaminophenol and 1:8-naphthol sulfonic acid-3-sulfomethyl-anilide are stirred for 2 hours at 90°-100° C. in 750 parts of water with a solution of ammonium chromium salicylate corresponding to 9.1 parts of chromium oxide (this solution being for instance obtained by neutralisation of a mixture of 1 mole of a chromi-salt, e. g. of chromium fluoride, and 2 moles of salicylic acid at an elevated temperature with ammonia). The dyestuff being for the greatest part still insoluble at the beginning of the chroming becomes dissolved within 20 to 30 minutes to a deep blue coloration under formation of the complex compound. The complex dyestuff is isolated by addition of sodium chloride and the product thus precipitated in a sandy form is dried. The dyestuff, a deep blue powder, is easily soluble in water and dyes wool from a formic acid bath in flowery blue shades of very good uniformity. The so-obtained dyeings possess very good fastness properties to light, to rubbing and in the moist state.

Example 2

28.1 parts of the dyestuff from diazotised 4-chloraminophenol and 1:8-naphtholsulfonic acid-3-sulfethyl-anilide are stirred in 1500 parts of water and boiled under reflux for several hours with 140 parts of a solution of ammonium chromium salicylate corresponding to 5.3 parts of chromium oxide until the formation of the complex dyestuff has completed. The deep bluish-violet solution is separated by filtration while hot from the difficultly soluble product containing chromium. By addition of sodium chloride to the filtrate the new dyestuff is obtained. It dyes wool from an acid bath in blue-violet uniform shades of very good fastness properties.

Example 3

53.4 parts of the dyestuff obtainable from diazotised 4-chloraminophenol and 1:8-naphthol sulfonic acid-3-sulfanilide are boiled in 3000 parts of water with 300 parts of a solution of ammonium chromium salicylate corresponding to 20 parts of chromium oxide until a test specimen has been proved fast to acids and to alkalis. Then there is hot filtered in order to separate the difficultly soluble, chromium-containing portion and the dyestuff is precipitated from the filtrate by addition of sodium chloride, thus giving a violet-blue powder. It dyes wool from an acid bath in pure blue-violet shades of very good fastness properties.

Example 4

56.6 parts of the sodium salt of the dyestuff from diazotised 5-nitroaminophenol and 1:8-naphthol sulfonic acid-3-sulfanilide are boiled for 50 hours under reflux and under stirring in 1000 parts of water with 600 parts of a solution

of ammonium chromium salicylate corresponding to 22.8 parts of chromium oxide. Thus, the dyestuff being first completely undissolved goes in solution to a deep blue coloration while forming the complex compound. The dyestuff containing chromium is precipitated by addition of sodium chloride. It dyes wool from an acid bath in greenish-blue shades of a pleasing even color.

Example 5

45.6 parts of the monosodium salt of the dyestuff obtainable from diazotised 4:6-dinitro-2-amino-1-phenol and 1-hydroxynaphthalene-5-sulfonic acid are dissolved in 700 parts of water, boiled for some hours with the chromium complex compound obtainable by neutralising with sodium carbonate a hot solution of 70.6 parts of sodium-2-hydroxy-5-sulfethyl-anilide-benzoate and of 8.4 parts of chromium oxide in form of chromium fluoride. The deep black solution is then treated with sodium chloride, whereby the new chromium-containing dyestuff is precipitated in a resinous form. It forms on drying a black powder. When applied from an acid bath this dyestuff gives black shades of very good fastness properties in the moist state and of a very good light-fastness.

Example 6

20.8 parts of the disodium salt of the dyestuff obtainable from diazotised 1-aminonaphthalene-4-sulfonic acid and 2-hydroxybenzoic acid are heated under reflux to boiling for 2 hours in 250 parts of water with 110 parts of a solution of ammonium chromium salicylate corresponding to 4.2 parts of chromium oxide. Thus, a brown-yellow solution is formed which, by a treatment with concentrated hydrochloric acid, becomes violet. The solution is evaporated in vacuo at a raised temperature. There remains a brown-yellow powder dyeing wool from an acid bath in golden-yellow shades of good uniformity.

Example 7

62.4 parts of the disodium salt of the dyestuff obtainable from diazotised 1-aminonaphthalene-5-sulfonic acid and 2-hydroxybenzoic acid are dissolved in 750 parts of hot water, heated for a short time to boiling with a solution of ammonium chromium salicylate corresponding to 12.6 parts of chromium oxide; then the chromium-containing dyestuff is isolated by addition of sodium chloride. It dyes wool from an acid bath in clear golden-yellow shades of good fastness to light.

Example 8

12 parts of the dyestuff obtainable from diazotised 4-nitro-2-amino-1-phenol-6-sulfonic acid and 4-isobutyl-2-methyl-1-phenol are stirred with 300 parts of water and 72 parts of a solution of ammonium chromium salicylate corresponding to 2.73 parts of chromium oxide and heated during 3 hours to 140° C. in a closed vessel. The chromed dyestuff, which has partly precipitated after cooling of the reaction mass, is completely precipitated by addition of sodium chloride. The chromium-containing dyestuff thus obtained dyes wool from an acid bath in full reddish-brown shades of excellent fastness properties.

Example 9

38 parts of the disodium salt of the dyestuff obtainable from diazotised 1-aminobenzene-3-sulfonic acid and 1-methyl-2-hydroxybenzene-3-carboxylic acid are dissolved in 600 parts of hot

5

water and stirred for some hours at the water-bath temperature with a solution of ammonium chromium salicylate corresponding to 9.1 parts of chromium oxide. The complex dyestuff thus formed is isolated in the usual manner. The same is obtained in form of a yellow-brown powder for instance by evaporating the brown-yellow solution and drying the remaining viscous mass in vacuo at a raised temperature. The resulting powder is again easily soluble in water and dyes wool from a formic acid bath in clear greenish-yellow shades of excellent evenness and of good fastness properties.

Example 10

36.6 parts of the disodium salt of the dyestuff obtainable from diazotised 1-aminobenzene-4-sulfonic acid and 2-hydroxybenzene-1-carboxylic acid are dissolved in 500 parts of hot water and, after addition of 240 parts of a solution of ammonium chromium salicylate corresponding to 9.1 parts of chromium oxide, boiled during 5 hours. The deep yellow solution of the resulting chromium complex dyestuff is treated with 200 parts of sodium chloride and 35 parts of concentrated hydrochloric acid. The precipitated dyestuff is filtered off and dried. Thus a bright brown powder is obtained which dyes wool from a formic acid bath in clear yellow shades of very good evenness and of good fastness properties.

Example 11

59.7 parts of the monosodium salt of the azo dyestuff obtainable from diazotised 5-nitro-2-aminophenol-(1) and 1-naphthol-8-sulfonic acid-3-sulfonic acid-4'-methoxyanilide (the coupling component is obtained by condensation of 1:8-naphthsultone-3-sulfochloride with 1-amino-4-methoxy-benzene and by subsequent alkaline saponification of the condensation product) are stirred in 750 parts of hot water, treated with a solution of ammonium chromium salicylate corresponding to 22.8 parts of chromium oxide and stirred at boiling temperature under reflux during 24 hours. Thus the dyestuff salt being at the beginning of the chroming nearly completely undissolved goes into solution to a deep blue coloration. This solution, which does not show any change of coloration on mixing it with dilute alkali or mineral acid, is hot filtered and the complex dyestuff is separated from the solution by addition of sodium chloride thus producing a dark blue powder. The new chromium-containing dyestuff is easily water-soluble and dyes wool from a formic acid bath in clear greenish-blue shades of good evenness. The dyeings possess generally good fastness properties in the moist state as well as a good fastness to rubbing and to light.

Example 12

59.9 parts of the disodium salt of the dyestuff obtainable from diazotised 2-aminobenzene-1-carboxylic acid and 1-naphthol-8-sulfonic acid-3-sulfethylanilide are stirred in 1000 parts of water and, after addition of 240 parts of a solution of ammonium chromium salicylate corresponding to 9.1 parts of chromium oxide, boiled under stirring and under reflux until the dyestuff has been transformed into the complex form, this being the case after 15 to 20 hours. The deep red solution is hot filtered in order to eliminate some insoluble, chromium-containing by-products; then the chromium complex dyestuff is isolated by saturation with sodium chloride. It constitutes, after drying, a dark wine-red powder which is very well soluble in water. From a formic acid bath it dyes

6

wool in pure, wine-red shades of complete evenness. The dyeings are distinguished by good fastness properties to fulling, perspiration and rubbing as well as by a very good light-fastness.

Example 13

58.3 parts of the sodium salt of the dyestuff obtainable from diazotised 5-nitro-2-aminophenol and 1:8-naphthol sulfonic acid-3-sulfethyl phenylamide are suspended in 2000 parts of water and heated to boiling for 15 hours with 240 parts of a solution of ammonium chromium salicylate corresponding to 9.1 parts of chromium oxide. Thus, by this chroming a deep blue solution is produced. The new chromium-containing dyestuff is isolated in the usual manner by precipitation with sodium chloride. It dyes wool from an acid bath in greenish-blue shades.

Example 14

59.7 parts of the dyestuff obtainable from diazotised 6-nitro-4-methyl-2-amino-1-phenol and 1:8-naphthol sulfonic acid-3-sulfethylanilide are dissolved in 1000 parts of hot water and, after addition of 240 parts of a solution of ammonium chromium salicylate corresponding to 9.1 parts of chromium oxide, boiled for several hours. The deep blue solution of the complex dyestuff is filtered and the dyestuff is precipitated from the filtrate by addition of sodium chloride. After drying the dyestuff constitutes a dark blue powder. It dyes wool from an acid bath in navy-blue shades of very good light-fastness and good fastness properties in the moist state.

Example 15

61.8 parts of the dyestuff obtainable from diazotised 4-chloro-5-nitro-2-amino-1-phenol and 1:8-naphthol sulfonic acid-3-sulfethylanilide are suspended in 1500 parts of hot water and stirred at boiling temperature during 5 hours with a solution of ammonium chromium salicylate corresponding to 9.1 parts of chromium oxide. Thus, under formation of the complex compound, a deep blue solution is formed which, after cooling, is treated with sodium chloride until all the dyestuff has precipitated. The dark blue-violet powder is filtered and dried. It dyes wool from an acid bath in flowery blue shades of very good fastness to light and to rubbing.

Example 16

59.7 parts of the sodium salt of the dyestuff obtainable from diazotised 5-nitro-4-methyl-2-amino-1-phenol and 1:8-naphthol sulfonic acid-3-sulfethylanilide are suspended in 1200 parts of hot water and then boiled during 3 hours with 250 parts of a solution of ammonium chromium salicylate corresponding to 8.36 parts of chromium oxide. At the beginning of the chroming there is rapidly formed a deep blue solution, from which the complex dyestuff finally begins to crystallise. Then, the whole is cooled and the blue-black, crystalline dyestuff is filtered by suction and dried at an elevated temperature. The chromium-containing dyestuff dyes wool from an acid bath in flowery reddish-blue shades of high evenness and of very good light-fastness.

Example 17

61.8 parts of the dyestuff obtainable from diazotised 6-nitro-4-chloro-2-amino-1-phenol and 1-hydroxynaphthalene-5-sulfonic acid ethyl-(3'-sulfonic acid phenyl)-amide are heated to boiling for 8 hours in 1000 parts of water with 600 parts of a solution of ammonium chromium sali-

cylate corresponding to 9.12 parts of chromium oxide. The still hot, navy-blue solution is treated with 80 parts of sodium chloride, whereupon the dyestuff precipitates in form of a dark-blue powder, which is sucked off and dried at an elevated temperature. The new dyestuff dyes wool from an acid bath in navy-blue shades of eminent light-fastness and of excellent fastness to potting.

The 1-hydroxynaphthalene-5-sulfonic acid ethyl-(3'-sulfonic acid phenyl)-amide is prepared by condensation of 1-carbomethoxy-hydroxynaphthalene-5-sulfonic acid chloride with 1-ethylaminobenzene-3-sulfonic acid in an aqueous, slightly alkaline medium and by saponification of the obtained condensation product with the calculated quantity of caustic soda lye.

Example 18

32.2 parts of the dyestuff obtainable from diazotised 1-aminobenzene-3-sulfonic acid and 2-hydroxybenzoic acid are dissolved in form of the ammonium salt in 200 parts of water and, under stirring, evaporated on the water-bath with 240 parts of a solution of ammonium chromium salicylate corresponding to 9.1 parts of chromium oxide. The remaining viscous mass is dried in vacuo at an elevated temperature. The chromium-containing dyestuff being an olive-yellow powder dyes wool from an acid bath in greenish-yellow clear shades of very good evenness.

Example 19

62.8 parts of the sodium salt of the dyestuff obtainable from diazotised 5-nitro-2-aminophenol and 1:8-naphthol sulfonic acid-3-sulfonic acid-ethyl-(3'-nitrophenyl)-amide are dissolved in 1500 parts of hot water, treated with 240 parts of a solution of ammonium chromium salicylate corresponding to 9.1 parts of chromium oxide and then heated to boiling. After a short time the dyestuff salt has been transformed into the complex form thus giving a deep blue coloration which, on addition of diluted mineral acid, undergoes no further change. Then the solution is treated with sodium chloride and the dyestuff precipitated as blue-black powder is filtered by suction and dried. It dyes wool from an acid bath in greenish-grey shades.

The 1:8-naphthol sulfonic acid-3-sulfonic acid-ethyl-(3'-nitrophenyl)-amide is made in the following manner: 1-ethylamino-3-nitrobenzene is condensed in anhydrous pyridine with naphthsultone-3-sulfochloride and the so-obtained naphthsultone-3-sulfonic acid-ethyl-(3'-nitrophenyl)-amide is saponified with the calculated quantity of hot dilute caustic soda lye.

Example 20

11.9 parts of the sodium salt of the dyestuff obtainable from diazotised 5-nitro-2-amino-1-phenol and 1:8-naphthol sulfonic acid-3-sulfonic acid-ethyl-(2'-methylphenyl)-amide are suspended in 150 parts of water and treated with 53 parts of a solution of ammonium chromium salicylate corresponding to 1.82 parts of chromium oxide. Thus a bronzy mass is formed which is now heated to boiling under reflux and under stirring. After some hours the complex formation is complete. The new chromium complex dyestuff precipitates almost completely on cooling the resulting solution. The precipitate is then filtered and dried. From an acid bath the dyestuff gives flowery blue shades of good evenness.

Example 21

12.2 parts of the sodium salt of the dyestuff obtainable from diazotised 5-nitro-4-methyl-2-amino-1-phenol and 1:8-naphthol sulfonic acid-3-sulfonic acid-ethyl-(2'-methylphenyl)-amide are partly dissolved in 150 parts of hot water and stirred at 90°-100° C. under reflux for 15 hours after having added 53 parts of a solution of ammonium chromium salicylate corresponding to 1.82 parts of chromium oxide. The formed chromium complex dyestuff, which partly separates already in the heat in a beautiful crystalline form, is completely precipitated by addition of sodium chloride and isolated. It dyes wool from an acid bath in beautiful, fiery, blue shades of good evenness.

Example 22

57.5 parts of the sodium salt of the dyestuff obtainable from diazotised 5-nitro-2-amino-1-phenol and 1:8-naphthol sulfonic acid-3-sulfonic acid-methylphenyl amide are dissolved in 750 parts of hot water and treated with 240 parts of a solution of ammonium chromium salicylate corresponding to 9.1 parts of chromium oxide. The mixture is heated to boiling and stirred under reflux until a clear, deep blue solution has been formed, which undergoes no further change in coloration upon addition of dilute mineral acid. The solution is treated with sodium chloride and the complex dyestuff precipitated in a crystalline form is filtered off and dried. The low chromium-containing dyestuff dyes wool from an acid bath in flowery blue shades of very good fastness to fulling and perspiration.

Example 23

58.9 parts of the dyestuff obtainable from diazotised 5-nitro-4-methyl-2-amino-1-phenol and 1:8-naphthol sulfonic acid-3-sulfonic acid-methylphenyl amide are stirred in 750 parts of water and, after addition of 240 parts of a solution of ammonium chromium salicylate, heated to boiling. By the chroming a clear, deep blue solution is formed after a short time, the same being, when still hot, treated with sodium chloride. After cooling the powdery dyestuff thus precipitated is filtered by suction and dried at elevated temperature. The new chromium-containing dyestuff dyes wool from an acid bath in very uniform, flowery, blue shades of good fastness properties to fulling and perspiration.

Example 24

57.5 parts of the sodium salt of the dyestuff obtainable from diazotised 5-nitro-2-amino-1-phenol and 1:8-naphthol sulfonic acid-5-sulfonic acid-methylphenyl-amide are boiled for 20 hours under reflux and under stirring in 1000 parts of a solution of ammonium chromium salicylate corresponding to 9.1 parts of chromium oxide. Thus, a deep blue solution is formed, from which the complex dyestuff partly crystallises already in the hot. In order to isolate the dyestuff the solution is treated with sodium chloride and the dyestuff thus precipitated as a dark blue powder is filtered by suction and dried. It dyes wool from an acid bath in greenish-grey shades of excellent fastness properties to fulling and to perspiration.

The 1:8-naphthol sulfonic acid-5-sulfonic acid-methyl phenyl-amide is produced by condensation of methylphenylamine with 1:8-naphthsultone-5-sulfochloride and by alkaline saponification of the obtained condensation prod-

uct. The 1:8-naphtholsulfone-5-sulfonic acid chloride is obtained by heating 1 mole of the sodium salt of the 1:8-naphtholsulfone-5-sulfonic acid with 1 mole of phosphorus pentachloride.

Example 25

61 parts of the dyestuff obtainable from diazotised 5-nitro-4-chloro-2-amino-1-phenol and 1:8-naphtholsulfonic acid-5-sulfonic acid-methylphenyl amide are suspended in 750 parts of water and heated to boiling with 240 parts of a solution of ammonium chromium salicylate corresponding to 9.1 parts of chromium oxide. After about one hour the chroming is complete. The clear, deep blue solution is allowed to cool down, while stirring, whereby the complex dyestuff crystallises out in form of beautiful crystals. It dyes wool from an acid bath in greenish-grey shades of excellent fastness properties to fulling and to perspiration.

Example 26

57.1 parts of the sodium salt of the dyestuff obtainable from diazotised 5-nitro-2-amino-1-acid-4'-methylphenyl ester are dissolved in 1000 parts of hot water and, after heating to 100° C., treated with 200 parts of a solution of ammonium chromium salicylate. Thus a bronzing precipitate is separated which, on further stirring at 100° C., rapidly dissolves to a deep blue solution. After 5 hours it is treated with sodium chloride and the precipitated complex dyestuff is filtered. The new dyestuff dyes wool from an acid bath in navy-blue shades of very good light-fastness and good fastness to potting.

The 1:8-naphthol sulfonic acid-3-sulfonic acid-4'-methylphenyl ester is produced by condensation of 1:8-naphtholsulfone-3-sulfonic acid chloride with 4-methyl-1-hydroxybenzene and by saponification of the condensation product with the calculated quantity of sodium carbonate.

Example 27

29.3 parts of the sodium salt of the dyestuff obtainable from diazotised 5-nitro-4-methyl-2-amino-1-phenol and 1:8-naphthol sulfonic acid-3-sulfonic acid-4'-methylphenyl ester are suspended in 500 parts of water and, after addition of 200 parts of a solution of ammonium chromium salicylate corresponding to 8.3 parts of chromium oxide, boiled under reflux and under stirring during 60 hours. By the chroming a blue-black powder is formed which is sucked off after cooling and dried. The so-obtained chromium-containing dyestuff dyes wool from an acid bath in navy-blue, flowery shades of very good light-fastness and of good evenness.

Example 28

4.89 parts of the dyestuff obtainable from diazotised 6-nitro-4-amyl-2-amino-1-phenol and 3'-sulphophenyl-3-methyl-5-pyrazolone are suspended in 75 parts of water and, after addition of 24 parts of a solution of ammonium chromium salicylate corresponding to 0.91 part of chromium oxide, stirred for some hours at 90°-100° C. Thus, a gelatinous solution is obtained, which is stable to dilute acid and which is evaporated to dryness in vacuo at elevated temperature. The new chromium-containing dyestuff, a red powder, dyes wool from an acid bath in clear, red shades of very good fastness properties to light, fulling and to perspiration.

Instead of the complex chromium compounds used in the above examples for the chroming, of

course also other o-hydroxycarboxylic acid compounds of the benzene series mentioned in the general part of this specification may be used; in view of economical reasons the simplest and cheapest compounds will especially be used.

What we claim is:

1. A process for chroming a chromable mono-azo dyestuff containing one sulfonic acid group and two aromatic nuclei selected from the class consisting of nuclei of the benzene and naphthalene series, which comprises chroming the said chromable mono-azo dyestuff with a complex chromium compound of an o-hydroxybenzoic acid in such proportions that at least one atom of chromium is present for each chromable group of said chromable compound.

2. A process for chroming a chromable mono-azo dyestuff containing one sulfonic acid group and two aromatic nuclei selected from the class consisting of nuclei of the benzene and naphthalene series, which comprises chroming the said dyestuff with the complex chromium compound of salicylic acid in such proportions that at least one atom of chromium is present for each chromable group of said chromable dyestuff.

3. A process for chroming a chromable mono-azo dyestuff containing one sulfonic acid group, two aromatic nuclei selected from the class consisting of nuclei of the benzene and naphthalene series, and a hydroxy group in at least one of the o- and o'-positions to the azo bridge, which comprises chroming the said dyestuff with a complex chromium compound of an o-hydroxybenzoic acid in such proportions that at least one atom of chromium is present for each chromable group of said chromable dyestuff.

4. A process for chroming a chromable mono-azo dyestuff containing one sulfonic acid group, two aromatic nuclei selected from the class consisting of the benzene and naphthalene series, and one o-hydroxy-carboxy-grouping, which comprises chroming the said dyestuff with a complex chromium compound of an o-hydroxybenzoic acid in such proportions that at least one atom of chromium is present for each chromable group of said chromable dyestuff.

5. A process for chroming a chromable mono-azo dyestuff containing one sulfonic acid group, two aromatic nuclei selected from the class consisting of nuclei of the benzene and naphthalene series, and a carboxy and a hydroxy group in o:o'-position to the azo bridge, which comprises chroming the said dyestuff with a complex chromium compound of an o-hydroxybenzoic acid in such proportions that at least one atom of chromium is present for each chromable groups of said chromable dyestuff.

6. A process for chroming a chromable mono-azo dyestuff containing one sulfonic acid group, two aromatic nuclei selected from the class consisting of nuclei of the benzene and naphthalene series, and a hydroxy group in at least one of the o- and o'-positions to the azo bridge, which comprises chroming the said dyestuff with a complex chromium compound of salicylic acid in such proportions that at least one atom of chromium is present for each chromable group of said chromable dyestuff.

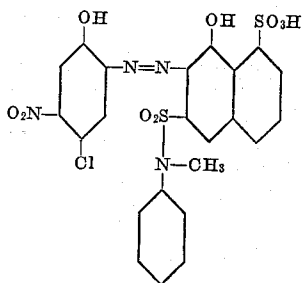
7. A process for chroming a chromable mono-azo dyestuff containing one sulfonic acid group, two aromatic nuclei selected from the class consisting of the benzene and naphthalene series, and one o-hydroxy-carboxy-grouping, which comprises chroming the said dyestuff with a complex chromium compound of salicylic acid in such

11

proportions that at least one atom of chromium is present for each chromable group of said chromable dyestuff.

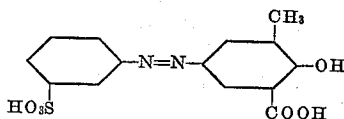
8. A process for chroming a chromable mono-azo dyestuff containing one sulfonic acid group, two aromatic nuclei selected from the class consisting of nuclei of the benzene and naphthalene series, and a carboxy and a hydroxy group in o:o'-position to the azo bridge, which comprises chroming the said dyestuff with a complex chromium compound of salicylic acid in such proportions that at least one atom of chromium is present for each chromable group of said chromable dyestuff.

9. A process for chroming the dyestuff of the formula



which comprises chroming the said dyestuff with the complex chromium compound of salicylic acid in such proportion that at least one atom of chromium is present for each chromable group of said dyestuff.

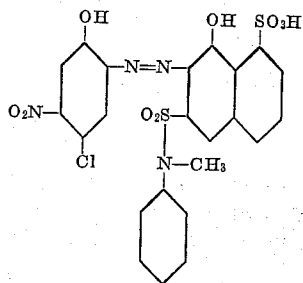
10. A process for chroming the dyestuff of the formula



which comprises chroming the said dyestuff with the complex chromium compound of salicylic acid in such proportion that at least one atom of chromium is present for each chromable group of said dyestuff.

11. A chromed chromable dyestuff containing one sulfonic acid group and two aromatic nuclei selected from the class consisting of nuclei of the benzene and naphthalene series, chromed by means of a complex chromium compound of an o-hydroxy-benzoic acid, and containing at least one atom of chromium for each chromable group of said dyestuff.

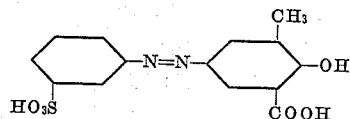
12. The chromed chromable dyestuff of the formula



being chromed by means of the complex chromium compound of salicylic acid and containing at least one atom of chromium for each chromable group of said dyestuff, and being an easily soluble blue powder dyeing wool in even blue shades.

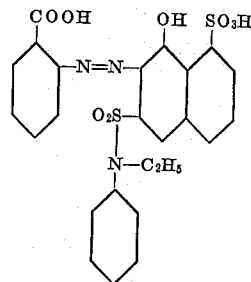
12

13. The chromed chromable dyestuff of the formula



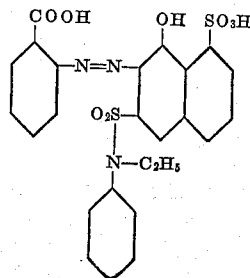
being chromed by means of the complex chromium compound of salicylic acid and containing at least one atom of chromium for each chromable group of said dyestuff, being a brownish-yellow powder, easily soluble in water and dyeing wool in bright greenish-yellow shades.

14. A process for chroming the dyestuff of the formula



which comprises chroming the said dyestuff with the complex chromium compound of salicylic acid in such proportion that at least one atom of chromium is present for each chromable group of said dyestuff.

15. The chromed chromable dyestuff of the formula



being chromed by means of the complex chromium compound of salicylic acid and containing at least one atom of chromium for each chromable group of said dyestuff, being a dark wine-red powder, easily soluble in water and dyeing animal fibres in light-fast pure wine-red shades.

ACHILLE CONZETTI.
GUIDO SCHETTY.
OTTO SCHMID.

REFERENCES CITED

The following references are of record in the file of this patent:

UNITED STATES PATENTS

Number	Name	Date
2,090,432	Straub	Aug. 17, 1937
2,054,057	Lange	Sept. 8, 1936
1,957,580	Delfs et al.	May 8, 1934
2,305,747	Straub	Dec. 22, 1942
2,353,675	Knecht et al.	July 18, 1944
2,317,671	Cook et al.	Apr. 27, 1943
2,054,489	Stusser	Sept. 15, 1936
2,362,988	Conzetti et al.	Nov. 21, 1944
2,010,921	Lange	Aug. 13, 1935
2,022,243	Lange	Nov. 26, 1935

FOREIGN PATENTS

Number	Country	Date
75 418,622	Great Britain	Oct. 29, 1934