Combined desizing, scouring and bleaching of cotton using ozone

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An attempt has been made to desize, scour and bleach grey cotton fabric simultaneously using ozone. The mechanical, chemical and dyeing properties of the ozonized fabric have been compared with those of the fabric subjected to conventional desizing, scouring and hydrogen peroxide bleaching. To achieve a high degree of whiteness with minimum damage to cellulose, a two-stage process is suggested wherein the ozonized fabric is further treated with hydrogen peroxide. An acceptable degree of whiteness (ready for dyeing) can be obtained by using ozone in a very short time. This process has additional advantages such as savings in thermal energy, water and chemicals.

Keywords: Bleaching, Cotton, Desizing, Dyeing, Scouring

1 Introduction

The impurities present in grey cotton fabric are sizing ingredients, fat, waxes, pectins and natural colouring matter. Efficient removal of these impurities during grey preparation is essential to guarantee proper dyeing, printing and finishing processes. Till today, the most commonly accepted sequence of operations for cotton grey preparation is acid or enzyme desizing, alkali scouring and hypochlorite or hydrogen peroxide bleaching. This sequence of operations is time consuming and needs a large quantity of water, energy and a variety of chemicals. Therefore in the past, different approaches have been made to simplify cotton grey preparation. One approach was to carry out all the three processes simultaneously (combined process). Some of the combined processes proposed are:

- A combined desizing, scouring and bleaching of medium and fine varieties of cotton fabrics was suggested by Parikh, which involves the use of DTPA as stabilizer for hydrogen peroxide.
- BTRA developed a single-stage process in kier which is claimed to produce high degree of whiteness with minimum damage to cellulose.
- Sahakari worked out a process which is based on solvent-nonionic emulsion system known as Scourex process.
- Gulrajani et al. suggested a solvent-assisted aqueous process in which sodium hydroxide (scouring agent) has been replaced by a solvent–nonionic surfactant–pine oil combination along with hydrogen peroxide.

Other combined processes reported in the literature use tetrapotassium perhydroxy phosphate (KPP), sodium dipersulfate (SPS) and various combinations of sequestering agents, wetting agents and peroxide stabilizers. In almost all these combined processes, the benefits of combining the processes are generally derived at the expense of some quality. Hence, they were accepted by the industry with a lot of reservations.

The increasing demand for the conservation of natural resources and environmental protection has forced the researchers to look for the processes which can be carried out at a low temperature using small amount of water in a short duration without the use of harmful chemicals such as hypochlorite. To fulfill these objectives, attempts are now being made to bleach cotton using ozone, ozone-UV radiation, peracetic acid and enzymes. Ozone being a powerful oxidizing agent can bleach cellulose much faster than hydrogen peroxide and hypochlorite. Today, it is
being used, to a large extent, as a substitute for chlorine in pulp bleaching. However, in cotton bleaching it is still at the infant stage. In 1995, two patents have been awarded for bleaching of cotton with ozone. These patents claim a continuous process using low-temperature plasma for desizing and scouring and ozone in the presence of UV for bleaching. Takahashi and Kaiga have studied the effect of ozone concentration and treatment time on the properties of bleached fabrics. It is expected that in a few years from now an enzyme cocktail will be developed which will perform continuous desizing, scouring and bleaching of cotton. The advantage of using enzymes is that it is ecofriendly and saves significant amount of energy.

In the present work, an attempt has been made to combine all the three grey preparatory processes, such as desizing, scouring and bleaching. Here, ozone is used to desize, dewax and decolour the grey cotton fabric. To improve the fabric properties, two-stage bleaching is suggested wherein the fabric is treated with ozone followed by hydrogen peroxide.

2 Materials and Methods

2.1 Materials

Commercial grey cotton fabric (ends/in, 134; picks/in, 78; and weight, 139.6 g/m²) sized with native starch was used for the study. The chemicals and dyes (monochlorotriazinyl and dichlorotriazinyl) used were of analytical and commercial grades respectively.

2.2 Apparatus

The equipment used for the bleaching with ozone has three components: the ozone generator, the applicator and the ozone destroyer. The ozone generator of 8 g/h capacity was supplied by Ozone Tek Ltd, India. The input for the generator is oxygen from a pressurized cylinder. The generator supplies the required concentration of ozone - oxygen mixture to the applicator. The applicator is a glass cylindrical tube with a diffuser at the bottom. The gas mixture is pumped continuously at the required flow rate into the applicator through the diffuser. The wet fabric samples are suitably placed in the applicator for the required time. The spent mixture is passed through the ozone destruction unit which has a heating element, where the ozone is completely converted into oxygen before being released into the atmosphere. An ozone analyzer is mounted on the applicator to measure ozone concentration both at the entry and the exit of the applicator.

2.3 Procedure

Wet grey cotton fabrics having ~24% moisture content (wet pickup) were placed in the application chamber and exposed to 100 g/m² concentration of ozone-oxygen gas mixture at pH 5 using acetic acid for a specified time (1-7 min) at room temperature (about 30°C) for the combined desizing, scouring and bleaching. The gas mixture flow was maintained at a constant rate of 0.5 litre/min for the all experiments.

Two-stage bleaching of grey cotton fabrics was first carried out with ozone and then with hydrogen peroxide. The wet grey fabrics with ~24% moisture content were first bleached with ozone (100 g/m²) at pH 5 for 1, 2 and 3 min and washed. These fabrics were then bleached with hydrogen peroxide for 45, 30 and 15 min respectively using standard procedure. All the bleached samples were then hot soap washed at 80°C, cold washed, dried and finally conditioned before testing for the properties.

Grey fabrics were also acid desized, alkali scoured and bleached with hydrogen peroxide and calcium hypochlorite using standard procedures.

2.4 Tests

The bleached samples were tested for whiteness index (WI) using the following Harrison equation:

\[ WI = 100-(R_{670}-R_{430}) \]

where \( R \) represents the reflectance values at 670 and 430 nm.

The per cent strength loss and per cent change in elongation-at-break were determined by the tensile testing method according to Indian standards procedure. The extent of chemical modification was measured in terms of aldehyde groups (cupric number), carboxyl groups, fluidity and degree of polymerization using Indian standards procedures. The per cent weight loss was measured by weighing the conditioned samples before and after bleaching. The per cent dewaxing was measured by soxhlet extraction and the absorbency was tested according to AATCC test method 39-1980.

In order to assess the dyeing properties of ozone bleached samples, the fabrics with WI ranging from 80% to 90% were separately dyed to medium shade (2.5% own) with two types of reactive dyes. The dyeing procedures were as specified by the dye manufacturers. The colour yield of the dyed samples was evaluated using a Hitachi spectrophotometer U-3210 and by applying the following Kubelka-Munk equation:
where, \( R \) is the decimal fraction of the reflectance of dyed fabric; \( R_0 \) the decimal fraction of the reflectance of undyed fabric; \( K \), the absorption coefficient; and \( S \), the scattering coefficient.

### 3 Results and Discussion

It is reported in the literature that the quality of ozone bleached cotton fabric depends on ozone concentration, treatment time, pH and the amount of moisture present on the fabric. The degree of whiteness and the extent of mechanical and chemical damages to cellulose are found to increase with the increase in either ozone concentration or treatment time. However, the latter is found to have more detrimental effect than the former. The results indicate that the quality of ozone bleached fabric could be brought in line by using the hydrogen peroxide bleaching, provided that the ozone bleaching is first carried out in a very short time with high ozone concentration. It is also reported that the presence of moisture during bleaching has a very significant effect on the degree of whiteness obtained and the rate of bleaching. It is found that the 8% moisture content (standard moisture regain) has very little bleaching effect, but it increases very rapidly as the per cent moisture content increases up to 24%. A further increase in moisture content (up to 80%) retards the bleaching action and thereafter the amount of moisture present seems to have no effect on the time taken for bleaching. The pH also plays a significant role in deciding the degree of whiteness obtained and the rate of bleaching. It is found that with the increase in pH from 2 to 9 there is a marginal decrease in WI; a further increase in pH up to 12 results in a very rapid decrease in WI. Based on these findings, the present investigation has been carried out wherein the grey cotton fabric with 24% moisture content is bleached with 100 g/m² ozone at pH 5. The properties of ozonized fabrics with those of fabrics processed by conventional methods have also been compared.

Table 1 shows the properties of ozone bleached fabrics. It is observed that with the increase in treatment time there is an increase in WI, strength loss and cellulose modification (in terms of copper number, carboxyl group, fluidity and degree of polymerization) of the bleached fabrics. For an acceptable degree of whiteness (84%) to dye medium shades, the strength loss of ozone bleached fabric is same as that of hydrogen peroxide bleached fabric. However, when WI is further increased, the strength loss is least for hydrogen peroxide followed by calcium hypochlorite and ozone. Table 1 also shows the change in elongation-at-break of ozone and conventionally bleached fabrics. There is no change in elongation-at-break when fabric is treated with ozone, while it is significantly high for conventionally processed samples. The reason for this might be due to the fact that the latter have undergone a number of hot-wet treatments for a long period during desizing, scouring and bleaching. During such treatments, the fabric is prone to shrink considerably, resulting in high crimp and thread density which leads to high elongation. On the other hand, ozone bleached grey fabrics are subjected to only a hot soap wash and a cold wash for a short duration. The changes in fabric construction parameters due to the wet processing.

<table>
<thead>
<tr>
<th>Property</th>
<th>Ozone</th>
<th>Hydrogen peroxide</th>
<th>Calcium hypochlorite</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1°</td>
<td>3°</td>
<td>5°</td>
</tr>
<tr>
<td>Whiteness index</td>
<td>80</td>
<td>84</td>
<td>88</td>
</tr>
<tr>
<td>Strength loss, %</td>
<td>14</td>
<td>16</td>
<td>23</td>
</tr>
<tr>
<td>Elongation-at-break, %</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Weight loss, %</td>
<td>5</td>
<td>6</td>
<td>6.5</td>
</tr>
<tr>
<td>De-waxing, %</td>
<td>24</td>
<td>31</td>
<td>35</td>
</tr>
<tr>
<td>Copper No.</td>
<td>0.12</td>
<td>0.27</td>
<td>0.36</td>
</tr>
<tr>
<td>Carboxyl content</td>
<td>5.38</td>
<td>6.00</td>
<td>6.97</td>
</tr>
<tr>
<td>Fluidity</td>
<td>4.18</td>
<td>5.13</td>
<td>7.80</td>
</tr>
<tr>
<td>Degree of polymerization</td>
<td>2150</td>
<td>1965</td>
<td>1654</td>
</tr>
</tbody>
</table>

*Treatment time (min)
operations of hydrogen peroxide, calcium hypochlorite and ozone bleached samples are given in Table 2.

The loss in weight after bleaching is an indication of the removal of impurities, such as sizing ingredients and natural waxes. During bleaching, ozone reacts with cellulose as well as non-cellulosic constituents such as starch and waxes present in the fabric. Chemically starch is poly-α-glucopyranose in which straight chain (amylose) and branched chain (amylopectin) polymers are present. These constituents are insoluble in water but can be solubilized by oxidation. Due to high oxidation potential of ozone, it readily oxidizes these constituents, thereby solubilising them. During oxidation, the 1-4 linked D-glucopyranose unit of starch is attacked by ozone, resulting in the formation of carbonyl and carboxyl groups as well as the cleavage of glycosidic bonds. Hence, the reactivity of waxes toward ozone largely depends on their chemical nature. It is well known that the waxes are esters of higher fatty alcohols and fatty acids. The principal components of waxes are considered to be long chain alcohols and acids, saturated and unsaturated hydrocarbons, resin and resin acids, sterols and sterol glucosides. Hence, the reactivity of waxes towards ozone largely depends on their chemical nature. It is generally agreed that while reacting with unsaturated hydrocarbon present in waxes, ozone gives an ozonide which, on hydrolysis in water, breaks down into a mixture of aldehydes and acids. Ozone may also give an aldehyde and acid type products by attacking the bond between carbonyl and alkoxy group present in the saturated waxes. Therefore, one would expect that during grey bleaching of cotton with ozone there is a possibility that some of these impurities are also removed, resulting in weight loss after bleaching. Table 1 also shows this phenomenon that with the increase in treatment time there is an increase in weight loss. The extent of impurities removed during ozonation is less than that of conventional method of desizing, scouring and bleaching. However, a weight loss ranging between 5.0% and 7.0% (depending upon treatment time) during ozonation clearly demonstrates that the ozone is capable of desizing and dewaxing to some extent. The extent of dewaxing during ozone bleaching is shown in Table 1. It is found that with the increase in treatment time the efficiency of dewaxing increases. To achieve an acceptable degree of whiteness (84%), the degree of dewaxing is found to be 31%. Though it is less when compared to the degree of dewaxing of fabrics scoured with alkali, the water drop absorbency is found to be satisfactory (<3 s). In this context, it is worthwhile to recall the flash scouring techniques such as vaporloc system, where the absorbency is satisfactory even though the extent of dewaxing is low because the wax present on the fibre surface develops cracks due to flash scouring and so the absorbency is satisfactory. It has also been reported in the literature that there is no correlation between water adsorption of cotton fibre and its natural wax content. In fact, it is mainly the distribution of the residual wax on the fibre surface that determines water absorbency. Hence, it is necessary to reduce the wax content to a level at which it can no longer form a continuous protective film around the fibre so that the subsequent wet operations like dyeing could be carried out without any problem.

It is well known that a higher degree of chemical modification in cellulose during ozone bleaching than that in conventional bleaching is because of the very high oxidation potential of ozone. While bleaching cotton fabrics with ozone, it is generally accepted that the cellulose molecules are oxidized into oxy-cellulose. Hence, in the present work, to study the influence of ozone on cellulose chemical modification, copper number, carboxyl group content, fluidity and degree of polymerization are measured. The results (Table 1) indicate that with the increase in treatment time the extent of chemical modification is increased. This modification is found to be higher than that caused during conventional hydrogen peroxide bleaching, especially at higher degree of WI.

One would expect a low colour yield during reactive dyeing with the increase in copper number and carboxyl group content. Therefore, another
method to assess the quality of bleached fabric was used to study the amount of reactive dye uptake after bleaching. Dyeing experiments were carried out on fabrics having WI of 80, 84, 88 and 90%. The colour yield of these dyed samples was compared with that of dyed fabrics that are processed by conventional methods. The K/S values for different WI are shown in Figs 1 and 2. It can be seen from these figures that with the increase in whiteness index the K/S values decrease for all the fabrics bleached with ozone, hydrogen peroxide and calcium hypochlorite. This indicates that during bleaching the hydroxyl groups are converted into carboxyl or aldehyde groups. For the acceptable degree of WI (84%), the dye uptake of the samples bleached with ozone is nearly same as that of the samples bleached with hydrogen peroxide and calcium hypochlorite. However, at higher degrees of WI, the dye uptake is more for the samples bleached with hydrogen peroxide followed by calcium hypochlorite and ozone. The wash fastness properties of dyed samples bleached with ozone were found to be same as those of peroxide bleached samples. This result further confirms that for the acceptable degree of WI, the quality of ozone bleached fabric is in line with that of conventionally processed fabrics.

From the above comparison, it could be concluded that up to a certain degree of whiteness (84%), which is sufficient for dyeing medium to dark shades with reactive dyes, the grey fabric processed with ozone exhibits a quality which is comparable to the quality of fabric processed by conventional method of desizing, scouring and hydrogen peroxide bleaching. Beyond this degree of whiteness which is necessary for dyeing pastel shades with reactive dyes, the quality of ozonized fabric is inferior to that of fabrics processed by conventional method. In the conventional method, two-stage bleaching is often used to obtain high degree of whiteness with minimum cellulose degradation at a competitive cost to dye pastel shades and also for OBA treatment. The best example is hypochlorite bleaching followed by hydrogen peroxide bleaching. It is reported in the literature that the ozone can be used as the sole-bleaching agent in pulp bleaching, provided that the required brightness is about 60 - 70%. For high brightness levels, it is used in a two-stage bleaching that would include treatment with other bleaching agents like oxygen, peroxide, chlorine dioxide and hypochlorites. This kind of two-stage bleaching is recommended to minimize severe loss in yield and fibre strength properties. In light of the above practice, in the present work an attempt has been made to carry out two-stage bleaching of grey fabric with ozone followed by hydrogen peroxide to achieve a high degree of whiteness with minimum cellulose degradation.

The wet grey fabrics with 24% moisture content at pH 5 were first bleached with ozone (100 g/m²) for 1.2 and 3 min and then bleached with hydrogen peroxide for 45, 30 and 15 min respectively. The process conditions were so adjusted that the final fabrics have 90% WI. The quality parameters of these bleached fabrics are reported in Table 3. This table also shows the fabric properties after single-stage bleaching with ozone, hydrogen peroxide and calcium hypochlorite separately to achieve 90% WI. It can be seen from this table that with the increase in ozone treatment time, the strength loss, copper number, carboxyl group content and fluidity increase and the degree of polymerization decreases. However, the strength loss, fluidity and degree of polymerization of grey fabric treated with ozone for 1 min followed by hydrogen peroxide are nearly same as that of the fabric bleached with hydrogen.
peroxide. The copper number and carboxyl group content for two-stage bleached fabrics are higher than that of the hydrogen peroxide bleached samples. From this data, it may appear that the extent of chemical modification due to ozone treatment followed by hydrogen peroxide bleaching is very high. However, it should be noted that two-stage bleaching is carried out on grey fabric while the conventional bleaching with hydrogen peroxide or calcium hypochlorite is carried out after desizing and scouring. The presence of residual size materials and natural impurities, which carry acidic and reducing groups in the grey two-stage bleached fabric, seem to be responsible for high copper number and carboxyl groups\textsuperscript{20}. It is also noted that the quality parameters of two-stage bleached fabrics are found to be better than that of the fabric bleached with only ozone or calcium hypochlorite. A remarkable drop in degree of polymerization is observed when fabric is treated separately with ozone and calcium hypochlorite to achieve 90\% whiteness.

To study the suitability of two-stage bleaching to dye pastel shades, experiments were carried out with two types of reactive dyes. The fabrics were dyed to 0.1\% (owm) shade and analyzed for $K/S$ values. These values are compared with that of dyed fabrics that are bleached by only ozone and by conventional methods. These results are reported in Table 3. Here also, as expected, the $K/S$ values are found to decrease with the increase in ozone treatment time for both the reactive dyes studied. However, the $K/S$ values for the fabrics bleached with ozone for 1 min followed by hydrogen peroxide are same as that of the fabrics bleached with hydrogen peroxide and higher than that of the fabrics bleached with calcium hypochlorite and ozone alone. This clearly indicates that the quality of two-stage bleached fabric is same as that of fabrics bleached with hydrogen peroxide and higher than that of fabric bleached with calcium hypochlorite and ozone alone. Therefore, the above work illustrates that it is possible to achieve a high degree of whiteness by two-stage bleaching of grey fabric, the quality of which is comparable to the quality of fabric processed by conventional method of desizing, scouring and hydrogen peroxide bleaching.

4 Conclusions

The above study shows that grey preparation with ozone can be completed in one or two minute. This process has additional advantages such as savings in thermal energy, water and chemicals. For an acceptable degree of whiteness which is sufficient for dyeing medium and dark shades with reactive dyes, the quality of the fabrics processed with ozone is comparable with that of the fabrics processed by conventional method of desizing, scouring and hydrogen peroxide bleaching. For high degree of whiteness, undoubtedly the quality of fabrics bleached with hydrogen peroxide is found to be superior to that of the fabrics bleached with ozone and calcium hypochlorite. However, it can be said that there is a scope to improve the quality of ozonized fabrics. A two-stage bleaching of grey fabric with ozone followed by hydrogen peroxide is recommended for achieving a high degree of whiteness with minimum cellulose modification, which may be suitable for dyeing pastel shades.

<table>
<thead>
<tr>
<th>Bleaching agent</th>
<th>Treatment time, min</th>
<th>Strength loss, %</th>
<th>Copper number</th>
<th>Carboxyl content</th>
<th>Fluidity</th>
<th>Degree of polymerization</th>
<th>KIS</th>
<th>MCT dye</th>
<th>DCT dye</th>
</tr>
</thead>
<tbody>
<tr>
<td>I - Ozone</td>
<td>1</td>
<td>45</td>
<td>18</td>
<td>0.17</td>
<td>5.85</td>
<td>4.48</td>
<td>2084</td>
<td>0.55</td>
<td>2.70</td>
</tr>
<tr>
<td>II - Ozone</td>
<td>2</td>
<td>30</td>
<td>19</td>
<td>0.22</td>
<td>6.21</td>
<td>5.72</td>
<td>1970</td>
<td>0.53</td>
<td>2.42</td>
</tr>
<tr>
<td>III - Hydrogen peroxide</td>
<td>3</td>
<td>15</td>
<td>23</td>
<td>0.32</td>
<td>6.55</td>
<td>7.90</td>
<td>1663</td>
<td>0.46</td>
<td>1.40</td>
</tr>
<tr>
<td>IV - Calcium hypochlorite</td>
<td>7</td>
<td>60</td>
<td>27</td>
<td>0.49</td>
<td>8.15</td>
<td>12.0</td>
<td>1308</td>
<td>0.31</td>
<td>0.70</td>
</tr>
</tbody>
</table>

Table 3 — Properties of two-stage and single-stage bleached fabrics to obtain 90\% $W_I$  
[Control grey fabric - Whiteness index, 70\%; Fluidity, 2.61; and Degree of polymerization, 2571]
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