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METHOD OF TREATING CELLULOSIC TEXTILE MATERIALS

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12 Claims. (Cl. 8—116.3)

This invention relates to the chemical modification of cellulosic textile materials. More particularly it relates to the chemical modification of cellulosic textile materials whereby to render the same receptive to acid and chrome dyes used with wool, and to improve the crush resistance of such materials.

Cellulosic fibers are being used in increasing amounts in admixture with wool to create novel textiles not obtainable with either fiber alone, and to lower the raw materials cost of wool-containing products. This situation has made it desirable to obtain modified cellulosic fibers which can be dyed with wool dyes in order to avoid the complications and expense arising from the use of a mixture of dyes or a two-bath dyeing process. Further, in certain instances it is desirable to improve simultaneously the crush resistance of cellulosic textile materials, which are notably inferior to wool in this respect.

A variety of treatments have been described for modifying cellulosic textiles in order to give them affinity for the acid and chrome dyes used with wool. For example, it has been proposed to react regenerated cellulose filaments and fibers with an aminoaldehyde, say dimethylaminoacetaldehyde, whereby the aldehyde group is attached to the cellulose by the formation of an acetal group. In still other processes heretofore described, the cellulosic textile material is first modified by treatment with an aldehyde, and is subsequently reacted with one or more of a large variety of nitrogenous compounds, prominent among which are the amines. In general, however, these methods have not been entirely satisfactory since the dyeings obtained are often deficient in fastness to light and washing and/or are dull and lack uniformity. In addition, high cost, complicated procedure, and lack of affinity for a wide range of dyestuffs make many of the previously described treatments unsatisfactory from a commercial standpoint.

Many of the treatments which have been proposed for improving the crush resistance of cellulosic textiles reduce the affinity of these materials for direct dyes to an objectionable degree. This is particularly true in treatments involving formaldehyde.

An object of this invention, therefore, is to modify cellulosic textile materials so that they will have good affinity for acid and chrome dyes and improved crush resistance, by a simple procedure utilizing inexpensive and readily available raw materials. Another object is to prepare new cellulosic textile materials which can be dyed to a full shade with a wide range of wool as well as direct cotton dyes to yield colored products having good fastness to light and soaping. A still further object resides in the treatment of regenerated cellulose textile materials with inexpensive reagents which render the materials receptive to a wide range of direct, acid, and chrome dyes and which, in addition, enhance the crush resistance of such materials. Further objects will appear hereinafter.

These objects are accomplished by this invention, the essentials of which, briefly stated, are as follows: Cellulosic textile materials are intimately contacted with an aqueous solution comprising formaldehyde or a formaldehyde-yielding material, a salt of a water-soluble tertiary hydroxyalkylamine, each hydroxyl group of which is at least 2 carbon atoms removed from the amino nitrogen, and an acidic catalyst; thereafter the materials are dried and the reaction is completed by heat-treating the dried materials at an elevated temperature. The resulting tertiary amino nitrogen-containing cellulosic textile materials, which are new and form a part of this invention, have excellent affinity for acid, chrome and direct dyes, and improved crush resistance.

In carrying out the process of this invention a preferred procedure is as follows: The cellulosic textile material is impregnated with an aqueous formaldehyde solution containing a salt of a water-soluble tertiary hydroxyalkylamine and an acidic catalyst. The excess solution is removed by suitable means from the cellulosic material which is then dried at a temperature below 70° C. and heated for one to ten minutes at a temperature in the range of 80° C. to 150° C. The treated material is rinsed with water, washed in a soap solution containing soda ash and again rinsed with water. The resulting products have excellent affinity for a wide range of acid and chrome as well as direct dyes.

The treating solution preferably contains, by weight, from 3 to 15% formaldehyde and 3 to 30% of the tertiary hydroxyalkylamine salt. The acid catalyst, preferably ammonium chloride, is used in such an amount, generally from 0.05 to 2% depending upon the particular catalyst, that the resulting impregnating solution has a pH in the range of 1.6 to 3.0. The production of crush resistant products is favored by the use of high baking temperatures, high concentrations of formaldehyde, and active catalysts which give a low pH value.

Salts suitable for use in this invention may be made by the addition of a strong mineral or organic acid to an equivalent quantity of a water-soluble tertiary hydroxyalkylamine. The preferred tertiary hydroxyalkylamines are the tertiary beta-hydroxyethylamines which are conveniently obtained by the interaction of ethylene oxide with an ammonia type compound having at least one hydrogen attached to the amino nitrogen, or by reacting a beta-hydroxyethylamine having at least one amino hydrogen with formal-

dehyde and thereafter with formic acid as described in U. S. Patent 2,163,099.

The drying step is preferably carried out at room temperature in a stream of air. If more rapid drying is desired, the material is heated at temperatures ranging up to 70° C.

Heating or baking the impregnated and dried yarn in rapidly circulating hot air improves the uniformity of the treatment and increases the reaction rate. Preferably the baking temperature is within the range of 90° C. to 140° C. If desired, inert liquids such as xylene can be used as the heating medium.

The unreacted tertiary hydroxyalkylamine salt is readily recovered from the treated yarn by concentrating the aqueous solution obtained when the yarn is rinsed after the baking step.

The invention is further illustrated by the following examples. Parts are given by weight.

Example I

There is described in U. S. Patent No. 2,249,745 a crimped viscose rayon yarn which will be referred to hereinafter as "Fiber D." Skeins of 2500 denier, 100 filament "Fiber D" yarn are impregnated with an aqueous solution containing 5% formaldehyde, 10% tris(beta-hydroxyethyl)-amine hydrochloride and 0.2% ammonium chloride. The treating solution has a pH of 1.9 and is used at room temperature. The impregnated yarn is centrifuged so that the amount of treating solution retained is about equal to the weight of the dry yarn. After being dried at room temperature, the yarn is heated for five minutes in a chamber in which hot air at 105° C. is rapidly circulated. The treated skeins are rinsed with water, heated at 70° C. for three minutes in a 0.1% soap solution, rinsed thoroughly with water and dried. "Fiber D" treated in this manner gains 5% in weight and contains 0.33% nitrogen. The treated yarn is believed to be characterized by the presence of the structural unit

$$\text{Cell—OCH}_2\text{OCH}_2\text{CH}_2\text{N(CH}_2\text{CH}_2\text{OH)}_2\cdot\text{HCl}$$

wherein Cell represents a cellulose residue. The modified yarn has excellent affinity for a wide range of dyestuffs commonly used in dyeing wool. The concentration of representative acid, chrome and direct dyes required to produce equivalent shades on wool and the modified "Fiber D" are given in the following table.

Table I

Dye	Rowe Color Index No.	Percentage used with—	
		Modified "Fiber D"	Wool
ACID DYES			
"Pontacyl" Light Yellow GX	639	1.0	2.0
Du Pont Orange G	27	1.0	2.5
"Pontacyl" Wool Blue GL	833	1.0	3.0
"Pontacyl" Fast Black BBO	307	2.0	8.0
"Pontacyl" Blue Black SX	246	2.0	10.0
CHROME DYES			
"Pontachrome" Fast Red E Conc	652	1.0	2.0
"Pontachrome" Black TA	203	6.0	12.0
DIRECT DYES			
"Pontamine" Blue RWG Conc	512	1.0	2.0
"Pontamine" Green BX	593	1.0	2.0

The above data show that the affinity of the tris(beta-hydroxyethyl)amine hydrochloride-formaldehyde modified "Fiber D" for these dyes is superior to that of wool in all cases. The results obtained by exposing the dyed yarns to light from a carbon arc for 15 and 40 hours indicate that the dyeings on the modified "Fiber D" are equivalent in light-fastness to those on wool. The dyeings on the modified yarn possess about the same degree of wash-fastness as similar dyeings on wool. The modified yarn also has good affinity for the following dyes.

Table II

Dye	Rowe Color Index number
ACID DYES	
Du Pont Brilliant Milling Green B Conc	667
Du Pont Anthraquinone Green G	1,078
CHROME DYES	
"Pontachrome" Flavine A	219
"Pontachrome" Azure Blue BR	720
DIRECT DYES	
"Pontamine" Fast Red 8BL	278
"Pontamine" Sky Blue 6B	518
"Pontamine" Black E	581
"Pontamine" Fast Black FF	539

In all cases the dyeings on the modified "Fiber D" are equal or superior in depth to the dyeings obtained with wool by the same procedure.

Example II

Skeins of bright, unfinished, 150 denier, 40 filament viscose rayon yarn are impregnated with an aqueous solution containing 5% formaldehyde, 15% methyl-bis(beta-hydroxyethyl) amine hydrochloride and 0.2% ammonium chloride. The treating solution has a pH of 2.3 and is used at room temperature. The yarn is centrifuged, dried at room temperature and heated in a current of air at 105° C. for four minutes. The treated yarn is rinsed with water, heated at 70° C. for three minutes in a 0.1% soap solution, rinsed with water, and dried. As a result of this treatment, the yarn gains 4.5% in weight and has a wet tenacity 28% greater than the untreated control. When dyed with the acid dye, 1-amino-4-para-toluido-anthraquinone-2,2′-disulfonic acid, and washed with a warm soap solution, the modified yarn has a blue color similar in shade and depth to that obtained with wool dyed and washed in an identical manner. Untreated viscose rayon is not colored by this dye.

It is to be noted that these advantageous results are not obtained when the salt of a primary or secondary hydroxyalkylamine is used. For example, a different result is obtained when the methyl-bis(beta-hydroxyethyl) amine hydrochloride in the above treatment is replaced with an equal quantity of beta-hydroxyethylamine hydrochloride and the viscose yarn is treated in a manner similar to that described above. The dye is not retained by the modified yarn when it is dyed with the acid dye, 1-amino-4-para-toluido-anthraquinone-2,2′-disulfonic acid, and washed in the same manner as the methyl-bis(beta-hydroxyethyl) amine hydrochloride-formaldehyde treated yarn. In addition, the treatment

lowers the wet strength of the yarn considerably. Similar negative results are obtained when the beta-hydroxyethylamine hydrochloride is replaced with bis(beta-hydroxyethyl) amine hydrochloride.

Example III

Skeins of 400 denier, 33 filament cellulose acetate yarn containing 45% combined acetic acid are impregnated at room temperature with an aqueous ethanol solution containing 40% ethanol, 10% formaldehyde, 15% tris-(beta-hydroxyethyl) amine hydrochloride and 0.2% ammonium chloride. The yarn is centrifuged, dried at room temperature, and heated in a forced draft oven at 125° C. for four minutes. The treated cellulose acetate yarn is rinsed with water, placed in a 0.1% soap solution at 70° C. for three minutes, rinsed with water and dried. The modified cellulose acetate yarn has good affinity for the acid wool dyes, 1-amino-4-para-toluido-anthraquinone-2,2'-disulfonic acid and Du Pont Milling Red SWB, Rowe Color Index No. 430. The dyeings on the modified acetate yarn possess about the same degree of fastness to soaping as similar dyeings on wool.

Example IV

Skeins of 2500 denier, 100 filament "Fiber D" yarn are impregnated with an aqueous solution containing 10% tris-(beta-hydroxyethyl) amine hydrochloride, 5% formaldehyde, and 0.3% ammonium chloride. The impregnated yarn is centrifuged so that the weight of treating solution retained is about equal to the weight of the dry yarn. The yarn is dried at room temperature in a stream of air and baked in a forced draft oven at 140° C. for three minutes. The treated yarn is rinsed with water, heated in a 0.1% soap solution at 70° C., rinsed again with water, and dried at room temperature. The treatment increases the wet strength of the yarn 100%. The modified "Fiber D" has good affinity for the acid wool dye, 1-amino-4-para-toluido-anthraquinone-2,2'-disulfonic acid, and the direct cotton dye, "Pontamine" Sky Blue 6BX, Rowe Color Index No. 518, and the dyeings are fast to soaping. The crease angle of the yarn is increased by this treatment from 66°, that of the untreated "Fiber D," to 158°. This indicates that the resilience of the treated yarn is markedly superior to the control.

The crease angle is determined by winding a single thread which has been conditioned at 50% relative humidity and 25° C. over a double-edged knife blade under a tension of 500 g., removing the tension after 10 minutes and cutting the thread along one edge of the knife blade. The creased segments of the yarn are allowed to relax for ten minutes while lying on a smooth horizontal surface. The degree that the thread recovers from creasing is an index of its resilience, and the angle formed by the thread is known as the crease angle. An increase in crease angle accordingly indicates improved resilience.

Example V

Skeins of 2500 denier, 100 filament "Fiber D" yarn impregnated with an aqueous solution containing 5.0% tris-(beta-hydroxyethyl) amine hydrochloride, 3% formaldehyde, and 0.4% ammonium chloride is centrifuged so that the amount of treating solution retained is equal to the original weight of the dry yarn. The skeins are dried at room temperature and then placed in xylene at 138° C. for one minute. The xylene is removed from the "Fiber D" either by evaporation or by rinsing with methanol. The yarn is then washed in a warm soap-soda ash solution, rinsed and dried. The yarn has gained 1.9% in weight and is improved 76% in wet strength. After being wet with water and centrifuged, the modified "Fiber D" retains only 33% as much water as the untreated yarn. The crease angle of the treated yarn is 100° as compared with 66° for the untreated "Fiber D." This indicates a considerable improvement in the resilience of the yarn.

Example VI

Bright, unfinished, 150 denier, 40 filament viscose rayon yarn is impregnated with an aqueous treating solution containing 4% formaldehyde, 15% phenyl-bis-(beta-hydroxyethyl) amine hydrochloride and 0.2% ammonium chloride. The treating solution, which has a pH of 1.8, is used at room temperature. The yarn is centrifuged, dried at room temperature and heated in a forced draft oven at 105° C. for four minutes. The treated yarn is placed in a 0.1% soap solution at 70° C. for three minutes, rinsed with water and dried. The modified viscose rayon has good affinity for the acid wool dye, 1-amino-4-para-toluido-anthraquinone-2,2'-disulfonic acid, and the dyeing is fast to soaping.

Example VII

Skeins of 700 denier-70 filament "Fiber D" yarn are impregnated with an aqueous solution containing 10% tris-(beta-hydroxyethyl) amine hydrochloride, 5% formaldehyde and 0.4% ammonium chloride. The yarn is centrifuged, dried at room temperature, and heated in a forced draft oven at 122° C. for two minutes. The treated yarn gains 2.4% in weight, is improved 115% in wet strength and has affinity for the acid dye, 1-amino-4-para-toluido-anthraquinone-2,2'-disulfonic acid, and the direct dye, "Pontamine" Sky Blue 6BX, Rowe Color Index No. 518.

It is to be understood, of course, that the above examples merely illustrate preferred embodiments and are not to be construed as defining the broad limits of the invention. On the contrary, a wide departure from the exact materials, reagents and conditions recited in the examples is obviously within the purview of this invention.

Thus, cellulosic textile materials suitable for use in this invention include natural cellulose products, such as cotton, jute, ramie, and linen; regenerated cellulose materials, such as viscose and cuprammonium rayon; and cellulose esters and ethers containing unsubstituted hydroxyl groups, such as cellulose acetate, cellulose nitrate, cellulose acetate propionate, methyl cellulose, ethyl cellulose, benzyl cellulose, glycol cellulose, and cellulose glycolic acid. The textile material may be treated in the form of a fabric, loose staple, continuous filament yarn, and yarn spun from staple fiber. The cellulosic material may be mixed with other textile products, such as wool, either before or after treatment. The cellulose derivatives, such as the esters or ethers, which have fewer unsubstituted hydroxyl groups than cellulose, require the use of a greater excess of formaldehyde than other cellulose textiles in order to obtain the desired degree of modification.

The concentration of formaldehyde used will depend somewhat on the other reaction variables and the nature of the product desired. For example, less formaldehyde is required when longer baking times, higher baking temperatures, more active catalysts, or higher concentrations of the tertiary hydroxyalkylamine salt are used. More

formaldehyde will be required when a crush resistant product is desired. In general, at least 1% formaldehyde is used and 5 to 15%, or even as much as 40%, may be employed. The term "formaldehyde" is meant to include monomeric formaldehyde and such polymers as trioxane and paraformaldehyde.

Salts suitable for use in this invention include those derived from strong acids and water-soluble tertiary hydroxyalkylamines, all hydroxyl groups of which are at least 2 carbon atoms removed from the amino nitrogen. Suitable strong acids include such mineral acids as hydrochloric, sulfuric, phosphoric, hydrobromic, and organic acids such as oxalic, chloroacetic and toluenesulfonic. The tertiary hydroxyalkylamines may have one, two, three or more hydroxyl groups and should be soluble in water to the extent of at least 2% at 25° C. Salts of these water-soluble tertiary hydroxyalkylamines are sufficiently reactive so that products having the desired affinity for acid and chrome dyes are obtainable. Salts of tertiary hydroxyalkylamines having a plurality of hydroxyl groups and a neutral equivalent less than 200 are preferred because they react more readily with the cellulosic materials, and for a given increase in weight there is introduced into the cellulosic textile materials a greater amount of tertiary amino nitrogen, which is essential for acid and chrome dye affinity.

In addition to the salts of the tertiary hydroxyalkylamines used in the examples, salts of the following water-soluble alkanolamines are suitable for use in this invention: ethyl-bis(beta-hydroxyethyl)amine, N-beta-hydroxyethylmorpholine, N,N'-bis(beta-hydroxyethyl)piperazine, tris(beta-hydroxypropyl)amine, N,N,N',N'-tetrakis(beta-hydroxyethyl)ethylenediamine, dimethyl-3-hydroxypropylamine, dimethyl-(2,3-dihydroxypropyl)amine, and dimethyl-(4-hydroxybutyl)amine.

It is desirable to employ at least 1% of the tertiary hydroxyalkylamine salt in the impregnating bath in order to obtain fibers having appreciable affinity for acid and chrome dyes, and concentrations of 5 to 20%, or even as high as 50% or more, give good results. With a given concentration of the tertiary hydroxyalkylamine salt, higher concentrations of formaldehyde, active catalysts, higher baking temperatures and longer baking times all lead to products having a higher degree of modification.

Acids and substances capable of liberating or becoming acids under the conditions of the treatment constitute suitable catalysts. Examples are mineral acids such as hydrochloric, sulfuric, phosphoric, and hydrobromic; acid salts of mineral acids such as sodium hydrogen sulfate, sodium dihydrogen phosphate; salts of strong acids and weak bases, such as ammonium chloride, ammonium sulfate, ammonium thiocyanate, and ferric chloride; and organic acids such as tartaric, citric and toluenesulfonic. The concentration of any particular catalyst may vary from 0.05% or lower to as high as 1% or more, depending upon its potential acidity. Preferably, sufficient catalyst is used so that the pH of the impregnating solution is between 1.6 and 3.0. Less catalyst will be required when more drastic baking conditions or higher concentrations of formaldehyde are employed. The amount and type of catalyst is selected so that the desired modification of the textile material takes place readily with little or no tendering.

The treating solution may be applied to the textile material in any of several ways. The material may be dipped in the solution and squeezed or centrifuged to remove excess solution. Yarn, rope and flat goods may be passed continuously through the solution or the solution may be applied by spraying and the excess solution may be removed by squeezing between rolls or by vacuum extraction. The treating solution is usually employed at room temperature although solutions at a higher or lower temperature may be used.

The impregnated cellulosic textile material may be dried in air at temperatures ranging from room temperature to 70° C. or more. Uniform and rapid drying is favored by the rapid circulation of air in the drying chamber.

The impregnated and dried textile material is heated at temperatures ranging from 70° to 200° C. or higher in order to bring about reaction between the textile material, formaldehyde and tertiary hydroxyalkylamine salt within a reasonable time. At lower baking temperatures it is necessary to heat as long as an hour or more while at the higher temperatures a heating time of a minute or less is often sufficient. The use of higher baking temperatures favors the formation of crush resistant products. A vigorous circulation of air in the baking chamber improves the uniformity of the treatment and reduces the time required for the reaction to take place. An inert liquid may be used as a heating medium. Suitable inert liquids include xylene, dioxane, and bis(methoxyethoxyethyl)ether. Other suitable heating media are described in Pinkney, U. S. application Serial No. 364,886, filed November 8, 1940, now Patent 2,311,080.

I claim:

1. The method of treating cellulosic textile materials to render them receptive to acid and chrome dyes while retaining their affinity for direct dyes which comprises impregnating the cellulosic textile material with an aqueous solution of a pH value within the range of 1.6 to 3.0 and which contains from 3 to 15% by weight of formaldehyde, from 0.05 to 2% of an acidic catalyst, and from 3 to 30% of a water-soluble salt of a water-soluble tertiary hydroxyalkylamine, each hydroxyl group of which is at least 2 carbon atoms removed from the amino nitrogen, substantially drying the impregnated material, and thereafter heating the same at a temperature of from about 70° C. to about 200° C. to complete the reaction.

2. The method of treating cellulosic textile materials to render them receptive to acid and chrome dyes while retaining their affinity for direct dyes which comprises impregnating the cellulosic textile material with an aqueous solution of a pH value within the range of 1.6 to 3.0 and which contains from 3 to 15% by weight of formaldehyde, from 0.05 to 2% of ammonium chloride as catalyst, and from 3 to 30% of a water-soluble salt of a water-soluble tertiary hydroxyalkylamine, each hydroxyl group of which is at least 2 carbon atoms removed from the amino nitrogen, substantially drying the impregnated material in air at temperatures ranging from room temperature to 70° C., and thereafter heating the same at a temperature of from about 70° C. to about 200° C. to complete the reaction.

3. The method of treating cellulosic textile materials to render them receptive to acid and chrome dyes while retaining their affinity for direct dyes which comprises impregnating the cel-

lulosic textile material with an aqueous solution of a pH value within the range of 1.6 to 3.0 and which contains from 3 to 15% by weight of formaldehyde, from 0.05 to 2% of an acidic catalyst, and from 3 to 30% of a water-soluble salt of a water-soluble tertiary hydroxyalkylamine having a plurality of hydroxyl groups and a neutral equivalent of less than 200, each hydroxyl group of which is at least 2 carbon atoms removed from the amino nitrogen, substantially drying the impregnated material, and thereafter heating the same at a temperature of from about 70° C. to about 200° C. to complete the reaction.

4. The method of treating cellulosic textile materials to render them receptive to acid and chrome dyes while retaining their affinity for direct dyes which comprises impregnating the cellulosic textile material with an aqueous solution of a pH value within the range of 1.6 to 3.0 and which contains from 3 to 15% by weight of formaldehyde, from 0.05 to 2% of an acidic catalyst, and from 3 to 30% of a water-soluble salt of a water-soluble tertiary beta-hydroxyethylamine, substantially drying the impregnated material, and thereafter heating the same at a temperature of from about 70° C. to about 200° C. to complete the reaction.

5. The method of treating cellulosic textile materials to render them receptive to acid and chrome dyes while retaining their affinity for direct dyes which comprises impregnating the cellulosic textile material with an aqueous solution of a pH value within the range of 1.6 to 3.0 and which contains from 3 to 15% by weight of formaldehyde, from 0.05 to 2% of ammonium chloride as catalyst, and from 3 to 30% of a water-soluble salt of a water-soluble tertiary beta-hydroxyethylamine, substantially drying the impregnated material in air at temperatures ranging from room temperature to 70° C., and thereafter heating the same at a temperature of from about 70° C. to about 200° C. to complete the reaction.

6. The method of treating cellulose textile materials to render them receptive to acid and chrome dyes while retaining their affinity for direct dyes which comprises impregnating the cellulose textile material with an aqueous solution of a pH value within the range of 1.6 to 3.0 and which contains from 3 to 15% by weight of formaldehyde, from 0.05 to 2% of ammonium chloride as catalyst, from 3 to 30% of a water-soluble salt of a water-soluble tertiary beta-hydroxyalkylamine, substantially drying the impregnated material in air at room temperature, and thereafter heating the same at a temperature within the range of 90° to 140° C. to complete the reaction.

7. The process of claim 1 wherein the cellulosic textile material is regenerated cellulose textile material.

8. The process of claim 2 wherein the cellulosic textile material is regenerated cellulose textile material.

9. The process of claim 5 wherein the cellulosic textile material is regenerated cellulose textile material.

10. The process of claim 6 wherein the cellulose textile material is regenerated cellulose textile material.

11. The method of treating cellulosic textile materials to render them receptive to acid and chrome dyes while retaining their affinity for direct dyes which comprises intimately contacting the cellulosic material with an aqueous solution of a pH value within the range of 1.6 to 3.0 comprising essentially from 3 to 15% by weight of formaldehyde, from 0.05 to 2% of an acidic catalyst, and from 3 to 30% of tris(beta-hydroxyethyl) amine hydrochloride, substantially drying said cellulosic textile material, and thereafter heat treating the same to complete the reaction.

12. The method of treating regenerated cellulose textile materials to render them receptive to acid and chrome dyes while retaining their affinity for direct dyes which comprises impregnating the textile material with an aqueous solution of a pH value within the range of 1.6 to 3.0 and which contains from 3 to 15% by weight of formaldehyde, from 0.05 to 2% of ammonium chloride as catalyst, and from 3 to 30% of tris(beta-hydroxyethyl) amine hydrochloride, substantially drying the impregnated material in air at room temperature, and thereafter heating the same at a temperature within the range of 90° to 140° C. to complete the reaction.

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CERTIFICATE OF CORRECTION.

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It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction as follows: Page 2, second column, line 31, for "6B" read --6BX--; 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.

Signed and sealed this 9th day of April, A. D. 1946.

Leslie Frazer

(Seal) First Assistant Commissioner of Patents.

lulosic textile material with an aqueous solution of a pH value within the range of 1.6 to 3.0 and which contains from 3 to 15% by weight of formaldehyde, from 0.05 to 2% of an acidic catalyst, and from 3 to 30% of a water-soluble salt of a water-soluble tertiary hydroxyalkylamine having a plurality of hydroxyl groups and a neutral equivalent of less than 200, each hydroxyl group of which is at least 2 carbon atoms removed from the amino nitrogen, substantially drying the impregnated material, and thereafter heating the same at a temperature of from about 70° C. to about 200° C. to complete the reaction.

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