

UNITED STATES PATENT OFFICE

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MANUFACTURE OF COLORING MATTERS AND DYEINGS THEREWITH

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Azo dyestuffs containing chromium and capable of dyeing wool are already known.

We have now found that chromium derivatives can also be prepared in a water-soluble form from direct coloring matters which contain groups enabling them to be chromed and that such chromium derivatives will still have the property of directly dyeing cotton or other cellulose fibres whether natural or artificial. They produce dyeings of excellent fastness. Water-soluble chromium derivatives of the aforesaid character can especially be obtained from azo dyestuffs containing two radicles of an ortho-hydroxy-carboxylic acid in their molecule. In some cases even chromium compounds of wool dyestuffs have the character of direct dyestuffs and may be employed like the chromated direct coloring matters.

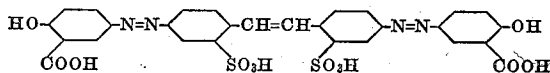
We have further found that it is not necessary to first prepare the chromium compounds of the dyestuffs, but the dyestuffs may be simply mixed with a soluble chromium salt. The mixture can serve for dyeing without further treatment and produces dyeings usually of greater fastness than those obtained with the coloring matters alone on chrome mordanted cotton or with afterchroming. Or the dyeing baths may be directly prepared from the dyestuffs and the chromium salts separately. For example fluoride, acetate, oxalate, formate and other salts of chromium may be used or mixtures of such and similar salts. For such mixtures direct azo dyestuffs containing, as aforesaid, two radicles of an ortho-hydroxy carboxylic acid in their molecule, and which are particularly adapted to give water-soluble chromium derivatives are especially suitable. Chromium salts of a complex character which contain chromium both in an anion and in a cation state may also particularly be mentioned.

Dyeing with the said chromium compounds of dyestuffs or with dyestuffs and chromium salts or mixtures made therefrom may be effected either in a hot bath or in the cold and it may often be advisable, in particular when working with cold baths, to employ an after-treatment with an alkaline agent.

The following examples illustrate more fully how the invention may be carried into practice but the invention is not restricted to these examples. The parts are by weight.

Example 1

10 parts of the direct azo dyestuff made from 4,4'-diamino-stilbene-2,2'-disulphonic acid and two molecular proportions of salicylic acid corresponding to the formula:

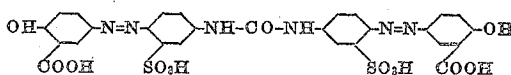


are dissolved in 400 parts of water, and boiled, after an addition of 5 parts of crystallized sodium acetate has been made, with 100 parts of a solution of a chromium salt, containing about 10 parts of chromium oxide Cr_2O_3 . Such chromium salt solution may be prepared from 6 molecular proportions of chromium formate, 4 molecular proportions of chromium fluoride and 1 molecular proportion of chromium sulphate. After boiling the dyestuff with the chromium salt solution for about 3 hours, the solution is filtered, if necessary, and the new compound salted out. It should be dried with caution. The quantity of chromium salts can be considerably reduced.

For dyeing, 100 parts of cotton are treated in a hot bath containing say 3 parts of the new chromium compound and a little Glauber's or common salt, for about an hour, or manipulated for several hours at ordinary temperature, then rinsed for a short time and put into lime water for a while. Fast orange shades are so obtained.

Example 2

3 parts of the direct azo dyestuff representing the urea of the azo combination paraphenylene-diamine sulfonic acid + salicylic acid, as expressed by the formula:



are mixed with so much of a mixture of chromium salts (composed of 6 molecular pro-

portions of chromium formate, 4 molecular proportions of chromium fluoride and 1 molecular proportion of chromium sulfate) as corresponds to 3 parts of chromium oxide, and with 3 parts of dehydrated sodium acetate. Such mixture may be used for dyeing cotton in a hot bath, while gradually adding a solution of common salt.

Example 3

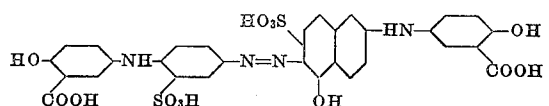
Instead of first making the chromated dye-stuff as described in Example 1, 10 parts of cotton may be dyed with 0.3 part of the azo dyestuff mentioned in said example, 0.3 part of crystallized sodium acetate, 3 parts of the chromium salt solution mentioned in Example 1 and 200 parts of water, while gradually adding 12 parts of saturated common salt solution.

The following dyestuffs may also be mixed with soluble chromium salts and the mixtures used for dyeing, or the dye-bath may be prepared with the coloring matters and an addition of a chromium salt:

A dyestuff from 2 molecular proportions

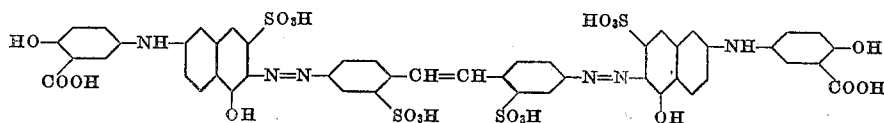
and 2 molecular proportions of 4'-hydroxy-3'-carboxylic acid-1'-phenyl-2-amino-5-naphthol-7-sulfonic acid (obtained by condensing 2-amino-5-naphthol-7-sulfonic acid with para-amino-salicylic acid in the presence of sodium bisulphite according to the British specification No. 18726 A. D. 1900): dyes violet.

The same amino-naphthol-sulfonic acid derivative with 1 molecular proportion of 4-amino-2-sulfonic acid-4'-hydroxy-5'-carboxylic acid-diphenylamine which gives a dyestuff corresponding to the formula:

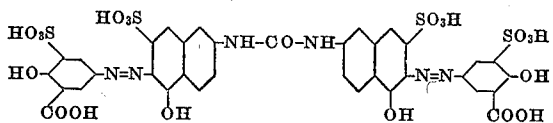


also dyes violet.

The same amino-naphthol-sulfonic acid derivative with 1 molecular proportion of 4,4'-diamino-stilbene-2,2'-disulfonic acid which gives a dyestuff corresponding to the formula:

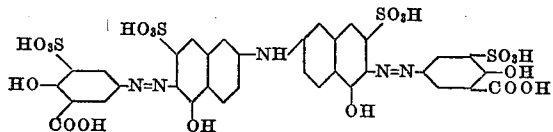


of diazotized para-amino-sulfo-salicylic acid (obtained by sulfonating para-amino-salicylic acid with fuming sulfuric acid of 23 per cent SO_3) and 1 molecular proportion of the urea from 2-amino-5-naphthol-7-sulfonic acid corresponding to the formula:



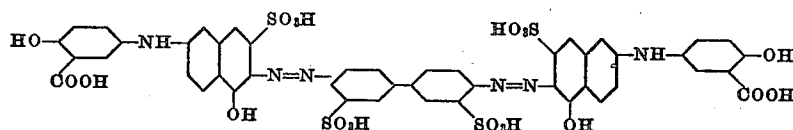
dyes red.

A similar dyestuff, but with 1 molecular proportion of 5,5'-dihydroxy-2,2'-dinaphthylamine-7,7'-disulfonic acid instead of the urea named which corresponds to the formula:



dyes violet. The same dyeings are obtained with a dyestuff derived from ortho-amino-para-sulfo-salicylic acid.

A dyestuff corresponding to the formula:

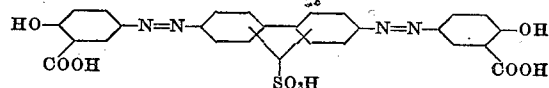


prepared from 1 molecular proportion of tetrazotized benzidine-o-o-disulfonic acid

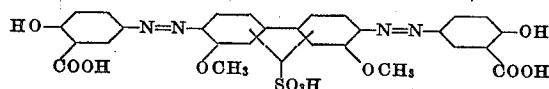
dyes blue.

As further examples may be cited the sulfonation products of the following disazo-dyestuffs, dyeing from golden yellow to orange yellow:

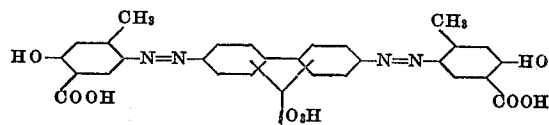
1 molecular proportion of benzidine + 2 molecular proportions of salicylic acid corresponding to the formula:



1 molecular proportion of o,o'-dianisidine + 2 molecular proportions of salicylic acid corresponding to the formula:

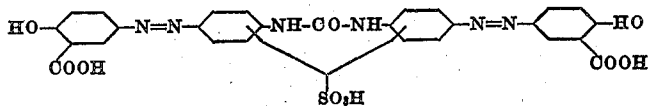


1 molecular proportion of benzidine + 2 molecular proportions of meta-cresotinic acid corresponding to the formula:



1 molecular proportion of p,p-diamino-diphenyl urea + 2 molecular proportions of

salicylic acid corresponding to the formula: of a direct azo dyestuff containing in its mole-



Example 4

100 parts of calico are dyed, for the space of an hour, in a hot bath containing 3 parts of the dyestuff p-p-diamino-stilbene disulfonic acid + 2 molecular proportions of salicylic acid described in Example 1, 3 parts of crystallized sodium acetate, 10 parts of common salt and a solution of chromium acetate-oxalate (2 molecules Cr_2O_3 : 4 molecules acetic acid: 4 molecules oxalic acid) containing 3 parts of Cr_2O_3 . After rinsing and drying, a bright orange shade of excellent fastness is obtained.

Chromium-formate-oxalate may also be employed, or a mixture of, for example, hexaformate-dihydroxo-tri-chromium-formate and potassium-tri-oxalate-chromate.

Example 5

30 parts of one of the dyestuffs mentioned in Example 3 are mixed with 9 parts of dried sodium acetate and 43 parts of dried chromium-acetate-oxalate (see Example 4) containing 35 per cent of chromium. For dyeing 100 parts of cotton, 8 parts of such mixture are used with 10 parts of common salt, and dyed in a hot bath for an hour.

We claim:

1. The process of manufacturing chromium derivatives, capable of dyeing cellulose fibers, of dyestuffs which consists in combining a direct azo dyestuff containing groups enabling it to be chromed, and free from any heavy metal, with a soluble chromium salt.

2. The process of manufacturing chromium derivatives, capable of dyeing cellulose fibers, of dyestuffs which consists in combining a direct azo dyestuff, containing in its molecule two residues of an ortho-hydroxy-carboxylic acid and free from any heavy metal, with a water-soluble chromium salt.

3. As an article of manufacture a directly dyeing water-soluble product containing chromium but no other heavy metal and a direct azo dye-stuff having groups enabling it to be chromed.

4. As an article of manufacture a directly dyeing water soluble product containing chromium but no other heavy metal and a direct azo dyestuff containing in its molecule two residues of an ortho-hydroxy-carboxylic acid.

5. As a composition of matter, a mixture of a direct azo dyestuff containing in its molecule two residues of an ortho-hydroxy-carboxylic acid and free from any heavy metal and a water-soluble chromium salt.

6. As a composition of matter, a mixture

cule two residues of an ortho-hydroxy-carboxylic acid and free from any heavy metal and a water-soluble complex chromium salt which composition is soluble in water and has the property of directly dyeing cellulosic fiber.

7. The process of dyeing cellulosic fiber which consists in applying a bath containing a dissolved direct azo dyestuff with two residues of an ortho-hydroxy-carboxylic acid in its molecule and a soluble chromium salt and aftertreating the dyeings in an alkaline bath.

8. The process of dyeing cellulosic fiber, which comprises applying thereto a bath containing a dissolved direct azo coloring matter having groups enabling it to be chromed and free from any heavy metal, and combining the said coloring matter with chromium in the same bath by means of a soluble chromium salt.

9. The process of dyeing cellulosic fiber, which comprises applying thereto a bath containing a dissolved direct azo dyestuff with two residues of an ortho-hydroxy-carboxylic acid in its molecule and free from any heavy metal, and combining the said dyestuff with chromium in the same bath by means of a soluble chromium salt.

In testimony whereof we have hereunto set our hands.

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