Process optimization in tetraacetyl ethylenediamine activated sodium perborate bleaching of cotton

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Received 17 March 2003; revised received 28 July 2003; accepted 24 September 2003

Cotton fabric has been bleached with tetraacetyl ethylenediamine (TAED) activated sodium perborate by varying sodium perborate concentration, TAED concentration and temperature. The effect of these process parameters on the quality of the bleached cotton has been studied and compared with the conventionally bleached cotton. Improved whiteness with minimum fibre damage can be obtained by activated sodium perborate bleaching at lower temperature and for shorter exposure duration. The process is found to reduce energy cost and effluent load on environment.

Keywords: Bleaching, Cotton, Desizing, Scouring, Whiteness index
IPC Code: Int. Cl. D06L 3/00, D06B 3/00

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. 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. Recently, the use of hypochlorites has been discouraged due to the liberation of harmful chlorinated organic compounds in the bleach plant effluents. Bleaching with hydrogen peroxide is a well-established process in textile industry. However, optimized bleaching is often dependent on processing conditions that can sometimes be detrimental to fibre quality, specially through the use of high temperatures, high pH values or extended reaction duration. The increasing demand for the conservation of natural resources, environmental protection and reducing energy cost has now forced researchers to look for the processes which can be carried out at a low temperature in a short duration without the use of harmful chemicals such as hypochlorite. Now, the textile industry is becoming increasingly aware of the potential benefits of using peroxide activated systems. It is reported[13] that by incorporating TAED, a bleach activator, into the bleach bath containing hydrogen peroxide or persalts, bleaching can be performed at both lower temperature and alkalinity with significant benefits in terms of retained fibre quality. Recently, the application of TAED in industrial textile bleaching, particularly for cotton/wool blends, has been reported[1-7]. In the detergent industry, the bleach activator TAED has been used for many years in combination with a persalt to provide effective bleaching by the production of peracetic anion at low temperature and residence time[8]. TAED is colourless, odourless, storage stable, safe and easy to handle. It has been established as a non-toxic, non-sensitizing and non-mutagenic product which readily biodegrades to form carbon dioxide, water, ammonia and nitrate. Sodium perborate is primarily used as a bleaching agent in detergent powders. It is used as a bleaching agent at 15-30% by weight of the total detergent composition. It is a crystalline compound formed by reaction between sodium borate and hydrogen peroxide. When dissolved in water, sodium perborate releases back hydrogen peroxide; its aqueous solution practically performs like a solution of hydrogen peroxide. Therefore, in this study, an attempt has been made to bleach cotton fabric with sodium perborate in presence of TAED. To optimize the process parameters, such as sodium perborate concentration, TAED concentration and temperature, the quality of the bleached fabric was assessed for the degree of

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whiteness, per cent strength loss and cellulose degradation in terms of carboxyl group content and copper number. The properties of TAED bleached fabrics were compared with the properties of hydrogen peroxide bleached fabrics.

2 Materials and Methods

2.1 Materials

The commercial medium quality desized cotton fabric having the following specifications was used for the study:

Weave, plain; ends/cm, 34; picks/cm, 26; warp count, 16.7 tex; weft count, 21 tex; and fabric weight, 120.8 g/m².

All the chemicals used were of analytical grade.

2.2 Methods

2.2.1 Experimental Design

The experiments were conducted using Box-Behnken second order composite design for three variables. The variables were selected at three levels (-1, 0, +1) and the response was given by a second-order polynomial. To test the estimated regression equation for the goodness of fit, Fisher F-test was employed and the multiple correlation coefficient $R^2$ was calculated. If the $R^2$ value lies between 0.75 and 1, the fitted regression equation is considered to be a good fit of the model.

2.2.2 Bleaching

The samples were bleached with sodium perborate and TAED solution for 1 h using the material-to-liquor ratio of 1:10. Bleaching with hydrogen peroxide involved the standard procedures.

2.2.3 Test Methods

The bleached samples were tested for whiteness index using the CIE formula for illuminant D65 and 1964 10° observer.

Whiteness index = $Y + 800 (0.3138 - x) + 1700 (0.3310 - y)$

where $Y$, $x$ and $y$ represent the chromaticity coordinates of the specimen; and 0.3138 and 0.3310 represent the $x$, $y$ chromaticity coordinates for the perfect diffuser respectively. Tensile strength was determined according to Indian standards specification, and from this the per cent strength loss was determined after bleaching. The extent of chemical modification was measured in terms of carboxyl groups and aldehyde groups (copper number).

3 Results and Discussion

In the standard sodium perborate bleaching method, the fabric should be bleached at high temperatures and high pH over a prolonged period in order to achieve a satisfactory whiteness. This operation is time consuming and needs a large quantity of energy. It is possible to reduce the bleach temperature to less than 60°C by adding organic activators into sodium perborate bleach solution. TAED reacts with hydrogen peroxide formed in the solution of sodium perborate to generate peracetic acid and peracetate anion in situ that are stronger bleaching agents than peroxide or perborate at low temperatures. The TAED activated sodium perborate rapidly generates peracetic acid over a wide temperature range, which improves the bleaching efficiency at both cold and medium temperatures. It is reported that peracetic acid, unlike hypochlorite, gives satisfactory bleaching results with overall improved substrate whiteness, improved cotton seed-coat removal and reduced fibre damage at low temperatures. However, a controlled reaction condition must be required to ensure maximum perhydrolysis of TAED to maintain bleach performance at low temperature and to minimize side reactions such as nucleophilic attack of peracetic acid anion on unreacted TAED molecule to form diacetyl peroxide, and the hydrolysis of TAED. Therefore, an attempt has been made to optimize the process variables to achieve a maximum whiteness with less fibre damage. The following limits for the process variables were fixed based on a preliminary study: sodium perborate concentration ($X_1$), 5 - 15 g/L; TAED concentration ($X_2$), 1 - 4g/L; and temperature ($X_3$), 30 - 70°C. To establish the relationship between the process variables, regression analysis was performed using the regression coefficients in the quadratic equation.

3.1 Effect of Process Parameters on Whiteness Index

3.1.1 Effect of Sodium Perborate

The effect of process parameters on whiteness index is shown in Table 1. The results were obtained from the following response surface equation of whiteness index:

Whiteness index = $44.9 + 1.75 X_1 - 0.75 X_2 + 9.75 X_3 + 2.175 X_1^2 + 1.675 X_2^2 - 4.325 X_3^2 - 5.75 X_1 X_2 + 5.25 X_1 X_3 - 4.75 X_2 X_3$

$R^2$ value = 0.9204
Table 1 - Effect of process parameters on fabric properties

<table>
<thead>
<tr>
<th>Sodium perborate g/L</th>
<th>TAED g/L</th>
<th>Whiteness index</th>
<th>Strength loss, %</th>
<th>Carboxyl content, milli-equiv./100g</th>
<th>Copper number</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
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<td>50°</td>
<td>70°</td>
<td>30°</td>
<td>50°</td>
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<td>5</td>
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<td>36.5</td>
<td>45.5</td>
<td>6.3</td>
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<td>4</td>
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<td>10.6</td>
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<tr>
<td>10</td>
<td>1</td>
<td>28.5</td>
<td>47.3</td>
<td>57.5</td>
<td>2.6</td>
</tr>
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<td>57</td>
<td>72.4</td>
<td>3.3</td>
</tr>
<tr>
<td></td>
<td>2.5</td>
<td>29.5</td>
<td>48.8</td>
<td>59.5</td>
<td>5.9</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>29.4</td>
<td>44</td>
<td>49.9</td>
<td>10.2</td>
</tr>
</tbody>
</table>

*Desized fabric – whiteness index, 22; maximum load at break, 539.5 N; carboxyl content, 5.93 milli equiv./100g; and copper number, 0.051.

Temperature in °C.

The table shows that a high degree of whiteness index could be achieved at higher concentration of sodium perborate as expected. This may be due to the liberation of more perhydroxyl ions which are mainly responsible for bleaching at higher concentration of sodium perborate. Fig. 1 shows the effect of sodium perborate and TAED on whiteness index for a given temperature. It is observed that at higher concentration of TAED, the whiteness index decreases with the increase in sodium perborate concentration. The maximum whiteness index is obtained at higher concentration of sodium perborate and lower concentration of TAED.

3.1.2 Effect of TAED

The concentration of TAED present in sodium perborate solution determines pH of the bleach liquor. As in the case of hydrogen peroxide and hypochlorites, the pH also plays a major role in activated sodium perborate bleaching. Based on pH, the following two mechanisms can be proposed for the bleaching action of peracetic acid formed from TAED activated sodium perborate: the liberation of either nascent oxygen (along with acetic acid) or perhydroxyl radical (along with carbonyl radical). The liberation of nascent oxygen occurs in the acidic and neutral medium while that of perhydroxyl radical occurs in alkaline media. Table 1 shows the effect of TAED on whiteness index. It can be seen from this table that with the increase in TAED concentration, there is an increase in whiteness index at lower sodium perborate concentration. However, a maximum degree of whiteness is achieved at higher concentration of sodium perborate but decreased concentration of TAED. Here, it should be noted that at lower concentration of sodium perborate (5g/L), initially the bleach bath pH was 9.5, which decreased to 6.5 upon the addition of TAED. Therefore, the maximum bleaching process was carried out at pH 6.5. At this pH, formation of nascent oxygen would be more responsible for effective bleaching action than the formation of perhydroxyl radical from peracetic acid. But, in the case of higher concentration of sodium perborate (above 10g/L), initially the bleach bath pH was 10.5, which decreased to 10 upon the addition of lower concentration of TAED into bleach bath and hence the bleaching was effectively performed at pH 10. This observation clearly indicates that the maximum degree of whiteness can be obtained when the bleaching is carried out with higher concentration of sodium perborate in presence...
of lower concentration of TAED. The probable reason for this is the formation of more perhydroxyl radical by the dissociation of peracetic acid at pH 10. This behaviour of peracetic acid in an alkaline pH is similar to the effect of pH on hydrogen peroxide bleaching. If the pH is below 10.5, the hydrogen peroxide decomposes very slowly and hence the formation of perhydroxyl radical would be less. It is also reported that the TAED gives maximum bleaching efficiency at pH ~10. At pH below 10, it is found that many of the existing bleach activators lose their effectiveness and undergo competing side reactions, which produce ineffective byproducts. The effect of TAED and temperature on whiteness index at given sodium perborate concentration is shown in Fig. 2.

3.1.3 Effect of Temperature

The stability of peracetic acid also depends on the temperature. At room temperature, it is relatively stable and starts to decompose with the increase in temperature. Therefore, an increase in whiteness index with increased temperature is expected, provided the decomposition rate is such that all the perhydroxyl radicals are available for bleaching. If the decomposition rate is very rapid, the radicals would escape into the atmosphere before they could bleach, as happens with a strongly alkaline pH. Preliminary studies have indicated that for a given set of process parameters, the whiteness index is very poor if bleaching occurs either below 30°C or above 70°C. The effect of temperature on whiteness index is shown in Table 1 and Fig. 3. At the lower concentration of sodium perborate (5g/L), the whiteness increases considerably when the temperature rises from 30°C to 50°C. But when the temperature further increases to 70°C, the whiteness index either remains constant or decreases marginally. However, at >5g/L sodium perborate concentration, the whiteness increases with the increase in temperature from 30°C to 70°C and is maximum at about 70°C. Rucker established a relationship between temperature and per cent peracetic acid decomposition and claimed that at pH 7 when the temperature increases from 20°C to 60°C, the per cent decomposition increases from 5.7 to 81 but the whiteness index increases up to 50°C, and then decreases slightly. He also found that the increased bleaching effectiveness with temperature was counteracted by decrease in peracetic acid stability and the maximum effectiveness was thus achieved at 50°C.

3.2 Effect of Process Parameters on Strength Loss

The major drawback of bleaching cellulose with oxidizing agents is the loss in tensile strength. This is due to the cellulose degradation owing to the drop in cellulose chain length and conversion of hydroxyl groups into aldehyde and carboxyl groups. It is always expected that a high degree of whiteness is accompanied by a high strength loss. Therefore, to establish commercial acceptability of the bleaching process, it is necessary to study the tensile properties of bleached samples. Table 1 shows the effect of all the process parameters on per cent strength loss. It can be seen from this table that with the increase in whiteness index, the per cent strength loss also
increases. It also shows that various combinations of process parameters can achieve a desired whiteness index, for example at a particular TAED concentration with either a low temperature and a high concentration of sodium perborate or a high temperature and a low concentration of sodium perborate. In such situations, it is found that the percent strength loss need not be same for these two samples. Therefore, it is worthwhile to determine which process parameter has a more detrimental effect on tensile properties. Also, to get a desired whiteness index, how can the per cent strength loss be minimized by changing the processing condition? The study of the regression equation, as shown below, for per cent strength loss clearly shows that it is most markedly influenced by changes in temperature than in TAED concentration:

\[
\text{Strength loss (\%)} = 7.967 - 0.15X_1 + 0.888X_2 + 2.0875X_3 + 0.929X_1^2 + 0.904X_2^2 - 0.746X_3^2 + 0.05X_1X_2 - 2.575X_2X_3,
\]

where \(X_1\) is sodium perborate concentration, \(X_2\) is temperature, and \(X_3\) is TAED concentration.

\[R^2\text{ value} = 0.9724\]

The negative coefficient of sodium perborate concentration indicates that a high concentration results in less strength loss than a lower one. From the regression equation for whiteness index, it is observed that the coefficient for sodium perborate concentration is positive, which means that as the sodium perborate concentration increases, the whiteness index also increases. Thus, there is little incentive to bleach in a low sodium perborate concentration as it not only increases the per cent strength loss but also reduces the whiteness index achieved.

Since three process parameters are involved, the optimum process conditions to achieve a desired whiteness with minimum per cent strength loss cannot be determined by manual examination of relevant graphs. Therefore, the regression equations obtained are optimized by the “complex search” method of Box using non-linear response surface equations. For this purpose, four constraints are set: three are implicit constraints (process parameters) limiting the values to the ranges used in the experimental design, and the fourth constraint is whiteness index which is set to be greater than or equal to successively higher values of 40 - 72 in steps of 4. The per cent strength loss equation is used as the objective function. The “complex search” method uses a hill climb technique similar to the concept of “simplex search” to minimize the objective function while ensuring that none of the constraints is violated. This is an iterative search and stops when successive iterations show only an insignificant improvement in the value of the objective function. Table 2 shows the optimized processing conditions for obtaining various whiteness levels with minimum per cent strength loss. These predicted processing conditions have been experimentally verified and found to be correct. The results show that for a desired whiteness, minimum per cent strength loss can be achieved when the bleaching is carried out with higher concentration of sodium perborate, keeping TAED concentration and temperature low.

### Table 2 — Optimum process conditions

<table>
<thead>
<tr>
<th>Whiteness index</th>
<th>Sodium perborate g/L</th>
<th>TAED concentration</th>
<th>Temperature °C</th>
<th>Strength loss, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>40</td>
<td>15</td>
<td>1</td>
<td>35</td>
<td>5.0</td>
</tr>
<tr>
<td>44</td>
<td>15</td>
<td>1</td>
<td>39</td>
<td>6.5</td>
</tr>
<tr>
<td>48</td>
<td>15</td>
<td>1</td>
<td>42</td>
<td>7.5</td>
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<tr>
<td>52</td>
<td>15</td>
<td>1</td>
<td>45</td>
<td>8.0</td>
</tr>
<tr>
<td>56</td>
<td>15</td>
<td>1</td>
<td>49</td>
<td>8.5</td>
</tr>
<tr>
<td>60</td>
<td>15</td>
<td>1</td>
<td>54</td>
<td>10.0</td>
</tr>
<tr>
<td>64</td>
<td>15</td>
<td>1</td>
<td>58</td>
<td>10.5</td>
</tr>
<tr>
<td>68</td>
<td>15</td>
<td>1</td>
<td>62</td>
<td>11.5</td>
</tr>
<tr>
<td>72</td>
<td>15</td>
<td>1</td>
<td>65</td>
<td>12.5</td>
</tr>
</tbody>
</table>

3.3 Effect on Extent of Chemical Damage

The measure of the presence of carboxyl and aldehyde groups in cellulose is an indication of the extent of damage during bleaching. The presence of these groups reduces reactive dye uptake. It is normally accepted that among conventional bleaching agents, hypochlorites give a higher degree of chemical damage than hydrogen peroxide, and hence lesser reactive dye uptake for the samples bleached with the former than with the latter. While assessing chemical damage, it is observed that on several occasions the carboxyl group content is less than that of the control sample. Similar observations are reported in the literature [19]. The reason for such observation is the removal of residual size materials and impurities (bearing acidic and reducing groups) from the fabric during bleaching treatment. It seems that the removal of acidic and reducing contents of these non-cellulose materials exceeds those created as a result of the chemical degradation of cotton cellulose. That is why the carboxyl group content of the treated fabric is less than that of the control sample. Table 1 shows the effect of process
parameters on extent of chemical degradation. The results were obtained from the following response surface equations of carboxyl and aldehyde group contents:

\[
\text{Carboxyl group content} = 5.439 + 0.0831 \, X_1 + 0.532 \, X_2 - 0.178 \, X_3 + 0.226 \, X_1^2 + 0.269 \, X_2^2 + 0.247 \, X_1 \, X_2 + 0.311 \, X_2 \, X_3 + 0.537 \, X_1 \, X_3 + 0.427 \, X_2 \, X_3.
\]

\[R^2 \text{ value} = 0.9684\]

\[
\text{Aldehyde group content} = 0.0347 - 0.0002 \, X_1 - 0.000725 \, X_2 - 0.004925 \, X_1 + 0.005296 \, X_1^2 + 0.002896 \, X_2^2 + 0.007396 \, X_1 \, X_2 + 0.003625 \, X_1 \, X_3 - 0.000975 \, X_2 \, X_3.
\]

\[R^2 \text{ value} = 0.8920\]

It can be clearly observed from the table that the formation of carboxyl groups during bleaching depends on the process parameters. From the regression equation of carboxyl group content, it is observed that the carboxyl groups of the treated fabric decrease by increasing the temperature and decreasing the concentration of TAED. The carboxyl group is also found to be high at low or high concentration of sodium perborate. Equation of aldehyde group content shows that aldehyde group content is most markedly influenced by the changes in temperature, followed by TAED concentration and sodium perborate concentration. It is generally found that the values of carboxyl group and aldehyde group contents are more at both low and high levels of process parameters. The probable reason for this is that at low levels of process parameters, the presence of impurities markedly influences the determination of carboxyl and aldehyde group contents. At high levels of process parameters, the impurities are not present and so the increase in carboxyl and aldehyde group contents may be attributed to the increase in cellulose degradation.

3.4 Comparison with Conventional Process

An attempt has also been made to compare the quality of TAED activated sodium perborate bleached material with that of hydrogen peroxide bleached material (Table 3). For a given whiteness index, the per cent strength loss and extent of chemical damage measured in terms of carboxyl and aldehyde group contents for the activated sodium perborate bleaching process are marginally better than that of hydrogen peroxide bleaching. These beneficial properties are due to bleaching under milder conditions at lower temperatures and for shorter exposure duration. The quality of activated sodium perborate bleached fabric was also compared with that of sodium perborate (without TAED) bleached fabric under the identical bleaching conditions. The results are found to be less satisfactory for the fabrics bleached with sodium perborate without activator.

<table>
<thead>
<tr>
<th>Bleaching agent</th>
<th>Whiteness index</th>
<th>Strength loss (%)</th>
<th>Carboxyl content (equiv./100g)</th>
<th>Copper number</th>
</tr>
</thead>
<tbody>
<tr>
<td>Activated</td>
<td>44</td>
<td>6.5</td>
<td>5.43</td>
<td>0.045</td>
</tr>
<tr>
<td>sodium</td>
<td>48</td>
<td>7.5</td>
<td>5.34</td>
<td>0.043</td>
</tr>
<tr>
<td>perborate</td>
<td>52</td>
<td>8.0</td>
<td>5.13</td>
<td>0.041</td>
</tr>
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<td>Hydrogen</td>
<td>44</td>
<td>7.0</td>
<td>5.52</td>
<td>0.047</td>
</tr>
<tr>
<td>peroxide</td>
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<td>7.8</td>
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</tr>
<tr>
<td>perborate</td>
<td>60</td>
<td>10.0</td>
<td>4.41</td>
<td>0.044</td>
</tr>
</tbody>
</table>

4 Conclusions

Bleaching of cotton using TAED activated sodium perborate is environment-friendly, energy saving and low-temperature process and is a good replacement of conventional bleaching processes. Bleaching can be done with 15 g/L of sodium perborate and 1 g/L of TAED at 50 - 60°C for 1 h in order to achieve an acceptable degree of whiteness (ready for dyeing) with minimum cellulose degradation. For the materials that undergo subsequent optical brightening agent treatment, the bleaching process can be done for about 90 min or so at 60 - 70°C. The quality of the bleached material is marginally better than that of hydrogen peroxide bleached material since the process is carried out at lower temperature and for shorter exposure duration. The process would also seem to be highly suitable for fibres, such as linen, linen blends and wool blends, which cannot withstand traditional severe bleaching condition.

Acknowledgement

The authors are thankful to the Foundation of Science and Technology, Government of Portugal, for providing the financial assistance.

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