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METHOD OF DYEING CELLULOSIC TEXTILES WITH MIXTURES OF THIOSULFONIC ACID-SULFUR DYES AND REACTIVE DYES AND COMPOSITIONS THEREOF

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This invention relates to dye compositions and methods of dyeing cellulosic textile materials therewith, and more particularly to dye compositions comprising as the principal constituents the alkali salts of thiosulfonic acids of sulfur dyestuffs, an alkali, a reducing agent for said sulfur dyestuffs and a reactive dyestuff as defined herein, said composition being capable of dyeing said textile materials in a single dye bath under controlled temperature conditions with good uniformity of color.

Heretofore, dyeing of textile materials with sulfur dyestuffs and reactive dyestuffs have usually been carried out in two dyeing steps, that is, using separate dye baths for the sulfur dyestuffs and the reactive dyestuffs, which is objectionable with respect to the time requirement and required chemicals.

The dyestuff compositions of the present invention have simplified the dyeing operation and produced better dyeing results with the combination of the sulfur dyestuffs and the reactive dyestuffs used in a single bath. This has been made possible by using the water soluble alkali salts of thiosulfonic acids of sulfur dyestuffs, instead of the usual sulfur dyestuffs, and by using an alkali that effects fixation of the reactive dyestuff and concurrently using a reducing agent that effects fixation of the sulfur dyestuff onto the textile fiber.

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, cellulosic constituents in blends or mixed fabrics may be dyed satisfactorily by the dyestuff compositions of this invention.

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 -phenylsulfonylethylpropionyl-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.

Regarding the controlled temperature feature of the dyeing method of the present invention, this involves dyeing of the textile material with the dyestuff composition above mentioned containing the alkali salt of the thiosulfonic acid of a sulfur dyestuff, the reactive dyestuff and an alkali, such as for example sodium carbonate, at a relatively low temperature, e.g. about 30° C., for a period of minutes and then adding a suitable reducing agent, such as for example sodium sulfide or sodium hydrosulfide, and increasing the temperature of the dye bath to about 60–90° C. for a further period of minutes; and subsequently rinsing and oxidizing the dyed textile material and applying the usual finishing operations.

A presently advantageous procedure for carrying out the dyeing process of the present invention comprises treating the cellulosic material to be dyed in a first step

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with dye liquors containing as an essential component, aside from the water-soluble alkali salt of the thiosulfonic acid of the sulfur dyestuff and the reactive dyestuff, only alkali which gives rise to the fixation of the reactive dyestuff, and then further treating at an elevated temperature, after the addition of the reducing agent necessary for the reduction of the sulfur dyestuff. Thus also the sulfur dyestuff goes onto the fiber, and after the usual finishing, full combination dyeings are obtained, having a very good uniformity.

Illustrative but non-limiting more specific examples of the dyestuff compositions containing a thiosulfonic acid group containing sulfur dyestuff in combination with a reactive dyestuff and the methods of dyeing textile materials therewith are as follows:

Example 1

A cotton cheese is processed in a circulating liquor containing 5% Hydrosol Fast Yellow-brown GL (C.I. Solubilized Sulfur Brown 60, C.I. No. 53326), 2% Procion-yellow M-RS (C.I. Reactive Yellow 4), 20 g./l. calcined sodium sulfate, and 10 g./l. sodium carbonate, during 45 minutes at 30° C. Then 7.5% of a 20% sodium hydrosulfide solution are added, dyeing is continued for a further 10 minutes at 30° C. and, after increasing the temperature of the liquor to 90° C., for a further 30 minutes at this temperature. Subsequently, the material is rinsed, oxidized at 40° C. with a liquor containing 1 g./l. sodium perborate, soaped, and rinsed again. A deep yellow-brown dyeing of good uniformity is thus obtained.

Example 2

A cotton cheese is first treated in a circulating bath containing 5% Hydrosol Blue FFG (C.I. Solubilized Sulfur Blue 2, C.I. No. 53481), 2% Cibacron Turquoise-blue G (C.I. Reactive Blue 7 constitution described in "Collection Czechoslov. Chem. Commun.," vol. 25 (1960), page 2797), 20 g./l. calcined sodium sulfate, 20 g./l. calcined sodium carbonate, and 7.5% of a 20% sodium hydrosulfide solution during 10 minutes at 30° C.; the temperature of the liquor is then increased during 20 minutes to 90° C., the material is dyed during 30 minutes at this temperature, then cooled down to 50–60° C., and treated for a further 10 minutes at this temperature. Subsequently, the dyeing is finished by rinsing, oxidizing with 1.5% potassium bichromate, and 3% of a 30% acetic acid at a temperature of 60–70° C., again rinsing, soaping, and rinsing once more.

Example 3

A cotton cheese is treated in a circulating bath containing 3% Hydrosol Blue R (C.I. Solubilized Sulfur Blue 7, C.I. No. 53441), and 2% Procion Brilliant-blue M-RS (C.I. Reactive Blue 4), 30 g./l. calcined sodium sulfate, and 15 g./l. calcined sodium carbonate during 30 minutes at 30° C.; then 4.5% of a 20% sodium hydrosulfide solution are added, the material is dyed for a further 10 minutes at 30° C. and, after the temperature of the liquor has been raised to 60° C., another 30 minutes at this temperature. Subsequently, the dyeing is rinsed, oxidized at 40° C. with 0.5% of 35% hydrogen peroxide, soaped, and rinsed again. Thus, a deep and brilliant blue dyeing of a good uniformity is obtained.

Example 4

A cheese of mixed cotton-cellulose yarn is first treated in a circulating bath containing 10% 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), page 1533/48), 2% Cibacron

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Turquoise-blue G (C.I. Reactive Blue 7, constitution described in "Collection Czechoslov. Chem. Commun.," vol 25 (1960), page 2797), 20 g./l. calcined sodium sulfate, 2% sodium sulfhydrate, and 10 g./l. calcined sodium carbonate, during 10 minutes at 30° C. The temperature of the liquor is then increased to 90° C. within 30 minutes, and the material is dyed during 30 minutes at this temperature. Subsequently, the dyeing is finished by rinsing, oxidizing at 40° C. with a liquor containing 1 g./l. sodium perborate, soaping and rinsing. A brilliant green dyeing is, thus, obtained which is impossible to obtain with sulfur dyes only.

Example 5

A cotton cheese is treated in a circulating bath containing 6% Hydrosol Fast Yellow-brown GL (C.I. Solubilized Sulfur Brown 60, C.I. No. 5326), 2% Cibacron Scarlet 2G (C.I. Reactive Red 9, constitution described in "Collection Czechoslov. Chem. Commun.," vol 25 (1960), page 2794/95), 30 g./l. calcined sodium sulfate, and 15 g./l. calcined sodium carbonate during 60 minutes at 60-65° C. The dye liquor is then cooled down to 30° C., admixed with 2% sodium hydrosulfide, and dyeing is continued for 10 minutes at 30° C. and, after the temperature of the liquor has been raised to 90° C., for another 30 minutes at 90° C. Subsequently, the dyeing is rinsed, oxidized at 40° C. with a liquor containing 1 g./l. sodium perborate, soaped, and rinsed again. Thus, a vivid red brown dyeing is obtained, having a very good uniformity.

What is claimed is:

1. A dyestuff composition for dyeing cellulosic textile materials comprising as the principal constituents a water soluble alkali salt of a thiosulfonic acid of a sulfur dyestuff, an alkali, a reducing agent for said sulfur dyestuff, and a reactive dyestuff, said composition being capable of dyeing said textile materials in a single dye bath under controlled temperature conditions with good uniformity of color.

2. A dyestuff composition as defined in claim 1 and in which the reactive dyestuff component is selected from the group of reactive dyestuffs containing haloacetyl-, β -halopropionyl-, acryloyl-, and β -phenylsulfonylpropionyl-amino groups.

3. A dyestuff composition as defined in claim 1 and in which the reactive dyestuff contains a reactive residue selected from the group consisting of a halotriazine-,

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halopyrimidine-, halopyridazine residue, a halopyridazine- and haloquinoxaline-carboxylic acid residue.

4. A method of dyeing cellulosic textile materials comprising subjecting the textile materials to a single dye bath containing as a dye composition therein a water soluble alkali salt of a thiosulfonic acid group-containing sulfur dyestuff, an alkali, a reducing agent for the sulfur dyestuff, and a reactive dyestuff, for a period of time to effect dyeing thereof; then subjecting the dyed material to the usual finishing treatments.

5. A method as defined in claim 4 wherein said reducing agent for the sulfur dyestuffs comprises an alkali sulfide.

6. A method as defined in claim 4 wherein the dye bath is maintained at a moderately elevated temperature for a period of time and subsequently raised to a higher temperature for a period of time.

7. A method as defined in claim 6 wherein the moderately elevated temperature is around 30° C. and the dye bath is maintained at said temperature for between 10 and 45 minutes, and wherein the higher temperature is between 60-90° C. and the dye bath is maintained at said higher temperature for approximately 30 minutes.

8. A method as defined in claim 6 wherein said dye bath is maintained at said moderately elevated temperature for a period of time prior to the addition of the reducing agent to the dye bath.

9. A method as defined in claim 6 wherein the dye bath, after being maintained at the higher temperature, is lowered to a temperature of approximately 50-60° C. prior to the usual finishing treatments.

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