

- [54] **PROCESS FOR WHITENING DURABLE-PRESS CELLULOSIC FABRICS WITH BASIC OPTICAL BRIGHTENERS**
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- [58] Field of Search ..... **8/185, 17, 18, 31, 1 W, 8/186, 100**

[56]

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### ABSTRACT

Durable-press cellulosic fabrics with increased response to basic optical brighteners have been produced by a novel process wherein ordinary chemical crosslinking formulations are modified by substituting an alpha-hydroxy carboxylic acid for the usual strong inorganic acid to provide a chemically modified cellulose with pendant carboxylic groups. The second phase of the process consists of submitting the chemically modified fabric to a relatively mild treatment with a basic optical brightener.

**13 Claims, No Drawings**

## PROCESS FOR WHITENING DURABLE-PRESS CELLULOSIC FABRICS WITH BASIC OPTICAL BRIGHTENERS

A non-exclusive, irrevocable, royalty-free license in the invention herein described, throughout the world for all purposes of the United States Government, with the power to grant sublicenses for such purposes, is hereby granted to the Government of the United States of America.

This invention relates to the preparation of cellulosic durable-press textiles. More specifically, this invention relates to a process for imparting durable-press characteristics to cotton fabrics and other cellulosic fabrics while rendering the finished product whiter than has been possible heretofore. The process of this invention comprises treating cellulosic textiles with a formulation containing a crosslinking reagent and an alpha-hydroxy carboxylic acid instead of the usual strong inorganic acid catalyst to produce a crosslinked durable-press fabric with acidic pendant groups which attract and accept basic optical brighteners.

In general, according to the invention, a process is provided for imparting to a cellulosic textile durable-press performance and the quality of improved response to, and acceptance of, basic optical brighteners. In carrying out the process, the cellulosic textile is impregnated with a formulation containing about from 1 to 15 percent of an agent for crosslinking cellulose, as, for example, dimethylol dihydroxyethyleneurea, and about from 0.5 to 10 percent of an alpha-hydroxy carboxylic acid, such as citric acid, glycolic acid, lactic acid, malic acid, mandelic acid, mucic acid, tartaric acid, and tropic acid, for catalyzing the crosslinking reaction between the textile cellulose and said crosslinking agent. The wet, impregnated textile is dried for about from 2 minutes to 24 hours at a temperature of about from 25° C. to 90° C. and the dry, impregnated cellulosic textile is then cured at a temperature of about from 100° C. to 170° C. for about from 30 seconds to 20 minutes, using the longer times with the lower temperatures, to effect the crosslinking reaction between the textile cellulose and the crosslinking agent and produce a crosslinked textile containing acidic pendant groups which attract and accept basic optical brighteners. Thereafter, the resulting crosslinked textile is whitened by treatment with a basic optical brightener, such as Fluorescent Brighteners 56, 101, and 159, and Phorwite DBS (a cationic pyrazoline brightener).

In essence, this invention relates to the use of 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 strength of this catalyst may arise from its action as a source of a strong acid (hydrochloric acid).

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 crosslink-

ing of the fabric. The objective of the use of large amounts (2-10 percent) 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 groups on the fabric. This carboxyl concentration (up to 1.9 percent depending upon acid type and concentration of the acid used in the finishing bath) gives the fabric a potential acidic characteristic.

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 is crosslinked using a hydroxy carboxylic acid as the catalyst. Examples of such hydroxy-carboxylic acids are citric acid, mucic acid, glycolic acid, lactic acid, mandelic acid, tropic acid, tartaric acid, and malic acid.

Because of the presence of these acidic carboxyl groups on fabric, it is now possible to whiten the fabrics by the application of certain special types of brighteners. These brighteners are the basic or cationic brighteners which are normally used on acid fabric such as acrylic fiber fabrics. The brighteners can be applied to the fabric either by using a mild dye bath procedure or by a padding procedure. At the option of the operator, the carboxyl-containing fabrics may be converted to the acid form by use of a mild acid (dilute hydrochloric acid-) followed by a distilled water wash, prior to treatment with the basic optical brightener. However, because many of the baths for treating the basic brightener are actually acidic, this eliminates the need for this intermediate treatment.

The basic brighteners are selectively absorbed by the crosslinked fabrics containing these grafted carboxylic groups. The absorption of the brightener leads to whiter fabrics under both regular and ultraviolet (UV) light. The effectiveness of the method has also been demonstrated by the use of a spectrofluorometer, which measures the fluorescence of the various fabrics. In general, it has been found that in a series of fabrics consisting of crosslinked fabrics with grafted carboxylic groups, conventionally crosslinked fabrics containing no grafted carboxylic groups and an untreated cotton, the fabrics with the carboxylic groups show the strongest affinity for optical brighteners. This affinity is not only better than that of the conventionally crosslinked fabrics but surprisingly in some instances, it is better than that of the untreated cotton fabrics. Moreover, because this absorption of brightener is due to the fact that the carboxyl groups are grafted onto the fabric, this brightness is a durable and enduring characteristic of the fabric. Thus, the whitening action of the brightener can be utilized or repeated after the fabric has been laundered 5, 10, or 20 times.

Currently, industry endeavors to solve the whiteness problem of fabrics by use of the brightener in the initial

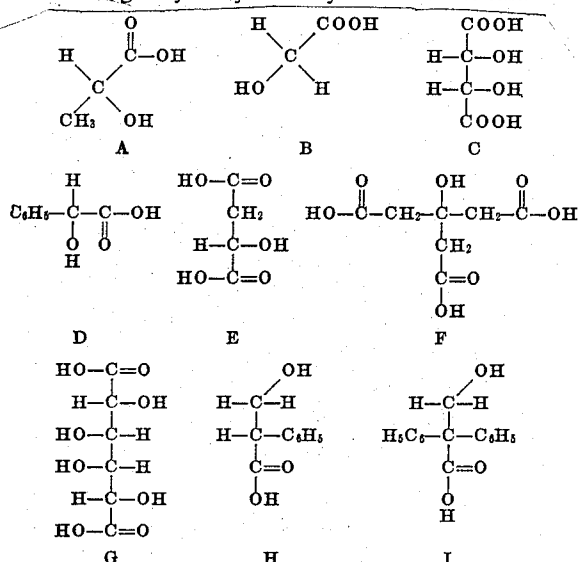
normal pad bath. While this method has its efficacy, it might be noted that it has certain deficiencies. First, the heat treatment used in curing (160°C for 3-15 minutes) frequently destroys about half of the effectiveness of many brighteners. Subsequent exposure to light, heat, laundering, detergents, and bleach also further reduce or destroy the original optical brightener applied to the fabric. Because of this, the fabric gradually acquires a grey or yellow cast or an off-white shade. The crosslinked character of the fabrics means that these fabrics have poor affinity for the brighteners normally found in laundry detergents.

The process developed in this method permits the facile application of the brighteners to fabrics either in normal padding operations such as are sometimes used with top softeners and under mild dye bath or washing conditions. It permits the housewife to do something to restore the whiteness of a durable-press fabric once greying has become a problem with a particular garment.

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 catalyst normally used in such solutions for the production of 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 then washed and brightened at any subsequent time with a bath containing the basic brightener.

#### DESCRIPTION OF AGENTS

Several hydroxy acids have 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), tropic acid (H), and benzylic acid (I). In general, this method would seem feasible with any formulation containing a hydroxy-carboxylic acid or its salt.



Because of the presence of an aromatic group in the structure, especially good results have been obtained with the mandelic acid (D).

#### CONCENTRATION OF AGENT IN PAD BATH SOLUTION

While from 0.5 to 10 percent 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 5 percent seems to be the optimum concentrations for the acid catalyst and coreactant.

To summarize, this invention can best be described as a two-phase process for whitening crosslinked fabrics subsequent to crosslinking. The first phase consists of the use of hydroxy acids as catalysts for crosslinking systems and as coreactants to lead to crosslinked fabrics containing pendant carboxyl groups. Due to the presence of these carboxyl groups, the second phase of this process can now be employed. This consists of the application of a basic brightener which is substantive to the crosslinked acid substrate. Neither cotton crosslinked in the normal manner nor untreated cotton fabrics have much substantivity for basic brighteners.

Only the standard 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. Similarly, a combination of hydroxy acids rather than a single acid can be utilized.

The following examples are provided to illustrate the invention and should not be construed as limiting the invention in any manner whatsoever.

#### 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 percent. The amounts of the acids and the properties of the resultant fabrics are listed in Table I.

TABLE I

| Acid Catalyst                                             | Cond.<br>WRA<br>(deg.) | Warp<br>Tearing<br>Strength<br>(g) | %<br>COOH |
|-----------------------------------------------------------|------------------------|------------------------------------|-----------|
| 0.5% Zn(NO <sub>3</sub> ) <sub>2</sub> ·6H <sub>2</sub> O | 285                    | 387                                | 0.25      |
| 2.0% Glycolic acid                                        | 287                    | 493                                | 0.81      |
| 3.0% Glycolic acid                                        | 281                    | 440                                | 1.06      |
| 4.0% Glycolic acid                                        | 277                    | 427                                | 1.32      |
| 5.0% Glycolic acid                                        | 269                    | 433                                | 1.46      |
| 2.0% Malic acid                                           | 287                    | 507                                | 0.60      |
| 4.0% Malic acid                                           | 294                    | 480                                | 1.29      |
| 2.0% Mandelic acid                                        | 276                    | 540                                | 0.43      |
| 4.0% Mandelic acid                                        | 275                    | 527                                | 0.61      |
| 6.0% Mandelic acid                                        | 276                    | 507                                | 0.91      |
| 2.0% Lactic acid                                          | 273                    | 533                                | —         |
| 4.0% Lactic acid                                          | 269                    | 473                                | —         |
| 10% Lactic acid                                           | 268                    | 433                                | —         |
| 0.5% Citric acid                                          | 280                    | 487                                | 0.50      |
| 1.0% Citric acid                                          | 279                    | 500                                | 0.49      |
| 2.0% Citric acid                                          | 289                    | 480                                | 0.83      |
| 4.0% Citric acid                                          | 294                    | 433                                | 1.36      |
| 6.0% Citric acid                                          | 297                    | 427                                | 1.85      |
| 1.0% Tartaric acid                                        | 274                    | 393                                | 0.55      |
| 2.0% Tartaric acid                                        | 278                    | 373                                | 0.69      |
| 4.0% Tartaric acid                                        | 273                    | 327                                | 1.22      |
| 3.0% Tropic acid                                          | 256                    | 573                                | 0.51      |

It can be seen that the effect of these treatments is to produce fabrics with high resiliency (wrinkle recovery) like a conventional durable press fabric (sample cross-linked with DMDHEU using zinc nitrate as a catalyst), and with somewhat improved tearing strength relative to the crosslinked control and fabrics with a significant amount of carboxyl groups on the fabric as illustrated in Table I. The tearing strength of most of the hydroxy acid treated were greater than the zinc nitrate catalyzed control. On the other hand, the use of an equivalent large amount of mixed catalyst would lead to substantial reduction in tearing strength relative to the zinc nitrate control.

#### EXAMPLE 2

Small samples of fabric prepared as in Example 1 were placed in a bath prepared from 0.5 part Fluorescent Brightener 56 and 99.5 parts water (pH had been adjusted to 5 with sodium hydroxide). The fabrics were treated in the bath for 20 minutes at 25°C, 15 minutes at 35°-40°C and 20 minutes at 50°C. They were then rinsed repeatedly in distilled water including one warm rinse—up to 40°C. After that, they were dried in a tumble dryer. The samples which had hydroxy acids cross-linked in the fabric were distinctly whiter under regular and UV light. In particular, the sample in which mandelic acid was used as a catalyst was superior to the others. The fluorescence of these fabrics was measured using a Farrand Spectrofluorometer. The data in Table II clearly indicate that the samples treated with hydroxy acids as the crosslinking catalysts show superior absorption of the basic optical brighteners both with respect to the crosslinked control and the untreated cotton fabric. This example provides a crosslinked fabric with grafted acid groups being whitened with a basic brightener.

TABLE II

| Crosslinking Catalyst                                | Conc. | %<br>Fluorescence <sup>11</sup> |
|------------------------------------------------------|-------|---------------------------------|
| Zn(NO <sub>3</sub> ) <sub>2</sub> ·6H <sub>2</sub> O | 0.5%  | 18                              |
| Glycolic acid                                        | 4.0%  | 36                              |
| Mandelic acid                                        | 4.0%  | 100                             |
| Lactic acid                                          | 4.0%  | 59                              |
| Citric acid                                          | 4.0%  | 46                              |
| Tartaric acid                                        | 4.0%  | 42                              |
| Untreated cotton                                     | —     | 12                              |

<sup>11</sup> Fluorescence of mandelic acid treated sample was taken as 100%. Fluorescence was measured at 455 mμ.

#### EXAMPLE 3

In this case, three series of fabrics were employed. One series was a regular cotton printcloth, the second was a mercerized cotton printcloth while the third was a 50—50 polyester-cotton. The fabrics were cross-linked and finished in the same manner as in Example 1. In one case (the control) the crosslinking catalyst was 0.5 percent zinc nitrate hexahydrate (all samples had 9 parts dimethylol dihydroxyethyleneurea). In the other cases hydroxy acid catalysts were used instead of zinc nitrate. The hydroxy acid catalysts were glycolic, mandelic, citric, malic, lactic and tartaric acid. In each case, 4 percent of these acids were used as the cross-linking catalyst and coreactant additive.

Samples of these fabrics subsequent to curing and laundering were placed in a bath prepared from 0.5 percent Fluorescent Brightener 159 (a basic brightener) and 99.5 percent water (the pH of this bath was 3). The samples were immersed in the bath for a period of 30 minutes at a temperature from 25°-30°C. The samples were rinsed repeatedly in distilled water and then laundered. In general, the samples with -COOH grafts were whiter under regular light than the pad-dry-cure control which used the zinc nitrate catalyst. Under UV light, it was apparent that all the samples with -COOH groups fluoresced strongly whereas both the crosslinked control and untreated control were grey, showing poor absorption of optical brightener. Samples of these fabrics were also treated with 0.5 percent solution of this same brightener (Fluorescent Brightener 159) in which the pH was adjusted to 4 and the bath temperature was 70°-75°C. The samples were kept in the bath for seven minutes, then rinsed repeatedly with distilled water, washed and dried.

Inspection revealed that selective uptake of this brightener was so strong by the -COOH containing fabrics that they acquired a greenish cast. (This brightener fluoresces at 465 mμ and this is the reason for the white produced by this brightener having a greenish cast to it.)

The relative fluorescence of these samples was measured (unmercerized cotton fabric series) using the Farrand Spectrofluorometer. In this case, the fluorescence of the sample with the glycolic acid graft was taken as 100 percent. On this same scale, the sample with the mandelic acid graft was 92 percent while the fluorescence of the crosslinked cotton control was only 10 percent of that of the glycolic acid treated sample. These results clearly demonstrate the effect of the presence of the -COOH grafts on the absorption of the basic brightener. Furthermore, the effect was demon-

strated on three types of fabrics, unmercerized cotton fabric, mercerized cotton fabric, and 50—50 polyester-cotton fabric

#### EXAMPLE 4

Swatches of samples of the series of treatments in Example 3 (regular cotton printcloth) were immersed in a bath (pH 7) prepared from 0.5 part Fluorescent Brightener 101 and 99.5 parts of water. The samples were immersed in the bath for a period of 20 minutes at 40°C, 20 minutes for a period while the temperature was between 40–50°C and 20 minutes while the water was cooling. The samples were rinsed 7 times in distilled water, warmed in distilled water at 40°C for 5 minutes and rinsed again. They were then tumble dried. The fluorescence of these samples was then measured using a Farrand Spectrofluorometer. While the fluorescence of the crosslinked sample with zinc nitrate as the catalyst was 33 percent of the untreated control, the values for the various samples with the hydroxy acid catalysts were glycolic acid 63 percent, mandelic acid 88 percent, malic acid 65 percent, lactic acid 78 percent, citric acid 50 percent, tartaric acid 65 percent. The effect of the phenyl substituent in conjunction with the carboxyl can be found in the increase in fluorescence with the mandelic acid sample.

#### EXAMPLE 5

Swatches of fabrics from the various treatments in Example 3 on regular cotton fabric were laundered seven times. They were then placed in a bath prepared from 0.5 percent Phorwite DBS (a cationic pyrazoline brightener) and 99.5 percent of solvent prepared from equal parts of water and ethanol. The samples were immersed in this bath for a period of 30 minutes at 45°C, then rinsed eight times in distilled water and tumble dried. The fluorescence of the various samples was then measured using the untreated cotton fluorescence as 100 percent. Under these conditions, the crosslinked control with the metal salt catalyst was 23 percent, while the values for the various hydroxy acid samples were glycolic acid 63 percent, mandelic acid 100 percent, malic acid 56 percent, lactic acid 90 percent, citric acid 60 percent, and tartaric acid 46 percent. The effect of the presence of the carboxy groups can be readily seen. The member of the series which seems to be most effective is again the mandelic acid in which the combination of phenyl and -COOH groups is present. The durable character of these treatments in enhancing optical brightener absorption was demonstrated by the fact that these samples were laundered seven times before being treated with the bath containing the optical brightener.

In another case, the samples from Example 3 were treated in the same manner as described in the forepart of this example (Example 5). In this case, however, one wash samples and mercerized fabrics were utilized. Furthermore, the samples were laundered with warm water with wetting agent, and were then tumble dried. When measured on the spectrofluorometer, the crosslinked control with zinc nitrate catalyst had 9 percent fluorescence value while the mandelic acid sample was 100 percent and the lactic acid catalyzed sample was 94 percent. These results again show the effect of the pendant -COOH groups for enhancement of the absorption and retention of basic brighteners.

#### EXAMPLE 6

In this case, swatches of samples from Example 3 including untreated cotton, crosslinked cotton with metal salt catalyst, and crosslinked cottons with hydroxy acid catalyst on a mercerized printcloth fabric were immersed in an aqueous bath containing 0.2 percent Fluorescent Brightener 159, 0.2 percent Fluorescent Brightener 101, and 0.2 percent of a cationic pyrazoline type brightener. The samples were treated at room temperature for 30 minutes and then 0.3 percent sodium sulfate was added and the samples treated an additional 20 minutes. After the samples were rinsed repeatedly in distilled water, they were laundered. The fluorescence values of the samples were measured at 450 and 465 mμ. The values measured were such that the fluorescent values for the various acid catalyzed samples (glycolic, mandelic, malic, lactic, citric, and tartaric acid) were 2.0 to 2.5 times that of the values of both the untreated cotton and the crosslinked cotton with the metal salt catalyst at each of the peaks measured. This experiment clearly indicates that a combination of basic brighteners will be selectively absorbed by these fabrics with the pendant acid groups.

We claim:

1. A process for imparting to a cellulosic textile durable-press performance and the quality of improved response to and acceptance of basic optical brighteners, the process comprising:

- a. impregnating the cellulosic textile with a formulation containing about from 1 to 15 percent of dimethylol dihydroxyethyleneurea as an agent for crosslinking cellulose, and about from 0.5 to 10 percent 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 for catalyzing the crosslinking reaction between the textile cellulose and the dimethylol dihydroxyethyleneurea;
  - b. drying the wet, impregnated textile for about from 2 minutes to 24 hours, at a temperature of about from 25° C. to 90° C.;
  - c. curing the dry, impregnated cellulosic textile at a temperature of about 100° C. to 170° C., for about from 30 seconds to 20 minutes, using the longer periods of time with the lower temperatures, to effect the crosslinking reaction between the textile cellulose and the dimethyl dihydroxyethyleneurea and produce a crosslinked textile containing acidic pendant groups which attract and accept basic optical brighteners; and then
  - d. whitening the resulting crosslinked textile with a basic optical brightener.
2. The process of claim 1 wherein the alpha-hydroxy acid is citric acid.
  3. The process of claim 1 wherein the alpha-hydroxy acid is glycolic acid.
  4. The process of claim 1 wherein the alpha-hydroxy acid is lactic acid.
  5. The process of claim 1 wherein the alpha-hydroxy acid is malic acid.
  6. The process of claim 1 wherein the alpha-hydroxy acid is mandelic acid.
  7. The process of claim 1 wherein the alpha-hydroxy acid is mucic acid.

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

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

10. The process of claim 1 wherein the basic optical brightener is Fluorescent Brightener 56.

11. The process of claim 1 wherein the basic optical

brightener is Fluorescent Brightener 101.

12. The process of claim 1 wherein the basic optical brightener is Fluorescent Brightener 159.

13. The process of claim 1 wherein the basic optical brightener is a cationic pyrazoline brightener.

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