

## UNITED STATES PATENT OFFICE

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METHOD OF CHROMING DYESTUFFS WITH  
ORTHO HYDROXY CARBOXYLIC ACID  
CHROMIUM COMPLEXES

Achille Conzetti, Basel, and Otto Schmid,  
Muttentz, near Basel, Switzerland, assignors to  
J. R. Geigy A. G., Basel, Switzerland, a Swiss  
firm

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1

In technical literature many processes for chroming mordant dyestuffs containing sulfonic acid groups have been published, which all consist in the use either of trivalent chromium salts or of chromium hydroxide or chromites.

According to all these known processes o-hydroxycarboxy dyestuffs, free from sulfonic acid groups, of the type of Eriochromazurol B (Schultz-Lehmann, Dyestuff tables, 7th edition, No. 838) or of Eriochromflavin A (loc. cit. No. 258) become completely insoluble compounds.

It is further known that o:o'-dihydroxy azo dyestuffs, free from sulfonic acid groups, can be converted into alcohol-soluble chromium compounds, which however are not water-soluble, by treatment with trivalent chromium salts in an aqueous alcoholic solution or by the action of chromium-yielding agents in alkaline medium in the presence of salts of aliphatic o-hydroxycarboxylic acids.

There has now been made the surprising discovery that mordant dyestuffs, free from sulfonic acid groups, of the above types can be converted into water-soluble chromium compounds by treating the same in an aqueous solution or suspension at a raised temperature, preferably at boiling temperature, open or under pressure, with complex chromium compounds of aromatic o-hydroxycarboxylic acids of the benzene and naphthalene series and in doing so using at least one atom of chromium for each mordant group of the dyestuff capable of being chromed.

Complex chromium compounds of aromatic o-hydroxycarboxylic acids are obtained in the known manner by treating their alkali salt solutions with trivalent chromium salts. Suitable aromatic o-hydroxycarboxylic acids are for example salicylic acid, its homologues and substitution products, such as sulfosalicylic acid, sulfocresotinic acids, further o-hydroxynaphthoic acids and their substitution products, such as sulfo- $\beta$ -hydroxynaphthoic acid and so on. Even diamine compounds of complex chromium compounds of aromatic o-hydroxycarboxylic acids, such as diamine chromium salicylic acid or its alkali salts, which are obtained in form of red-violet crystallised compounds, for example from chromium salicylate alkali salts when standing with excess amines, such as ammonia, alkyl amines, ethylene diamine or pyridine, are suitable for use according to the present invention.

The formation of water-soluble chromium compounds of mordant dyestuffs, free from sulfonic acid groups, could not be foreseen and the very smooth course of the chroming is surprising,

2

particularly as complex chromium compounds of aliphatic o-hydroxycarboxylic acids, as shown by experiments, are not very suitable as chromium-yielding agents for chroming mordant dyestuffs.

The new water-soluble chromium compounds of o-hydroxycarboxy dyestuffs, free from sulfonic acid groups, extend the field of application of many dyestuffs known for a long time. They may be used for example for dyeing cellulose, such as cotton or paper, for dyeing silk from a weak acid bath or leather. In comparison with the analogous, completely water-insoluble chromium compounds, obtainable by known chroming processes, the new water-soluble chromium compounds constitute a substantial enrichment of technology.

The new water-soluble chromium compounds of o:o'-dihydroxy azo dyestuffs, free from sulfonic acid groups, draw uniformly, from a weak acid bath, on animal fibres and partially also on cotton. They are also suitable for dyeing leather.

The present invention is illustrated, but not limited, by the following examples. Their parts are by weight unless otherwise indicated.

25

## EXAMPLE 1

9.6 parts of Eriochromazurol B (sodium salt) (Schultz, Dyestuff tables, 7th edition, No. 838) are dissolved in 100 parts of water and stirred for about 20 minutes at 90–100° C. with 100 parts of a solution of ammonium chromium salicylate, containing 1 gram atom of chromium in 2500 g. of solution. The yellow-red solution changes within 5 minutes, with a temporary violet coloring, into a pure blue. By salting out the cooled solution, the new chromium compound can be isolated as a violet-blue powder. It is easily soluble in water with a pure blue coloration. From the organic acid bath it dyes animal and vegetable fibres with pure blue shades. Very pure blue color shades are obtained on leather.

The apple green solution of ammonium chromium salicylate is obtained for example by stirring the solutions of 1 mol. chromium acetate in 2000 parts of water and 2 mol. ammonium salicylate in 400 parts of water at 90–100° C. and neutralising with ammonia until the reaction remains neutral to litmus.

Similar complex dyestuff chromium compounds are obtained with analogous chromium compounds of the homologous salicylic acids, of the salicylic acid mono- or di-sulphonic acids, of the o-hydroxynaphthoic acids and of their sulfonic acids.

## EXAMPLE 2

9.7 parts of the dyestuff Eriochrome flavin A (Schultz No. 258) are dissolved in 100 parts of water and boiled by reflux with a solution of sodium chromium salicylate, corresponding to 4.5 parts of chromium oxide. In a short time the brown-olive solution of the water-soluble chromium compound of the dyestuff is formed. The new chromium-containing dyestuff can be obtained as an olive-yellow powder by salting out. It produces, from a weak acid bath, on animal

um sulfosalicylate is obtained from ammonium chromium sulfosalicylate as peach-bloom red little crystals by allowing the solution, saturated with  $\text{NH}_3$ , to stand. Analogous compounds are obtained with amines such as ethylene diamine, alkyl amines, pyridine and piperidine and the like.

By treating the above mentioned dyestuff with sodium chromium salicylate a water-soluble chromium compound is obtained which is very suitable for dyeing leather.

Table

Dyestuff	Chromed with: Na/NH <sub>4</sub> chromium salicylate (a) Na/NH <sub>4</sub> chromium sulfo salicylate (b)	Color of the chromium compound	Dyeing of wool (W), Silk (S), leather (L), cellulose (C)
1. Eriochrome-azuroil B.....	a	Blue.....	S, L, C: blue.
2. Eriochrome-azuroil G.....	a	do.....	S, L, C: blue.
3. Naphthochrome-green G (Schultz No. 851).....	a	Green.....	S, L, C: green.
4. 2-(4'-diethylamino-2'-oxy)-benzoyl benzoic acid condensed with $\beta$ -resorcylic acid and oxidised.....	a	Red.....	S, L, C: red.
5. Methylene-di-o-cresotic acid hydrol condensed with 1-phenyl-3-methyl-5-pyrazolone and oxidised.....	a	Brown.....	S, L, C: brown.
6. 4-dimethylamino-2-chlorobenzaldehyde condensed with o-cresotic acid and oxidised.....	a	Violet.....	S, L, C: violet.
7. Eriochrome flavin A (Schultz No. 258).....	a	Yellow.....	S, C, L: yellow.
8. Anthranilic acid $\rightarrow$ 1-phenyl-3-methyl-5-pyrazolone.....	b	do.....	W: yellow.
9. Anthranilic acid $\rightarrow$ 2,4-dihydroxy quinoline.....	b	do.....	W, L: yellow.
10. 4-nitro-2-amino-phenol $\rightarrow$ 1-phenyl-3-methyl-5-pyrazolone.....	b	Yellow-orange.....	W, L: orange.
11. 6-methyl-4-nitro-2-amino-phenol $\rightarrow$ 1-phenyl-3-methyl-5-pyrazolone.....	b	Orange.....	W, L: orange.
12. 4-nitro-2-amino-phenol $\rightarrow$ 2,4-dihydroxy quinoline.....	b	do.....	W, L: orange.
13. Anthranilic acid $\rightarrow$ p-cresol.....	b	Red.....	W, L: red.
14. 4-chloro-2-amino-phenol $\rightarrow$ 2,4-dihydroxy quinoline.....	b	Bordeaux.....	W, L: Bordeaux.
15. 4-nitro-2-amino-phenol $\rightarrow$ p-cresol.....	b	do.....	W, L: Bordeaux.
	b	Red-brown.....	W, L: red-brown.

fibres, bright yellow dyeings of good fastness properties.

The sodium chromium salicylate is obtained for example, by boiling a chromium acetate solution, which contains 1 gram atom of chromium in 1.5 litres, with 2 gram molecules of sodium salicylate, whilst neutralising with sodium carbonate the acetic acid set free until the reaction remains neutral to litmus.

Chromium compounds of Eriochrome flavin A of similar properties are obtained with analogous complex chromium solutions from homologous salicylic acids, salicylic acid mono- or di-sulfonic acid, sulfo cresotic acids, o-hydroxy-naphthoic acids and their sulfonic acids.

## EXAMPLE 3

19.6 parts of the dyestuff, free from sulfonic acid groups, obtained from diazotised 4-nitro-2-amino-phenol and 1-phenyl-3-methyl-5-pyrazolone are dissolved in 800 parts of hot water with 100 parts of 34% soda lye and boiled by reflux with 130 parts of a solution of sodium chromium sulfosalicylate (corresponding to 5 parts of chromium oxide). The orange colored solution thereby separates about 5 parts of brown little crystals of a water-insoluble, but alcohol-soluble chromium complex compound, which are filtered off hot after 2 hours. The new water-soluble chromium compound is recovered from the filtrate by salting out. It produces, from the weak acid bath, good light-fast, uniform yellow-orange dyeings on animal fibres.

Similar products are obtained with ammonium chromium sulfosalicylate and ammonium diamine chromium sulfosalicylate.

The said chroming agents are obtained by dissolving 1 gram atom of chromium hydroxide in a solution of 2 gram atoms of sulfosalicylic acid in 1 litre of water and neutralisation with sodium carbonate or ammonia until the reaction remains neutral to litmus. Ammonium diamine chromi-

What we claim is:

1. Process for chroming dyestuffs capable of being chromed and free from sulfonic acid groups consisting in chroming such a dyestuff in an aqueous medium at a raised temperature with a complex chromium compound of a member selected from the group consisting of the aromatic o-hydroxycarboxylic acids of the benzene and naphthalene series, using at least one atom of chromium for each mordant group of the dyestuff capable of being chromed.

2. Process for chroming dyestuffs capable of being chromed and free from sulfonic acid groups consisting in chroming such a dyestuff in an aqueous medium at boiling temperature with a complex chromium compound of an o-hydroxybenzoic acid, using at least one atom of chromium for each mordant group of the dyestuff capable of being chromed.

3. Process for chroming Eriochromazurol B, consisting in chroming this dyestuff in an aqueous medium at 90°-100° C. with ammonium chromium salicylate, using at least one atom of chromium for each o-hydroxy-carboxy group of the dyestuff.

4. Process for chroming Eriochromflavin A, consisting in chroming this dyestuff in an aqueous medium at 90°-100° C. with sodium chromium salicylate, using at least one atom of chromium for each o-hydroxy-carboxy group of the dyestuff.

5. Process for chroming the azo dyestuff from diazotized 4-nitro-2-aminophenol and 1-phenyl-3-methyl-5-pyrazolone, consisting in chroming this dyestuff in an aqueous medium at boiling temperature with sodium chromium sulfosalicylate using at least one atom of chromium for each mordant group of the dyestuff.

6. A dyestuff which is free from sulfonic acid groups and which contains, in complex union, trivalent chromium and an aromatic o-hydroxycarboxylic acid, said dyestuff being obtained by

5

chroming a chromable dyestuff which is free from sulfonic acid groups with a complex chromium compound of a member selected from the group consisting of the aromatic o-hydroxycarboxylic acids of the benzene and naphthalene series, at least one atom of chromium being present for each mordant group of the chromable dyestuff.

7. A dyestuff which is free from sulfonic acid groups and which contains, in complex union, trivalent chromium and an o-hydroxybenzoic acid, said dyestuff being obtained by chroming a chromable dyestuff which is free from sulfonic acid groups with a complex chromium compound of the o-hydroxybenzoic acid, at least one atom of chromium being present for each mordant group of the chromable dyestuff.

8. A dyestuff which is free from sulfonic acid groups and which contains, in complex union, trivalent chromium and ammonium salicylate, said dyestuff being obtained by chroming Eriochromazurol B with a complex chromium compound of ammonium salicylate, at least one atom of chromium being present for each o-hydroxycarboxy group of the chromable dyestuff.

9. A dyestuff which is free from sulfonic acid groups and which contains, in complex union, trivalent chromium and sodium salicylate, said dyestuff being obtained by chroming Eriochromflavin A with a complex chromium compound of sodium salicylate, at least one atom of chromium being present for each o-hydroxycarboxy group of the chromable dyestuff.

10. A dyestuff which is free from sulfonic acid

6

groups and which contains, in complex union, trivalent chromium and sodium sulfosalicylate, said dyestuff being obtained by chroming the azo dyestuff from diazotized 4-nitro-2-aminophenol and 1-phenyl-3-methyl-5-pyrazolone with a complex chromium compound of sodium sulfosalicylate, at least one atom of chromium being present for each mordant group of the chromable dyestuff.

ACHILLE CONZETTI.  
OTTO SCHMID.

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