PROCESS FOR FINISHING TEXTILES

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Appl. No.: 12/083,262
PCT Filed: Sep. 21, 2006
PCT No.: PCT/EP2006/066563

§ 371 (c)(1), (2), (4) Date: Apr. 7, 2008

FOREIGN APPLICATION PRIORITY DATA

Oct. 12, 2005 (EP) ........................................ 05292137.6

PUBLICATION CLASSIFICATION

Int. Cl. D06M 13/352 (2006.01)

U.S. Cl. .............................................................. 8/189

ABSTRACT

The instant invention relates to a process for the finishing of textiles with a non formaldehyde cross-linking agent based on 2-imidazolidinones wherein by certain process parameters in drying and curing the undesired yellowing and unpleasant amine smell is avoided.
PROCESS FOR FINISHING TEXTILES

[0001] The present invention relates to a process for finishing a cellulose-based textile as well as a cellulose-based textile finished according to this process.
[0002] Cross-linking textile finishes are currently used for conferring on cellulose fabrics properties of durable press and resistance to creasing or crease recovery, a dimensional stability to domestic washes as well as easy care (easy ironing or no ironing), among other properties.
[0003] Most of these cross-linking textile finishes contain free or combined formaldehyde which is released either in the finishing shop or when using fabrics finished in this way. However, formaldehyde is now considered to be a noxious product, exposure doses of which are limited to very low values by certain national regulations.
[0004] In U.S. Pat. No. 3,304,312 4,5-dihydroxy or 4,5-dialkoy derivatives of 2-imidazolidinones, are disclosed as non-formaldehyde textile finishing agents for imparting crease resistance. The impregnated material is subjected to drying and curing operations at a temperature in the range of 82° C. to 232° C.
[0005] These compounds are widely used in Pad-Dry and Cure or Pad-Dry-Cure finishing processes where a cellulose containing fabric is impregnated with a bath containing these non-formaldehyde cross-linking agents, a catalyst and additives. The impregnated fabric is dried and cured at elevated temperatures; the drying and curing steps may be consecutive or simultaneous. In the case where the fabric is first dried, curing temperatures from 120° C. to 230° C. are described (U.S. Pat. No. 4,295,846)
[0006] Unfortunately, finished fabrics according to this prior art, have low resistance to tearing, show a great tendency to yellowing, and may generate an unpleasant amine smell.
[0007] Furthermore to increase the easy-care properties of the finished fabrics, one can increase the concentration of these non-formaldehyde crosslinkers but at the expense of the whiteness and the tear strength. The bad amine smell is then also promoted.
[0008] It is known by the artisan, as described in Textile Chemist and Colorist 1982 (Cooke and al. 14(5), 100-106, 1982), that the necessary acid conditions (pH from 3 to 5) not only catalyze the etherification of the cellulose, but also give an undesired side reaction where dialkyldantoins are formed thus reducing the efficiency of the crosslinker (degrees of fixation of the resin of from 50 to 70% are generally observed).
[0009] Surprisingly, it has now been discovered that non-formaldehyde crosslinkers can be applied under extreme acidic conditions to a cellulose based fabric in a moist cure process (a combination of impregnation, padding, gentle drying, low temperature curing and washing) to give good easy-care properties. The finished fabrics according to this invention have an excellent whiteness level, a very high tear strength, and no unpleasant amine smell.
[0010] This invention provides a formaldehyde free cross-linking finishing process of cellulose fabrics or cellulose containing fabrics.

[0011] The compounds used in this invention have the general formula (I):

\[
\begin{align*}
\text{(I)} & \\
R^1 \text{-} & N \overset{X}{\text{-}} N \overset{R^2}{\text{-}} & R^4 \text{O or OR}^3
\end{align*}
\]

[0012] Either the cis or trans isomer type or mixtures thereof may be used,
wherein
X is O or S, preferably O,
R^1, R^2 are the same or different and are
[0013] linear or branched C_{1-23}-alkyl, preferably C_1-C_4-alkyl, most preferably methyl,
[0014] or
[0015] linear or branched C_{2-23}-alkyl, preferably C_{2-4}-alkyl, substituted by one or more functional groups like hydroxyl, amino, carboxyl, amide, ester, ether, and halogen (fluorine, chlorine, bromine and iodine),
R^3, R^4 are the same or different (R^3 and R^4 may be part of the same ring structure)
[0016] and are H
[0017] or
[0018] linear or branched C_{1-23}-alkyl, preferably C_{1-4}-alkyl, eventually substituted by one or more functional groups like hydroxyl, amino, carboxyl, amide, ester, ether, and halogen (fluorine, chlorine, bromine and iodine),
[0019] or
[0020] groups like

\[
\text{CH}_2 - \text{CH} = \text{O} \]

[0021] where
[0022] n is 1-20, preferably 1-6, most preferably 2, and
[0023] R^3 is H or linear or branched chain alkyl C_1-C_4, preferably II.
[0024] Most preferably R^1 and R^2 are methyl and R^3 and R^4 are H or methyl or —(CH_2)_3OH.
[0025] Preferred compounds of the invention are 1,3-Dimethyl-4,5-dihydroxy-2-imidazolidinone (also called DMED-HEU, DiMethylDiHydroxYEthyleneUrea) and its etherified derivatives. To partly or completely etherify the DMEDHEU, the preferred alcohols are methanol or DEG (diethyleneglycol) or mixtures thereof.
[0026] These products are generally commercial and sold by example under the trade name Arkofix NZF New (Clariant) or can be prepared by different techniques known to the man skilled in the art as described among other possible processes in U.S. Pat. No. 3,304,312, U.S. Pat. No. 4,295,846, EP 0 141 755, or U.S. Pat. No. 5,707,404. The process is generally a condensation of glyoxal and a di-substituted urea followed or not by an etherification step with one or more alcohol or polyol.
Process of this Invention:

0027. The process of this invention is characterised by the following steps:

0028. a) Impregnation of a cellulose containing fabric with a bath containing a non-formaldehyde cross-linking agent of formula (I) and a catalyst or a mixture of catalysts under acidic conditions,

0029. b) Drying at a temperature of 130° C. or below to a residual moisture of from 3 to 30%,

0030. c) Curing at a temperature of 50° C. or below.

0031. Afterwards the fabric is washed, neutralised and dried by operations known in the art.

0032. Optionally an additional top-finishing step may complete the instant process.

DETAILED DESCRIPTION OF THE INVENTION

0033. A cellulose containing fabric is impregnated with a bath containing a non-formaldehyde cross-linking agent of formula (I) and a catalyst or a mixture of catalysts.

0034. The concentration of the finishing agent of formula (I) in the bath calculated as solid is generally governed by the desired effect. As a rule it is between 30 and 500 g/l, preferably between 100 and 300 g/l, most preferably between 120 and 240 g/l.

0035. Catalysts suitable for this process are one single acid or combinations of organic and inorganic acids or acid donors. The cross-linking of the cellulose is acid-catalysed, the bath pH is adjusted to 3 or below, preferably to 2 or below, and most preferably to 0.8-1.5.

0036. Typical catalysts include acids such as hydrochloric, sulphuric, fluoroboric, phosphoric, nitric, acetic, glycolic, maleic, lactric, citric, tartaric, muriatic and oxalic acids; metal salts such as magnesium chloride, nitrate, fluoroborate, or fluorosilicate; zinc chloride, nitrate, fluoroborate, or fluorosilicate; ammonium chloride, zirconium oxychloride, sodium or potassium bisulphate; amine hydrochlorides such as the hydrochloride of 2-amino-2-methyl-1-propanol; and the like or mixtures thereof. Preferred are hydrochloric acid, sulphuric acid, phosphoric acid or ammonium chloride.

0037. Optionally, additives may be added to the bath. Conventional additives such as wetting agents, lubricants, softeners, bodying agents, water repellents, flame retardants, soil shedding agents, mildew inhibitors, anti-wet soiling agents, fluorescent brighteners, biocides (anti-microbial, anti-bacterial, anti-algae, anti-fungi, insect repellent, anti-dust mite, anti-mould) and the like may be used in the treating bath in conventional amounts as long as the stability of the bath is compatible with the very low pH range of the invention. Such auxiliaries must not, however, interfere with the proper functioning of the finishing resin, must not themselves have a deleterious effect on the fabric, and desirably are free of formaldehyde. Preferred are wetting agents, lubricants and softeners.

0038. The impregnated fabric is dried at low temperature below 130° C., preferably below 100° C. and most preferably between 60 and 90° C. to a residual moisture of from 3 to 30%, preferably from 5 to 15% and most preferably from 6 to 10%.

0039. The fabric being kept at this humidity either by being wrapped with a plastic film or by any other means, is cured at low temperature, below 50° C., preferably below 40° C., to avoid fibre damage for 5 to 30 h, preferentially for 15 to 25 h. During that curing stage the fabric is preferentially kept under rotation to avoid migration and local over-concentration of the catalyst that could damage the fabric.

0040. After the curing, the fabric is washed and neutralised with any conventional method generally used by the man skilled in the art. Neutralisation may be achieved for example with a base like caustic soda or just by rinsing.

0041. After the washing and neutralisation step, the fabric is dried. Optionally, but preferably, the fabric is top-finished with a bath containing additives. This step can be subsequent to the drying or the fabric can be padded after the washing in a wet-in-wet process and then dried.

0042. Conventional additives such as wetting agents, lubricants, softeners, bodying agents, water repellents, flame retardants, soil shedding agents, mildew inhibitors, anti-wet soiling agents, fluorescent brighteners, biocides (anti-microbial, anti-bacterial, anti-algae, anti-fungi, insect repellent, anti-dust mite, anti-mould) and the like may be used in the top-finish bath in conventional amounts as long as the bath is stable. Such auxiliaries must not, however, interfere with the proper functioning of the finishing resin, must not themselves have a deleterious effect on the fabric, and desirably are free of formaldehyde.

0043. The non-formaldehyde finished fabrics according to the disclosed process, have easy-care properties and furthermore have a better tear strength, a high whiteness level (no yellowing) and do not generate any unpleasant amine smell.

0044. The following examples shall explain the instant invention in more detail.

<table>
<thead>
<tr>
<th>parameter</th>
<th>method</th>
</tr>
</thead>
<tbody>
<tr>
<td>Durable Press</td>
<td>AATCC 124</td>
</tr>
<tr>
<td>Tear strength</td>
<td>NF G07-149</td>
</tr>
<tr>
<td>Tensile strength</td>
<td>NF G07-091</td>
</tr>
</tbody>
</table>

Degree of Fixation

0045. The degree of fixation is obtained by the nitrogen determination (N%) of the fabric before and after washing by elementary analysis.

| Degree of fixation=100xN% washed fabric/N% finished fabric |

EXAMPLE 1

Moist Cure with a DMDEHEU Based Crosslinker

0046. A bleached white 100% cotton toile 1/1 (116 g/m², 40x27.5 threads/cm) was impregnated in a bath according to recipe #1. The material was squeezed to a wet pick-up of 65%, and then it was dried with hot air having 70° C. to a residual moisture of 7-8%. The material was wrapped in a plastic bag and was allowed to stand at 35° C. for 24 hours (curing). Thereupon it was promptly washed, neutralised, rinsed with water at 30° C. for 5 minutes then squeezed and dried at 120° C. After the drying, the material was impregnated and squeezed with recipe A to a wet pick up of 60%, and dried at 130° C. (top-finish).

COMPARATIVE EXAMPLE 1

Pad-Dry-Cure with a DMDEHEU Based Crosslinker

0047. The fabric of example 1 is impregnated in a bath according to recipe #2. The material was squeezed to a wet
The details of the recipes are shown in Table 1.

<table>
<thead>
<tr>
<th>Products</th>
<th>Recipes</th>
<th>1</th>
<th>A</th>
<th>2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sandzoin MRN liq cone</td>
<td>g/l</td>
<td>0.3</td>
<td>0.3</td>
<td>0.3</td>
</tr>
<tr>
<td>(commercial wetting agent*)</td>
<td>Arkofox NZF New liq</td>
<td>g/l</td>
<td>440</td>
<td>440</td>
</tr>
<tr>
<td>(commercial DMeDHEU based crosslinker*)</td>
<td>Catalyst MC1 liq (commercial mixture of organic and inorganic acids*)</td>
<td>g/l</td>
<td>110</td>
<td>18</td>
</tr>
<tr>
<td>Sandolube SVN ZP liq (commercial non ionic polyethylene softener*)</td>
<td>g/l</td>
<td>40</td>
<td>20</td>
<td>40</td>
</tr>
<tr>
<td>Sandoperm MEW liq (non ionic silicone microemulsion*)</td>
<td>g/l</td>
<td>30</td>
<td>10</td>
<td>30</td>
</tr>
<tr>
<td>Sandoperm RPU liq (commercial polyurethane softener*)</td>
<td>g/l</td>
<td>30</td>
<td></td>
<td></td>
</tr>
<tr>
<td>pH of bath</td>
<td>1.2</td>
<td>4.2</td>
<td>3.9</td>
<td></td>
</tr>
</tbody>
</table>

*available from Clariant

Results:

**0–untreated fabric**

<table>
<thead>
<tr>
<th>Durmple Press (5 x 60°C washes, tumble-dried)</th>
<th>Example</th>
<th>0</th>
<th>example 1</th>
<th>comp ex 1</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tear strength - Elmdorf (weft)</td>
<td>cN</td>
<td>1059</td>
<td>1483</td>
<td>958</td>
</tr>
<tr>
<td>Tensile strength (weft)</td>
<td>dN</td>
<td>57.2</td>
<td>36.4</td>
<td>37.5</td>
</tr>
<tr>
<td>Degree of fixation</td>
<td>%</td>
<td>45</td>
<td>64</td>
<td></td>
</tr>
</tbody>
</table>

These results clearly demonstrate a surprising increase of the tear strength when the fabric is treated by the instant moist cure process.

**EXAMPLE 2**

Moist Cure with a DMeDHEU Based Crosslinker

A bleached white 100% cotton poplin (120 g/m²) was impregnated in a bath according to recipe #3. The material was squeezed to a wet pick-up of 75%, then it was dried with hot air having 90°C to a residual moisture of 9%. The material was wrapped in a plastic bag and was allowed to stand at 20°C for 22 hours. Thereupon it was promptly rinsed, neutralised with caustic soda, rinsed with water for 10 minutes, acidified with acetic acid, rinsed again then squeezed and dried at 120°C. After the drying, the material was impregnated and squeezed with recipe B to a wet pick-up of 75%, and dried at 120°C.

**COMPARATIVE EXAMPLE 2**

Pad-Dry-Cure with a DMeDHEU Based Crosslinker

The fabric of example 2 is impregnated in a bath according to recipe #4. The material was squeezed to a wet pick-up of 75% then it was dried for 45 seconds at 120°C. and cured for 30 seconds at 160°C.

**COMPARATIVE EXAMPLE 3**

The finished material of comparative example 2 was washed with 1 g/l of a detergent/wetting and dispersing agent for 15 minutes at 45°C. then was rinsed with water, squeezed and dried for 45” at 120°C.

**Details of the recipes are shown in Table 3.**

<table>
<thead>
<tr>
<th>Products</th>
<th>Recipes</th>
<th>3</th>
<th>B</th>
<th>4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sandzoin RW liq cone (commercial wetting agent*)</td>
<td>g/l</td>
<td>0.3</td>
<td>0.3</td>
<td>0.3</td>
</tr>
<tr>
<td>Arkofox NZF New liq (commercial DMeDHEU based crosslinker*)</td>
<td>g/l</td>
<td>440</td>
<td>200</td>
<td></td>
</tr>
<tr>
<td>Concentrated sulfuric acid</td>
<td>cc/l</td>
<td>11</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Catalyst NKD liq (commercial magnesium chloride based catalyst*)</td>
<td>g/l</td>
<td>18</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sandolube SVN liq (commercial non ionic polyethylene softener*)</td>
<td>g/l</td>
<td>50</td>
<td>50</td>
<td></td>
</tr>
<tr>
<td>Ceraperm MW liq (non ionic silicone microemulsion*)</td>
<td>g/l</td>
<td>30</td>
<td>30</td>
<td></td>
</tr>
<tr>
<td>pH of bath</td>
<td>1.1</td>
<td>4.2</td>
<td>3.5</td>
<td></td>
</tr>
</tbody>
</table>

*available from Clariant

**Results:**

**0–untreated fabric**

<table>
<thead>
<tr>
<th>Durmple Press (1 x 60°C C. wash, tumble-dried)</th>
<th>Example</th>
<th>0</th>
<th>2</th>
<th>comp ex 2</th>
<th>comp ex 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tear strength - Elmdorf (warp)</td>
<td>cN</td>
<td>995</td>
<td>1148</td>
<td>802</td>
<td>795</td>
</tr>
<tr>
<td>Tear strength - Elmdorf (weft)</td>
<td>cN</td>
<td>683</td>
<td>694</td>
<td>540</td>
<td>545</td>
</tr>
<tr>
<td>Degree of whiteness (CIE)</td>
<td>°</td>
<td>75.1</td>
<td>77.8</td>
<td>73.5</td>
<td>74.9</td>
</tr>
<tr>
<td>Degree of fixation</td>
<td>%</td>
<td>48</td>
<td>67</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The results clearly show that the instant process leads to better properties of the textile fabric, especially the problem of yellowing has been solved and the tear strength is far better. It can also be seen that the improvement of tear strength and whiteness cannot be achieved from an additional washing step after a pad-dry-cure process, but is only obtainable with the instant process.
I. A process for finishing textiles comprising the steps of:
a) impregnating a cellulose containing fabric under acidic conditions with a bath containing a catalyst or a mixture of catalysts and either the cis or trans isomer type or mixtures thereof of a non-formaldehyde cross-linking agent of formula (I)

\[
R^2 \quad \text{X} \quad R^1
\]

\[
\text{R}^3 \quad \text{R}^4
\]

wherein
X is O or S,
R\(^1\), R\(^2\) are the same or different and are linear or branched C\(_1\) - C\(_{20}\) alkyl, or
linear or branched C\(_2\) - C\(_{20}\) alkyl, substituted by at least one functional group selected from the group consisting of: hydroxyl, amino, carboxyl, amide, ester, ether, and halogen,
R\(^3\), R\(^4\) are the same or different and may be part of the same ring structure and are H or linear or branched C\(_1\) - C\(_{20}\) alkyl, or

\[
\text{CH}_2 - \text{CH} - \text{O} - \text{H}
\]

wherein
n is 1 - 6, and
R\(^5\) is H.

3. A process according to claim 1, wherein
X is O,
R\(^1\) and R\(^2\) are methyl,
R\(^3\) and R\(^4\) are H or \(-\text{CH}_2 - \text{CH}_2 - \text{OH}\).

4. A process according to claim 1, wherein the non-formaldehyde cross-linking agent of formula (I) is 1,3-Dimethyl-4,5-dihydroxy-2-imidazolidinone.

5. A process according to claim 1, wherein
a) the impregnating step is done in a bath containing from 30 to 500 g/l of the non-formaldehyde cross-linking agent of formula (I), at a pH below 3,
b) the drying step is done at a temperature below 100\(^\circ\) C. to a residual moisture content of from 5 to 15%,
c) the curing step is done at a temperature below 40\(^\circ\) C. for 5 to 30 hours.

6. A process according to claim 1, wherein
a) the impregnating step is done in a bath containing from 10 to 300 g/l of the non-formaldehyde cross-linking agent of formula (I), at a pH below 2,
b) the drying step is done at a temperature below 100\(^\circ\) C. to a residual moisture content of from 5 to 15%,
c) the curing step is done at a temperature below 40\(^\circ\) C. for 5 to 30 hours.

7. A process according to claim 1, wherein
a) the impregnating step is done in a bath containing from 10 to 300 g/l of the non-formaldehyde cross-linking agent of formula (I), at a pH from 0.8 to 1.5,
b) the drying step is done at a temperature from 60 to 90\(^\circ\) C. to a residual moisture content of from 6 to 10%,
c) the curing step is done at a temperature below 40\(^\circ\) C. for 15 to 25 hours and the fabric is kept under rotation.

8. A process according to claim 1, wherein the fabric is treated with an additional top-finish.

9. A process according to claim 1, wherein the catalyst or mixture of catalysts is selected from the group consisting of: hydrochloric acid, sulphuric acid, phosphoric acid and ammonium chloride.

10. A process according to claim 1, wherein the impregnating bath further comprises wetting agents, lubricants or softening agents.

11. A textile obtained from a process according to claim 1.