

# UNITED STATES PATENT OFFICE

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## PROCESS FOR PRODUCING FAST TINTS ON ANIMAL FIBERS

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In dyeing animal fibers with chromiferous azo-dyestuffs the dyeing is conducted in a bath acid with sulfuric acid. This entails a considerable disadvantage because a number of chromiferous dyestuffs is precipitated in the acid dye-bath so that the dyeings obtained are not fast and are feeble; furthermore, in many cases, notwithstanding that the dyestuffs are fully taken up by the fiber, the correct strength of color cannot be attained.

It has been proposed to use the chromiferous azo-dyestuffs in dye-baths acid with organic acids. Here again, in spite of the fact that the dyestuffs are fully taken up by the fiber, in many cases the correct color strength or the valuable properties of fastness, or both, are not attained.

It is also known that the chromiferous azo-dyestuffs can be used in dye-baths which, beside mineral acids, such as, for example, sulfuric acid, contain aliphatic acids, such as, for example, formic acid or acetic acid. In dyeing in this manner the defects belonging to the other known processes are in large part avoided.

The present invention is based on the observation that in respect of the yield of dyeing, improved uniformity of dyeing and dyeing throughout the fabric, and, further, more particularly the production of colored effects and combinations, results are obtained which are even better than those produced by dyeing the animal fibers, for instance silk and wool, in baths which, beside mineral acids, such as, for example, sulfuric acid, contain aliphatic acids, by using dye-baths which, beside inorganic acids, such as, for example, sulfuric acid, contain aromatic acids.

This new process has the advantage that it requires a smaller proportion of mineral acid than is necessary in the known process.

The present invention, therefore, relates to a process according to which there are used for dyeing animal fibers, on the one part, chromium compounds of azo-dyestuffs of the general formula  $R-N=N-R_1$  wherein R stands for an aromatic radical containing a group capable of being chromed, and  $R_1$  for the radical of a coupling component, and, on the other part, dye-baths which, beside inorganic acids, contain aromatic acids.

The chromium compounds of azo-dyestuffs which are dyed according to the present proc-

ess may contain not only one atom of chromium but also more or less than one atom of chromium for each group of the dyestuff molecule capable of being chromed.

The azo-dyestuffs which are the basis of these chromium compounds may be obtained from such diazotized aromatic amines of the benzene and naphthalene series which contain groups capable of being chromed, such as, for example, a hydroxyl group or a carboxyl group standing in ortho-position to the amino group, or a hydroxyl group standing in ortho-position to a carboxyl group, by coupling with any coupling components, such as, for example, the hydroxy- and amino-compounds of the benzene- and naphthalene series which are capable of being chromed, as well as compounds of which the carbon atom capable of coupling belongs to a heterocyclic ring (pyrazolones, hydroxyquinolines and barbituric acids) or to an open chain (aceto acetic acid derivatives and benzoylaceto-o-carboxylic acids).

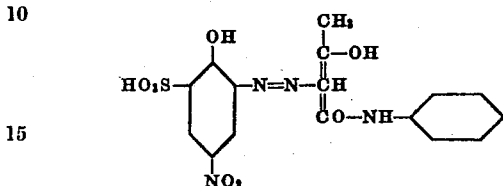
The present process may, for example, be carried out by using dye-baths at first containing only the aromatic acid, the mineral acid being added in the course of the dyeing only, or dye-baths which at first contain both the aromatic acid and a part of the necessary mineral acid, the rest of the mineral acid being added in the course of the dyeing only, or by using dye-baths which contain the aromatic acid and the total quantity of mineral acid already at the beginning of the dyeing. By this latter procedure it is possible to avoid the two stages of the known process, and to carry out the dyeing in a single step. In case the mineral acid is present in the dye-bath already at the beginning of the dyeing operation, the aromatic acids may be added to the dye-baths also in the form of their salts, such as, for example, the sodium salt, potassium salt or ammonium salt.

As aromatic acids there may be used aromatic sulfonic acids, aromatic carboxylic acids or aromatic sulfocarboxylic acids; also substitution products of these acids can be used, for instance amino-acids, hydroxy-acids, amino-hydroxy-acids, halogenated acids, nitrated acids; furthermore, the so-called exo-acids, such as  $\omega$ -benzyl-sulfonic acids, sulfamic acids,  $\omega$ -methane-sulfonic acids or oxamic acids. In the examples a number of these products are named.

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

**Example 1**

5 Into a bath consisting of 2000 parts of water, 0.5 part of benzenemonosulfonic acid, 3 parts of the chromium compound of the dyestuff from diazotized 4-nitro-2-amino-1-phenol-6-sulfonic acid and acetic acid anilide of the formula



are entered 100 parts of wool at 60–70° C. The temperature is raised in the course of ½ hour to the boil, 4 parts of sulfuric acid are added and boiling is continued for 1–1½ hours; the goods are then rinsed and dried.

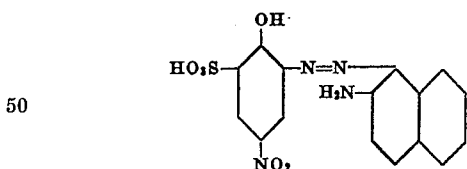
There are obtained full, pure yellow tints of very good properties.

25 Like results are obtained when 1:5-naphthalene-disulfonic acid is used in place of benzenemonosulfonic acid in this example.

30 Instead of the acid used in this example, other aromatic acids may be used, for instance aminosulfonic acids or poly-sulfonic acids of the benzene, naphthalene and anthracene series; naphthalenesulfonic acids, their analogues and substitution products; naphthylaminesulfonic acids; aminonaphtholsulfonic acids; arylcarboxylic acids, such as benzoic acid, hydroxybenzoic acids, phthalic acids and their sulfonic acids, such as sulfosalicylic acid or sulfophthalic acid.

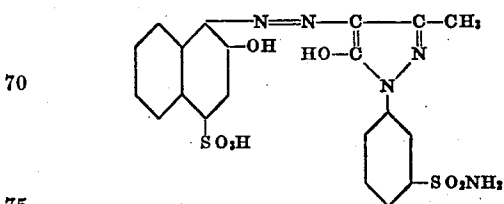
**Example 2**

40 Into a dye-bath consisting of 2000 parts of water, 0.6 part of benzenemonosulfonic acid, 2 parts of the chromium compound of the dyestuff from diazotized 4-nitro-2-amino-1-phenol-6-sulfonic acid and 2-amino-naphthalene of the formula.

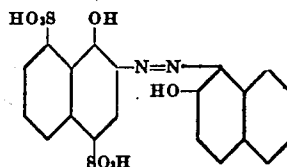


55 there are entered 100 parts of wool at 60–70° C.; the temperature is raised in the course of half an hour to the boil, 4 parts of sulfuric acid are then added and boiling is continued for 1–1½ hours. The goods are then rinsed and dried.

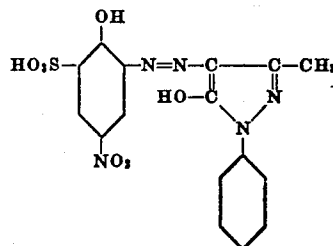
60 Full, pure green tints of very good fastness are obtained. Instead of the chromium compounds of the dyestuffs named in these examples, other chromium compounds may be used, for instance those of the dyestuffs from diazotized 1-amino-2-hydroxynaphthalene-4-sulfonic acid and 1-(3'-sulfamido)-phenyl-3-methyl-5-pyrazolone of the formula



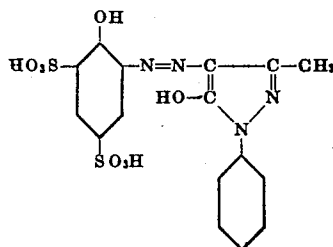
diazotized 2-amino-1-hydroxynaphthalene-4:8-disulfonic acid and β-naphthol of the formula



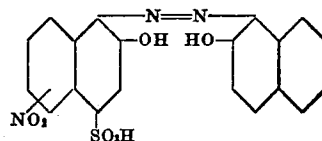
15 diazotized 4-nitro-2-amino-1-phenol-6-sulfonic acid and 1-phenyl-3-methyl-5-pyrazolone of the formula



25 diazotized 2-amino-1-phenol-4:6-disulfonic acid and 1-phenyl-3-methyl-5-pyrazolone of the formula

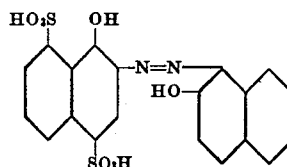


40 nitrated 1-diazo-2-hydroxynaphthalene-4-sulfonic acid and 2-hydroxynaphthalene of the formula

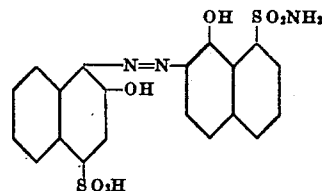


**Example 3**

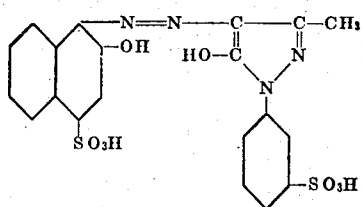
50 100 parts of wool are introduced into a dye-bath at 60–70° C. consisting of 2000 parts of water, 5 parts of sulfuric acid, 4.5 parts of the chromium compound of the dyestuff from diazotized 2-amino-1-naphthol-4:8-disulfonic acid and 2-hydroxynaphthalene of the formula



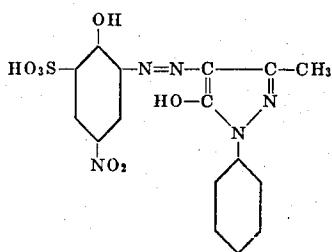
65 1.2 parts of the chromium compound of the dyestuff from diazotized 1-amino-2-naphthol-4-sulfonic acid and 1:8-naphtholsulfamide of the formula



1 part of the chromium compound of the dyestuff from diazotized 1-amino-2-naphthol-4-sulfonic acid and 1-(3'-sulfo)-phenyl-3-methyl-pyrazolone of the formula



0.3 part of the chromium compound of the dyestuff from diazotized 4-nitro-2-amino-1-phenol-6-sulfonic acid and 1-phenyl-3-methyl-5-pyrazolone of the formula

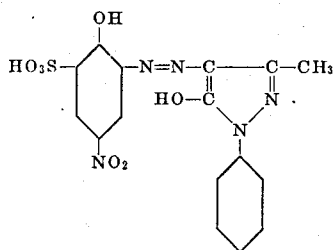


and 5 parts of a solution of 0.66 per cent. strength of 1-amino-2-naphthol-4-sulfonic acid; the temperature is raised in the course of half an hour to boiling and is kept at this point for 1-1½ hours. The goods are then rinsed and dried.

Marine blue dyeings are obtained which are remarkable for their strong, full tones and are of very good fastness to rubbing and, in spite of the proportion of sulfuric acid used, quite essentially improved fastness to fulling as compared with the dyeings obtained by the known processes, which require essentially larger quantities of sulfuric acid for development of the properties.

#### Example 4

Into a dye-bath consisting of 2000 parts of water, 4 parts of sulfuric acid, 3 parts of the chromium compound of the dyestuff from diazotized 4-nitro-2-amino-1-phenol-6-sulfonic acid and 1-phenyl-3-methyl-5-pyrazolone of the formula



and 10 parts of a solution of 5 per cent. strength of 1:3-dihydroxybenzene-4-carboxylic acid there are entered 100 parts of wool at 60-70° C.; the temperature is raised in the course of ½ hour to boiling, boiling is continued for 1 hour to an hour and a half and the goods are then rinsed and dried.

Orange tints are obtained which are fuller and finer and of better properties of fastness, notwithstanding that only half of the sulfuric acid usual in the known process has been employed in the dyeing.

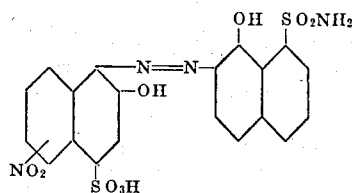
If, in this example there be substituted for the 1:3-dihydroxybenzene-4-carboxylic acid, for in-

stance 2-hydroxynaphthalene-3-carboxy-8-sulfonic acid, similar results are obtained.

Instead of the chromium compound of the dyestuff named in this example there may be used other chromium compounds for the dyeing, for instance the chromium compound of the dyestuff from diazotized 1-amino-2-hydroxynaphthalene-4-sulfonic acid and 1-(3'-sulfamido)-phenyl-3-methyl-5-pyrazolone; or from diazotized 2-amino-1-hydroxynaphthalene-4:8-disulfonic acid and β-naphthol.

#### Example 5

Into a dye-bath consisting of 2000 parts of water, 0.5 part of benzenesulfonic acid, 2 parts of concentrated sulfuric acid and 7 parts of the chromium compound of the dyestuff from nitrated 1-diazo-2-hydroxynaphthalene-4-sulfonic acid and 1-hydroxynaphthalene-8-sulfamide of the formula



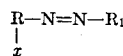
there are entered 100 parts of wool at 60-70° C. The temperature is raised to boiling in the course of half an hour, 3 per cent. of concentrated sulfuric acid are added, boiling is continued for 1½ hours and the goods are then rinsed and dried.

There are obtained full, very fast black shades. Similar results are obtained when, from the first, 0.5 part of benzenesulfonic acid and 5 per cent. of sulfuric acid are present in the bath.

What we claim is:—

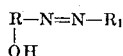
1. Process for producing fast tints on animal fibers, consisting in using for the dyeing, on the one part, chromium compounds of azo-dyestuffs of the general formula  $R-N=N-R_1$  wherein R stands for an aromatic radical containing a group capable of being chromed, and  $R_1$  for the radical of a coupling component, and on the other part, dye-baths which, beside inorganic acids, contain aromatic acids.

2. Process for producing fast tints on animal fibers, consisting in using for the dyeing, on the one part, chromium compounds of azo-dyestuffs of the general formula



wherein R stands for an aromatic radical,  $R_1$  for the radical of a coupling component, and x for a group capable of being chromed standing in ortho-position to the azo-bridge, and, on the other part, dye-baths which, beside inorganic acids, contain aromatic acids.

3. Process for producing fast tints on animal fibers, consisting in using for the dyeing, on the one part, chromium compounds of azo-dyestuffs of the general formula



wherein R stands for an aromatic radical,  $R_1$  for the radical of a coupling component, and where- in the hydroxyl-group stands in ortho-position to the azo-bridge, and, on the other part, dye-baths which, beside inorganic acids, contain aromatic acids.

4. Process for producing fast tints on animal

fibers, consisting in using for the dyeing, on the one part, chromium compounds of azo-dyestuffs of the general formula



wherein R stands for a radical of the benzene or naphthalene series, R<sub>1</sub> for the radical of a coupling component, and wherein the hydroxyl-group stands in ortho-position to the azo-bridge, and, on the other part, dye-baths which, beside inorganic acids, contain aromatic acids.

5. Process for producing fast tints on animal fibers, consisting in using for the dyeing, on the one part, chromium compounds of azo-dyestuffs of the general formula



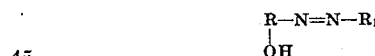
wherein R stands for a radical of the benzene or naphthalene series, R<sub>1</sub> for the radical of a coupling component, and wherein the hydroxyl-group stands in ortho-position to the azo-bridge, and, on the other part, dye-baths which, beside inorganic acids, contain aromatic sulfonic acids.

6. Process for producing fast tints on animal fibers, consisting in using for the dyeing, on the one part, chromium compounds of azo-dyestuffs of the general formula



wherein R stands for a radical of the naphthalene series, R<sub>1</sub> for the radical of a coupling component, and wherein the hydroxyl-group stands in ortho-position to the azo-bridge, and, on the other part, dye-baths which, beside inorganic acids, contain aromatic sulfonic acids.

7. Process for producing fast tints on animal fibers, consisting in using for the dyeing, on the one part, chromium compounds of azo-dyestuffs of the general formula



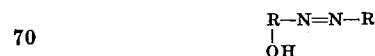
wherein R stands for a radical of the naphthalene series, R<sub>1</sub> for a naphthol radical, and wherein the hydroxyl-group stands in ortho-position to the azo-bridge, and, on the other part, dye-baths which, beside inorganic acids, contain aromatic sulfonic acids.

8. Process for producing fast tints on animal fibers, consisting in using for the dyeing, on the one part, chromium compounds of azo-dyestuffs of the general formula



wherein R stands for a radical of the naphthalene series, R<sub>1</sub> for a naphthol radical, and wherein the hydroxyl-group stands in ortho-position to the azo-bridge, and, on the other part, dye-baths which, beside inorganic acids, contain aromatic mono-sulfonic acids.

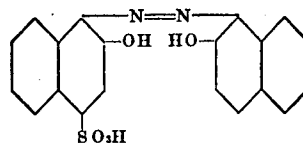
9. Process for producing fast tints on animal fibers, consisting in using for the dyeing, on the one part, chromium compounds of azo-dyestuffs of the general formula



wherein R stands for a radical of the naphthalene

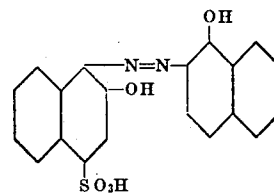
series, R<sub>1</sub> for a naphthol radical, and wherein the hydroxyl-group stands in ortho-position to the azo-bridge, and, on the other part, dye-baths which, beside inorganic acids, contain benzene-mono-sulfonic acid.

10. Process for producing fast tints on animal fibers, consisting in using for the dyeing, on the one part, chromium compounds of azo-dyestuffs of the formula



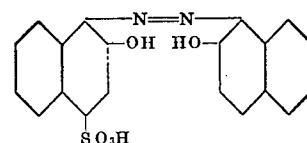
and, on the other part, dye-baths which, beside inorganic acids, contain benzene-mono-sulfonic acid.

11. Process for producing fast tints on animal fibers, consisting in using for the dyeing, on the one part, chromium compounds of azo-dyestuffs of the formula



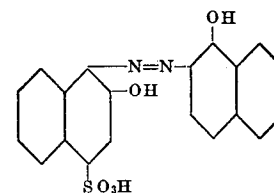
and, on the other part, dye-baths which, beside inorganic acids, contain benzene-mono-sulfonic acid.

12. Process for producing fast tints on animal fibers, consisting in using for the dyeing, on the one part, chromium compounds of azo-dyestuffs of the formula



and, on the other part, dye-baths which, beside sulfuric acid, contain benzene-mono-sulfonic acid.

13. Process for producing fast tints on animal fibers, consisting in using for the dyeing, on the one part, chromium compounds of azo-dyestuffs of the formula



and, on the other part, dye-baths which, beside sulfuric acid, contain benzene-mono-sulfonic acid.

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