

1

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**PROCESS FOR DYEING TEXTILE MATERIALS
WITH SULFUR DYESTUFFS AND REAC-
TIVE DYESTUFFS**

Christian Heid and Karl Holoubek, Fechenheim, Germany, assignors to Cassella Farbwerke Mainkur Aktiengesellschaft, Frankfurt am Main-Fechenheim, Germany, a German company

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4 Claims. (Cl. 8—25)

This invention relates to dyeing of cellulosic textile materials and more particularly to a process of dyeing such materials with a combination of sulfur dyestuffs and reactive dyestuffs to obtain improved wet fastness properties, especially when washing the dyed textile materials with peroxide.

Heretofore, when using sulfur dyestuffs in combination or in conjunction with other dyestuffs for dyeing cellulosic textile materials, it has been common practice to complete the dyeing with the sulfur dyestuffs including oxidation of the dyestuffs and then topping the finished dyeings with a different type of dyestuff, such as for example substantive or basic dyestuffs.

In accordance with the present invention, we have found that substantially improved dyeing properties may be obtained by applying the sulfur dyestuff to the textile material, and prior to oxidation of the sulfur dyestuff, applying the reactive dyestuff in conjunction with suitable chemicals, and subsequently oxidizing the sulfur dyestuff and finishing the dyed goods. When the process is carried out in this sequential manner, and particularly when the reactive dyestuff is applied before the previously applied sulfur dyestuff is oxidized, more vivid colors and improved fastness to washing is obtained than heretofore possible with the prior art processes.

The textile material to be treated in accordance with this invention, may be in any of the usual forms, such as fibers, yarns, and woven or knitted fabrics. Likewise, the basic fiber of this material may be any of the presently known cellulosic textile fibers, e.g. cotton, rayon, linen. Also, blends or mixed fabrics containing two or more of the above synthetic and cellulosic fibers may be dyed satisfactorily by the dyestuff compositions of this invention.

For the sulfur dyestuff component any of the commonly known sulfur dyestuffs may be employed, such as sulfur dyestuffs insoluble and soluble in water. Especially suited for the last-mentioned group of sulfur dyestuffs are for example the alkali salts of thiosulfonic acids of sulfur dyestuffs.

For the reactive dyestuff component, any of the commonly known reactive dyestuffs may be employed, such as for example those with haloacetyl-, β -halopropionyl-, acryloyl-, and β -phenylsulfonylpropionyl-amino groups. Particularly suitable are reactive dyestuffs containing as a reactive residue a halotriazine-, halopyrimidine-, or halopyridazine residue, or the residue of a halopyridazine- or haloquinoxaline-carboxylic acid.

Illustrative but non-limiting more specific examples of the process of our invention utilizing the combination of a sulfur dyestuff and a reactive dyestuff and carried out in accordance with the foregoing principles, are as follows:

Example 1

A dyeing of Hydrosol Fast Yellow G (C.I. Solubilized Sulfur Yellow 5 being the thiosulfonic acid of C.I. Sulfur Yellow 5, the constitution of which is described in "Collection Czechoslov. Chem. Commun.," vol. 27 (1962), pp. 1533-48) on cotton yarn (obtained with 10%

2

of the dyestuff, 4 g./l. calcined sodium carbonate, 20 g./l. calcined sodium sulfate, and 1.2 g./l. sodium hydrosulfide in a liquor ratio of 1:20 at 90° C.) is rinsed and treated at 90° C. during 30 minutes in a fresh bath with 2% Cibacron Scarlet 2G (C.I. Reactive Red 9, constitution described in "Collection Czechoslov. Chem. Commun.," vol. 25 (1960), pp. 2794-95), 20 g./l. calcined sodium sulfate, and 5 g./l. calcined sodium carbonate in a liquor ratio of 1:20. Subsequently, the dyeing is rinsed, oxidized at 40° C. with a liquor containing 1 g./l. sodium perborate, soaped, and rinsed again. A vivid orange dyeing of a very good fastness to washing and to washing with peroxide is obtained.

A dyeing from Hydrosol Fast Yellow G which has been oxidized with perborate and then topped with Cibacron Scarlet 2G, is much weaker and shows a more yellowish tint. Furthermore, it possesses only poor wet fastness properties.

Example 2

A dyeing of Hydrosol Blue FFG (C.I. Solubilized Sulfur Blue 2, C.I. No. 53481), on cotton yarn (obtained with 5% of the dyestuff, 4 g./l. calcined sodium carbonate, 20 g./l. calcined sodium sulfate, and 1.2 g./l. sodium hydrosulfide in a liquor ratio of 1:20 at 60° C.) is rinsed and treated at 90° C. during 30 minutes in a fresh bath with 2% Cibacron Ruby R (C.I. Reactive Red 7, constitution described in "Collection Czechoslov. Chem. Comm.," vol. 25 (1960), p. 2795), 20 g./l. calcined sodium sulfate, and 5 g./l. calcined sodium carbonate in a liquor ratio of 1:20. Subsequently, the dyeing is rinsed, oxidized at 40° C. with a liquor containing 0.5 cc./l. H_2O_2 , soaped, and rinsed again. A vivid violet dyeing is obtained possessing, as compared to a dyeing of Hydrosol Blue FFG which has been oxidized before topping with Cibacron Ruby R, an improved fastness to washing and to washing with peroxide.

Example 3

A dyeing of Immedial Fast Brilliant-green BBL (C.I. Sulfur Green 25) on cotton yarn (obtained with 10% of the dyestuff dissolved in the same amount of crystalline Na_2S , 4 g./l. calcined sodium carbonate, and 20 g./l. calcined sodium sulfate in a liquor ratio of 1:20 at 90° C.) is rinsed and treated at 70° C. during 30 minutes in a fresh bath with 4% Cibacron Yellow G (C.I. Reactive Yellow 6), 20 g./l. calcined sodium sulfate, and 5 g./l. calcined sodium carbonate in a liquor ratio of 1:20. Subsequently, the dyeing is rinsed, oxidized at 40° C. with a liquor containing 1 g./l. sodium perborate, soaped, and rinsed again.

A brilliant, yellowish green dyeing is obtained showing improved wet fastness properties, in particular a good fastness to washing with peroxide.

Example 4

A dyeing of Hydrosol Fast Yellow G (C.I. Solubilized Sulfur Yellow 5) on cotton yarn, obtained as described in Example 1, is treated, after rinsing, at 90° C. during 30 minutes with 2% Drimaren Scarlet Z-GL (C.I. Reactive Red 19), 20 g./l. calcined sodium sulfate, and 5 g./l. calcined sodium carbonate in a liquor ratio of 1:20. Subsequently, the dyeing is rinsed, oxidized at 40° C. with 1 g./l. perborate, soaped, and rinsed again. A reddish yellow dyeing is obtained showing improved wet fastness properties.

If the dyeing from Hydrosol Fast Yellow G is oxidized with perborate before being treated with Drimaren Scarlet Z-GL, a weaker, less reddish yellow dyeing is obtained.

Example 5

A dyeing of Hydrosol Fast Yellow G (C.I. Solubilized Sulfur Yellow 5, being the thiosulfonic acid of C.I. Sul-

fur Yellow 5, the constitution of which is described in "Collection Czechoslov. Chem. Commun.," vol. 27 (1962), pp. 1533-48) on cotton yarn, obtained as described in Example 1, is treated, after rinsing, at 90° C. during 30 minutes with 3% Remazol Red B (C.I. Reactive Red 22, constitution described in "Collection Czechoslov. Chem. Commun.," vol. 27 (1962), p. 273), 20 g./l. calcined sodium sulfate, and 5 g./l. calcined sodium carbonate in a liquor ratio of 1:20. Subsequently, the dyeing is rinsed, squeezed off, soaped, and rinsed again. A reddish yellow dyeing is obtained showing good wet fastness properties.

If the dyeing from Hydrosol Fast Yellow G is oxidized with perborate or bichromate acetic acid, before being treated with Remazol Red B, a weaker, less reddish yellow dyeing is obtained.

What is claimed is:

1. A process for dyeing cellulosic textile materials as defined herein, with sulfur dyestuffs and reactive dyestuffs, comprising treating the textile material with the sulfur

dyestuff together with an alkali and a reducing agent, rinsing the thus treated textile material, next treating the textile material with a solution of a reactive dyestuff, then oxidizing the sulfur dyestuff, and then finishing the thus dyed material.

2. A process as defined in claim 1 and in which the sulfur dyestuff is a water soluble alkali salt of a thiosulfonic acid of a sulfur dyestuff.

3. A process as defined in claim 1 and in which the reactive dyestuff contains a group selected from the class consisting of haloacetyl-, β -halopropionyl-, acryloyl-, and β -phenyl-sulfonyl-propionyl-amino.

4. A process as defined in claim 1 and in which the reactive dyestuff contains a reactive residue selected from the class consisting of a halotriazine, halopyrimidine, halopyridazine, halo-pyridazine carboxylic acid and halo-quinoxaline carboxylic acid.

No references cited.

J. TRAVIS BROWN, *Primary Examiner*.