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**METHOD OF PREVENTING YELLOWING BY NITROGEN CONTAINING RESINS CURED ON CELLULOSE FIBERS BY ADDING HYDROGEN PEROXIDE OR UREA PEROXIDE**

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This invention relates to the finishing of cellulosic fibers, and particularly to an improved method of finishing cellulosic fibers with nitrogenous resins, in accordance with which the discoloration normally imparted to the fibers by these resins, is substantially reduced.

In recent years, the fabrics industry has benefited greatly from the development of the so-called wash-and-wear fabrics. For example, cellulosic fiber products such as cotton cloth are rendered crease-resistant and easily laundered by application to them of an essentially permanent resin finish which surrounds the fibers and reacts with them, thereby rendering them resistant to soiling and capable of retaining a smooth, wrinkle-free appearance. Resins particularly useful in this treatment are the polymethylol and polyalkoxymethyl ureas and melamines, such as the dimethylol ethylene urea resins, the methylated dimethylol urea resins, and the trimethylol melamine resins. In use, these resins are compounded with acidic curing agents and impregnated into the fibers, where they are cured in combination with the fibers by the application of heat.

Fiber products treated in this fashion have met with considerable commercial success, by reason of their improved properties which provide them with many of the characteristics of the more expensive synthetic fiber products. However, the treatment has one major drawback which limits its use. The cured resin-fiber product is often yellowed, or discolored, to an objectionable degree by the resin treatment. This yellowing is magnified in cases where the resin is even slightly overcured, with the result that undue care must be exercised to assure that the resin will be cured completely, and therefore will perform its function, and yet will not cause yellowing of the product.

The art has recognized that the use of resin-treated cellulosic fiber products could be broadened if the undesirable tendency of the resins to yellow the fibers on curing could be reduced, and white products of this type reliably provided.

It is a feature of this invention to provide an improved method of resin-treating cellulosic fibers, whereby the tendency of the treated fibers to be yellowed by the treatment is substantially reduced.

It is a further feature of this invention to provide such a method which provides resin-treated cellulosic fibers which are not substantially discolored, and which otherwise have the desirable physical and chemical properties of treated fibers.

It has now been found, quite surprisingly, that a very small amount of hydrogen peroxide or urea peroxide added to an aqueous solution of a nitrogenous resin used in the treatment of cellulosic fibers, essentially eliminates yellowing of the fibers by the resin. At the same time, the use of these particular peroxygen additive does

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not interfere with the crease resistances, physical strengths and the like of fibers treated with the resins in the absence of the additives.

In practice of the present invention, cellulosic fibers are impregnated with an aqueous solution of a nitrogenous resin from the class of the polymethylol and polyalkoxymethyl ureas and melamines, an acidic catalyst, and on the weight of the resin about 0.012% to 0.2% of 100% hydrogen peroxide introduced as aqueous hydrogen peroxide of any desired concentration, or as urea peroxide. The impregnated fibers are partially dried, and if desired, mechanically treated or manipulated to provide a particular finish on the fibers while they are in a wet condition, and thereafter the treated fibers are heated at a temperature of about 225° to 500° F. for a time sufficient to react the cellulose of the fibers with the nitrogenous resin. The resulting fiber product is found to have the desirable properties of fiber products treated with the resin in the absence of the peroxide, and also to be free of the objectionable yellowness of such products. The important improvements in the products would not be expected to result from the simple addition to the resin formulation of the present small amounts of peroxide.

This invention is applicable to a variety of cellulosic fibers, particularly to woven and non-woven fabrics made of cotton, rayon formed of regenerated celluloses, such as viscose and cuproammonium rayons, ramie, jute, linen, or other cellulosic fibers or cellulose derivatives which contain hydroxyl groups available for reaction with the nitrogenous resin. Mixtures of two or more of such fibers may also be treated. Cottons should be free of waxes before treatment, and if desired, they may have been mercerized.

The nitrogenous resin is employed on the fibers in the amount of about 1 to 15% of resin solids on fabric dry weight, and may be introduced by conventional means, such as with padding equipment and squeeze rolls. It is employed as an aqueous solution having any desired concentration which will provide the desired amount of resin on the fibers. Normally, a solution of about 5 to 20% concentration in water will be employed. More or less of the resin may be employed, however, the particular amount used will be determined on the basis of the degree of modification of the fibers desired. Normally, the indicated amount of 1 to 15% of the resin will provide excellent crease-resistance and washing resistance in the fabric, yet will provide a desirable hand or feel in the fabric.

The acidic catalyst employed for promoting the curing reaction of the nitrogenous resin, which is believed to involve reaction of the nitrogenous resin with cellulose hydroxy groups present in the fibers being treated, is not critical. Normally, about 0.1 to 2% of the acid catalyst on the weight of the resin will be employed, although more of the acid catalyst may be employed if desired. The acids commonly employed as catalysts for curing these resins may be employed, particularly the amine hydrochlorides such as morpholine hydrochloride, 2-amino-propanol hydrochloride and the like, ammonium salts of strong acids, for example, ammonium chloride, diammonium phosphate, ammonium sulfate and the like, the fluoroborates such as the zinc and other heavy metal salts, as well as the common acids such as phosphoric,

hydrochloric, acetic, oxalic, tartaric, p-toluenesulfonic, and the like. The solution may also contain wetting agents, which assist in the impregnation of the fabric by the resin solution. Likewise, it may contain such materials as softeners or lubricants, or other materials known for the treatment of cloth.

The treating solution importantly contains a small amount of hydrogen peroxide or urea peroxide, which serves to reduce markedly any yellowing which may be imparted to the cloth by the cured resin. It has been found that certain other active-oxygen chemicals, for example, the persulfates such as ammonium and potassium persulfate, degrade the cloth under the conditions of curing, and do not eliminate the yellowing problem, even in some cases contributing to the yellowing rather than to avoidance of it. It has been found that about 0.012 to 0.2% of 100% hydrogen peroxide on the weight of the resin is sufficient to avoid yellowing of the cloth. Use of less than the indicated lower amount of peroxide results in fiber products having little improvement in whiteness. Use of more than the indicated upper amount of peroxide is not desirable as little or no improvement in the fiber product is achieved by the additional peroxide, and its additional expense is therefore not justified. The hydrogen peroxide may be introduced in the form of aqueous hydrogen peroxide of any desired concentration, or as the urea peroxide. It has been noted that substantially no reduction in crease recovery, tensile strength or tear strength is imparted to the fibers by incorporation of the peroxide in the resin mix.

The present resin solutions are impregnated into the fibers by conventional means, for example, by passing the fibers through a solution of the resin followed by squeezing excess resin off with rolls, by spraying the resin onto the fibers and the like. Curing of the resin-treated fibers is effected by either simultaneously curing and drying the treated fibers in conventional heating equipment, or by first partially or completely drying the fibers and then curing with heat. In either case, a drying tenter-frame, heated metal cans or the like may be employed to provide the heat required for curing. Normally, the resins will cure at a temperature of about 225° F. to 500° F. The time of curing will, of course, vary in accordance with the temperature employed, from about ten seconds to half an hour. It is preferred to cure at a temperature of about 250° F. to 350° F., and for about two to ten minutes.

The following examples demonstrate the effect of the active-oxygen additive on the resin-treatment of cellulosic fabrics. The information presented in these examples is not intended to limit the scope of the present method or materials, it being apparent that modifications in the process may be made without departing from the invention.

#### EXAMPLE 1

(a) A cotton cloth sample having an 80 x 80 thread count and a weight of 4.0 yds./lb., measuring 10 inches wide by 3 feet long, was weighed and dipped into an aqueous solution containing 10% of dimethylol ethylene urea and 0.31% of morpholine hydrochloride on the weight of the resin. The sample was then passed through squeeze rolls to provide a pick-up of about 87% of resin solution on the weight of the cloth. Following this, the wet cloth was dried at room temperature, and cured at 320° F. for 5 minutes. It was then tested, with the results reported in Table I.

(b) The procedure of Example 1(a) was followed with the exception that the resin solution contained in addition to the indicated ingredients, 0.05% of 35% hydrogen peroxide on the weight of the resin. The cloth

sample was treated in the same fashion as was the sample in 1(a) above, with the results reported in Table I.

Table I

Property	Sample from Example 1(b)	Sample from Example 1(a)
Warp Tensile Strength, Washed <sup>1</sup> (lbs.)	24.8	25.0
Warp Tensile Strength, Unwashed (lbs.)	26.0	26.5
Warp Tear Strength, (grams)	442	409
Warp Crease Recovery, Unwashed (degrees)	140	137
Warp Crease Recovery, Washed (degrees)	131	141
Reflectance <sup>2</sup> (percent)	82.8	77
Reflectance of Untreated Cloth (percent)	83.2	

<sup>1</sup> The samples were washed at 130° to 140° F. in 14 gallons of water containing 79 grams of an alkaline, anionic built detergent and 205 cc. of a 5.25% solution of sodium hypochlorite. Two pounds of resin-treated cloth and 6 pounds of white filler cloth made up the load. The wash consisted of 15 minutes of a hot wash and about 15 minutes of rinsing and spin drying. After being washed, the cloth was ironed until it was dry to the touch, by being passed three times through an automatic ironer set at 70° F. Washes were repeated five times. The samples were ironed dry after each wash.

<sup>2</sup> Reflectances were determined on a Gardner Multi-Purpose Reflectometer employing a blue filter. Five readings were taken on each sample in the warp direction, and the results were averaged.

All samples were conditioned for 18 hours at 72° F. and 60 to 65% relative humidity prior to testing. U.S. Government Federal Specification Textile Test Methods identified as CCC-T-191b and dated January 25, 1956, were followed. Tensile tests were carried out according to CCC-T-191b test method 5102, tear tests according to method 5132, and crease recovery tests according to method 5212.

#### EXAMPLE 2

The procedures of Examples 1(a) and 1(b) were followed with the exception that the wetted resin samples were dried at 257° F. for 4 minutes, after which they were cured for 5 minutes at 320° F., whereas in Examples 1(a) and 1(b) the wet cloth samples were dried at room temperature. The sample treated with the solution containing hydrogen peroxide had a reflectance of 80.3%, whereas the sample treated without hydrogen peroxide had a reflectance of 63.2%. This demonstrates that the fabric can be dried at elevated temperatures before curing without destruction of the active-oxygen component.

#### EXAMPLE 3

This example demonstrates the amounts of hydrogen peroxide which may be employed in the present process. The procedure of Example 1(b) was followed, with the amounts of hydrogen peroxide reported in Table II as 100% hydrogen peroxide, being employed on the weight of the resin. The peroxide was introduced at 35% hydrogen peroxide.

Table II

Amount of 100% H <sub>2</sub> O <sub>2</sub> :	Reflectance, percent
0	68.7
0.2	80.1
0.15	80.5
0.035	81.6
0.02	82.2
0.012	80.4
0.01	71.2
Original cloth	82.7

#### EXAMPLE 4

In this example, the hydrogen peroxide was introduced as urea peroxide. The procedure followed was that of Example 1(b). Table III reports the percent reflectance values of resin-treated cloth products prepared with solutions containing varying amounts of urea peroxide, with amounts reported as 100% hydrogen peroxide.

Table III

Amount of 100% H <sub>2</sub> O <sub>2</sub>	Reflectance, percent
0	71.3
0.075	81.3
0.035	79.6
0.016	81.0
Original cloth	82.7

## EXAMPLE 5

In this example the dimethylol ethylene urea resin was replaced with trimethylol melamine. In all respects, the experimental procedures of Example 1(a) and 1(b) above were followed, with Example 5(a) showing the effect of having no peroxide in the resin solution, and Example 5(b) showing the effect of using hydrogen peroxide in the solution. Results of these examples are shown in Table IV.

Table IV

Property	Sample from Example 5(b)	Sample from Example 5(a)
Warp Tensile Strength, Washed (lbs.)	26.3	25.0
Warp Tensile Strength, Unwashed (lbs.)	25.3	24.2
Warp Tear Strength (grams)	488	442
Warp Crease Recovery, Unwashed (degrees)	140	141
Warp Crease Recovery, Washed (degrees)	133	137
Reflectance, percent	82.6	65.9
Reflectance, Original Cloth, percent	83.7	

## EXAMPLE 6

In this example, the resin employed was dimethoxy methyl urea. The procedures of Example 1(a) and 1(b) were followed, with Example 6(a) showing the effect of treating the cloth with a resin formulation not containing hydrogen peroxide, and Example 6(b) showing the effect of employing hydrogen peroxide, in the solution. Results of these examples appear in Table V below.

Table V

Property	Sample from Example 6(b)	Sample from Example 6(a)
Warp Tensile Strength, Washed (lbs.)	29.0	26.5
Warp Tensile Strength, Unwashed (lbs.)	25.8	25.3
Warp Tear Strength (grams)	537	493
Warp Crease Recovery, Unwashed (degrees)	127	141
Warp Crease Recovery, Washed (degrees)	133	131
Reflectance, percent	80.4	67.0
Reflectance of Original Cloth, percent	83.7	

## EXAMPLE 7

This example demonstrates the results obtained when the hydrogen peroxide is replaced with ammonium persulfate or potassium persulfate. In this example, the procedure of Example 1(a) was followed, with the exception that 0.15% of ammonium persulfate, and 0.15% of potassium persulfate, on the weight of the resin, were used in place of the hydrogen peroxide. The results of these experiments are reported in Table VI which follows.

Table VI

Sample	Warp Tensile Strength, Unwashed (lbs.)	Reflectance, percent
No Active Oxygen Additive	28.2	74.4
With Ammonium Persulfate	14.0	52.0
With Potassium Persulfate	23.0	64.3
Original Cloth		82.8

It will be seen from these examples that hydrogen peroxide introduced as such or as urea peroxide into a nitrogenous resin solution is an effective additive in the treatment of cellulosic fibers with the resin. The peroxide serves virtually to eliminate the undesirable yellowing of cellulosic fibers which is produced by treatment of the fibers with a resin solution not containing the peroxide.

Fibers treated with the peroxide-containing resin solutions are essentially as bright as are the original fibers, in each case having a reflectance value of more than 80%, whereas the brightness of fibers treated with resin solutions containing no peroxygen compound are much lower, having reflectances even as low as about 65%.

Furthermore, the other properties of the resin-treated fibers are not deleteriously affected by addition of the active oxygen compound to the resin used to treat the fibers. It is important to note that certain other active-oxygen compounds, for example ammonium and potassium persulfates, do not reduce yellowing of the fibers, and even damage the cloth when used with the resin. This is despite their effectiveness as carriers of active oxygen in many other applications.

Pursuant to the requirements of the patent statutes, the principle of this invention has been explained and exemplified in a manner so that it can be readily practiced by those skilled in the art, such exemplification including what is considered to represent the best embodiment of the invention. However, it should be clearly understood that, within the scope of the appended claims, the invention may be practiced by those skilled in the art, and having the benefit of this disclosure, otherwise than as specifically described and exemplified herein.

What is claimed is:

1. Method of providing a soil-resistant and crease-resistant product having a high reflectance value and otherwise good physical properties from cellulose fibers from the group consisting of natural cellulose fibers and regenerated cellulose fibers, comprising introducing onto said cellulose fibers, about 1 to 15% on the dry weight of said fibers of a nitrogenous resin which yellows on being heat cured on said fibers, said resin being from the group consisting of the polyfunctional methylol and alkoxymethyl urea resins and the polyfunctional methylol and alkoxymethyl melamine resins, an acidic curing agent for said resin, and a peroxide from the group consisting of hydrogen peroxide and urea peroxide in an amount to provide, on the weight of said resin, about 0.012 to 0.2% of hydrogen peroxide, and heating the treated cellulose fibers until the nitrogenous resin is cured to a thermo-set condition.

2. Method of claim 1 in which the hydrogen peroxide is introduced as hydrogen peroxide.

3. Method of claim 1 in which the hydrogen peroxide is introduced as urea peroxide.

4. Method of claim 1 in which resin on the treated cellulosic fibers is cured to a thermo-set condition by being heated at about 225° to 500° F.

5. Method of claim 1 in which the nitrogenous resin is dimethylol ethylene urea.

6. Method of claim 1 in which the nitrogenous resin is dimethoxy methyl urea.

7. Method of claim 1 in which the nitrogenous resin is dimethylol melamine.

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