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UNITED STATES PATENT OFFICE

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PROCESS FOR PRODUCING FAST TINTS ON CELLULOSE FIBERS

Fritz Straub, Kaiseraugst, near Basel, and Walter Hanhart, Riehen, Switzerland, assignors to the firm Society of Chemical Industry in Basle, Basel, Switzerland

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3 Claims. (Cl. 8—42)

It has been found that fast tints are produced on cellulose fibers when the fibers dyed with direct dyeing azo-dyestuffs capable of combining with metal which are derived from tetrazotised 4:4'-diamino-3:3'-dialkoxydiphenyls, are treated in a medium alkaline with alkali carbonate with an agent yielding metal and stable at least in the cold to aqueous alkali carbonate solution.

Cellulose fibers suitable for treatment by the invention are for example the various vegetable fibers, for instance cotton and linen and fibers from regenerated cellulose, for instance artificial silk and staple fiber which may be made by the viscose process, the cuprammonium process or any other process.

Direct dyeing azo-dyestuffs capable of combining with metal which are derived from tetrazotised 4:4'-diamino-3:3'-dialkoxydiphenyls having alkoxy groups of the lower aliphatic series, for example 4:4'-diamino-3:3'-dimethoxydiphenyl or -diethoxydiphenyl are those dis- and poly-azo dyestuffs in which the coupling of both or at least one diazo group of the tetrazotized 4:4'-diamino-3:3'-dialkoxydiphenyl occurs in ortho-position to the auxochrome groups, preferably hydroxyl groups of the coupling components, for instance in hydroxy benzenes or hydroxy naphthalenes, which components may contain for instance sulphonic groups or amino groups, and where by suitable choice of components it is ensured that the dyestuff produced has affinity for cellulose fiber.

The cellulose fibers may be dyed with the said dyestuffs by usual methods for dyeing with direct dyeing dyestuffs, for example in a bath containing sodium sulphate and if desired alkali carbonate, for instance sodium carbonate. The cellulose fibers serving as the starting material for the process dyed in the manner described are treated in a bath alkaline with alkali carbonate, for example a bath alkaline with sodium carbonate with an agent yielding metal, for example one yielding nickel, cobalt or especially copper which is stable to aqueous alkaline carbonate solution, at least in the cold and preferably also in the hot, that is to say an agent which has no tendency or only insignificant tendency to precipitate an insoluble metal compound, for instance an hydroxide or an oxide. Such agents are for example metal compounds, especially copper compounds of organic compounds containing hydroxyl groups, for instance, hydroxy carboxylic acids, for example aliphatic hydroxy carboxylic acids. They may be prepared in simple manner, for instance by mixing an aqueous solution of an ordinary metal salt, for instance copper sulfate with an aqueous solution of an organic compound containing a hydroxyl group, for instance an hydroxy carboxylic acid like tartaric acid and if desired neutralising the mixture by means of alkalihydroxide or alkali carbonate. Other hydroxy carboxylic acids which are applicable for the purpose are for instance lactic acid, glycollic acid, hydroxy-tartaric acid, malic acid, citric acid, saccharic acid and heptoic acid. The complex copper compounds of such hydroxy acids have the property of not being hydrolytically split with separation of copper oxide in an alkali carbonate bath in the cold or to any appreciable extent when heated.

The goods may be treated with this agent either in a fresh bath or in the same bath in which they have been dyed and if desired before the dyestuff has become completely fixed on the fiber. The temperature of the bath is preferably similar to that usual for the dyeing; it may be either somewhat lower or somewhat higher. There may also be used for the process dyestuffs of the kind in question which already contain metal in complex union in a dyestuff molecule but are still capable of combining further metal. In this case the agent yielding metal may supply the same metal as is in the dyestuff molecule or a different metal.

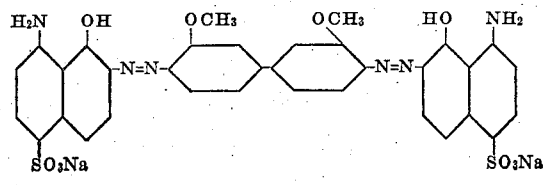
The invention produces dyeings which differ advantageously from those obtainable by the usual process involving after-coppering of the dyeings of the same dyestuffs with copper sulphate in neutral or feebly acid medium. From the properties of the dyeings produced it may be concluded that at least one alkoxy-group of the dyestuff used is saponified to a hydroxyl group.

Owing to the stability to washing of the metal complex compounds, the fastness to light of the dyeings produced by the invention is not affected or is only slightly affected by washing, namely less affected than those obtained by the usual processes.

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

Example 1

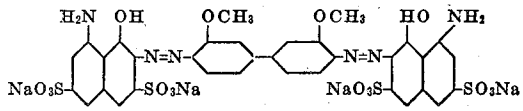
0.1 part of Chicago Blue B (Colour Index No. 516) of the formula



is dissolved in 200 parts of water with the addition of 0.2 part of sodium carbonate. 10 parts of cotton are entered into this bath at 30–40° C. and the temperature is then raised to the boil and 3 parts of crystallised sodium sulfate are added; dyeing is continued for ¾ hour at 90–95° C. There are then added to the bath 10 parts by volume of a solution made by dissolving 10 parts of crystallised copper sulfate, 12 parts of tartaric acid and the amount of caustic soda lye necessary for neutralisation in 1000 parts of water. Dyeing is continued for ½ hour at 90–95° C. and the goods are then thoroughly rinsed with cold water and soaped if desired. There is obtained a green-blue dyeing which differs from that obtained by the ordinary process by its greener tints.

Example 2

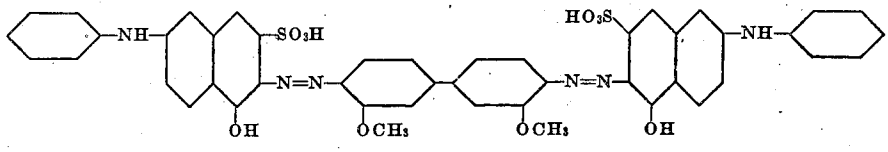
0.1 part of Diamine Sky Blue (Colour Index No. 520) of the formula



is dissolved with addition of 0.2 part of sodium carbonate in 200 parts of water. 10 parts of cotton are entered in this bath at 30–40° C. and the temperature is raised to the boil and 3 parts of crystallised sodium sulfate are added and dyeing is continued for ¾ hour at 90–95° C. There are then added to the bath 10 parts by volume of the solution made by dissolving 10 parts of crystallised copper sulfate, 12 parts of tartaric acid and the quantity of soda lye necessary for neutralisation in 1000 parts of water. Dyeing is continued for ½ hour at 90–95° C. The goods are then thoroughly rinsed with cold water and soaped if desired. There is obtained a green-blue dyeing which is greener and faster to light than a dyeing produced by the usual method.

Example 3

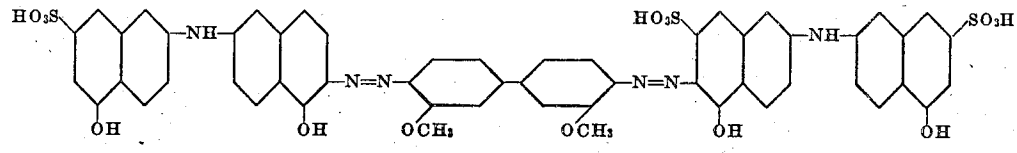
0.1 part of the dyestuff of the formula



is dissolved in the form of its sodium salt in 200 parts of water to which 0.2 part of sodium carbonate is added. 10 parts of cotton are entered in this bath at 30–40° C. The temperature is raised to boiling. 3 parts of crystallised sodium sulfate are added and dyeing is continued for ¾ hour at 90–95° C. There is then added to the bath 10 parts by volume of a solution made by dissolving 10 parts of crystallised copper sulfate, 12 parts of tartaric acid and the quantity of caustic soda lye necessary for neutralisation in 1000 parts of water. Dyeing is continued for about ½ hour at 90–95° C. and the goods are then thoroughly rinsed in cold water. The blue dyeing obtained in this manner differs from that obtained by the usual after-coppering process in that it has a bluer tint and suffers less change of colour when soaped or washed.

Example 4

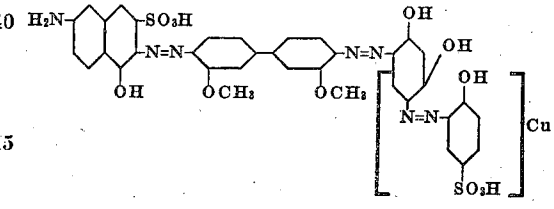
0.1 part of the dyestuff of the formula



is dissolved in the form of its sodium salt in 200 parts of water to which 0.2 part of sodium carbonate has been added. 10 parts of cotton are entered in this bath at 30–40° C., the temperature is raised to the boil, 3 parts of crystallised sodium sulfate is added and dyeing is continued for ¾ hour at 90–95° C. 10 parts by volume of the solution made by dissolving 10 parts of crystallised copper sulfate, 12 parts of tartaric acid and the quantity of soda lye necessary for neutralisation in 1000 parts of water is then added to the bath. Dyeing is continued for about ½ hour at 90–95° C. and the goods are then thoroughly washed with cold water and soaped if desired. The dyeing obtained is greenish-blue and differs from one produced by the usual process by a greener tint and improved fastness to light.

Example 5

A dye bath is prepared from 4000 parts of water, 2 parts of sodium carbonate and 1 part of the dyestuff of the formula



and 100 parts of cotton are entered into the bath at 40–50° C. After ¼ to ½ hour the temperature of the bath is raised to 95° C. whereupon there are added 30 parts of crystallised sodium sulfate and dyeing is continued for about 15–20 minutes; there are then added 66 parts of an aqueous solution containing per litre 10 parts of crystallised copper sulfate, 12 parts of tartaric acid and the quantity of caustic soda lye necessary to complete neutralisation; dyeing is continued for about 30 minutes at 90–95° C. and the goods are finally washed with cold water. A violet tint is obtained of improved fastness to light, especially in the washed dyeings, as compared with the tint obtained by after-coppering with copper sulfate.

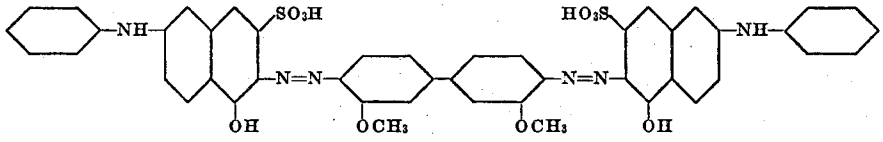
Similar dyeings are obtained if instead of the dyestuff containing copper one containing nickel, chromium or cobalt is used.

The dyestuff of the formula last given is ob-

tained by treating at a raised temperature, the monoazo-dyestuff from 18.9 parts of diazotized 2-amino-1-phenol-4-sulfonic acid and 11 parts of 1:3-dihydroxybenzene with an agent yielding copper in the proportion of 1 mol dyestuff to 1 mol copper, coupling in a solution alkaline with sodium carbonate the aqueous solution of the metal compound of the dyestuff thus obtained with 24.4 parts of tetrazotized dianisidine and then coupling the intermediate dyestuff product thus produced with 24 parts of 2-amino-5-hydroxynaphthalene-7-sulfonic acid and working up the final dyestuff in the usual manner.

Example 6

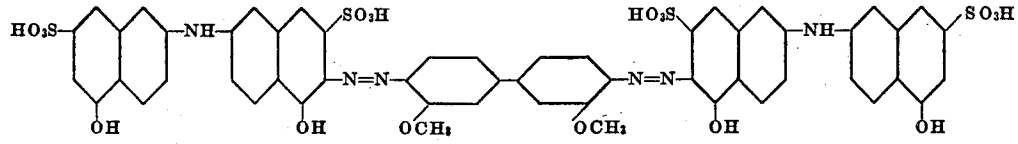
0.1 part of the dyestuff of the formula



(sodium salt) is dissolved in 200 parts of water to which 0.2 part of sodium carbonate has been added. 10 parts of cotton are entered in this bath at 30–40° C., the temperature is raised to the boil, 3 parts of crystallised sodium sulfate are added and dyeing is continued for 1¼ hours at 90–95° C. The material is then rinsed in cold water and after-treated for ½ hour at 60–70° C. in a fresh bath consisting of 200 parts of water, 0.2 part of sodium carbonate and 10 parts by volume of a solution obtained by dissolving 10 parts of crystallized copper sulfate, 12 parts of tartaric acid and the quantity of caustic soda solution necessary for neutralisation in 1000 parts of water. The goods are then thoroughly rinsed in cold water. The dyeing obtained is blue and differs from one produced by the usual after-coppering process by a greener tint and improved fastness to light.

Example 7

0.1 part of the dyestuff of the formula



(sodium salt) is dissolved in 200 parts of water to which 0.2 part of sodium carbonate has been added. 10 parts of cotton are entered in this bath at 30–40° C., the temperature is raised to the boil, 3 parts of crystallised sodium sulfate are added and dyeing is continued for 1¼ hours at 90–95° C. The material is then rinsed in cold water and after-treated for ½ hour at 60–70° C. in a fresh bath consisting of 200 parts of water, 0.2 part of sodium carbonate and 10 parts by volume of a solution obtained by dissolving 10 parts of crystallised copper sulfate, 12 parts of tartaric acid and the quantity of caustic soda solution necessary for neutralisation in 1000 parts of water. The goods are then thoroughly rinsed in cold water. The dyeing obtained is blue and differs from that obtained by the usual after-coppering process in that it has a bluer tint and a somewhat better fastness to light and suffers less change of color when soaped and washed.

What we claim is:

1. A process for producing fast tints on cellulose fibers, which comprises reacting, in an aqueous medium rendered alkaline with alkali metal carbonate, a metal-yielding agent which is stable to aqueous alkali metal carbonate solutions at least in the cold and which contains metal bound in complex form to an aliphatic hydroxy carboxylic acid, with cellulose fibers which have been dyed with a direct dyeing azo-dyestuff which is capable of being metallized and which is produced by coupling, on both sides, a tetrazotized 4:4'-diamino-3:3'-dialkoxy-diphenyl, the alkoxy groups of which belong to the lower aliphatic series, with coupling components which contain SO_3H groups and which are selected from coupling components of the benzene and naphthalene series.

2. A process for producing fast tints on cellulose fibers, which comprises reacting, in an aqueous medium rendered alkaline with alkali metal carbonate, a copper-yielding agent which is stable to aqueous alkali metal carbonate solutions at least in the cold and which contains copper bound in complex form to an aliphatic hydroxy carboxylic acid, with cellulose fibers which have been dyed with a direct dyeing azo-dyestuff which is capable of being metallized and which is produced by coupling, on both sides, a tetrazotized 4:4'-diamino-3:3'-dialkoxy-diphenyl, the alkoxy groups of which belong to the lower aliphatic series, with coupling components which contain SO_3H groups and which are selected from coupling components of the benzene and naphthalene series.

3. A process for producing fast tints on cellulose fibers, which comprises reacting, in an aqueous medium rendered alkaline with alkali metal carbonate, a complex copper salt of tartaric acid, with cellulose fibers which have been dyed with a direct dyeing azo-dyestuff which is capable of being metallized and which is produced by coupling, on both sides, a tetrazotized 4:4'-diamino-3:3'-dialkoxy-diphenyl, the alkoxy groups of which belong to the lower aliphatic series, with coupling components which contain SO_3H groups and which are selected from coupling components of the benzene and naphthalene series.

FRITZ STRAUB.
WALTER HANHART.