

UNITED STATES PATENT OFFICE

2,115,136

DYEING

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10 Claims. (Cl. 8—5)

A. The present invention relates to improvements in dyeing whereby fast shades may be obtained on animal or vegetable fibers, including fibers made of cellulose esters, (e. g. cellulose acetate) or on fabrics consisting of mixtures of any

B. It is well known that animal and certain of the vegetable fibers are sensitive to caustic alkalis, and that this has restricted the dyeing of cellulose acetate, wool, and other alkali sensitive fibers with azo dyes.

C. An object of the invention is to dye alkali sensitive fibers of either animal or vegetable origin with an azo dyestuff without subjecting the fiber to the degrading influence of a caustic alkali. Another object of the invention is to dye materials with ice colors in a bath free from caustic alkalis.

D. The objects of the invention are accomplished, generally speaking, by treating an alkali sensitive animal or vegetable fiber, or a material derived therefrom, with an amino-arylamide of 2:3-hydroxy-naphthoic acid containing a solubilizing group (sulfo, carboxy, or thioglycollic acid groups) in the aminoaryl radical in the presence of a mild base and in the absence of a caustic alkali, and developing the color by treatment with a solution of a diazo compound or with a nitrous acid solution. Among the materials to which the process can be applied are wool, cellulose esters, regenerated cellulose. The basic substance may be either organic or inorganic.

E. Exemplary of the very large number of primary arylamines which may be used as the diazo components in this invention are the following: 4-nitro-2-amino-anisole; 2:5-dichlor-aniline; 4-chloro-2-amino-toluene; 2-methoxy-1-naphthylamine; 2-methoxy-aniline; 2-phenoxy-aniline; 2-ethoxy-aniline; 2-chlor-5-methyl-aniline; 2-methyl-aniline; 2-methoxy-5-methyl-aniline; 2-methoxy-4-chlor-5-methyl-aniline; 2:5-dimethoxy-aniline; 2:5-diethoxy-aniline; 2:5-dimethoxy-4-chlor-aniline; 5-brom-2-methoxy-aniline; 3-iodo-6-methoxy-aniline; 3-iodo-6-ethoxy-aniline; 3-methyl-4-chlor-aniline; 3-brom-6-ethoxy-aniline; 3-chlor-6-ethoxy-aniline; 3-ethoxy-aniline; 3-phenoxy-aniline; 3-methoxy-aniline; 3-brom-6-phenoxy-aniline; 3-iodo-6-phenoxy-aniline; 3-brom-6-methyl-aniline; 3-chlor-6-methyl-aniline; 3-methyl-aniline; 3-brom-5-methyl-aniline; 3-chlor-6-phenoxy-aniline; 2:5-dimethyl-4-chlor-aniline; 4-ethyl-aniline; 4-amino-benzotrifluoride; 4-chlor-2-methoxy-aniline; 4-brom-2-methoxy-aniline; 4-brom-2-ethoxy-aniline; 4-iodo-2-methoxy-aniline; 4-methoxy-aniline; 4-chlor-2-ethoxy-aniline; 4-phenoxy-aniline; 4-ethoxy-aniline; 4-brom-2-phenoxy-aniline; 4-methoxy-2-chlor-aniline; 4-chlor-2-methyl-aniline; 4-methyl-3-brom-aniline; 4-brom-3-methyl-aniline; 4-methyl-3-chlor-aniline;

line; 4-methyl-aniline; 4-chlor-2-phenoxy-aniline; 4-methoxy-3-chlor-aniline; 4-phenoxy-2-chlor-aniline; 4-chlor-2:5-diethoxy-aniline; 3-chlor-2-methyl-aniline; 3-chlor-2-methoxy-aniline; alpha-naphthylamine; beta-naphthylamine; ortho-chlor-aniline; meta-chlor-aniline; meta-nitraniline; 4-chloro-2-nitraniline; 4-chloro-2-amino-anisole; 5-nitro-2-amino-anisole; 1-amino-4-benzoylamino-2:5-diethoxy-benzene; N-(para-amino-benzoyl)-aniline; dianisidine; alpha-amino-anthraquinone; 3-amino-carbazole; 2-nitro-4-methyl-benzene-azo-cresidine; 4:4'-diamino-diphenylamine.

F. On wool a full shade having good fastness to milling is obtained notwithstanding that there is no caustic alkali in the padding bath. This is highly advantageous; with 2:3-hydroxynaphthoic arylamides which are void of solubilizing groups production of full shades can only be affected by the use of caustic alkali in the padding bath.

G. On natural silk similarly good results are obtained, the shades when sodium carbonate is used in the padding bath being even fuller than when caustic alkali is used. The affinity of the arylamide is good and the resulting dyeings are of fair fastness to degumming.

H. On cotton the affinity is good and the shades produced are fast to soaping. The fastness to chlorine is also good.

I. The following examples illustrate the invention, without limiting it.

EXAMPLE I

Cotton dyeing

2 parts of 2:3-hydroxynaphthoic-4'-amino-3'-sulfoanilide are pasted with 9 parts of Turkey-red oil and 100 parts of boiling water are added. The mixture is heated, 10 parts of soda ash being added, and boiled until clear. The clear brown solution is then made up with water to 1000 parts.

Cotton is steeped in the solution (20 parts solution to 1 part of cotton) for ½ hour at 25°-30° C.; squeezed and then developed in a diazo bath in the way usual in the "ice-color" process. After the customary finishing treatment by soaping the following shades are obtained:

Diazo compound from	Shade obtained
2:5-dichloroaniline	Yellowish scarlet.
3-Chloroaniline	Do.
o-Nitroaniline	Bright orange brown.
3-nitro-p-toluidine	Brick red.
4-chloro-2-nitroaniline	Do.
5-nitro-o-toluidine	Do.
5-nitro-o-anisidine	Do.
5-chloro-o-toluidine	Bluish red.
4-chloro-o-toluidine	Dull red.
4-chloro-o-anisidine	Bluish red.
Dianisidine	Blue black.
4-benzoylamino-2:5-diethoxyaniline	Navy blue.

EXAMPLE II

Dyeing or printing animal fibers especially wool and natural silk

- 5 a. 1 part of 2:3-hydroxynaphthoic-4'-amino-3'-sulfo-anilide is mixed with 4 parts of triethanolamine and the solution poured into 95 parts of water at 40° C.

- 10 Wool or silk material is padded in the above liquor, dried and then printed with a thickened solution of a diazotized amine which may be prepared according to the recipe:—

	Parts
Salt from diazotized 5-chloro-ortho-toluidine and naphthalene-1:5-disulfo acid	4
Water	26
Wheat starch-tragacanth thickening	70

- 20 The printed fabric is dried, washed in water and finally soaped at 60° C. A bright red shade is produced.

- 25 b. 2:3-hydroxynaphthoic-4'-amino-3'-sulfoanilide may also be suitably brought into solution by pasting 1.5 parts with a little water and 0.3 part sulfonated alkylated petroleum (British specification No. 274,611), adding 75 parts of boiling water then 4 parts of soda ash. The clear solution thus obtained is made up to 1000 parts with water.

- 30 Wool (1 part in 20 parts of solution) is steeped in the above solution for ½ hour at 50° C., squeezed and rinsed with water and then developed in a diazo bath. Diazotized 5-chloro-ortho-toluidine gives a brick red shade.

- 35 c. 5 parts of wool are treated in a bath containing 5% of 2:3-hydroxynaphthoic-4'-amino-3'-sulfoanilide (on the weight of cloth), the bath being prepared as follows:

- 40 0.25 part of product is pasted with 0.7 part of commercial triethanolamine and 150 parts of water are added. The wool is immersed into the warm liquor, which is gradually heated to boiling during the course of 20-30 minutes. After boiling for 10 minutes 0.5 part of salt is added and a second similar addition is made after a further 10 minutes boiling. Boiling is continued for 30-40 minutes in all.

- 45 The wool is rinsed in water and then immersed in a cold bath of a diazotized amine containing approximately 0.25 part of amine per 100. After ½ hour, the shade is fully developed and the dyed wool is rinsed and soaped for 2-3 minutes at 40°. Diazotized 5-chloro-ortho-toluidine gives a red shade.

- 50 d. The 5 parts of wool which has been padded as in "c" above is immersed for ½ hour in 100 parts of water containing 0.25 part of sodium nitrite and 0.25 part of formic acid. Finally it is treated for 10 minutes in a cold 0.05% aqueous solution of sodium carbonate. After rinsing and soaping, the wool is dyed in a brownish-claret shade. On silk the shade is claret.

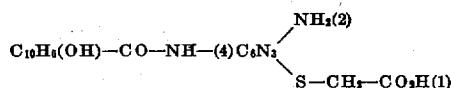
EXAMPLE III

Application to cellulose acetate

- 65 10 parts of scoured cellulose acetate are immersed in 300 parts of an ethanolamine solution of 0.5 part of 2:3-hydroxynaphthoic-4'-amino-3'-sulfoanilide made as described in Example II. The temperature is gradually raised to 85° C. and kept at that for ½ hour. The material is then rinsed in water and entered into a bath containing 0.5 part sodium nitrite and 0.5 part of formic acid in 250 parts of cold water. After ½ hour the material is treated for 10 minutes in cold

0.02% aqueous sodium carbonate and finally soaped at 60°. A bright crimson shade possessing very good fastness to soap and free from marking off is produced.

5 If instead of 2:3-hydroxynaphthoic-4'-amino-3'-sulfoanilide there is used the 3'-amino-4'-sulfoanilide, the shade produced is a bright red. A similar shade is produced by the compound



10 which is described in U. S. application, Serial No. 710,374.

EXAMPLE IV

Application to union materials

15 Wool-cotton union materials are dyed in solid shades by applying the products in the manner described in Example II. Application of the compound is commenced at or near the boil with addition of salt. The bath is then cooled and if necessary more compound is added to fill in the cotton. Development is carried out as already described.

25 J. As many apparently widely different embodiments of this invention may be made without departing from the spirit and scope thereof, it is to be understood that we do not limit ourselves to the specific embodiments thereof except as defined in the appended claims.

We claim:

1. The method of dyeing wool which comprises mixing 2:3-hydroxynaphthoic-4'-amino-3'-sulfoanilide with triethanolamine and diluting with water, impregnating wool with the said solution and coupling with the salt from diazotized 5-chloro-ortho-toluidine and naphthalene-1:5-disulfonic acid.

2. The method of dyeing which comprises impregnating a textile material with an aminoaryl-amide of 2:3-hydroxynaphthoic acid containing one of the group consisting of COOH and SO₃H in lactam-forming position in the aminoaryl radical, and coupling it with a diazotized primary arylamine in the presence of a mild alkali.

3. The method of dyeing which comprises impregnating a fibrous material with an aminoaryl-amide of 2:3-hydroxynaphthoic acid containing in the aminoaryl radical a group from the class consisting of COOH and SO₃H, and coupling it in the presence of a mild alkali and in the absence of caustic alkali to a diazotized primary arylamine.

4. A textile fiber dyed with a compound formed by the coupling of a diazotized arylamine with 2:3-hydroxynaphthoic-4'-amino-3'-sulfoanilide in the presence of a mild alkali.

5. A textile fiber dyed with a compound formed by the coupling in the presence of a mild alkali of a diazotized arylamine with an aminoaryl-amide of 2:3-hydroxynaphthoic acid containing a lactam-forming, water-solubilizing group adjacent to the amino group.

6. Textile fibers dyed with the dyestuff resulting from the coupling in the presence of a mild alkali of 2:3-hydroxynaphthoic-4'-amino-3'-sulfoanilide with diazotized 2:5-dichloro-aniline.

7. Textile fibers dyed with the dyestuff resulting from the coupling in the presence of a mild alkali of 2:3-hydroxynaphthoic-4'-amino-3'-sulfoanilide with diazotized 3-nitro-para-toluidine.

8. Textile fibers dyed with the dyestuff resulting from the coupling in the presence of a mild alkali of 2:3-hydroxynaphthoic-4'-amino-3'-sul-

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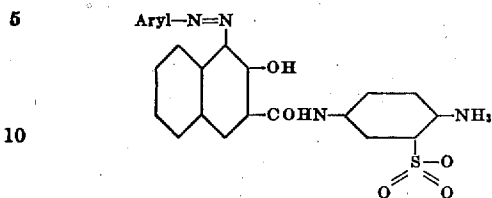
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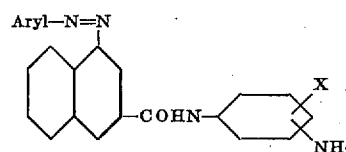
foanilide with diazotized 5-nitro-ortho-anisidine.

9. Material of the class described dyed with the compound represented in the form of its free acid by the formula:



10. Material of the class described dyed with

a compound represented in the form of its free acid by the formula



in which X is a lactam-forming radical in lactam-forming position in respect to the NH₂ group.

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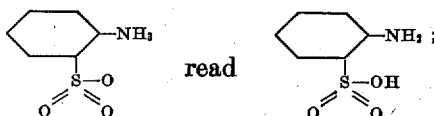
Certificate of Correction

Patent No. 2,115,136.

April 26, 1938.

HAROLD BLACKSHAW, ET AL.

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction as follows: Page 3, first column, lines 5-14, claim 9, in the formula, for the last nucleus



and that the said Letters Patent should be read with this correction therein that the same may conform to the record of the case in the Patent Office.

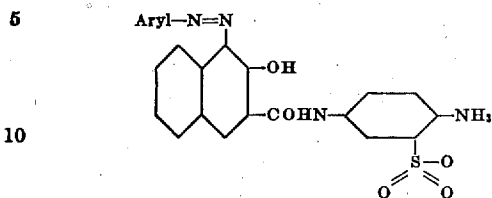
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HENRY VAN ARSDALE,
Acting Commissioner of Patents.

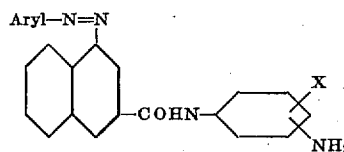
foanilide with diazotized 5-nitro-ortho-anisidine.

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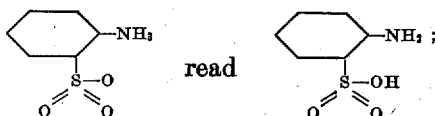
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