Influence of Dyeing Techniques on Strength-Abrasion of DCT-Dyed DMDHEU-Finished Cotton Fabric

J VARGHESE, S K PATEL, B A Doshi and P R MISTRY
The Bombay Textile Research Association, Lal Bahadur Shastri Marg, Ghatkopar(West), Bombay 400 086, India
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Bleached mercerized cotton sheeting (200g/m²) samples, dyed with a dichlorotriazinyl dye, CI Reactive Blue 4, by exhaust (Exh) and pad batch (PB) techniques, were subjected to catalyst control (20g/l MgCl₂·6H₂O) treatment and DMDHEU finishing by pad-dry-cure treatment and evaluated for resilience and strength-abrasion properties. The samples dyed by Exh technique suffer greater loss in strength-abrasion properties than the corresponding samples dyed by PB technique. This is corroborated by the higher cuprammonium fluidity values of the samples blank dyed using Exh technique and subjected to catalyst control treatment as well as by the greater surface damage observed on scanning electron microscopic examination of samples dyed by the Exh technique.

Keywords: Cotton fabric, Dichlorotriazinyl dye, Dimethyloldihydroxyethyleneurea, Dyeing, Finishing, Strength-abrasion properties

1 Introduction
The use of cotton for apparel purposes is gaining ground all over the world now-a-days. To enhance the aesthetic appeal of the apparels, they are dyed or printed with bright colours and further resin finished to improve easy care properties. In this connection, the use of chlorotriazine based reactive dyes for dyeing of cotton has gained wide popularity. Resin finishing of these dyed fabrics could lead to concomitant loss in strength-abrasion and some changes in tone, depth and fastness characteristics of the dyed finished fabrics. Braun and Rieker have reported the use of factorial trial procedure and regression analysis for optimization of resin finishing on reactive dyed cotton fabric. Recently, it has been reported that dyeing of cotton sheeting with monoclorotriazinyl (MCT) dyes by pad-dry-cure technique leads to better strength-abrasion retention on finishing with DMDHEU than the dyeing of corresponding samples by pad-dry-steam technique. The dichloro-s-triazinyl (DCT) based reactive dyes, because of their high reactivity, could be used at low temperature for dyeing of cotton by exhaust (Exh) or pad-batch (PB) technique, thus enabling substantial savings in energy during the dyeing operation. Therefore, in the present study, a comparative evaluation of the influence of these two dyeing techniques (Exh and PB) on resilience and strength-abrasion retention of cotton sheeting dyed with C.I. Reactive Blue 4 and further finished with dimethyloldihydroxyethyleneurea (DMDHEU) has been made.

2 Materials and Methods
2.1 Materials
Mill bleached-mercerized cotton sheeting (grey particulars: count, 17s × 9s; reeds × picks per inch, 81 × 31 and weight, 202 g/m²) was used for dyeing and finishing experiments. The details of the pretreatments of the sheeting have been reported elsewhere. One commercially available DCT dye (CI Reactive Blue 4) was used for dyeing experiments. Dimethyloldihydroxyethyleneurea (DMDHEU) having 44% solid content was used for finishing experiments. All other chemicals used were laboratory reagent (LR) grade.

2.2 Methods
2.2.1 Dyeing
Dyeing of sheeting fabric by Exh technique was carried out in a laboratory jigger with a material-to-liquor ratio of 1:5 using 2% C.I. Reactive Blue 4 (on the weight of fabric) along with 50 g/l sodium chloride and 15 g/l sodium carbonate as per dye supplier’s recommendations. The whole dyeing operation took about 180-200 min including the dye fixation period of around 60 min with alkali. The dyed fabric was thoroughly washed with cold and hot water (60°C) and then again with hot water (85°C) for 20 min, followed by rinsing with cold water and then line-dried.

For dyeing by pad-batch technique, the fabric was padded with a solution containing 20 g/l C.I. Reactive Blue 4, 80 g/l urea, 5.8 g/l sodium carbonate and 14.2 g/l sodium bicarbonate at 95% wet pick-
up, followed by batching on a roller and rotating for 20 h. The fabric was then thoroughly washed as mentioned above.

Dyed fabrics were finished with 60, 120 and 150 g/l DMDHEU using magnesium chloride hexahydrate (MgCl₂, 6H₂O) as catalyst. For 60 g/l DMDHEU, 15 g/l catalyst and for 120 and 150 g/l DMDHEU, 20 g/l catalyst was used. The dyed fabrics were padded with the finishing solution at 80% wet pick-up, dried at 80°C for 5 min, and then cured at 150°C for 5 min. Pad-dry-cure treatments were also carried out using water alone (water control) and a solution of 20 g/l MgCl₂.6H₂O (catalyst control). The cured fabrics were washed with cold and hot water and then soaped (5 g/l soap and 2 g/l sodium carbonate) at 60°C for 30 min, followed by thorough hot and cold water rinsing and finally line-dried.

2.2.3 Blank Dyeing Treatment

The bleached mercerized sheeting was subjected to blank treatment, i.e. dyeing without the dye but with all other dyeing ingredients as per the details of Exh and PB techniques. These samples were also subjected to water and catalyst control treatments as mentioned above.

2.2.4 Test Methods

Cuprammonium (Cuam) fluidity of samples was determined by AATCC Test Method No.82-1979. The nitrogen content was determined by Kjeldahl’s method. Durable press (DP) rating was assessed after machine wash (41 ± 2°C for 12 min) and line drying (AATCC Test Method No.124-1982). Conditioned and wet wrinkle recovery angles (WRA) were determined by using a Monsanto tester (AATCC Test Method No.66-1976). Tensile strength and elongation at break were determined by the ravelled strip method as per ASTM D-1682-54. Tear strength was determined on Elemendorf tear strength tester (ASTM D-1424-67). Flex abrasion was determined by the ravelled strip method on Stoll’s universal wear tester using 1 lb head load and 4 lb tension load (ASTM D-1175-71). Accelerator weight loss was determined using Carborundum universal liner No 320 as liner at a rotor speed of 2000 rpm for 2 min (AATCC Test Method No.74-1974). For Scanning electron microscopic (SEM) examination, samples were mounted on specimen holder and coated with gold platinum in a sputter. The coated samples were then examined in a Hitachi scanning electron microscope (model No 510) at a suitable accelerating voltage.

3 Results and Discussion

The mill bleached mercerized sheeting, used in the study, possessed barium activity number 140, drop absorbency of less than 1s, cuprammonium fluidity of 3.4 poise⁻¹, total non-cotton content of 1.17% and whiteness index (Hunter 1958 equation) of 86.8. From these results, it could be concluded that the fabric has undergone safe and efficient bleaching and mercerization operations in the mill and it is good for dyeing.

3.1 Resilience Properties

The resilience and related properties of sheeting dyed with C.I. Reactive Blue 4 and then finished with 60, 120 and 150 g/l DMDHEU are given in Table 1. This table shows that DMDHEU finishing of the dyed fabric improved the resilience properties with increasing amount of DMDHEU applied, and near about durable press level of resilience is attained at 150 g/l DMDHEU. However, it is observed that on finishing with 120 and 150 g/l DMDHEU the samples dyed by Exh technique give higher values of both conditioned and wet WRA as compared to the corresponding samples dyed by PB technique. This may be due to the higher level of DMDHEU reaction with cellulose hydroxyl, as seen in the finishing.

<table>
<thead>
<tr>
<th>SI No.</th>
<th>Sample</th>
<th>Finishing</th>
<th>Nitrogen (% owf)</th>
<th>DP rating</th>
<th>WRA (W + F)</th>
<th>Total resilience (R) score</th>
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</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>DMDHEU</td>
<td>MgCl₂,6H₂O</td>
<td>Exh/Exh</td>
<td>Wet/Exh</td>
<td>Exh/Exh</td>
</tr>
<tr>
<td>1</td>
<td>Dyed control (C)</td>
<td>—</td>
<td>—</td>
<td>0.12/0.08</td>
<td>1.9/1.9</td>
<td>194/197</td>
</tr>
<tr>
<td>2</td>
<td>Dyed water control (FW)</td>
<td>—</td>
<td>—</td>
<td>0.14/0.07</td>
<td>1.9/1.9</td>
<td>195/199</td>
</tr>
<tr>
<td>3</td>
<td>Dyed and catalyst treated (F0)</td>
<td>—</td>
<td>20</td>
<td>0.17/0.12</td>
<td>1.8/1.8</td>
<td>195/192</td>
</tr>
<tr>
<td>4</td>
<td>Dyed and finished (F1)</td>
<td>60</td>
<td>15</td>
<td>0.30/0.30</td>
<td>3.0/3.0</td>
<td>230/234</td>
</tr>
<tr>
<td>5</td>
<td>Dyed and finished (F2)</td>
<td>120</td>
<td>20</td>
<td>0.66/0.53</td>
<td>3.2/3.3</td>
<td>261/257</td>
</tr>
<tr>
<td>6</td>
<td>Dyed and finished (F3)</td>
<td>150</td>
<td>20</td>
<td>0.76/0.65</td>
<td>3.4/3.5</td>
<td>275/268</td>
</tr>
</tbody>
</table>

Exh—Exhaust; PB—Pad batch; owf—on the weight of fabric
Table 2—Data on Strength-Abrasion Properties of Sheeting Dyed with 2% Reactive Blue 4 by Exh and PB Techniques and Finished with DMDHEU

<table>
<thead>
<tr>
<th>SI No.</th>
<th>Sample Description</th>
<th>Tensile strength at break (kg/2.5 cm) (W+F)% Rtn. Exh/PB</th>
<th>Elongation at break (%) (W+F)% Rtn. Exh/PB</th>
<th>Tear strength (g) (W+F)% Rtn. Exh/PB</th>
<th>Flex Abrasion (cycles) Exh/PB</th>
<th>Accelerator wt. loss (Exh/PB)</th>
<th>Total strength abrasion (S) score</th>
<th>Retention in strength abrasion score (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Dyed control (C)</td>
<td>100/100</td>
<td>100/100</td>
<td>100/100</td>
<td>100/100</td>
<td>2.9/3.1</td>
<td>147.1/146.9</td>
<td>100/100</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(68.4/68.1)*</td>
<td>(30.3/31.3)*</td>
<td>(8256/8213)</td>
<td>(1874/1921)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>Dyed water control (FW)</td>
<td>97/97</td>
<td>108/101</td>
<td>99/87</td>
<td>85/85</td>
<td>4.1/3.5</td>
<td>135.9/133.9</td>
<td>92/91</td>
</tr>
<tr>
<td>3</td>
<td>Dyed and catalyst treated (F0)</td>
<td>89/85</td>
<td>87/96</td>
<td>70/78</td>
<td>41/74</td>
<td>6.7/4.5</td>
<td>101.6/118.9</td>
<td>69/81</td>
</tr>
<tr>
<td>4</td>
<td>Dyed and finished (F1)</td>
<td>73/72</td>
<td>83/88</td>
<td>62/67</td>
<td>31/48</td>
<td>10.9/9.1</td>
<td>82.0/92.1</td>
<td>56/63</td>
</tr>
<tr>
<td>5</td>
<td>Dyed and finished (F2)</td>
<td>69/59</td>
<td>71/88</td>
<td>44/48</td>
<td>10/25</td>
<td>13.9/11.4</td>
<td>58.1/67.0</td>
<td>39/46</td>
</tr>
<tr>
<td>6</td>
<td>Dyed and finished (F3)</td>
<td>65/53</td>
<td>63/73</td>
<td>38/34</td>
<td>7/20</td>
<td>15.5/13.5</td>
<td>49.1/49.3</td>
<td>33/34</td>
</tr>
</tbody>
</table>

*Values within the parantheses are the original values.

from the higher amount of nitrogen fixed on Exh dyed samples than on the corresponding samples dyed by PB technique. However, it is surprising to note that this has not been reflected on DP rating values of the Exh dyed samples.

3.2 Strength-Abrasion Properties and Performance Profile Chart

The strength-abrasion values of sheeting fabrics dyed with C.I. Reactive Blue 4 by both the dyeing techniques show progressive loss with increasing amount of DMDHEU applied (Table 2). In most of the strength-abrasion properties including elongation at break, the samples dyed by PB technique and finished with DMDHEU give better retention properties than those dyed by Exh technique. However, it is surprising to note that in the case of tensile strength converse trend is seen. Thus, the resilience properties do not go hand in hand with all the strength-abrasion properties and hence, it is difficult to assess the influence of dyeing technique on these properties. Hence, a performance profile chart (Fig. 1) similar to the one used in an earlier study was used to assess the various resilience and strength-abrasion properties based on a common rating scale. It included three resilience properties, viz. conditioned WRA, Wet WRA and DP rating, and five strength-abrasion properties, viz. tensile strength, elongation at break, tear strength, flex abrasion and accelerator weight loss. Using this chart, scores for resilience and strength-abrasion properties were read from the common rating scale. The scores for resilience properties were added up to give the total resilience (R) score. Similarly, the total strength-abrasion (S) score was obtained by adding up the individual score for each strength-abrasion test (Table 2).

3.3 Overall Performance Profile

To evaluate the influence of Exh and PB dyeing techniques on the performance of DCT-dyed DMDHEU-finished sheeting, total 'S' scores were plotted against total 'R' scores obtained for all the finished samples. The profiles thus obtained, i.e. overall performance profiles of the Exh and PB techniques, are shown in Fig. 2. From these profiles, the 'S' scores obtained at 'R' scores of 50 (wash and
wear level of resilience) and 80 (durable press level of resilience) and their slope values were read. These values are given in Table 3. It is observed from the values that S score obtained at R score of 50 for sheeting dyed with the reactive dye by PB technique is significantly higher than that obtained for similar samples dyed by Exh technique. The reasons for obtaining this advantage are the higher order of retentions in abrasion properties and to a limited extent in tear strength and elongation at break of those finished samples which were dyed by PB technique. However, since the slope of the profile of the former being high, the initial higher value of S score gets reduced as R score increases and at durable press level it becomes nearly equal to that obtained on samples dyed by Exh technique. Thus, it appears that the dyeing technique has some role on the total S score obtained at wash and wear level of resilience, when the dyed fabric is finished with a low amount of DMDHEU.

3.4 Total Scores of Water and Catalyst Control Treated Samples

From the total ‘S’ scores of samples dyed by the two techniques and subjected to water control and catalyst control treatments (Table 2), it is observed that there is about 8-9% reduction in these scores on water controls and they are nearly equal for samples dyed either by Exh or PB technique. The Cuan fluidity of blank dyed samples subjected to water and catalyst control treatments are given in Table 4. It is observed that the increase in Cuan fluidity of these samples on water control treatment is only nominal. Thus, it could be concluded that the thermal damage occurring on the dyed cotton during the pad-dry-curing operation is low and it is not influenced by the dyeing technique employed.

As regards the reduction in total S score of catalyst controls, it has been reported in an earlier study that the pad-dry-cure treatment of mercerized scoured poplin (MS) with 20 g/l MgCl₂.6H₂O at 150°C for 5 min causes a reduction of around 15% in total S score with the resultant reduction in degree of polymerization of cotton cellulose. In the present study also, sheeting dyed with the reactive dye by PB technique gives rise to 19% reduction in total S score during catalyst control treatment. However, the sample dyed by Exh technique gives 31% reduction in total S score as compared to 19% by PB technique. The same trend prevails during finishing with low amounts of DMDHEU.

Dyeing of cotton with direct dye by exhaust technique is reported to adversely affect the strength characteristics of cotton. According to Noah et al., there is a direct relationship between the loss of fibre strength of cotton and increase in the number of sulphonic acid groups present in the dye as well as the molecular weight of the dye. As suggested by Sumner, the internal pH of a cotton fabric undergoing dyeing with either reactive or direct dye by Exh technique gets reduced when the fabric containing the dye and the electrolyte is washed with water. The external dye-bath pH is reduced by the dilution of alkali and the internal pH within the fibre is reduced even more due to the greater ionization of electrolyte on dilution. It is reported that the magnitude of the difference between internal and external pH increases with the amount and basicity

### Table 4—Cuprammonium Fluidity Values of Undyed (BM) and Blank Dyed Sheeting Samples

<table>
<thead>
<tr>
<th>No.</th>
<th>Sample</th>
<th>Cuan fluidity, poise⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Bleached mercerized sheeting (BM)</td>
<td>3.82</td>
</tr>
<tr>
<td>2</td>
<td>Blank dyed sheeting (b)</td>
<td>4.63/4.18</td>
</tr>
<tr>
<td>3</td>
<td>Blank dyed water control</td>
<td>5.77/4.98</td>
</tr>
<tr>
<td>4</td>
<td>Blank dyed catalyst control</td>
<td>16.30/13.50</td>
</tr>
</tbody>
</table>
of dye, quality of wash water and the number of washes that the dyed fabric undergoes. Thus, using water at pH 7 containing approximately 120 mg/l of neutral electrolyte (sodium chloride), the internal pH may decrease progressively with repeated washing to reach 4.5-5.5 after six washes. If the purity of wash water is extremely high, the internal pH developed is as low as 2-3. The internal pH begins to rise as the drying of the dyed fabric proceeds due to the increasing concentration of electrolyte in the entrapped water. However, the interior of the fibre will remain acidic throughout most of the drying process. In the present investigation dyeing of cotton fabric with a reactive dye was carried out by the Exh technique in the presence of an electrolyte (sodium chloride). Therefore, during the washing off stage, the internal pH of the fabric dyed by this technique would have been reduced. This reduction in internal pH has not resulted in any appreciable difference in the extent of damage of samples dyed by Exh and PB techniques at the water control treatment stage, as is clear from the comparable values of total strength-abrasion scores obtained for samples dyed by both the techniques (Table 2). However, on catalyst control treatment using a solution of 20 g/l MgCl₂.6H₂O the sample dyed by Exh technique gives rise to significantly lower value for the total strength-abrasion score as compared to the similar value obtained in the case of sample dyed by PB technique (Table 2). Possibly the samples dyed by Exh technique would have undergone higher order of thermohydrolytic damage due to the greater acidity developed by the combined effect of low internal pH of the dyed fabric coupled with the use of Lewis acid salt (MgCl₂.6H₂O) as catalyst at the high temperature of curing than the corresponding samples dyed by PB technique, wherein no electrolyte was used during dyeing.

3.5 Cuprammonium Fluidity

To check the above possibility, the samples blank dyed using Exh and PB techniques were subjected to catalyst control treatment. The Cuam fluidity values of these samples are given in Table 4. From these values, it is observed that the blank dyeing operations involving the two techniques of dyeing do not bring about any significant degradation of cotton. However, subsequent water control and catalyst control treatments do bring about some molecular degradation of cotton and more so during catalyst control treatment. Similar observations have been reported by Shih and Rowland⁹. According to them, the degree of polymerization of untreated cotton cellulose, as determined by viscosity measurements of nitrated cellulose in ethylacetate, drops

Fig. 3—Scanning electron micrographs of cotton sheeting dyed with C.I. Reactive Blue 4 by Exh technique [a—Control (low magnification), b—Control (high magnification), and c—Finished with 150 g/1DMDHEU]
from around 4000 to about 1000 on pad-dry-curing at 160°C for 3 min with a solution of 25 g/l MgCl₂·6H₂O. In the present study, Cuam fluidity increases from 3.82 to 13.5 and 16.3 for catalyst controls of PB and Exh technique respectively (Table 4). This four-fold increase in fluidity indicates that there is extensive molecular degradation occurring during catalyst control treatment and it is more so on sample processed through Exh technique of dyeing.

3.6 Scanning Electron Microscopic Studies

The scanning electron micrographs of sheeting dyed with C.I. Reactive Blue 4 by Exh and PB techniques as such and after finishing with DMDHEU were taken at a number of places and the most representative ones are shown in Figs 3 and 4. The dyeing by Exh technique in a jigger leads to clustering of the fibres due to repetitive rubbing of the fabric surface on the guide rollers of the jigger (Fig. 3a). However, no such clustering is seen on the samples dyed by PB technique (Fig. 4a), wherein the fabric undergoes only simple padding operation. This clustering of fibre is partly due to the loose construction of the sheeting fabric. Hence, the fibres of the fabric dyed by former technique are likely to undergo higher order of damage when they are subjected to pad-dry-cure treatment during finishing. Thus, more cracks are observed on the sample dyed by Exh technique (Fig. 3b) as compared to that on the sample dyed by PB technique (Fig. 4b). This damage persists on finishing with DMDHEU and leads to fibrillar type of damage on sample dyed by Exh technique (Fig. 3c) as against the sample dyed by PB technique (Fig. 4c).

4 Conclusions

Cotton sheetings dyed with DCT dye by Exh technique suffer greater loss in strength-abrasion properties on finishing with DMDHEU than the corresponding samples dyed by the PB technique. This higher loss in strength-abrasion of samples dyed by the Exh technique could be attributed to the two unfavourable factors that this technique possesses, viz. (1) the use of electrolyte in the dyebath for obtaining good exhaustion of the dye onto the fabric which may lead to lowering of internal pH of the dyed fabric in subsequent washing off treatment as seen by the higher cuprammonium fluidity value of these samples when subjected to catalyst control treatment, i.e. pad-dry-cure with 20 g/l MgCl₂·6H₂O and, (ii) the physical damage due to loosening and clustering of fibres of the yarn which get rubbed repetitively on the guide rollers of the jigger as seen from the scanning electron micrographs.

Fig. 4—Scanning electron micrographs of cotton sheeting dyed with C.I. Reactive Blue 4 by PB technique [a—Control (low magnification), b—Control (high magnification), and c—Finished with 150 g/l DMDHEU]
These two factors are not contributing to any added damage at the dyed stage since samples dyed with the DCT dye by either technique possess comparable strength-abrasion properties.

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