Effect of Aftertreatments on the Ion Exchange Properties of Phosphorylated Cotton

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An effective and safe fire retardant finish for cotton has been developed. Application of the finish involves phosphorylation of cotton employing suitable chemicals and its subsequent aftertreatment with mixtures of metal salts. The duration and temperature of application in the phosphorylation reaction have been standardized with respect to the fire retardant and strength properties of the treated fabric. The phosphorylated cotton was subjected to aftertreatment with zirconium, titanium and antimony salts used individually as well as in mixed compositions. Mixtures of these salts gave better results than those given by the individual salts. The durability of the finish against hard water and soaping has been studied.

Fire retardant finishing of cotton has acquired considerable importance during the last few years. Many a time it becomes obligatory for the textile chemist to apply fire retardant finishes on textiles for special end uses, e.g. fabrics required by the fire fighting forces, certain military purposes and many other such applications. Fire retardant finishing of cotton has been studied extensively. Out of the many finishes developed so far, the organophosphorus compounds have been found to give all-round fastness properties on cotton. However, many of these chemicals are known to cause health hazards and are uneconomical. On the other hand, phosphorylation of cotton, which is known for many years now, imparts excellent flame and glow resistance properties to cotton and the finish is found to be safe from health point of view. However, this finish has a major drawback which is responsible for its failure commercially. Due to the presence of free ester-OH groups, as shown below, the finish picks up Ca and Mg ions when cleansing is done using hard water.

As a result of this ion exchange reaction, the finish is rendered ineffective. This is believed to happen due to the non-availability of phosphorus during the burning of cotton (around 450°C), because Ca or Mg phosphates formed during heating are thermally stable even up to 650°C. To avoid the ion exchange phenomenon in phosphorylated cotton, a few aftertreatments to block the free ester-OH groups have been suggested. It has been observed that if cellulose phosphate is treated with certain metal ions so that it forms a complex, as shown below, the finish shows reduced ion exchange behaviour.

This phosphate-metal complex is stable to washing and soaping. At the same time, during burning, it breaks and the phosphorus is made available for the fire retardant reaction.

A detailed study of these aftertreatments employing single metal salts as well as their mixtures is reported in this paper.

Materials and Methods
All the experiments were carried out on a scoured, bleached and mercerized medium cotton poplin fabric. The chemicals used in the phosphorylation and aftertreatment reactions were of chemically pure grade and those used in analysis work were of Analar grade.

Phosphorylation of cotton—Six moles of urea and one mole of phosphoric acid were taken in an evaporating dish and heated at 160°C for 30 min. The contents were cooled and dissolved in water such that a 49% (wt/vol) solution of the salt was obtained. Cotton samples were padded with this solution, keeping the pick up at 80%. The fabric was then dried at 80°C for 5 min and cured at different temperatures for different periods, as desired. However, the fabric cured at 180°C...
for 3 min was adopted uniformly for aftertreatments with metal compounds. The samples were washed thoroughly in cold distilled water and dried at room temperature.

Aftertreatment of the phosphorylated cotton samples—Phosphorylated cotton samples were padded with a solution containing the appropriate quantity of the metal salt in HCl and batched for 5 min. Subsequently, the samples were treated with a solution containing 15% Na₂CO₃. They were then washed in running water, soaped, washed and dried.

Estimation of phosphorus—The sample was digested in a Kjeldahl flask using concentrated H₂SO₄ and HNO₃ and ammonium molybdate reagent was added to form ammonium phosphomolybdate. This was filtered and washed first with distilled water and then with potassium nitrate solution (1%). The precipitate was dissolved in excess standard alkali solution and the unreacted alkali was back titrated with standard acid.

Testing of fire retardancy—The fire retardancy of the fabric sample was measured by the vertical flammability test method. A fabric sample strip (7 × 25.4 cm) was suspended vertically in the vertical flammability test equipment and Burshege gas flame of known flame height was applied at the bottom of the fabric for 12 sec. The char length was estimated by measuring the charred portion of the fabric. The duration of afterglow was measured with a stopwatch after removal of the flame source.

Determination of tensile and tear strengths—The tensile strength of the ravelled strips (specimen size, 2.5 × 10 cm) was determined on a pendulum type tester at a constant rate of traverse of 45 cm/min. The tear strength was measured by the Elmendorf method using 7 × 10 cm strips.

Wash fastness of the fire retardant fabrics—The fire retardant fabrics were subjected to washing operations of varying severity. A mild washing treatment consisted of an operation at 60°C in a bath containing 5 g/litre soap and 2 g/litre soda ash for 30 min. In a severe washing treatment, the sample was boiled for 30 min in a solution containing 5 g/litre soap and 2 g/litre soda ash.

<table>
<thead>
<tr>
<th>Curing conditions</th>
<th>Add-on Phosphorus content</th>
<th>Tensile strength retained, %</th>
<th>Tear strength retained, %</th>
<th>Char length in</th>
<th>Afterglow sec</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temp. C</td>
<td>Duration min</td>
<td>%</td>
<td>%</td>
<td>%</td>
<td>%</td>
</tr>
<tr>
<td>Untreated cotton</td>
<td>150</td>
<td>15</td>
<td>12.2</td>
<td>1.50</td>
<td>100</td>
</tr>
<tr>
<td></td>
<td>160</td>
<td>13</td>
<td>12.2</td>
<td>1.50</td>
<td>58</td>
</tr>
<tr>
<td></td>
<td>175</td>
<td>5</td>
<td>12.2</td>
<td>1.50</td>
<td>59</td>
</tr>
<tr>
<td></td>
<td>180</td>
<td>3</td>
<td>11.6</td>
<td>2.80</td>
<td>69</td>
</tr>
</tbody>
</table>

*BEL = Burning entire length.
Table 2—Aftertreatment of Phosphorylated Cotton with Various Metal Salts

<table>
<thead>
<tr>
<th>Inorganic compound</th>
<th>Concentration in pad bath %</th>
<th>Add-on to the fabric %</th>
<th>Char length in sec</th>
<th>Afterglow Char length in sec</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO₂</td>
<td>16</td>
<td>4.0</td>
<td>BEL* 40</td>
<td></td>
</tr>
<tr>
<td>Sb₂O₃</td>
<td>30</td>
<td>12.0</td>
<td>BEL* 40</td>
<td></td>
</tr>
<tr>
<td>TiO₂/Sb₂O₃</td>
<td>16/30</td>
<td>15.6</td>
<td>2.9 8</td>
<td></td>
</tr>
<tr>
<td>ZrOCl₂·8H₂O</td>
<td>30</td>
<td>10.5</td>
<td>BEL* 0</td>
<td></td>
</tr>
<tr>
<td>Sb₂O₃</td>
<td>30/32</td>
<td>16.0</td>
<td>2.9 8</td>
<td></td>
</tr>
<tr>
<td>ZrOCl₂·8H₂O</td>
<td>15/16</td>
<td>8.1</td>
<td>4.0 193</td>
<td></td>
</tr>
<tr>
<td>Sb₂O₃</td>
<td>7.5/8.0</td>
<td>5.4</td>
<td>3.6 317</td>
<td></td>
</tr>
</tbody>
</table>

*BEL = Burning entire length.

Table 3—Effect of the Soaping Ingredients on the Char Length and Afterglow of the Treated Sample

<table>
<thead>
<tr>
<th>Soaping ingredients in severe washing</th>
<th>No. of washes</th>
<th>Char length in sec</th>
<th>Afterglow</th>
</tr>
</thead>
<tbody>
<tr>
<td>Soap (5 g/litre)</td>
<td>1</td>
<td>2.5</td>
<td>7.0</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>3.0</td>
<td>11.5</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>3.0</td>
<td>9</td>
</tr>
<tr>
<td>Soap (5 g/litre) + Soda ash (2 g/litre)</td>
<td>1</td>
<td>2.5</td>
<td>15</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>3.0</td>
<td>46</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>3.0</td>
<td>56</td>
</tr>
<tr>
<td>Det detergent (2 g/litre)</td>
<td>1</td>
<td>1.5</td>
<td>8</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>3.0</td>
<td>8</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>3.5</td>
<td>10</td>
</tr>
</tbody>
</table>

This leaves two ester-OH groups free on two separate cellulose molecules, which are unable to pick up Ca or Mg ions, but during subsequent soaping treatment the fabric picks up Na ions and this causes increased glowing.

Except for the afterglow during soaping in the presence of soda ash, the phosphorylated aftertreated samples show very good durability against washing. The finish has been found to withstand five mild soaping treatments with hard water of up to 1400 ppm hardness (Table 4). This further shows that in the modified cellulose, during the aftertreatment with the combination of metal salts, a complex is formed between ester-OH groups on two separate cellulose chains and the metal oxide. Therefore, the modified product has no tendency to pick up Ca and Mg ions and retains flame resistance over a number of soaping treatments, but can easily pick up sodium ions and exhibit glowing. Leblanc and Leblanc⁶, from their study on the blocking of ester hydroxyls with metal salts, did not find any afterglow, which according to us is highly unlikely. In this type of finishing treatment, in the presence of sodium ions, the fabric is bound to give afterglow during burning.

Conclusion
Phosphorylation of cotton and its subsequent aftertreatment with zirconium and antimony salts in combination results in better fire retardant properties.
than when single metal salts are used. The finish is durable over a number of severe soaping treatments. However, the glowing tendency of the modified cotton could not be overcome completely, although it was reduced considerably.

Acknowledgement

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References