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IMPROVING THE DYEING PROPERTIES OF CELLULOSIC TEXTILES BY TREATMENT WITH FORMALDEHYDE AND A GUANIDINE SALT OF AN ALPHA-BETA UNSATURATED CARBOXYLIC ACID

James Hutchison MacGregor, Bocking Braintree, England, assignor to Courtaulds Limited, London, England, a British company

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2 Claims. (Cl. 8—100)

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This invention relates to the treatment of cellulosic textile materials and in particular to improving the dyeing affinity of such materials.

It has already been proposed in British specification No. 433,143 to treat cellulosic fibres with formaldehyde condensation products obtained by condensing formaldehyde with dicyandiamide, guanidine or heat-treated urea and to dye the treated fibre with wool or silk dyestuffs. It has also been proposed in British specification No. 450,516 to produce differential colour effects upon textile materials by locally impregnating with a nitrogenous synthetic resin and subsequently condensing to produce the synthetic resin on the material and applying a dyestuff to the material. Among the large number of synthetic resins cited in the specification are the compounds of formaldehyde with guanidine and its derivatives. In my prior British patent specification No. 549,214 I have described the improvement of the dyeing affinity of cellulosic textile material by treating it with an aqueous solution containing formaldehyde and a guanidine salt of a long chain aliphatic dicarboxylic acid, either as such or in the form of their water-soluble condensation product and then heating the material to convert the guanidine salt and formaldehyde into a water-insoluble condensation product. The affinity of the material for many classes of dyestuffs is improved by this process.

I have now found that the affinity of undyed cellulosic textile material for chrome dyestuffs applied by the "metachrome" or "after-chrome" process and for such classes of dyestuffs as acid wool, direct cotton, solubilized vat (i. e. sulphuric ester salts of the leuco vat dyestuffs), aqueous dispersions of insoluble amino- and hydroxy-azo compounds and of insoluble amino- and acylaminoanthraquinones is improved if the material is treated prior to dyeing with an aqueous solution containing formaldehyde and a guanidine salt of an unsaturated carboxylic acid, such as an aliphatic or aromatic monobasic or dibasic acid either as such or in the form of their water-soluble condensation product and then converting to the water-insoluble condensation product. The process can be carried out under acid, neutral or alkaline conditions, and if desired a catalyst, such for example as ammonium thiocyanate, may be present.

As examples of suitable guanidine salts which may be used in carrying out the process of the present invention I may mention guanidine acrylate, guanidine methacrylate (salt of guanidine and alpha-methylacrylic acid) guanidine styryl-acrylate, guanidine alpha-chloroacrylate, guanidine maleate and guanidine cinnamate.

Cellulosic mterial when treated according to

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the present invention gives dyeings with chrome dyestuffs of the same depth of shade as similar dyeings on wool. A good affinity for chrome dyestuffs can be obtained on cellulosic material by the process of the present invention even when the impregnation with formaldehyde and the guanidine salt of an unsaturated carboxylic acid is carried out under alkaline conditions whereas in order to obtain a good affinity for chrome dyestuffs with other guanidine salts and formaldehyde the treatment must be carried out in presence of ammonium thiocyanate as acid catalyst.

Further the light-fastness of dyeings produced by acid wool, direct cotton and chrome dyestuffs on cellulosic material treated according to the present invention is equal to or even better than corresponding dyeings on wool.

The treatment according to this invention, in addition to improving the affinity of the cellulosic material for the dyestuffs hereinbefore mentioned, also imparts an improved, resilient, soft handle, and this improved handle persists after dyeing. Cellulosic material treated according to the present invention possesses very good fastness to crabbing, this is particularly the case when the treating solution used is in the alkaline pH range, for example, at a pH of 8.0.

The following examples illustrate the present invention without the invention being limited to these examples. The percentage of the compounds used is based on the weight of the fibre being treated.

Example 1

Guanidine-methacrylate

$$\left(\begin{matrix}H_2N.C.NH_2\text{—}HOOC.C(CH_3)=CH_2\\ \|\\ NH\end{matrix}\right)$$

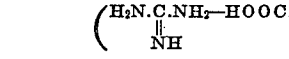
is prepared at room temperature by the careful addition over a period of 15 minutes of a concentrated aqueous solution of 1 mol of guanidine carbonate to an ethanol solution of 2 mols of methacrylic acid (stabilised with hydroquinone). After filtering, the filtrate is concentrated and the guanidine methacrylate obtained as an almost colourless crystalline product, which is readily soluble in warm water.

Viscose staple fibre is soaked at ordinary room temperature in an aqueous solution, the pH of which has been adjusted to 8.0, containing 3 parts of guanidine methacrylate and 16 parts of 40 per cent formaldehyde in 100 parts of solution. After saturation, the staple fibre is hydroextracted until it contains approximately its own weight of liquid, then dried at under 100° centigrade and heated at 140° centigrade for 10 minutes. It is then entered at 60° centigrade along with an equal weight of scoured wool, into 40 volumes of a dyebath containing 2 per cent of

Eriochrome Azurol B (Colour Index 720), 2 per cent of potassium chromate and 4 per cent of ammonium sulphate. The temperature of the dyebath is then raised to 95° centigrade and dyeing continued at this temperature for 1¼ hours. After removing from the dyebath, rinsing and drying it is found that both the animalized staple fibre and the wool are dyed to approximately the same depth and a fast solid blue shade is obtained.

Example 2

Guanidine alpha-chloroacrylate



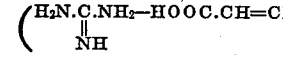
is prepared at room temperature by the careful addition over a period of 15 minutes of a concentrated aqueous solution of 1 mol of guanidine carbonate to an ethanol solution of 2 mols of alpha-chloroacrylic acid (stabilised with hydroquinone). After filtering, the filtrate is concentrated and guanidine alpha-chloroacrylate obtained as an almost colourless crystalline product, readily soluble in warm water.

Viscose staple fibre is soaked at ordinary room temperature in an aqueous solution, the pH of which is 3.4, containing 3 parts of guanidine alpha-chloroacrylate and 16 parts of 40 per cent formaldehyde in 100 parts of solution. After saturation, the staple fibre is hydroextracted until it contains approximately its own weight of liquid, then dried at under 100° centigrade, and heated at 140° centigrade for 10 minutes. It is then entered, along with an equal weight of scoured wool, into 40 volumes of a dyebath at 60° centigrade containing 6 per cent of Eriochrome Black T (Colour Index No. 203) and 2 per cent of acetic acid. The temperature of the dyebath is raised to 95° centigrade and dyeing continued at this temperature for 30 minutes. 2 per cent of formic acid is then added and dyeing continued at the same temperature for a further 30 minutes. Finally, 2 per cent of sodium dichromate is added and the dyeing completed after another 30 minutes at 95° centigrade. A full shade of black is obtained on both fibres which are dyed to approximately the same depth.

Example 3

Styrylacrylic acid is prepared by refluxing 300 grams of cinnamic aldehyde, 300 grams of malonic acid and 250 grams of pyridine essentially as described by A. Riedel (Annalen, vol. 361, page 99)—this being a modification of Doebner's process (Berichte der deutschen chemischen Gesellschaft, 1902, vol. 35, page 2137).

Guanidine styrylacrylate



is prepared at room temperature by the careful addition over a period of 15 minutes of a concentrated aqueous solution of 1 mol of guanidine carbonate to an ethanol solution of 2 mols of styrylacrylic acid. After filtering, the filtrate is concentrated and guanidine styrylacrylate obtained as a colourless crystalline product readily soluble in water but readily decomposed on the addition of acid to its aqueous solutions. For this reason it is necessary to use formaldehyde-guanidine styrylacrylate solutions in an alkaline pH range.

Viscose staple fibre is soaked at ordinary room temperature in an aqueous solution, the pH of which has been adjusted to 8.0, containing 3 parts of guanidine styrylacrylate and 16 parts of 40 per cent formaldehyde in 100 parts of solution. After saturation the staple fibre is hydroextracted until it contains approximately its own weight of liquid, then dried at under 100° centigrade and finally heated at 140° centigrade for 10 minutes. The so-treated staple fibre along with an equal weight of scoured wool is entered at 60° centigrade into 40 volumes of a dyebath containing 2 per cent of Solochrome Brown M. O. S. (Imperial Chemical Industries Ltd.), 2 per cent of potassium chromate and 4 per cent of ammonium sulphate. The temperature of the dyebath is then raised to 95° centigrade and dyeing continued at this temperature for 1¼ hours. A deep shade of brown of practically the same depth is obtained on both fibres.

Example 4

Viscose staple fibre is soaked at ordinary room temperature in an aqueous solution, the pH of which is 4.5, containing 3 parts of guanidine cinnamate and 16 parts of 40 per cent formaldehyde in 100 parts of solution. After saturation, the staple fibre is hydroextracted until it contains approximately its own weight of liquid, then dried at under 100° centigrade and finally heated at 140° centigrade for 10 minutes. The so-treated staple fibre is then entered at 60° centigrade into 40 volumes of a dyebath containing 1 per cent of Coomassie Navy Blue 2RNS (Colour Index No. 289), and 2 per cent of acetic acid based on the weight of fibre. The temperature is raised over a period of ½ an hour to 95° centigrade and dyeing continued for another ½ an hour at this temperature, when 0.25 per cent of potassium dichromate is added and dyeing continued for a further ½ an hour at 95° centigrade. The staple fibre is dyed a full navy shade of equal light-fastness to a similar dyeing on wool.

What I claim is:

1. A process of improving the dyeing affinity of cellulosic textile material and imparting a soft silky handle thereto, which comprises treating the material before dyeing with an aqueous solution containing formaldehyde and a guanidine salt of an alpha-beta unsaturated carboxylic acid which is devoid of amino groups, and thereafter converting the mixture to a water-insoluble condensation product.

2. A process of improving the dyeing affinity of cellulosic textile material and imparting a soft silky handle thereto, which comprises treating the material before dyeing with an aqueous solution containing formaldehyde and a guanidine salt of an alpha-beta unsaturated carboxylic acid which is devoid of amino groups, in the form of their water-soluble condensate and thereafter converting the water-soluble condensate into a water-insoluble condensation product.

JAMES HUTCHISON MacGREGOR.

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The following references are of record in the file of this patent:

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