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PROCESS FOR DYEING DURABLE PRESS CELLULOSIC FABRICS WITH BASIC DYES

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ABSTRACT OF THE DISCLOSURE

Durable-press cellulosic fabrics have been prepared in a process which simultaneously renders them responsive to basic dyes. In a two-phase process the cellulosic component is crosslinked using a crosslinking agent and an alpha-hydroxy carboxylic acid in the first phase (the carboxylic acids serving the dual purpose of catalyst and reactive additive), thus producing a crosslinked cellulosic fabric with pendant carboxylic groups. In the second phase, a basic dye is selectively absorbed by the chemically modified cellulosic textile, due to the presence of the carboxylic groups.

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This invention relates to chemical treatments which impart wrinkle resistance to cellulosic textiles. Specifically, this invention relates to chemical treatments to cellulosic textiles to render them wrinkle resistant as well as highly receptive to basic dyes. In addition to the improved dye receptivity imparted by the new process considerable improvement in certain other properties, such as tearing strength and moisture regain, can be achieved.

This invention also relates to the use of alpha-hydroxy-carboxylic acids as crosslinking catalysts in finishing. The normal catalyst used in crosslinking cotton is a metal salt catalyst such as magnesium chloride or zinc nitrate.

Another catalyst which has found considerable use is the mixed catalyst system. This so-called mixed catalyst is a complex formed by the combination of a metal salt and a hydroxy acid such as magnesium chloride-citric acid. This complex catalyst is a very powerful catalyst and small concentrations are sufficient to promote the desired crosslinking of the fabric.

The catalysts used for this work are the hydroxy acids themselves without any metal salt additive. Because these hydroxy acids are relatively weak acids, large amounts can be used to promote the desired crosslinking of the fabric. The objective of the use of large amounts (2–10%) is that this permits a significant quantity of these agents to be grafted onto the fabric. The reason that this occurs is that the hydroxyl group of the hydroxy acid is reactive with the N-methylol moiety of the crosslinking agent. When another N-methylol group of the crosslinking agent reacts with cotton the hydroxy acid then becomes attached to cotton. In this respect, an agent such as dimethylol dihydroxyethyleneurea is a particularly effective crosslinking agent because it has four N-methylol groups available for the grafting of the hydroxy acids or available for crosslinking. As a result of using this agent and the hydroxy acid in finishing, one obtains a crosslinked fabric with high conditioned wrinkle recovery, good durable press rating and a titratable amount

of carboxyl group on the fabric. This carboxyl concentration (up to 1.9% depending upon acid type and concentration of acid used in the finishing bath) gives the fabric a potential acidic character.

Thus, one should consider three fabrics. One fabric is the untreated cotton, the second is a fabric crosslinked in a conventional manner with a metal salt catalyst, and the third was crosslinked using a hydroxy carboxylic acid as the catalyst. Examples of such hydroxy-carboxylic acids are glycolic acid, lactic acid, mandelic acid, tropic acid, tartaric acid, and malic acid. To permit dyeing of these fabrics, the samples are treated with dilute hydrochloric acid to convert the pendant carboxyl groups from the salt form to the acid form. Then, the fabrics are washed with distilled water several times and dried (optional). (This pretreatment may be omitted depending upon dye bath and dyestuff subsequently employed.) The fabrics are then dyed in a dye bath containing a basic dyestuff and the other normal reagents commonly found in a basic dye bath. After the fabrics are dyed in the normal manner, the resultant fabrics are rinsed and laundered. While the untreated cotton and the cotton crosslinked with the metal salt catalyst have poor affinity for the basic dyestuff, the samples of fabric containing the carboxyl groups are dyed a significantly deeper color. Examples of some typical basic dyes with which this approach has found merit are C.I. (Color Index) Basic Blue 11, (C.I. 44040), C.I. Basic Violet 10 (C.I. 45170). and C.I. Basic Violet 1 (C.I. 42535).

In addition to dyeing the fabric with an acidic character with the basic dye, it is also possible to dye with a basic dye a fabric in which the acid grouping has been converted to the salt form. This technique involves the replacement of the proton on metal salt (for example sodium carboxylate) with the ammonium or quaternary or hydrochloride form of the basic dye. This technique has been used with methylene blue chloride (salt Basic Blue 9 C.I. 52015).

By contrast, the fabric crosslinked in the normal manner shows poor dye receptivity. This is true not only of the basic dyes used in this work but for other types of cotton dyes as well. The option of being able to dye after fabric has been crosslinked may have certain distinct marketing, processing, and technical advantages. First, it would be possible to dye white goods a different color should a demand arise for special colored fabrics. Such an option of selling fabrics either white or colored might be advantageous for inventory control. Second, due to the high temperatures commonly used in textile finishing, the sublimation of dyestuffs means that certain bright shades might not be readily available. Also, the effects of metal salt catalysts and heat to improper shade change might be easily corrected if fabric could be dyed after crosslinking. The fact that these fabrics could be dyed after finishing adds an element of flexibility that is not currently available either in processing conditions or choice of dyestuff. Finally, it would be possible to adjust fabric colors should any undesirable shade changes occur in curing or other steps. In addition to the dyeing characteristics of these fabrics, the use of these mild acid catalysts enhances certain other fabric properties. First, the fabrics usually have a higher level of tearing strength retention. Second, moisture regain of the fabric is usually increased. Increased moisture regain is usually associated with improved comfort characteristics. Third, the fabrics usually show improved soil release performance due to the presence of the carboxylic groups which are permanently cross-linked into the fabric.

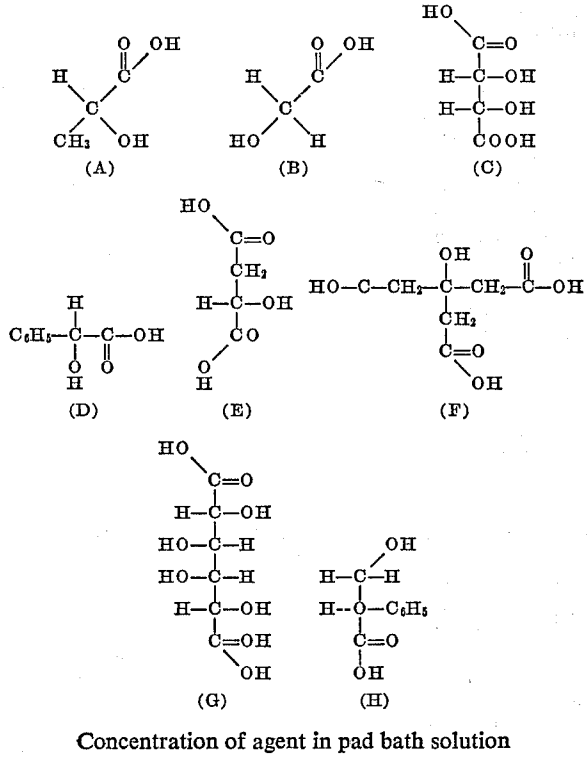
In general terms, the process of this invention starts with the incorporation of the hydroxy acid in a normal pad bath solution instead of the metal salt latent acid

normally used in such solutions to produce wash-wear or durable press cottons. From this point on, fabric is finished in a standard manner according to contemporary textile practice. This method can be used with a number of textile formulations, the only requirement being that the metal salt catalyst and the appropriate amount of water be replaced by the hydroxy acid catalyst. The method is readily applicable to either precure or postcure one-bath, one-step treatments. The fabric is washed and then dyed with a basic dye utilizing normal dyestuff practices.

DESCRIPTION OF AGENTS

A number of hydroxy acids has been employed as the hydroxy acid catalyst. Typical of such agents are lactic acid (A), glycolic acid (B), tartaric acid (C), mandelic acid (D), malic acid (E), citric acid (F), mucic acid (G), and tropic acid (H). In general, the method would seem feasible to almost any formulation containing a hydroxy carboxylic acid or its salt.

Examples of suitable hydroxy acids are the following:



Concentration of agent in pad bath solution

While a quantity of about from 0.5% to 10% of the various acids have been shown to be effective in promoting an adequate fabric cure, the carboxyl content of the fabric increases progressively with the use of larger amounts of hydroxy acid in the finishing bath. For the purposes of maximizing carboxyl content as well as because of economic considerations a concentration of acid ranging from about 2% to about 5% seems to be about the optimum concentration for the acid catalysts and coreactant.

To summarize, the invention can best be described as a process for imparting receptivity for basic dyes to crosslinked cotton fabrics. This improvement consists of the use of hydroxy acids as catalysts for crosslinking systems as well as coreactants to lead to crosslinked fabrics containing pendant carboxyl groups. Due to the presence of these carboxyl groups, dye procedures can now be applied to these fabrics using basic dyes, which would be substantive to an acid substrate. Neither cotton crosslinked in the normal manner nor untreated cotton fabrics have good substantitivity for basic dyestuffs.

Only the basic formulations have been used in the examples. Variations using softeners, wetting agents, and polymer additives are readily accessible for anyone skilled in the art of textile finishing.

EXAMPLE 1

Cotton printcloth was padded with a solution containing 9 parts dimethylol dihydroxyethyleneurea, 0.5 part zinc nitrate hexahydrate, and 90.5 parts of water. The fabric was dried for 7 minutes at 60° C. and cured for 5 minutes at 160° C. The fabric was then laundered and tumble dried. A second sample of cotton printcloth was padded with 9 parts dimethylol dihydroxyethyleneurea, 2 parts glycolic acid and 89 parts water. The sample was then dried, cured and washed in the same manner as the first sample. In addition to these samples, other samples were treated with 9 parts dimethylol dihydroxyethyleneurea, varying amounts of hydroxy acids and sufficient water to total 100 parts or 100%. The amounts of the acids and the properties of the resultant fabrics are listed in Table I. It can be seen that the effect of these treatments is to produce fabrics with high resilliency (wrinkle recovery) like a conventional durable press fabric [sample crosslinked with dimethylol dihydroxyethyleneurea (DMDHEU) using zinc nitrate catalyst]. However, an improvement of approximately 50–150 g. in warp tearing strength is usually observed. Furthermore, an increase in moisture regain from 0.3% to 1.4% higher than the crosslinked control was achieved. Increased moisture regain is generally associated with improved comfort characteristics. Finally, titration indicated a substantial increase in the carboxyl content of these crosslinked fabrics. Because of this increase in carboxyl content, the fabric now possesses an acid character which may have advantages for specific application purposes.

TABLE I.—PROPERTIES OF FABRICS CROSSLINKED USING HYDROXY ACID CATALYSTS

Acid catalyst	Cond. WRA (deg.)	Warp tearing strength (g.)	Percent COOH	Percent moisture regain
0.5% $Zn(NO_3)_2 \cdot 6H_2O$	285	387	0.25	3.8
2.0% glycolic acid	287	493	0.81	4.1
3.0% glycolic acid	281	440	1.06	4.1
4.0% glycolic acid	277	427	1.32	4.3
5.0% glycolic acid	269	433	1.46	4.5
2.0% malic acid	287	507	0.60	----
4.0% malic acid	294	480	1.29	----
2.0% mandelic acid	276	540	0.43	4.9
4.0% mandelic acid	275	527	0.61	4.9
6.0% mandelic acid	276	507	0.91	5.0
2.0% lactic acid	273	533	----	----
4.0% lactic acid	269	473	----	----
10.0% lactic acid	268	433	----	----
0.5% citric acid	280	487	0.50	5.3
1.0% citric acid	279	500	0.49	4.8
2.0% citric acid	289	480	0.83	4.6
4.0% citric acid	294	433	1.36	4.6
6.0% citric acid	297	427	1.85	4.7
1.0% tartaric acid	274	393	0.55	5.0
2.0% tartaric acid	278	373	0.69	5.2
4.0% tartaric acid	273	327	1.22	5.1
3.0% tropic acid	256	573	0.51	5.4

EXAMPLE 2

Swatches of the samples listed in Table I were immersed in 1% hydrochloric acid for about 30 minutes. They were, then, repeatedly washed with distilled water. After these samples were dried, they were immersed in a dye bath prepared from 15 g. of Basic Blue 11 (C.I. 44040), 22 g. of glacial acetic acid and 1500 ml. of distilled water.

The fabrics were dyed at room temperature about 15 minutes, 40° C. for about 15 minutes, and 60° C. for about 10 minutes. They were also dyed for the period of time during which the temperature was being raised. This corresponded to a period of 20 minutes in going from room temperature to 40° C. and about 20 minutes in going from 40° C. to 60° C.

The samples were rinsed repeatedly in distilled water, then heated in distilled water 60° to 90° C. changing water on several occasions. The fabrics were then tumble dried. Inspection of the samples was then made. It was found that while the crosslinked control (catalyzed with

a metal salt catalyst) and untreated cotton were dyed a light blue, all the samples in Table I, which had been catalyzed with hydroxy acids were dyed a deep blue. With a given acid, the samples had a deeper dye shade as the amount of the acid in the formulation increased. Morover, hydroxy acids which contained a phenyl ring (such as mandelic or tropic acid) dyed an even deeper shade of blue.

A portion of each sample was then cut off and laundered in a machine. After these samples were tumble dried, they again were inspected. The same relationships as had been observed previously still prevailed, namely, the untreated cotton and crosslinked cotton were a light blue while the samples containing carboxyl groups crosslinked into the fabric were a dark blue.

EXAMPLE 3

The same procedures were employed as in Examples 1 and 2 using the conventional treatment (9% DMDHEU and 0.5% zinc nitrate acid catalyst), the acid catalyzed treatments (9% DMDHEU and from 2–5% of the acid catalyst) and untreated control samples on mercerized cotton fabric and on polyester-cotton blended fabrics. The results are listed in Table II and clearly demonstrate that the use of the hydroxy acid catalyst leads to fabric with better tearing strength, moisture regain and accessibility to basic dyes than does fabric given a conventional treatment.

0.5% zinc nitrate hexahydrate. The sample was dried for 7 minutes at 60° C. and cured for 5 minutes at 160° C. Then an untreated sample of each fabric was treated in a similar manner except that the zinc nitrate in the finishing formulation was replaced by each of the following catalysts: 4% glycolic acid, 4% lactic acid, 4% mandelic acid, 4% malic acid, 4% citric acid, and 4% tartaric acid. These samples yielded fabrics in which the glycolic, mandelic, malic, citric, lactic, and tartaric acids were grafted onto the fabrics. The samples were then washed and tumble dried together with an untreated sample of each fabric. Then, swatches of each fabric were placed in a dye bath prepared from 8 g. of C.I. Basic Violet 1 (C.I. 42535) and 800 g. of distilled water, and 20 drops of glacial acetic acid.

The fabrics were inserted at room temperature and then the temperature raised to 95° C. at which point 100 cc. of distilled water were added to the bath. The bath was then allowed to cool slowly. After that, the samples were removed, rinsed in distilled water several times, then inserted in a distilled water bath several times. On one occasion the bath was raised to 40° C., the next bath, the temperature was raised to 50° C., and with the next distilled water bath the temperature was raised to 60° C. The samples were again rinsed several times in distilled water and tumble dried.

Inspection of the samples revealed that all samples containing carboxyl groups were dyed a deep purple violet. By contrast, the untreated samples or samples using a conventional crosslinking catalyst were dyed a pale violet. This relationship held for the mercerized and unmercerized cotton series as well as for the cotton-polyester series. In this respect, the cotton-polyester had its own peculiar shade changes due to the poor uptake of dye by the polyester component but relative relationships remained the same.

TABLE II.—PROPERTIES OF BLENDED FABRICS AND MERCERIZED FABRICS USING HYDROXY ACID CATALYST

Fabric	Acid catalyst	Cond. WRA (deg.)	Warp tearing strength (g.)	Percent COOH	Percent moisture regain	Dye shade
Merc. cotton	0.5% $Zn(NO_3)_2 \cdot 6H_2O$	304	580	0.3	5.2	Light blue.
Do	3% glycolic acid	281	680	0.8	6.3	Do.
Do	5% glycolic acid	281	700	1.2	6.2	Do.
Do	2% malic acid	287	780	0.5		Do.
Do	4% malic acid	282	720	0.8	6.1	Do.
Do	Untreated	172	1,010	0.2	7.2	Light blue.
50–50 polyester-cotton	0.5% $Zn(NO_3)_2 \cdot 6H_2O$	308	513	0.4	2.1	Light blue.[1]
Do	2% glycolic acid	307	553	0.7	2.9	Dark blue.
Do	3% glycolic acid	303	540	0.8	2.8	Do.
Do	5% glycolic acid	303	553	0.9	2.9	Do.
Do	2% malic acid	312	560	0.5	2.7	Do.
Do	4% malic acid	310	533	0.7	2.6	Do.
Do	Untreated	264	880	0.2	3.6	Light blue.

[1] Only cotton component dyed.

Swatches of the samples listed in Table I were inserted in 1% hydrochloric acid for a short period, then rinsed repeatedly in distilled water. Then the fabric was dipped in a dye bath prepared from 10 g. of C.I. Basic Violet 10 (C.I. 45170), 5 cc. of glacial acetic acid, and 1000 ml. water. The fabrics were immersed in the dye bath at 40° C., the temperature was raised to 60° C. over a period of 30 minutes, allowed to cool back to 35° C. during a period of 1 hour, 15 cc. of glacial acetic acid was added, temperature raised to 70° C. over a period of 30 minutes, then allowed to cool to 50° C. The fabric was washed in distilled water, then tap water. After repeated washing the samples were inspected.

The crosslinked control with a metal salt catalyst was a pale pink, the untreated control was a very light pink. On the other hand, the samples catalyzed with glycolic acid, mandelic acid, citric acid, malic acid, lactic acid or tartaric acids were dyed a bright violet in color. These samples provide another example of the fact that a basic dye can be used to dye fabrics containing acid groups crosslinked into the fabric.

EXAMPLE 4

Three types of fabrics were employed in this experiment. One was an unmercerized all-cotton printcloth, a second was a mercerized all-cotton printcloth, and a third was a 50–50 polyester-cotton blend. One sample of each fabric was padded with a solution of 9% DMDHEU and

EXAMPLE 5

Several representative fabrics treated with crosslinking agent and acid catalysts (examples from Table I) as well as appropriate controls were treated with a dye bath prepared from 1% methylene blue chloride(salt Basic Blue 9, C.I. 52015). The samples were in the dye bath for 40 minutes at room temperature and then for an additional 35 minutes while the bath was heated to 60° C. The fabrics were then washed repeatedly with distilled water. Included in this group of washings, the fabrics were heated in warm (40° C.) distilled water. The fabrics were then tumble dried. The sample prepared by crosslinking the fabric with a zinc nitrate based catalyst was light blue, the untreated cotton fabric was a light blue while the fabrics utilizing the hydroxy acid catalysts were dyed a dark blue. Examples of such acid catalysts included in this group were 4% tartaric acid, 6% citric acid, 5% glycolic acid, 6% lactic acid, 6% mandelic acid, 4% glycolic acid, 4% malic acid, 4% mandelic acid, and 3% tropic acid with 0.5% $Zn(NO_3)_2 \cdot 6H_2O$. The results from this ex-

periment clearly demonstrate that a salt of a basic dye can be applied to crosslinked fabric, in which a carboxyl group has been crosslinked into the fabric.

We claim:

1. A process for imparting to a cellulosic textile durable-press performance and the quality of being able to respond to and accept basic dyes, the process comprising:

(a) impregnating the cellulosic textile with a formulation consisting of about from 1% to 15% of the crosslinking reagent dimethylol dihydroxyethyleneurea and about from 0.5% to 10% of an alpha-hydroxy carboxylic acid selected from the group consisting of citric acid, glycolic acid, lactic acid, malic acid, mandelic acid, mucic acid, tartaric acid, and tropic acid;

(b) drying the wet impregnated textile for about from 2 minutes to 24 hours, at temperatures about from 25° to 90° C.;

(c) curing the dry impregnated cellulosic textile at temperatures about from 100° to 170° C. for periods of time about from 30 seconds to 20 minutes, using the longer periods of time with the lower temperatures; then

(d) dyeing the crosslinked textile with a basic dye.

2. The process of claim 1 wherein the alpha-hydroxy carboxylic acid is citric.

3. The process of claim 1 wherein the alpha-hydroxy carboxylic acid is glycolic.

4. The process of claim 1 wherein the alpha-hydroxy carboxylic acid is lactic.

5. The process of claim 1 wherein the alpha-hydroxy carboxylic acid is malic.

6. The process of claim 1 wherein the alpha-hydroxy carboxylic acid is mandelic.

7. The process of claim 1 wherein the alpha-hydroxy carboxylic acid is mucic.

8. The process of claim 1 wherein the alpha-hydroxy carboxylic acid is tartaric.

9. The process of claim 1 wherein the alpha-hydroxy carboxylic acid is tropic.

References Cited

UNITED STATES PATENTS

3,441,367	4/1969	Pierce et al.	8—185
2,950,553	8/1960	Hurwitz	8—185
3,374,107	3/1968	Cotton	8—18
3,411,860	11/1968	Braun et al.	8—18
3,046,075	7/1962	Kanter et al.	8—18 X
3,142,529	7/1964	Freyermuth et al.	8—18
3,702,230	11/1972	Blanchard et al.	8—31 X

HERBERT B. GUYNN, Primary Examiner

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