SEM and IR studies on scouring and bleaching of linen

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Sequential removal of wax, water-soluble substances, pectin, hemicellulose and lignin afforded a fabric that mainly contained cellulose along with very small amount of non-cellulosic constituents. The whiteness index of the resultant fabric (59.4) was set as a target for commercial production of bleached linen fabrics and was well achieved by appropriate selection of scouring formulation at pre-bleaching stage and by proper manipulation of bleaching sequences. The durability parameters could be maintained at a satisfactory level by controlled defibrillation of the filaments and optimum retention of the non-cellulosic constituents. The entire chemical process was monitored using a Cambridge SEM (Stereoscan 250) and 250-30 Hitachi Spectrophotometer.

Keywords: Bleaching, Linen, Scouring, Scanning electron microscopy

1 Introduction

Linen requires a lengthy and expensive bleaching operation to furnish a satisfactory level of whiteness. Although complete removal of lignin imparts full whiteness, the process is prohibitive for industrial application since the fibre practically disintegrates into ultimate cells in the process. Hence, optimum retention of lignin, which acts as inter-cellular cementing material, and other non-cellulosic constituents (NCs) is essential. But the removal of the undesirable impurities from the fabric surface prior to bleaching is equally important. Most of these impurities are removed by scouring with Na$_2$CO$_3$, NaOH or mixed alkali solutions, and further inclusion of a wetting agent improves the scouring efficiency.

Various formulations have been suggested for bleaching of linen and allied ligno-cellulosic fibres, making use of acidic/alkaline NaOCl, NaClO$_2$ or H$_2$O$_2$ solutions, but peroxide does not produce satisfactory whiteness on linen without pretreatments. The single-stage bleaching processes usually result in low levels of whiteness and hence, two-stage and multi-stage bleaching processes have been developed to achieve various degrees of whiteness. Irrespective of the mode of bleaching operation, linen encounters a considerable loss in tensile strength owing to the dissolution of NCs.

The present work is aimed at improving the available techniques for bleaching linen with a view to achieve full whiteness, without causing appreciable damage to the fibre through optimum retention of NCs.

2 Materials and Methods

2.1 Fabric and Chemicals

The representative grey fabric was made from Belgium variety (Grade T-240) of fibre and had the following structural specifications: weave, plain; mass, 220 g/m$^2$; ends/dm, 150; picks/dm, 158; and yarn count of 25 lea (66 tex) in both warp and weft directions. Unless stated otherwise, reagents of analytical grade (mostly products of BDH or E. Merck) were used.

2.2 Instrumental and Analytical Techniques

The infrared spectra of the fabric samples were recorded by KBr pellet technique, using 250-30 Hitachi infrared spectrophotometer. The samples for studying the morphological features were prepared according to a reported method and the photomicrographs were taken using a Cambridge SEM, model Stereoscan 250. The reflectance of fabrics was measured using a Diano Colorspec Spectrophotometer (a product of Milton Roy) equipped with Jay Pak 4800-II software for compu-
tation of colour. Tensile strength was measured in the warp direction only with an Instron strength tester (model 1026) using 3.75 cm wide strips and 15.0 cm grip length, and the values were corrected for changes in thread density. Cuprammonium fluidity (Cu-f) was measured following British Specification BS 3090-1959.

The reflectance values were recorded at 10° observer angle for computing yellowness index (YI) and whiteness index (WI) and at 2° for redness index (RI), using the following equations:

\[
YI = \frac{(128 \times X - 106 \times Z)}{Y}, \quad \ldots (1)
\]

where \(X\), \(Y\) and \(Z\) are the tristimulus values.

\[
WI = L - 3b \quad \ldots (2)
\]

where \(L = 10 \times Y\) and \(b = 7(\times - 0.847 \times Z)/Y\)

\[
RI = R_{655} - R_{535} \quad \ldots (3)
\]

2.3 Scouring

The fabrics were scoured with (1) \(Na_2CO_3\) (10g/l) and NOPCO 1535, a proprietary surfactant (2g/l), and (2) \(Na_2CO_3\) (10g/l), NaOH(2g/l) and same surfactant (2g/l), keeping the fabric-to-liquor ratio at 1:30 (w/v), at 95± 1°C for 30 min in case of (1) and for 2 h in case of (2). Scoured fabrics were neutralized with dil. acetic acid and washed successively with hot and cold water.

2.4 Bleaching

The scoured fabrics were subjected to single-stage bleaching by \(NaOCl\) (B), \(NaClO_2\) (B2) or \(H_2O_2\) (B3) and sequential 2-stage (B2-B3) and 3-stage (B2-B1-B3) bleaching. The single-stage bleaching conditions are given in Table 1. Identical procedures were adopted for individual operations in multi-stage bleaching. The concentrations of bleaching agents in the stock solutions were estimated before use. Each treated fabric was air dried, manually flattened and conditioned (67% RH; 27°C) prior to experimentation and evaluation.

3 Results and Discussion

The quality parameters of grey and treated linen fabrics are given in Table 2. The grey fabric shows a high degree of YI and RI and a poor WI. Sequential removal of wax (T-I), water-soluble substances (T-II) and pectins (T-III) from the fabric results in marginal improvement in WI, while subsequent removal of alkali-soluble substances (T-IV) results in a significant increase in WI. The change may be attributed to the partial removal of lignin along with hemicellulose. Remarkable improvement in WI is observed upon delignification through T-V. This is accompanied by a sharp decrease in both YI and RI, a steep rise in cuprammonium fluidity and a cumulative loss of ~50% in tensile strength. Thus, extensive removal of NCs produces a high degree of WI (~75% with respect to white standard tile, Tables 2 and 3), but the process causes intensive defibrillation of the filaments and excessive degradation of cellulose as
Table 2—Quality parameters of linen fabrics treated with different chemicals

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Treatment</th>
<th>Reflectance*</th>
<th>Weight Cuprammonium loss fluidity</th>
<th>Loss in tensile strengthb, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Grey fabrics</td>
<td></td>
<td>YI</td>
<td>WI</td>
<td>RI</td>
</tr>
<tr>
<td>T₀</td>
<td>Nil</td>
<td>46.5 ± 1.5</td>
<td>11.4 ± 1.6</td>
<td>11.3 ± 0.4</td>
</tr>
<tr>
<td>T₁</td>
<td>T - I</td>
<td>43.6 ± 1.7</td>
<td>12.6 ± 1.6</td>
<td>11.3 ± 0.6</td>
</tr>
<tr>
<td>T₂</td>
<td>T - II</td>
<td>38.2 ± 1.5</td>
<td>15.7 ± 1.3</td>
<td>9.3 ± 0.5</td>
</tr>
<tr>
<td>T₃</td>
<td>T - III</td>
<td>37.4 ± 1.2</td>
<td>13.0 ± 1.2</td>
<td>9.9 ± 0.5</td>
</tr>
<tr>
<td>T₄</td>
<td>T - IV</td>
<td>31.0 ± 1.7</td>
<td>22.7 ± 1.2</td>
<td>8.4 ± 0.3</td>
</tr>
<tr>
<td>T₅</td>
<td>T - V</td>
<td>12.9 ± 0.9</td>
<td>59.4 ± 1.8</td>
<td>3.7 ± 0.1</td>
</tr>
<tr>
<td>T₆</td>
<td>Scouring recipe 1</td>
<td>35.0 ± 0.5</td>
<td>20.1 ± 0.5</td>
<td>10.0 ± 0.1</td>
</tr>
<tr>
<td>T₇</td>
<td>Scouring recipe 2</td>
<td>34.6 ± 0.5</td>
<td>21.6 ± 0.2</td>
<td>9.8 ± 0.2</td>
</tr>
<tr>
<td>Scoured fabrics</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>T₆</td>
<td>B₁</td>
<td>27.5 ± 0.5</td>
<td>37.0 ± 0.6</td>
<td>12.1 ± 0.2</td>
</tr>
<tr>
<td>T₆</td>
<td>B₂</td>
<td>24.7 ± 0.9</td>
<td>42.0 ± 1.3</td>
<td>11.6 ± 0.4</td>
</tr>
<tr>
<td>T₆</td>
<td>B₃</td>
<td>25.6 ± 1.8</td>
<td>42.9 ± 0.2</td>
<td>9.4 ± 0.9</td>
</tr>
<tr>
<td>T₆</td>
<td>B₂-rinse-B₃</td>
<td>17.6 ± 0.3</td>
<td>53.8 ± 0.2</td>
<td>5.3 ± 0.1</td>
</tr>
<tr>
<td>T₆</td>
<td>B₂-B₁-B₃</td>
<td>13.2 ± 0.1</td>
<td>62.7 ± 0.3</td>
<td>3.1 ± 0.2</td>
</tr>
<tr>
<td>T₆</td>
<td>B₃</td>
<td>15.7 ± 0.2</td>
<td>40.6 ± 0.3</td>
<td>10.8 ± 0.2</td>
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<tr>
<td>T₆</td>
<td>B₂</td>
<td>22.6 ± 0.3</td>
<td>44.0 ± 0.6</td>
<td>10.8 ± 0.3</td>
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<tr>
<td>T₆</td>
<td>B₁</td>
<td>23.2 ± 0.2</td>
<td>45.0 ± 0.1</td>
<td>9.3 ± 0.9</td>
</tr>
<tr>
<td>T₆</td>
<td>B₂-rinse-B₃</td>
<td>16.3 ± 0.4</td>
<td>55.8 ± 0.5</td>
<td>5.1 ± 0.1</td>
</tr>
<tr>
<td>T₆</td>
<td>B₂-B₁-B₃</td>
<td>12.5 ± 0.1</td>
<td>63.1 ± 0.1</td>
<td>3.1 ± 0.1</td>
</tr>
<tr>
<td>White std.</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

- Av. of 10 readings (+ indicates 95% confidence interval).
- Av. of 5 readings.

T-I — Soxhletting (6h) with benzene; T-II — Refluxing (6h) with water; T-III — Refluxing (6h) with 0.5% ammonium oxalate; T-IV — Refluxing (6h) with 2.0% NaOH (refs 25 & 26); and T-V — Delignification through a series of treatment in tandem (ref.22).

Table 3—Chemical composition of linen at various stages of bleaching process

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Composition, %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>WI</td>
</tr>
<tr>
<td>Grey &amp; scoured</td>
<td>(A)</td>
</tr>
<tr>
<td>T₀</td>
<td>11.4</td>
</tr>
<tr>
<td>T₅</td>
<td>59.4</td>
</tr>
<tr>
<td>T₆</td>
<td>20.1</td>
</tr>
<tr>
<td>T₇</td>
<td>21.6</td>
</tr>
<tr>
<td>Scoured &amp; bleached</td>
<td></td>
</tr>
<tr>
<td>T₆(B₂-B₃)</td>
<td>53.9</td>
</tr>
<tr>
<td>T₆(B₂-B₁-B₃)</td>
<td>62.7</td>
</tr>
<tr>
<td>T₇(B₂-B₁)</td>
<td>55.8</td>
</tr>
<tr>
<td>T₇(B₂-B₁-B₃)</td>
<td>63.1</td>
</tr>
</tbody>
</table>

- Determined by soxhletting with benzene (6h).
- Determined by refluxing (6h) with 0.5% ammonium oxalate.
- Determined by refluxing (6h) with water.
- Determined by refluxing (6h) with 2% NaOH (refs 21 & 22).
- Estimated by (A) a series of treatments in tandem according to Turner22 with some modifications23; and (B) H₂SO₄ method22.
- Figures in parentheses indicate removal efficiency (11) of non-cellulosic constituents (NC)

η = [100 - (%NC in sample/%NC in grey fabric) × 100]
evident from its cuprammonium fluidity and loss in tensile strength. The inference is in conformity with the morphological changes observed during these treatments. The SEM photomicrograph of grey linen (Fig.1A) shows that the ultimate cells are tightly bound to one another by intercellular substances. Deposits of impurities are clearly visible on the surface of filaments. These impurities might have originated from the residual cell wall debris that remained adhered to the fibre during the preceding process of fibre extraction. The fabric surface shows surface of filaments. These impurities might have bound to one another by intercellular substances. The SEM photomicrograph of grey linen (Fig.1B) is more prominent, presumably due to the partial removal of intercellular encrusting materials. Removal of lignin to the extent of 90% in T5 causes excessive decementation and promotes in profound defibrillation and severe damage to the surface (Fig.1C).

Notwithstanding the physico-chemical changes, the WI of T5 was set as a target in the subsequent studies. The T-1—T-V sequence is not a commercially viable proposal because of (a) high cost involvement, and (b) excessive deterioration in the durability parameters. Hence, the subsequent studies were focussed on manipulation of the chemical processing to achieve the target WI, without causing damage to the textile properties to an appreciable extent.

The inherent impurities hinder the reactions at bleaching stage and, therefore, are removed by scouring. The treatment not only minimizes impurities but also facilitates better penetration of the bleaching agents. Scouring with recipes (1) and (2) solubilized 9.5% and 16% of NCs respectively. Although the second recipe slightly improves the whiteness (Table 2), the fabric suffers greater cellulose degradation, as evidenced from the cuprammonium fluidity values. The enhanced degradation may be attributed to the prolonged exposure of the fabric at higher alkalinities. The photomicrographs of T6 and T7 (Figs 1D and 1E) reveal that both the scouring recipes are equally effective in removing the non-fibrous impurities, since the deposits of these impurities, which were frequently visible over the filament surface of the parent fabric, are conspicuously absent in the scoured fabrics.

Application of single- and multi-stage bleaching sequences on scoured T6 and T7 substrates furnished two separate series of fabrics. The efficacy of bleaching in both the series, as envisaged from the WI, increases in the order B3 < B2 < B1 < B2—B3, while the YI and RI increase in the reverse order. Increase in whiteness is accompanied by increase in weight loss and cuprammonium fluidity values and decrease in tensile strength. Among the single-stage bleaching processes, the hypochlorite affects the durability parameters most severely.

A careful scrutiny of the data reveals that the initial scouring parameters have strong influence in determining the properties of the fabric at the final stage of bleaching process. The initial difference in whiteness between T6 and T7 is carried over in all the bleaching processes, except in the B2—B1—B3 sequence which gives fabrics of comparable whiteness with either substrate. Samples of T7 series suffer greater loss of NCs (~17-23%) than the corresponding samples of T6 series (~10-17%). This phenomenon may be attributed to the enhanced openness of the filaments in T7, which, in turn, makes the reagents more accessible to the reaction sites. The augmented reactivity of T7 has detrimental effect on the durability parameters of the bleached fabrics. The comparative values of cuprammonium fluidity in T6 (2.8-7.5) and T7 (3.9-11.4) series indicate a higher trend of cellulose degradation in the latter series. This degradative action has direct bearing on the tensile properties and the observed tensile data agree well with the contention. The loss in tensile strength of T7 series is much higher (22-36%) as compared to that in T6 series (11.5-34%). The most important outcome of this investigation is that a whiteness exceeding the target value (59.4) could be achieved by the application of B2—B1—B3 bleaching sequence, using either T6 or T7 as substrate. The whiteness just fall short of the target value in the two-stage bleaching sequence. Even then the process may be adopted to derive satisfactory functional properties by using T7 and B2—B3 bleach combination sequence.

The surface characteristics of T6 and T7 samples subjected to B2—B3 bleach combination sequence (Figs 1F and 1G respectively) are quite satisfactory since none of them shows any sign of damages. The SEM photomicrograph of T6 sample subjected to B2—B—B3 bleach combination sequence (Fig.1H) is satisfactory in all respects, while the corresponding sample derived from T7 shows surface damage at various places (Fig.1I). Considering all these aspects, the scouring recipe 1 has been found to have the following advantages:

(i) The duration of scouring treatment per batch is substantially low (30 min) compared to that for recipe 2 (120 min) and for other formulations (180 min). The alkali consumption is also significantly low and hence causes reduction in the overall process cost.
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Fig. 1—SEM photomicrographs of different linen fabrics [A—Grey (T<sub>0</sub>); B—Alkali extracted (T<sub>1</sub>); C—Delignified (T<sub>2</sub>); D—Optimally scoured (T<sub>3</sub>); E—Conventionally scoured (T<sub>4</sub>); F—T<sub>5</sub> bleached with B<sub>2</sub>—B<sub>3</sub> sequence; G—T<sub>6</sub> bleached with B<sub>3</sub>—B<sub>1</sub> sequence; H—T<sub>7</sub> bleached with B<sub>1</sub>—B<sub>2</sub>—B<sub>3</sub> sequence; I—T<sub>8</sub> bleached with B<sub>2</sub>—B<sub>1</sub>—B<sub>3</sub> sequence.
The entire process of scouring and bleaching was also monitored by infrared spectroscopy. The IR spectrum of grey linen (Fig.2) shows the characteristic bands of a typical ligno-cellulosic substance. The notable absorption bands are: 3400 cm\(^{-1}\) for O-H, 2900 cm\(^{-1}\) for C-H, 1732 cm\(^{-1}\) for C=O stretching vibrations, and 1620-1680 cm\(^{-1}\) for aromatic skeletal vibrations. The absorption bands below 1500 cm\(^{-1}\) are highly superimposed and do not provide useful information about various functional groups. The nature and intensity of absorption bands at 3400 cm\(^{-1}\) and 2900 cm\(^{-1}\) did not change appreciably after scouring or bleaching treatments since cellulose was retained as a major component in the treated fabrics. The free or esterified carboxylic acid groups give rise to absorption band at 1732 cm\(^{-1}\) for the grey fabric. This functional group probably originates from the pectin component or lignin-carbohydrate ester functions or both. The latter type of functional group has been shown to exist in allied vegetable fibres\(^{24-26}\) and hence its presence in linen appears to be highly probable. The scouring treatment ruptures the ester bonds and neutralizes the free carboxylic acid groups. The liberated carboxylate anions absorbed strongly in the region of 1550-1610 cm\(^{-1}\) and 1300-1400 cm\(^{-1}\) and hence could not be identified separately due to strong interference of absorption bands already present in that region in the IR spectrum of the grey fabric. From the hemicellulose and lignin contents of the bleached fabrics (Table 3), it is apparent that these components are retained to various degrees in all the samples. In spite of this, the band at 1732 cm\(^{-1}\) was absent from all the samples, indicating that the carboxylic acids exist as carboxylate anions in the bleached fabrics (Fig.3).

4 Conclusions
For a given set of bleaching sequence, the scouring parameters at pre-bleaching stage play a key role in determining the ultimate whiteness and durability parameters of the linen. The optimized scouring formulation 1 has been found to be better in this respect. Extensive removal of the NCs produced a whiteness of \(\sim 75\%\) w.r.t. the standard white tile and this was set as a target value for industrial application. The single-stage bleaching always produced low levels of whiteness (\(\sim 47-57\%\)), irrespective of the method of scouring and the nature of bleaching agent. Application of \(B_2-B_1-B_3\) combination bleach sequence on fabrics scoured by either recipe 1 or recipe 2 produced a whiteness of \(\sim 79\%\), which well exceeded the target value, but the loss in tensile strength and cellulosic degradation were less in the case of optimally scoured fabric. Depending on the
end use, the $B_2-B_3$ sequence may also be utilized to achieve a whiteness of $\sim 68-70\%$.

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References
10 Mukherjee R R & Radhakrishnan T, Text Prog, 4(4) (1972) 1.
21 Turner A J, Quality in flax (Linen Research Institute, Lambergh, Lisburn, N. Ireland), 1954, 118-125.