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## TEXTILE TREATMENT

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1 Claim. (Cl. 8—55)

The present invention relates to the dyeing, with an acid dye, of a cellulose yarn, fabric or other textile material. More particularly it relates to the acid dyeing of a cellulose textile material chemically modified to promote the affinity thereof for the acid dye.

With the present trend toward increased use of viscose rayon staple, particularly crimped staple, in admixture with wool in yarns and fabrics, the need for a satisfactory procedure for dyeing cellulose fibers with acid wool dyes is becoming more and more acute. Such a procedure would permit dyeing of cellulose and wool fabrics with the same acid dyes and in the same bath to eliminate the expense and inconvenience of using mixtures of dyes or a two-bath dyeing process.

Many methods have been proposed for modifying viscose rayon to give it an affinity for acid dyes. In general, these have not proved fully satisfactory in practice on account of lack of uniformity, brilliance or light fastness of the dyeings. They have also the disadvantages of high cost, difficulty of application, or lack of affinity for more than a very narrow range of dyes.

One method which has been proposed for modifying viscose rayon to give it an affinity for acid dyes has been to incorporate in the viscose spinning solution one of a number of nitrogenous resinous materials, for example, an ethylenimine-aromatic isocyanate reaction product, a carbon disulfide-ethylenimine reaction product, a carbon disulfide-ethylenimine-aromatic isocyanate reaction product, or a protein-amine-aromatic isocyanate reaction product. This method has the disadvantage of requiring the step of preparing a resin from materials which, as in the case of ethylenimine, are not generally available.

Another method which has been proposed is to treat the cellulose fibers with isocyanates containing an aliphatic residue of at least four carbon atoms containing, in addition to the nitrogen atom of the isocyanate group, a tertiary nitrogen atom. Such isocyanates are available only through a complicated series of chemical reactions involving expensive starting materials.

It is, therefore, an object of the present invention to produce an improved acid-dyed, chemically-modified cellulose textile material.

It is also an object of the present invention to provide an improved process for the production of the above product.

Other objects of the invention will appear hereinafter.

The objects of the invention may be accomplished, in general, by dyeing, with an acid dye, a cellulose textile material chemically modified by reaction with a hydrocarbon isocyanate containing at least six carbon atoms.

Several convenient procedures are available for modifying cellulose textile materials by chemical reaction with hydrocarbon isocyanates containing at least six carbon atoms. Any known process for reacting a cellulose textile with a hydrocarbon isocyanate containing at least six carbon atoms which will not otherwise affect the textile structure will be suitable for use in accordance with the present invention. In almost all cases heat is required to effect sufficient reaction between the cellulose and the isocyanate within a conveniently short time. The less volatile isocyanates, hexamethylene diisocyanate for example, may be applied from an inert volatile solvent. The textile may be impregnated with the solution, the solvent evaporated, and the textile heated in an oven. Long-chain non-volatile isocyanates may also be applied conveniently in some cases in the form of an aqueous emulsion or dispersion. Both of these procedures are described and illustrated in British Patent No. 461,179. The latter procedure is also described in the copending application of William E. Hanford and Donald F. Holmes, Serial No. 168,084, filed October 8, 1937, now Patent No. 2,284,895.

The more volatile isocyanates, such as hexyl and phenyl isocyanates, are preferably applied by other procedures. Cellulose textiles may conveniently be brought into reaction with these more volatile isocyanates merely by immersing the textile in the isocyanate which has been heated to reaction temperature. In some cases, use of a catalyst such as pyridine is advantageous. This procedure is described in Hartmann U. S. Patent No. 1,875,452. An even more convenient method for treating cellulose textiles with the more volatile isocyanates involves immersing the textile in a hot solution of the isocyanate in an inert solvent such as xylene. This

procedure is illustrated by Examples 2 and 3 below.

The cellulose textile material which has been modified by chemical reaction with a hydrocarbon isocyanate containing at least six carbon atoms through use of any of the available procedures is dyed with an acid dye by any of the common procedures used for applying acid dyes to wool. One of the common procedures used for dyeing wool with acid dyes is that described in the 1939 Year Book of the American Association of Textile Chemists and Colorists, Volume XVI, page 185. The dyed modified cellulose textiles of this invention are similar in color to wool dyed in an identical manner. The dyeings obtained are in most cases equal in brilliance and in fastness to light to those obtained on wool.

Although the present invention is applicable to any cellulose textile material, natural or artificial, it has particular applicability to yarns and fabrics prepared from the new, crimped, wool-like regenerated cellulose fibers, filaments and yarns disclosed in Charch and Underwood Patent No. 2,249,745. The process as defined in that patent comprises generally the extrusion of viscose into a coagulating bath having a rapid coagulating action and a slow, or no, regenerating action with a velocity of extrusion at least four times the velocity of draw-off. The streams of viscose issuing from the spinneret into the coagulating bath under the aforementioned conditions spontaneously assume a finely crimped form which persists as a permanent structural characteristic in the filaments.

The resulting yarn is composed of substantially non-crenulated filaments having an inherent and substantially permanent crimp, the crimps in the several filaments of the yarn being out-of-phase with each other. The filaments exhibit substantially no orientation in the direction of the fiber axis.

For purposes of convenience and ready identification, this yarn will hereinafter be referred to as "Fiber D" yarn.

The following examples are given to illustrate preferred methods of carrying out the present invention, it being understood that the invention is not limited to the details set forth in these examples:

*Example I*

Skeins of "Fiber D" yarn and of continuous, straight-filament, viscose rayon yarn, free from finishing agents and the like, are wet with water and dried by solvent interchange with methanol and benzene. This drying procedure consists in thoroughly washing the water out of the yarn with methanol and then washing the methanol out with dry benzene. The skeins of dry swollen yarn are immersed for ten minutes in dry benzene containing in solution 10% of hexamethylene diisocyanate by weight. They are centrifuged to remove excess solution, dried at room temperature for forty-five minutes, baked for one hour in an oven at 140°–145° C., washed with a warm aqueous soap-sodium carbonate solution, rinsed and dried. The gains in weight of the yarns due to reaction with hexamethylene diisocyanate are 5.1% and 13.1% for the straight-filament yarn and the "Fiber D" yarn, respectively.

The treated yarns are dyed with Brilliant Milling Green B Conc. (Rowe Color Index No. 667). Fifty parts of dye bath are used for one part of yarn. The bath contains 1% of dye, 10% of Glauber's salt, and 5% of acetic acid, all based on the weight of the yarn. The yarn is wet with water and placed in the dye bath. The bath is then gradually heated to boiling over a period of about fifteen minutes. During this step, the yarn is agitated to insure level dyeing. Boiling is continued for thirty minutes. Then the yarn is lifted out of the bath and 1% of sulfuric acid based on yarn weight is added. The yarn is replaced in the bath and boiling is continued for fifteen minutes. Then the yarn is removed from the bath, rinsed and dried. The yarns dyed in this manner are colored a green shade similar to that of wool dyed in an identical manner. Control yarns of "Fiber D" and straight-filament viscose rayon, which have not first been modified in the manner above set forth, are scarcely tinted by this dye.

The treated yarns are also dyed with the acid dye having Rowe Color Index No. 1088. The procedure is similar to that used in the application of Brilliant Milling Green B Conc. except that the bath is initially acidified with 3% of sulfuric acid, based on yarn weight, rather than with acetic acid. The yarns are colored a blue shade similar to that of wool dyed in an identical manner. Unmodified viscose rayon yarns are not colored by this dye.

*Example II*

Skeins of "Fiber D" and continuous straight-filament viscose rayon yarn are wet with water and dried by solvent interchange with methanol and benzene, as described in Example I. They are then immersed for one hour in a boiling 3% solution of n-hexyl isocyanate in xylene (one part of yarn to 20 parts of solution), rinsed with benzene, dried, washed with warm aqueous 0.25% soap-0.1% sodium carbonate solution, rinsed and dried. The gains in weight of the yarns due to reaction with the isocyanate are 2% and 8.5% for the straight-filament viscose rayon yarn and the "Fiber D" yarn, respectively. The treated "Fiber D" yarn contains 0.77% nitrogen. The treated yarns are dyed as described in Example I with Brilliant Milling Green B Concentrated (Rowe Color Index No. 667) and the acid dye having Rowe Color Index No. 1088. They take on colors similar to those of wool dyed in an identical manner. When the "Fiber D" yarn dyed with Brilliant Milling Green B Conc. by this process is exposed to light from a carbon arc, the dye does not fade as it does on wool but becomes darker.

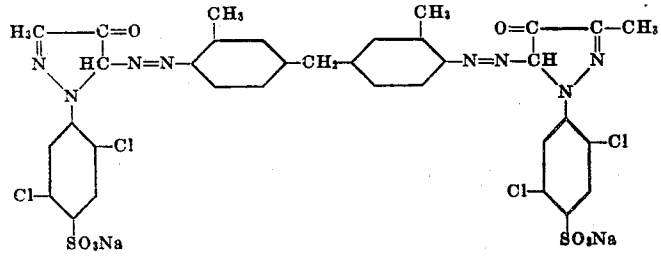
*Example III*

Skeins of "Fiber D" viscose rayon yarn, 140 parts, are wet with water and dried by solvent interchange with methanol and benzene. They are immersed in 2,340 parts of a boiling 3% solution of phenyl isocyanate in xylene for one hour, rinsed with benzene, methanol, and water in turn, and dried. The yarn treated in this way contains 2.03% nitrogen. It is dyed in acid baths by procedures standard for wool with the following acid wool dyes.

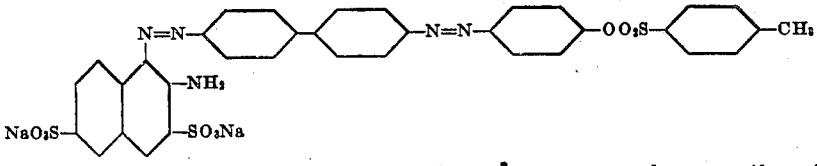
| | Rowe Color Index No. |
|---|---|
| "Pontacyl" Light Yellow GX | 639 |
| Du Pont Milling Red SWB | 430 |
| "Pontacyl" Wool Blue GL | 833 |
| Du Pont Brilliant Milling Green B. Conc | 667 |

An acid dye, Rowe Color Index No. 1088, and the acid dyes having the following chemical constitutions will also dye cellulose yarn modified

by the isocyanate treatment as hereinabove described:



and



In all cases the dyeings on the modified yarn are definitely superior in depth to dyeings which are obtained on unmodified "Fiber D" yarn by the same procedures in separate baths. Furthermore, most acid dyes give dyeings on the modified "Fiber D" yarn which are deeper than dyeings obtained with equivalent dye concentrations on wool. Exposures of the dyed yarns to light from a carbon arc for twenty and forty hours indicate that the dyeings on modified "Fiber D" are equivalent in light-fastness to those on wool.

Dyeings carried out in neutral solution with the above acid dyes on modified "Fiber D" and wool in the same bath indicate that the two fibers are equal in affinity for "Pontacyl" Light Yellow GX and the acid dye having Rowe Color Index No. 1088 and that the modified "Fiber D" has even greater affinity than wool for the other acid dyes.

The modified "Fiber D" also has good affinity for the direct cotton dye, "Pontamine" Sky Blue 6 BX (Rowe Color Index No. 518).

In general, if any cellulose textile material which has been modified by chemical reaction with any hydrocarbon isocyanate containing at least six carbon atoms is dyed with any acid dye, it assumes a shade similar to that of wool dyed with the same dye by the same procedure, while unmodified cellulose textile materials dyed by the same procedure are colored very slightly if at all.

The term "cellulose textile material," as used throughout the specification and claims, specifically refers to natural cellulose materials, such as cotton, linen, jute, ramie, and regenerated cellulose materials, such as viscose rayon and cuprammonium rayon. It includes fibers, staple fibers, continuous filaments and yarns, and fabrics produced therefrom. Before it is dyed, the isocyanate-treated cellulose textile material may be mixed with wool to produce a substantially uniformly dyed mixed fiber product, or it may be mixed with textile materials which do not have affinity for acid dyes, such as untreated cotton, viscose rayon, and cellulose acetate rayon, to produce a cross-dyed effect. Although there will be no serious damage to any cellulose material as the result of its reaction with the above-said isocyanate, regenerated cellulose will be less damaged than natural cellulose materials such as cotton and linen and, therefore, the present invention is particularly applicable to the acid dyeing of regenerated cellulose textile materials.

In addition to the isocyanates used in the above examples to render cellulosic textile materials suitable for use in this process, there may be used other aliphatic, aromatic, or alicyclic mono- or polyisocyanates including octyl, decyl, dodecyl, octadecyl, para-tolyl, para-ethylphenyl, para-dodecylphenyl, 2 - phenylethylcyclohexyl, and naphthylisocyanates and pentamethylene, octamethylene and meta- and para-phenylene diisocyanates. To obtain the best results, it is preferred that the hydrocarbon isocyanate have from six to twelve carbon atoms. Hydrocarbon isocyanates having less than six carbon atoms or more than twelve carbon atoms impart considerably less affinity for acid dyes to the cellulose material than those having six to twelve carbon atoms.

Any on the dyes known as acid dyes to those skilled in the art of dyeing can be used in this process. They may be applied in any of the dyeing procedures commonly followed in their application to wool. However, it must be kept in mind that in each case the depth of dyeing obtained with any given concentration of dye will vary with the isocyanate which has been used for modification of the textile material and with the extent of the reaction between the isocyanate and the cellulose. In general, as the nitrogen content of the cellulose increases, the depth of dyeing obtained with a given concentration of a given dye increases. The concentration of dye necessary to obtain the desired depth of dyeing can readily be determined in each case by carrying out a dyeing test.

By the present invention, cellulose textile materials can be dyed with acid dyes commonly used in the dyeing of wool. The modified cellulose materials will, in general, have substantially the same dyeing characteristics as wool; i. e., they will dye to substantially the same color, shade and depth as wool, to produce a uniformly dyed product comprising a mixture of wool with the chemically modified cellulose material with a single dyeing step with an acid dye.

Since it is obvious that many changes and modifications can be made in the above-described details without departing from the nature and spirit of the invention, it is to be understood that the invention is not to be limited to the said details except as set forth in the appended claim.

I claim:

The process which comprises dyeing, with an acid dye, a "Fiber D" regenerated cellulose textile material which has been reacted with phenyl isocyanate, said isocyanate imparting to said cellulose material an affinity for said acid dye.

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