HIGH STRENGTH WRINKLE RESISTANT COTTON FABRICS PRODUCED BY A PROCESS INVOLVING BOTH MONOSUBSTITUTION AND CROSSLINKING OF THE COTTON

Inventor: Domenick Donald Gagliardi, East Greenwich, R.I.
Assignee: Cotton, Incorporated, Memphis, Tenn.
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Primary Examiner—George F. Lesmes
Assistant Examiner—J. Cannon
Attorney—Kemon, Palmer and Estabrook

ABSTRACT

Improvement in the wear resistance of cotton fabrics in so-called wash-wear or durable press garments is attained using a concept of treatment referred to as SSX involving swelling conducted to increase sites for chemical reactions, substitution to introduce bulky, plasticizing side groups and crosslinking the distended polymer network in cotton fibers to achieve more uniformly placed crosslinks than in prior known wrinkle resistance treatments.

10 Claims, No Drawings
HIGH STRENGTH WRINKLE RESISTANT COTTON FABRICS PRODUCED BY A PROCESS INVOLVING BOTH MONOSUBSTITUTION AND CROSSLINING OF THE COTTON

BACKGROUND OF THE INVENTION

For many years it has been generally recognized that crosslinking of cellulosic fibers causes reduction in tensele strength, tear strength and abrasion resistance of the treated fabrics. In the first generation of wrinkle resistant cotton fabrics, only minor modification of the fibers was effected to yield wrinkle recovery values \( W + F \) of about 200° – 230° in the fabric. In the second generation of wash- and wear-fabrics, the modification or crosslinking was increased to produce wrinkle recovery angles of about 240° – 260°. Now some concern was felt about the reduced tensile strength, tear strength and abrasion resistance of the fabrics. To alleviate the problem, fabrics with stronger and heavier yarns were constructed, mercerization was increased, and softeners or thermoplastic resins were added to the treating bath. In the third and present generation of durable press fabrics, which demand 270° – 300° wrinkle recovery rating and high smoothness and crease retention ratings, the crosslinking agent concentration has had to be greatly increased. This increase now presents a very serious problem in the wear life of cotton durable press garments and has been of great concern both to the cotton industry and to the man-made fibers industry which needs cotton to produce many suitable fabric blends.

Many investigators have been at work to try to find a practical solution to producing high strength cotton in durable press fabrics. Some of the developments which have had varying degrees of success and are beginning to be commercially exploited include: Differential Crosslinking of Cotton Fabrics (1) (2); Vapor Phase Permanent Press (3) (4); Vapor Phase Grafting and Permanent Press (5) (6); crosslinking cotton in the presence of a non-reactive, non-volatile celluloid (7) (8); use of high loadings of thermoplastic polymers (9); two stage crosslinking (10); wet fixing (11); polymer loading and crosslinking (12) and fabrics from crosslinked and uncrosslinked fibers (13). In some of these prior operations, fiber reactive compositions having inherent fiber swelling properties have been used in crease-proofing treatments, but these have not been utilized to produce higher strength fabrics because they have always been used in non-swelling concentration ranges.

In spite of the extensive investigation and other work mentioned above, there is still a need for other methods and techniques to achieve more profound improvements in all properties of durable press cottons under simplified plant treating conditions.

OBJECTS

A principal object of this invention is the provision of a new concept for attaining improvements in the wear resistance of cellulosic fabrics treated to impart wrinkle resistance characteristics, so-called wash-wear or durable press treatments. Further objects include the provision of:

1. Substantial improvements in all properties of crease-proof treated cotton fabrics;

2. Such improvements which may be attained under simplified treating conditions;

3. Information concerning the SSX concept for creating high strength cotton through swelling, substitution and crosslinking;

4. Major improvements in the tensile strength, elongation, tear strength, toughness, flexing resistance, and surface abrasion resistance of wrinkle resistant cotton fabrics;

5. Information on the swelling effect of various organic structures and on the synthesis of cellulose reactive, non-functional and polyfunctional swelling analogs.

Other objects and further scope of applicability of the present invention will become apparent from the detailed description given hereinafter; it should be understood, however, that the detailed description and specific examples, while indicating preferred embodiments of the invention, are given by way of illustration only, since various changes and modifications within the spirit and scope of the invention will become apparent to those skilled in the art from this detailed description.

SUMMARY OF THE INVENTION

The wear resistance of a cotton fabric is a complex phenomenon which depends on fabric weight, fabric geometry, yarn structure and size, and fiber properties. Secondarily it depends on the absence or presence of lubricating or sizing finishing agents. It is known that cotton is made up of long-chain cellulose molecules and that these are held together by strong hydrogen bonds in certain crystalline regions. There are other regions, however, having less or no crystallinity. These contribute to fiber elongation and flexibility. The combination of long-chain length, hydrogen bonding and flexibility contribute to the normal high toughness of cotton. When chain slippage occurs, as in forming a wrinkle, this structure, however, is not capable of recovering to its initial state and permanent deformation occurs. It has now been established as a result of the present invention that in the normal process of treating cotton with crosslinking agents, only about 10–15 percent of the cellulose structure is accessible to the reagent. This limited accessibility results in crosslinkages being concentrated in the flexible, accessible regions. While this concentration of crosslinkages is desirable for preventing chain slippage and producing wrinkle resistance, it is, on the other hand, undesirable for maintaining toughness. Now the original flexible joint has become rigid, brittle and subject to localized stress accumulation. Under stress, this brittle joint can no longer distribute the applied load among all the structural elements and lower tensile, elongation and toughness results so there is a reduction of both mechanical and tensile strength and toughness. The magnitude of these changes is highest for linen medium for cotton and least for rayon. The overall results of this lowering of fiber elongation and tensile strength are reflected in a lowering of the area under a stress-strain curve drawn for any cellulosic fiber. This area relates directly to the work \( W \) required to rupture a fiber and can be approximated by the empirical equation for toughness \( L \times E \times C \). Resistance of a fabric to abrasion \( A \) is related to the work \( W \) to rupture fibers and to the toughness value \( 15 \).

It has now been found that mitigation of the loss of abrasion resistance in crosslinked cellulosic fibers can be attained by not reducing the fiber toughness though eliminating the formation of localized, brittle joints formed in prior known crosslinking treatments.

Broadly stated, the new methods of treating cellulosic fabrics involves: a) swelling the cotton fibers, b) introducing bulky, plasticizing side groups and c) crosslinking the stretched polymer structure. By eliminating or minimizing the sharp distinction between crystalline and amorphous, or more accessible, regions there results a more even distribution of crosslinkages through the polymer network. Secondly, the presence of bulky side groups provides for an internal plasticizing effect and further minimizes localized stress accumulation in the fibers.

Advantageously, attainment of high strength, creaseproofed cellulosic fabrics according to the present invention comprises:

a. swelling the fibers of the fabric in a medium capable of swelling cellulose to a greater extent than water;

b. conducting a multifunctional substitution of cellulose molecules in the fibers when so swollen and,

c. crosslinking the substituted and swollen fibers.

Success of this invention is, in part, due to the discovery that cotton fabric properties are greatly dependent on the highly crystalline hydrogen bonded regions and on the flexible, so-called amorphous regions and that the rigid, brittle, joint introduced by wrinkle proofing agents may be plasticized by the
dissolution of hydrogen bonds in the crystalline regions by the presence of a highly polar compound, e.g., urea. This leads to a more flexible structure and to restoration of tensile strength. This SSX invention concept further involves the discovery that if one eliminates or minimizes the wide differences between crystalline and amorphous regions in resin treating or crosslinking of cotton to obtain improved wrinkle resistance, then critical improvements in ultimate strength properties of the treated fabric may be obtained.

EXAMPLES

The SSX technique as referred to herein may be accomplished in a number of sequential reactions which involve separate steps of swelling, substitution and crosslinking. Advantageously, from a commercial viewpoint, the SSX method may be accomplished in a version of lesser number of steps by the use of certain classes of reagents. Preferably, one uses pairs of highly polar, cellulose swelling, monofunctional and polyfunctional cellulose reactive organic compounds and performs a precure or delayed cure durable press process in a single step.

The following details of operations in accordance with the invention and reported data illustrate the further principles and practice of the invention to those skilled in the art. In these examples and throughout the remainder of this specification and claims, all parts and percentages are by weight unless otherwise specified.

EXAMPLE 1

This example concerns pairs of monofunctional and polyfunctional reactive swelling agents for cotton.

In one case of evaluation of pairs of reagents, swelling measurements were made on different relative mixtures of monomethylol and dimethylol formamides and acetamides. All mixtures gave swelling indices greater than 2.0. The acetamide series, however, all caused greater cotton swelling than the formamide pairs.

As a separate operation, pairs of N-methylol polyol compounds were prepared in aqueous solutions under alkaline conditions and, then, when reaction was completed, the solutions were neutralized with hydrochloric acid to pH 7.0-7.5. These solutions were then used to treat 7 oz. kier boiled and bleached cotton twill fabric. The fabrics were padded with the solutions of reactant pairs at 70-80 percent wet pickup, frame dried 5 minutes at 250°F, cured 10 minutes at 320°F, scoured, refarmed and dried in air at 70°F.

In yet another operation, cuff wear tests were made with the twill fabric which was padded and dried 5 minutes at 220°F. Then it was made into trouser cuffs, hot-head pressed and then finally cured 10 minutes at 320°F. Wear tests were made in an automatic washing machine using a built synthetic detergent.

One pair of reagents for cotton containing 10 percent of monomethylol acetamide (MMA) and 30 percent of polyfunctional reagents at 10 percent concentration:

dimethylol ethylene urea (DMEU)
dimethylol dihydroxy ethylene urea (DMDHEU)
polyacrylamide methoxyethyl carbamate (PMMC)
methylated urea-formaldehyde resin (MUF)

Also, fabric was treated with aqueous solutions containing 10 percent of these polyfunctional reagents without the MMA. The crease resistance properties of the treated fabrics (MCRA, W+F) are reported in the following table.

<table>
<thead>
<tr>
<th>Reagent</th>
<th>Percent MMA Added</th>
<th>0</th>
<th>5</th>
<th>10</th>
<th>20</th>
<th>30</th>
</tr>
</thead>
<tbody>
<tr>
<td>DMEU</td>
<td>298</td>
<td>295</td>
<td>297</td>
<td>300</td>
<td>296</td>
<td></td>
</tr>
<tr>
<td>DMDHEU</td>
<td>396</td>
<td>396</td>
<td>396</td>
<td>396</td>
<td>396</td>
<td></td>
</tr>
</tbody>
</table>

In the case of DMEU, no change in wrinkle recovery occurred by adding increasing amounts of MMA. In contrast, with PMMC a fast drop in wrinkle recovery was found. In the case of DMDHEU, there was no change at lower percentages of MMA and at higher amounts of MMA a slow drop in wrinkle recovery occurred. With MUF, the addition of MMA brought a measurable increase in wrinkle resistance performance.

EXAMPLE 2

This example concerns fabric treatments with DMEU-MMA combinations.

The general procedures of Example 1 were repeated using a series of solutions containing 10 percent of MMA and varying proportions of N-methylol acetamide. The results of the tests on the resulting fabrics are reported in the following table:

<table>
<thead>
<tr>
<th>Reagent</th>
<th>Percent MMA Added</th>
<th>0</th>
<th>5</th>
<th>10</th>
<th>20</th>
<th>30</th>
</tr>
</thead>
<tbody>
<tr>
<td>DMEU</td>
<td>298</td>
<td>295</td>
<td>297</td>
<td>300</td>
<td>296</td>
<td></td>
</tr>
<tr>
<td>DMDHEU</td>
<td>396</td>
<td>396</td>
<td>396</td>
<td>396</td>
<td>396</td>
<td></td>
</tr>
</tbody>
</table>

In the case of DMEU, no change in wrinkle recovery occurred by adding increasing amounts of MMA. In contrast, with PMMC a fast drop in wrinkle recovery was found. In the case of DMDHEU, there was no change at lower percentages of MMA and at higher amounts of MMA a slow drop in wrinkle recovery occurred. With MUF, the addition of MMA brought a measurable increase in wrinkle resistance performance.

EXAMPLE 3

A series of fabric treatments was performed repeating the general procedures of Example 1 with solutions containing 10 percent DMDHEU and varying concentrations of MMA. The results of the standard tests for wrinkle resistance, strength, etc., performed on the resulting fabrics are reported in the following table:

<table>
<thead>
<tr>
<th>Reagent</th>
<th>Percent MMA Added</th>
<th>0</th>
<th>5</th>
<th>10</th>
<th>20</th>
<th>30</th>
</tr>
</thead>
<tbody>
<tr>
<td>DMEU</td>
<td>298</td>
<td>295</td>
<td>297</td>
<td>300</td>
<td>296</td>
<td></td>
</tr>
<tr>
<td>DMDHEU</td>
<td>396</td>
<td>396</td>
<td>396</td>
<td>396</td>
<td>396</td>
<td></td>
</tr>
</tbody>
</table>

The data of the table show that wrinkle resistance is not substantially changed by the addition of the MMA. However, the tensile strength is materially increased as are Stoll Flex abrasion and practical wear resistance. With no MMA, the first hole formed in four washes and after five washes there were also four total failures in the trouser cuffs. As the amount of MMA in the solutions increased, the number of washes to form a hole greatly increased. Also the total number of failures after five washes decreased (Failure equals one thread broken or one hole).

The table demonstrates the value of the concept of using a combination of monofunctional and difunctional cellulose reactive swelling agent in durable press cellulose fiber fabric treatments to obtain better overall strength.

EXAMPLE 4

Practical delayed cure cuff wear tests were performed using the general procedures of Example 1 to treat fabric with two separate solutions, one containing 10 percent DMEU without MMA and the other containing 10 percent DMEU and 10 percent MMA (plus in both cases the standard 1 percent zinc.
nitrates). The test results are reported in the following table:

<p>| TABLE XIII |</p>
<table>
<thead>
<tr>
<th>Percent DMEU in bath</th>
<th>Percent N-methyl acrylamide</th>
<th>Cuff No.</th>
<th>No. of washes for 1st hole</th>
<th>Total No. of failures 100 washes</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>None A</td>
<td>3, 3</td>
<td>8, 10</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>None B</td>
<td>4, 4</td>
<td>9, 9</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>None C</td>
<td>5, 5</td>
<td>9, 9</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>None D</td>
<td>6, 6</td>
<td>9, 9</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>10 F</td>
<td>7, 7</td>
<td>3, 3</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>10 G</td>
<td>8, 8</td>
<td>2, 2</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>10 H</td>
<td>9, 9</td>
<td>2, 2</td>
<td></td>
</tr>
</tbody>
</table>

1 Percent MMA.

The reported data show the mixed pair of reagents produced about three times the wear life of the control durable press treatment.

EXAMPLE 5

The procedure of Example 4 was repeated using DMDHHEU in place of DMEU. The results are reported in the following table:

<p>| TABLE XIV |</p>
<table>
<thead>
<tr>
<th>Percent DMDHHEU in bath</th>
<th>Percent N-methyl acrylamide</th>
<th>Cuff No.</th>
<th>No. of washes for 1st hole</th>
<th>Total No. of failures 100 washes</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>None A</td>
<td>4, 4</td>
<td>13, 13</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>None B</td>
<td>5, 5</td>
<td>13, 13</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>None C</td>
<td>6, 6</td>
<td>13, 13</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>None D</td>
<td>7, 7</td>
<td>13, 13</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>10 F</td>
<td>8, 8</td>
<td>5, 5</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>10 G</td>
<td>9, 9</td>
<td>5, 5</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>10 H</td>
<td>10, 10</td>
<td>5, 5</td>
<td></td>
</tr>
</tbody>
</table>

1 Percent MMA.

The reported data show dramatic increase in wear performance of durable press treatments using dimethyl dihydroxyethylene urea with N-methyl acrylamide as compared to the DMDHHEU alone.

EXAMPLE 6

This example concerns the use of N-methyl pyrolidone (NMP), i.e.,

\[
\text{CH}_2 = \text{C} = \text{O} \quad \text{N} - \text{CH}_2 \text{OH} \\
\text{CH}_2 = \text{C} = \text{O} \quad \text{N} - \text{CH}_2 \text{OH}
\]

and N-methyl acrylamide (MMA), i.e.,

\[
\text{CH}_2 = \text{C} = \text{O} \quad \text{N} - \text{C} - \text{H}_2 \text{O} \text{H} \\
\text{CH}_2 = \text{C} = \text{O} \quad \text{N} - \text{C} - \text{H}_2 \text{O} \text{H}
\]
as the monofunctional cellulose reactive swelling agents in combination with difunctional cellulose reactive creaseproofing agents.

The NMP and MMA were used in 10 percent concentration with DMEU as a representative member of the known class of polyfunctional organic cellulose reactive creaseproofing agents. Results of tests on fabrics treated with these solutions for comparison with DP control solution containing 10 percent DMEU without the monofunctional reagent NMP or MMA are reported in the following table:

<p>| TABLE XV |</p>
<table>
<thead>
<tr>
<th>Finishing bath</th>
<th>Percent N-methyl compound</th>
<th>MCRA</th>
<th>Toughness</th>
<th>Tear</th>
<th>Stoll flex</th>
<th>Wear test</th>
</tr>
</thead>
<tbody>
<tr>
<td>Untreated</td>
<td>Untreated</td>
<td>149</td>
<td>793</td>
<td>1,826</td>
<td>615</td>
<td>1,435</td>
</tr>
<tr>
<td>DP control</td>
<td>None</td>
<td>281</td>
<td>1,166</td>
<td>166</td>
<td>592</td>
<td>1,081</td>
</tr>
<tr>
<td>10% DMEU</td>
<td>10% MMA</td>
<td>281</td>
<td>1,166</td>
<td>166</td>
<td>592</td>
<td>1,081</td>
</tr>
<tr>
<td>10% DMEU</td>
<td>10% MMA</td>
<td>335</td>
<td>1,585</td>
<td>110</td>
<td>710</td>
<td>8,316</td>
</tr>
</tbody>
</table>

1 MMA.

The usefulness of dimethyl succinimide as a creaseproofing agent is limited because of limited water solubility of the compound and the lack of chlorine resistance in the treated fabric.

TEST VALUES

The physical tests employed to evaluate the effects produced in the treated fabrics in the above examples are as follows:

| Note: Wet MCRA values are obtained by soaking the test specimen in distilled water with 0.1 percent wetting agent at room temperature for 1 hour, blotting with blotting paper and testing as above. |
| Flex Abrasion Resistance - Cycles to Failure C.S.I. Stoll Flex Tester, 1 lb. tension/1.2 lb. load. ASTM Method D1175-55T. |
| Surface abrasion - Wyzenbeek surface abrasion test of the American Association of Textile Chemists and Colorists expressed in cycles to failure. |
| Appearance - Procedure for wash-wear items after home laundering, AATCC 88A-1964T. |
| Wrinkle Recovery - Wrinkle recovery test method AATCC66-1959T. |

DISCUSSION OF DETAILS

Treating compositions used in carrying out the SSX crease resistant improving procedures of this invention are aqueous.
solutions containing two essential ingredients, namely, (a) water-soluble, heat-curable, polyfunctional nitrogen-containing organic material known to possess crease-proofing properties when used in the treatment of cellulosic fabrics, and (b) a monofunctional organic compound having the ability to react with cellulose to form a substitution product. The invention is preferably conducted using water-soluble amine-aldehyde reaction products known to be useful in the crease-proofing of cotton or other cellulosic fabrics. However, the invention is contemplated for use with any other form of nitrogen-containing, water-soluble organic materials now known to be useful for crease-proofing of cellulosic fabrics or found in the future to be useful for this purpose, e.g., water-soluble alkylated amine-aldehyde reaction products, aziridinyl phosphine oxides or comparable materials.

Specific examples of nitrogen-containing, water-soluble, heat-curable organic cellulose fabric crease-proofing materials which may advantageously be used in accordance with the invention include:

From the class of amino-aldehyde reaction products, the monomers and water-soluble polymers of:

- dimethylol urea
- trimethylol melamines
- dimethylol ethylene urea
- polyacrylamide melamine
- polyacrylamide alkyl carbamates
- polyalkylated monoureins (see U.S. Pat. No. 3,209,010)
- N,N-dimethyl or dialkoxymethyl monoheterocyclic ureas represented by the following generic structure:

\[
\begin{align*}
R - O \cdot CH-N \cdot N \cdot CH-O \cdot R
\end{align*}
\]

where \( R \) is: 
- \( \mathrm{CO}_2 \mathrm{H}, \mathrm{CN}, \mathrm{CH}_3 \mathrm{CN}, \) or \( \mathrm{SO}_2 \mathrm{H} \)
- \( \mathrm{NH}_2 \) or a lower alkyl
- \( Y \) is: a di- or tri-valent alkylene or substituted alkylene radical, as for example:

\[
\begin{align*}
- \mathrm{CH}_2\mathrm{CH}=& - & - \mathrm{CH} \cdot \mathrm{CH} = \mathrm{CH}_2 = - & - \mathrm{CH} \cdot \mathrm{CH} = - \\
& & - & - \mathrm{CR} \cdot \mathrm{CR} & - \\
& & & & - \mathrm{OH} \cdot \mathrm{OR} \cdot \mathrm{OR} \\
& & & & - \mathrm{OH} \cdot \mathrm{OR} \cdot \mathrm{OR} \\
& & & & - \mathrm{OR} \cdot \mathrm{OR} \cdot \mathrm{OR} \\
& & & & - \mathrm{OR} \cdot \mathrm{OR} \cdot \mathrm{OR} \\
& & & & - \mathrm{OR} \cdot \mathrm{OR} \cdot \mathrm{OR} \\
& & & & - \mathrm{OR} \cdot \mathrm{OR} \cdot \mathrm{OR} \\
\end{align*}
\]

From the class of alkylated amino-aldehyde reaction products, the monomers and water-soluble polymers of:

- dimethoxyethyl urea
- trimethoxyethyl melamine
- from the class of aziridinyl phosphine oxides:
  - tris aziridinyl phosphine oxide
  - tris methyl aziridinyl phosphine oxide

In the preferred methods of the invention, the monofunctional reagent is one which has the capability of swelling cellulose to a greater degree than water and advantageously has a swelling index as hereinbefore defined of at least 1.5, especially 1.8 to 2.5. However, the SSX concept also involves the use of a suitable monofunctional, cellulose reactive reagent in combination with a non-reactive cellulosidator to produce the desired swelling of the cellulose. Such swelling with the separate non-reactive cellulosidator may precede the application of the reagents (a) and (b) mentioned above and continue through their application or the swelling may be accomplished simultaneously with the application of the reagents (a) or (b) or (a) with (b).

Various cellulose non-reactive organic and inorganic cellulosidators are known and have been used in various prior processes to dilate cellulose molecules in chemical reactions. This reagent must dilate the cellulosic fibers and keep them dilated during the curing of the creaseproofing agent, even after water has evaporated. It has been found that from this known class of materials, aprotic organic compounds are unique in the new methods of this invention. Dimethyl sulfoxide is the preferred aprotic organic cellulosidator, but other usable organic cellulosidators include dimethyl formamide, dimethyl acetamide, N-methylpyrrolidone, 2-pyrrolidone, tetramethyl urea, vinyl pyrrolidone, sodium xylene sulfonate, butyrolactone and dimethyl sulfone.

Lithium thiocyanate is an example of an inorganic cellulosidator. Other inorganic salts higher in the lyotropic series than lithium thiocyanate are also contemplated for use, i.e., water-soluble inorganic salts having greater water of hydration than lithium thiocyanate, e.g., LiBr, CaBr\(_2\), MgCl\(_2\), CaCl\(_2\), zirconium chlorohydrate and aluminum chlorohydrate.

Mixtures of aprotic organic cellulosidators with inorganic cellulosidators may advantageously be used. Such mixtures may comprise ratios of organic to inorganic between 100:1 and 1:100 and preferably between 5:1 and 1:5, especially 4:1 and 1:2.

The treating compositions used to impart wet and dry crease resistance to cellulosic fabrics in accordance with the invention are aqueous solutions containing dissolved therein the nitrogen-containing organic anti-crease agent, the monofunctional organic reagent, a separate cellulosidator if this is used and, preferably, in addition, an acidic aminoplast forming catalyst. Generally, the solutions will contain 1 to 20 percent reactive compound, 0 to 20 percent non-reactive cellulosidator and 1 to 5 percent of the acidic catalyst.

Specific examples of acidic catalysts which may be used in accelerating the curing of nitrogen-containing compounds and reaction thereof with cellulose in the fabrics include zine nitrate, zinc chloride, zinc fluoroborate and comparable acid reaction metal salts. In addition, acid reacting salts of ammonia or amines may be used, e.g., ammonium silicotungstate, diammonium phosphate, ammonium bisulfate, ethanolamine hydrochloride and the like. Suitable catalysts also include free acids, e.g., hydrochloric, phthalic, tartaric, citric and similar acids.

No special form of equipment is required in carrying out the procedures of the invention. This constitutes an important advantage of the new procedures for it makes possible the easy addition of the operation to established textile finishing and handling plants. Likewise, generally available, commercially used drying, shaping and textile handling equipment may be employed in carrying out the drying, heating and dimension controlling steps of the new operations. Furthermore, the new procedures may be applied in conjunction with other textile processing operations generally considered useful by the textile industry. Such procedures include waterproofing, mildep proofing, calendering, embossing, dyeing, printing and the like. Other known finishing agents not incompatible or detrimental to these new treatments may be applied in conjunction with the creaseproofing agents of this invention, e.g., lubricants, sizing materials, mothproofing agents, waterproofing agents, brighteners, dyes, pigments and the like. Some or all of these types of materials may be included in the actual treating compositions of this invention in amounts advantageously about 1 to 10 percent.

The impregnation of the aqueous treating compositions is probably most easily accomplished by standard padding procedures may be employed, e.g., spraying, brush application, roller coating, transfer from saturated webs or the like. Whatever procedure is employed, the fabric should be impregnated with sufficient of the aqueous composition so that when the fabric is completely dried, there will remain in the fabric as the non-volatile residue, between about 1 and 20 percent of the nitrogen-containing, creaseproofing agent, and advantageously, 3 to 10 percent by weight of the creaseproofing agent. With the preferred aqueous compositions, this can readily be accomplished by adjusting the impregnation to give a pickup of 50 to 100 percent by weight based upon the dried weight of the fabric or other fiber substrate to which the solution is applied.

Solution composition and fabric pickup is preferably controlled to place in the fabric before the curing step a polyfunctional nitrogen-containing, creaseproofing agent to
monofunctional cellulose reactive agent weight ratio of between about 10:1 and 3:20, and a weight ratio of the creaseproofing agent to curing catalyst of between about 100:1 and 1.5.

The aqueous solution impregnated fabrics or other fibrous webs are dried, preparatory to the heat curing step. This can be accomplished by air drying at room temperature using forced air circulation or, preferably, by heating such as with radiant or convection heat in ovens, tunnels or the like to an elevated temperature between about 50° and 100°C. and especially by 100° to 150°C. for between about 1 to 60 minutes. The drying step need not be conducted any longer than necessary to effect substantial complete drying and generally shorter times will be required for higher temperatures.

After the substrate is dried, it is subjected to an elevated heating step in order to effect a curing which appears to involve a condensation of the solid residue materials in the fabric with themselves and with the cellulose. The heat curing is advantageously conducted at a temperature above 100°C. and below the decomposition temperature of the fabrics, preferably between 100° and 200°C. and usually for between about 1 to 60 minutes, longer times generally being employed at the lower temperatures and vice versa. Drying and curing can take place at the same temperature if this is above about 100°C. and in the same oven or dryer if desired.

Following the heat curing step, it is advantageous to wash or scour the fabric in order to remove unreacted material. During this stage of the operation, it may be found desirable to treat the fabric with softening agents, sizing agents, lubricants or the like. Following this cleansing, the fabric is dried, preferably using some type of dimension control such as tensers or other dimension control frames or equipment to ensure even drying and squaring of the fabric.

The new creaseproofing operations are particularly useful for the finishing of cotton fabric which will be used for wearing apparel, such as men's shirts, women's dresses, children's clothing or the like, yard goods, sheeting and similar household fabrics. However, the operations are also useful with any other form of fabric including non-woven as well as woven webs, knitted goods and the like composed of fibers of cellulose origin, e.g., cotton, viscose rayon, acetate rayon, linen and the like. Cloth or other fibrous webs composed partially or wholly of fibers of cellulose origin and partially of other natural or synthetic fibers may also be treated, e.g., webs, containing in part, wool, silk, nylon, acrylic fibers, modacrylic fibers, polyester fibers and the like.

The SSX technique may be done in various ways, for example:

a. pad, dry, cure immediately;
b. pad, air dry 24 hours, then cure;
c. soak 1 hour, pad, dry, cure.

The cotton or other cellulose fabric may be sequentially modified by swelling, introducing side groups through alkyla-
tion, esterification or grafting, and finally crosslinking. Such reactions might be done in solvents, in a vapor phase or under aqueous conditions.

As an alternative, one may utilize pairs of monofunctional and polyfunctional cellulose reactive agents which also swell cotton to a much greater degree than water, e.g., to a swelling index of at least 1.8.

Additional swelling agents generally usable in the SSX operations include:

Concentrated zinc chloride solutions
Sodium zinicate
Concentrated sulfuric acid
Pyridine
Anhydro ethyl amine
Alkaline earth hydroxides
Quaternary ammonium bases
Cellulose solvents
Formic and acetic acid
Cellulose enymes

CONCLUSION

New improvements in methods of treating cotton and other cellulose fabrics to create strong wrinkle-resistant fabrics have been described. Such operations involve introducing bulky side groups and crosslinking the cellulose in a swollen state to eliminate the normally rigid and brittle joints of known crosslinking methods. Such a system produces a crosslinked fiber with greater flexibility and toughness. A series of sequential treatments are reported which have yielded stronger wrinkle-resistant cotton than is given by conventional treating methods.

The embodiments of the invention in which an exclusive property or right is claimed are defined as follows:

1. A process for the creation of wrinkle resistance characteristics in cellulose fabrics while preserving high strength and wear properties which comprises:

a. swelling a cellulose fabric by impregnating it in a solution consisting essentially of N-methylol acetamide, a polyfunctional cellulose creaseproofing agent, a catalyst and water;
b. drying; and
c. heat curing the fabric to effect simultaneously both a sub-
stitution of the cellulose by reaction with the N-methylol acetamide and a crosslinking of the cellulose with the creaseproofing agent so as to substantially increase the wrinkle recovery of the fabric.

2. A process according to claim 1 wherein the solution in step (a) contains from 5 to 30 percent N-methylol acetamide by weight.

3. A process according to claim 2 wherein the creaseproofing agent is a polymethylol cyclic urea and is present in the solution in step (a) in a concentration giving a weight ratio of creaseproofing agent to N-methylol acetamide of between about 10:1 and 3:20.

4. A process according to claim 3 wherein the creaseproofing agent is dimethylol dihydroxy ethylene urea.

5. A process for the creation of wrinkle resistance character-
cistics in cellulose fabrics while preserving high strength and wear properties which comprises:

a. swelling a cellulose fabric by impregnating it in an aque-
ous solution consisting essentially of 5 to 30 percent N-
methylol acetamide, 0 to 20 percent non-reactive cellu-
loidilator capable of swelling cellulose to a greater degree
than water, and water;
b. reacting the cellulose with the N-methylol acetamide so
as to introduce plasticizing side groups into the cellulose
while the fabric is swollen;
c. drying the fabric; d. impregnating the fabric with an aque-
ous solution containing a creaseproofing agent and a
catalyst; and
e. drying; and

f. heat curing the fabric.

6. A process according to claim 5 wherein the fabric is a
cotton-containing fabric and wherein the creaseproofing
agent is a polymethylol urea.

7. A process according to claim 5 wherein the fabric is a
cotton-containing fabric and the creaseproofing agent is
dimethylol dihydroxy ethylene urea.

8. A durable press treated cellulose fabric containing cellu-
lose substituted by reaction with N-methylol acetamide,
pre pared by the process of claim 3 and having a wrinkle
recovery angle greater than 260° and a tear strength retention
of at least 60 percent.

9. A durable press treated fabric according to claim 4
wherein the fabric contains cotton.

10. A composition for the treatment of cellulose fabrics to
impair wrinkle resistance characteristics thereto while
preserving high strength and wear properties comprising:

a. N-methylol acetamide, and
b. a polymethylol cyclic urea selected from the group con-
sisting of dimethylol ethylene urea and dimethylol dihydroxy ethylene urea,

the weight ratio of (a) to (b) being between 1:10 and 20:3.

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