Effect of water hardness on reactive dyeing of cotton

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Abstract
Dye-house water quality is the most important parameter to be confirmed before dyeing; precisely the presence of metal content i.e. Hardness. This study focused on the impact of water hardness (i.e. Calcium, Magnesium & Iron) in dyeing of cotton with reactive dyes. From evaluation of dyed fabric the range of metal content is sorted out where the quality starts to fluctuate as distinctive visible & spectral change of shade & fixation rate of the dye molecules has been found. The result of the work will help for further projection about water quality degradation in upcoming years & its effect on dyeing behavior, also the sustainability of present dyeing process to cope with the ever degrading quality of water.
The purpose of this project work is to determine the effect of hardness of water on dyeing with the reactive dyes the dyeing method is exhaust method. The project work is done on different hardness of water such as 20ppm, 200ppm, 500ppm, 1000ppm, 1500ppm, 2000ppm. The water hardness is increase as depth of shade is decrease.
Keyword: Hardness of water, reactive dye, exhaustion, rotadyer machine, Spectrophotometer.

I. INTRODUCTION
In textile wet processing, the most substantial & influential role is played by water. Although several alternatives are getting into consideration, water is undoubtedly the most suitable as dyeing medium. So the quality of coloration is vastly dependent on quality of water. Throughout the time there have been lots of studies & works to evaluate & standardize dye house quality, however chronologically the water quality is degrading so alarmingly that dye houses are required to be more conscious about this. Right first time dyeing hugely depended on the quality of water; quality of water is vast idea, the most important are the presence of metal ions (i.e. Hardness), alkalinity, turbidity etc. So before dyeing these parameters should be in control. This experimental work is to investigate the effect of Hardness in reactive dyeing, precisely the dyeing properties, build-up, strength & fastness etc. Hardness is generally referred to presence of calcium & magnesium in water. In this research dyeing with reactive dyes in different amount of hardness, artificially created in water, is done to investigate the dyeing behavior & other qualities which might be affected by Hardness. Dye-house water-hardness is defined as the presence of soluble calcium and magnesium salts in the water and is expressed as the CaCO3 equivalent (1). The presence of hardness in the water can cause dye precipitation, and the precipitates can further promote dye aggregations, which results in color specks and loss of depth (2).
The objectives of this study is as to investigate different aspects of increased hardness as decrease in strength and k/s value

Hardness creates many other undesirable effects in wet processing. The textile dyes for each fiber are designed to have low solubility in water and these become difficult to dissolve in very hard water. Due to insufficient solubility the dye-shade becomes weaker and may also produce spots on the dyed fabric. Further on heating or on coming in contact with alkalis during dyeing and soaping, calcium and magnesium ions are precipitated on fabrics as whitish carbonates and hydroxide particles.
The objectives of this study is as to investigate different aspects of increased hardness as change in wash off and fixation percentage. Usually the dyeing with reactive dye is commenced in neutral solution in presence of electrolyte. Here electrolyte acts to promote the exhaustion of the dye. Electrolyte neutralizes the negative charge formed in the fiber surface & puts extra energy to increase absorption. During this period dye just only migrate into the fiber surface but do not react with the fiber. Usually the higher shade percentage is ensured by higher electrolyte percentage and higher temperature. In dye Fixation stage, by the reaction of the reactive group of the dye and the fiber, dye-fiber covalent bond is formed. And running the exhaustion stage for few minutes an appropriate alkali is added to increase its PH (>10). The hydroxyl group of the cellulose is slightly acidic and due to the hydroxyl ion of the alkali, there causes some disassociation, forming cellulose ion.

Hardness creates many other undesirable effects in wet processing. The textile dyes for each fibre are designed to have low solubility in water and these become difficult to dissolve in very hard water due to insufficient solubility the dye shade becomes weaker and may also produce spots on dyed fabric. Further on heating or on coming in contact with alkalis during dyeing and soaping, calcium and magnesium ions are precipitated on fabrics as whitish carbonates and hydroxide particles.

LITERATURE SURVEY
Water is classified as hard and soft depending upon the presence or absence of dissolved salts of calcium or magnesium in it.
1) Hard water
2) Soft water
The hardness of water can be either
- Temporary hardness
- Permanent hardness

Temporary hardness can be removed simply by boiling the water (see later).
Permanent hardness cannot be removed by boiling but can often be removed by chemical treatment (see later). Temporary hardness is caused by calcium and/or magnesium hydrogen carbonate. These are formed as carbonated rain water passes over rocks containing carbonate ions, for example

$$H_2O(l) + CO_2(g) + CaCO_3(s) \rightarrow Ca(HCO_3)_2(aq)$$

$$H_2O(l) + CO_2(g) + MgCO_3(s) \rightarrow Mg(HCO_3)_2(aq)$$

Permanent hardness is caused by calcium and/or magnesium sulphate. These are formed as water passes over rocks containing sulphate ions, for example

$$aq\ CaSO_4(s) \rightarrow Ca^{2+}(aq) + SO_4^{2-}(aq)$$

$$aq\ MgSO_4(s) \rightarrow Mg^{2+}(aq) + SO_4^{2-}(aq)$$

**Expression of hardness:**

Hardness of water is expressed usually in terms of parts per million (ppm). The ppm value of an ion (or salt) is a number which denotes the amount of equivalent calcium carbonates per million parts of water.

Where \( W \) = weight of ion (or salt) in one million parts of water. Since the equivalent weight of calcium carbonate is 50,

$$ppm = \frac{W \times 50}{\text{weight of ion (or salt)}}$$

This can be illustrated by an example. Suppose a solution contains 0.9524 gms of magnesium chloride per litre and it is required to find out the hardness in ppm of magnesium chloride in the solution. Now 1000 ml. of water contains 0.9524 gms of magnesium chloride.

One million ml of water contains $$= \frac{0.9524}{1000 \times \text{one million gm}}$$

Of MgCl\(_2\) i.e. 952.4 gms of MgCl\(_2\).

Equivalent weight of MgCl\(_2\) = 47.62

Hardness in ppm = 47.62 \times 50 = 1000

The hardness of water, is therefore, 1000 ppm.

Water can be classified into 4 categories depending on its hardness as under:

- 0 upto 4 or 0 upto 57 ppm : Soft water
- 4 upto 7 or 57 upto 100 ppm : Moderately hard water.
- 7 upto 20 or 100 upto 300 ppm : Hard water
- Above 20 or above 300 ppm : Very hard water

**II. EXPERIMENTAL WORK**

This experiment deals with the material and chemicals that were used for the experiment various testing of the material and chemicals, procedure of experimental work, machine and instrument were used and the evaluation method of sample.

**Material:** Material used for the experiment were 100% cotton RFD 34single jersey knitted fabric is selected for the study. They are process for scouring, bleaching and use for dyeing.

**Dyes & Chemicals**

**Reactive dye (FNR Series) – Manufactured by Huntsman**
- Novacron Red FNR
- Novacron Yellow F4G
- Novacron Blue FNR
- Novacron Black R

**Vinyl Sulphone Dyes – Manufactured by Dystar**
- Remazol Yellow RGB
- Turquise Blue sky G

**Chemicals:**
1. Magnesium chloride (MgCl\(_2\))
2. Calcium chloride (CaCl\(_2\))
3. Glauber’s salt (Na\(_2\)SO\(_4\).10H\(_2\)O) - Exhausting agent
4. Sodium Carbonate (Na\(_2\)CO\(_3\)) - for dye fixing
5. Soap- Dekol FBSN (Non ionic detergent) - Soaping agent
6. Acetic Acid (CH\(_3\)COOH) - Neutralizing agent

**Laboratory Instruments**
1) Rota dyeing machine:
2) Spectrophotometer:

In this experiments Reactive dye, (Hot brand, Cold-brand & FNR series) dyeing with 2% shade with different Concentration of hardness of water i.e. 20ppm, 200ppm, 500ppm, 1000ppm, 1500ppm, 2000ppm and same condition like time, temperature and PH.

**Method**
Dyeing was carried out using exhaust method of dyeing on Rota dye machine.

**Parameters of RFD fabric:**
1. Absorbency : 3 Sec
2. Whiteness: 67.12
3. pH: 6 to 6.5

Dyeing process
Dye dissolution: The required amount of dye is pasted with small amount of water and addition of warm water to complete dissolution of dye. Then the solution was made to required volume (which is required for stock solution). When dye is completely soluble form it is check by spotting on filter paper.

Dyeing: Dye baths were set with required amount of dyes solution and water as per material to liquor ratio (MLR) of 1:30. Fabric samples were introduced into bath at room temperature. Dyeing is started at Room temperature. Then after 10 minutes gluaber’s salt of 80 g/l was added and run for 10 more minutes at 60°C. Then 20 g/l soda ash was added and dyeing was carried out at 60°C for 60 min. After complete fixation the dyed samples were washed, neutralized and soaped.

Sequence of dyeing (FNR series reactive dye)
Fabric is loaded at RT with Dye and water
Run at RT for 10 min
Salt addition
Run at 60°C for 10 min
Soda addition
Run at 60°C for 60 min
Washing
Neutralization
Soaking
Cold Wash
Dry fabric

Evaluation of dyed samples: Dyed samples were evaluated for K/S and color difference values using spectrophotometer.

III. RESULTS AND DISCUSSION
Table 1: Colour Strength and K/S values of samples dyed with Novacron Yellow F4G in presence of water having different hardness.

<table>
<thead>
<tr>
<th>Water Hardness in PPM</th>
<th>DL*</th>
<th>Da*</th>
<th>Db*</th>
<th>De*</th>
<th>DH*</th>
<th>DE*</th>
<th>%Strength</th>
<th>K/S</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>100</td>
<td>11.2</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>200</td>
<td>0.25</td>
<td>0.09</td>
<td>-1.30</td>
<td>-1.30</td>
<td>-0.01</td>
<td>1.33</td>
<td>97.84</td>
<td>9.9</td>
</tr>
<tr>
<td>500</td>
<td>0.32</td>
<td>-0.67</td>
<td>-2.49</td>
<td>-2.44</td>
<td>0.83</td>
<td>2.60</td>
<td>95.93</td>
<td>9.6</td>
</tr>
<tr>
<td>1000</td>
<td>0.24</td>
<td>0.65</td>
<td>1.52</td>
<td>1.49</td>
<td>0.73</td>
<td>1.67</td>
<td>93.25</td>
<td>9.3</td>
</tr>
<tr>
<td>1500</td>
<td>0.58</td>
<td>0.13</td>
<td>-0.25</td>
<td>0.26</td>
<td>-0.11</td>
<td>0.65</td>
<td>89.16</td>
<td>8.7</td>
</tr>
<tr>
<td>2000</td>
<td>1.04</td>
<td>-0.39</td>
<td>-2.23</td>
<td>-2.20</td>
<td>0.50</td>
<td>2.49</td>
<td>83.27</td>
<td>7.8</td>
</tr>
</tbody>
</table>

Figure 1: Effect of Water Hardness on Dyeing with Novacron Yellow F4G
Cotton knitted fabric samples were dyed with Novacron Yellow F4G and the results are shown in Table 1 and presented in Figure 1. From Table 1, it was observed that as water hardness increased, the colour strength and K/S values decreased. At water hardness of 2000 ppm, the colour strength decreased to about 83%. At higher water hardness, the decrease in colour strength and K/S values may be due to the detrimental effect of heavy metal salts on dyeing. The metal salts may be reacted with the reactive dye and inhibit the exhaustion and fixation of dye.
Table 2: Colour Strength and K/S values of samples dyed with Novacron Red FNR in presence of water having different hardness.

<table>
<thead>
<tr>
<th>Water Hardness in PPM</th>
<th>DL*</th>
<th>Da*</th>
<th>Db*</th>
<th>Dc*</th>
<th>DH*</th>
<th>DE*</th>
<th>%Strength</th>
<th>K/S</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>0.23</td>
<td>0.10</td>
<td>-0.36</td>
<td>0.12</td>
<td>-0.36</td>
<td>0.44</td>
<td>98.55</td>
<td>9.9</td>
</tr>
<tr>
<td>200</td>
<td>0.68</td>
<td>0.14</td>
<td>-0.24</td>
<td>0.16</td>
<td>-0.23</td>
<td>0.74</td>
<td>95.12</td>
<td>9.6</td>
</tr>
<tr>
<td>500</td>
<td>0.89</td>
<td>-0.45</td>
<td>-4.85</td>
<td>-4.82</td>
<td>0.72</td>
<td>4.95</td>
<td>88.54</td>
<td>8.0</td>
</tr>
<tr>
<td>1000</td>
<td>0.67</td>
<td>-0.11</td>
<td>-1.91</td>
<td>0.21</td>
<td>0.21</td>
<td>2.06</td>
<td>86.56</td>
<td>7.8</td>
</tr>
<tr>
<td>1500</td>
<td>2.14</td>
<td>-0.83</td>
<td>0.14</td>
<td>-0.84</td>
<td>-0.84</td>
<td>2.31</td>
<td>84.51</td>
<td>7.5</td>
</tr>
<tr>
<td>2000</td>
<td>2.10</td>
<td>-1.10</td>
<td>0.85</td>
<td>1.25</td>
<td>0.96</td>
<td>2.21</td>
<td>85.12</td>
<td>7.7</td>
</tr>
</tbody>
</table>

Figure 2: Effect of Water Hardness on Dyeing with Novacron Red FNR

From Table 2, it was observed that as water hardness increased, the colour strength and K/s values decreased. At water hardness of 2000 ppm, the colour strength decreased to 84%. At higher water hardness, the decrease in colour strength and K/s values may be due to the detrimental effect of heavy metal salts on dyeing. The metal salts may be reacted with the reactive dye and inhibit the exhaustion and fixation of dye on the fabric.

Table 3: Colour Strength and K/S values of samples dyed with Novacron Blue FNR in presence of water having different hardness.

<table>
<thead>
<tr>
<th>Water Hardness in PPM</th>
<th>DL*</th>
<th>Da*</th>
<th>Db*</th>
<th>Dc*</th>
<th>DH*</th>
<th>DE*</th>
<th>%Strength</th>
<th>K/S</th>
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<td>-0.99</td>
<td>0.25</td>
<td>-0.25</td>
<td>-0.10</td>
<td>0.27</td>
<td>99.24</td>
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<tr>
<td>200</td>
<td>0.49</td>
<td>-0.04</td>
<td>-0.21</td>
<td>0.21</td>
<td>-0.03</td>
<td>0.54</td>
<td>96.74</td>
<td>8.9</td>
</tr>
<tr>
<td>500</td>
<td>0.86</td>
<td>-0.17</td>
<td>0.03</td>
<td>-0.03</td>
<td>-0.17</td>
<td>0.88</td>
<td>94.21</td>
<td>8.6</td>
</tr>
<tr>
<td>1000</td>
<td>1.56</td>
<td>-0.19</td>
<td>-0.14</td>
<td>0.15</td>
<td>-0.18</td>
<td>1.57</td>
<td>89.27</td>
<td>8.2</td>
</tr>
<tr>
<td>1500</td>
<td>2.10</td>
<td>-1.10</td>
<td>0.85</td>
<td>1.25</td>
<td>0.96</td>
<td>2.21</td>
<td>85.12</td>
<td>7.7</td>
</tr>
<tr>
<td>2000</td>
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<td></td>
<td></td>
<td></td>
<td></td>
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</tbody>
</table>
Figure 3: Effect of Water Hardness on Dyeing with Novacron blue FNR

Samples were dyed with RemazolNovacron Blue FNR and the results are shown in Table 3 and presented in Figure 3. From Table 3, it was observed that as water hardness increased, the colour strength and K/s values decreased. At water hardness of 2000 ppm, the colour strength decreased to 85%. At higher water hardness, the decrease in colour strength and K/s values may be due to the detrimental effect of heavy metal salts on dyeing. The metal salts may be reacted with the reactive dye and inhibit the exhaustion and fixation of dye on the fabric.

Table 4: Colour Strength and K/S values of samples dyed with Novacron Black R in presence of water having different hardness.

<table>
<thead>
<tr>
<th>Water Hardness in PPM</th>
<th>DL*</th>
<th>Da*</th>
<th>Db*</th>
<th>Dc*</th>
<th>DH*</th>
<th>DE*</th>
<th>%Strength</th>
<th>K/S</th>
</tr>
</thead>
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<tr>
<td>20</td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td>100</td>
<td>23</td>
</tr>
<tr>
<td>200</td>
<td>0.20</td>
<td>0.08</td>
<td>-0.14</td>
<td>0.16</td>
<td>-0.02</td>
<td>0.25</td>
<td>98.24</td>
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<tr>
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<td>-0.24</td>
<td>0.15</td>
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</tr>
<tr>
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<td>-0.32</td>
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<td>0.62</td>
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<tr>
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<td>0.61</td>
<td>-0.06</td>
<td>-0.49</td>
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<td>-0.33</td>
<td>0.78</td>
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<tr>
<td>2000</td>
<td>0.82</td>
<td>-0.71</td>
<td>-1.11</td>
<td>0.71</td>
<td>-0.95</td>
<td>1.21</td>
<td>89.15</td>
<td>21.1</td>
</tr>
</tbody>
</table>

Figure 4: Effect of Water Hardness on Dyeing with Novacron Black R

From Table 4, it was observed that as water hardness increased, the colour strength and K/s values decreased. At water hardness of 2000 ppm, the colour strength decreased to 89%. At higher water hardness, the decrease in
colour strength and K/s values may be due to the detrimental effect of heavy metal salts on dyeing. The metal salts may be reacted with the reactive dye and inhibit the exhaustion and fixation of dye on the fabric

Table 5: Colour Strength and K/S values of samples dyed with Remazol Yellow RGB in presence of water having different hardness.

<table>
<thead>
<tr>
<th>Water Hardness in PPM</th>
<th>DL*</th>
<th>Da*</th>
<th>Db*</th>
<th>Dc*</th>
<th>DH*</th>
<th>DE*</th>
<th>%Strength</th>
<th>K/S</th>
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</thead>
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<tr>
<td>20</td>
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<td>100</td>
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<tr>
<td>200</td>
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<td>-0.45</td>
<td>-0.49</td>
<td>0.02</td>
<td>0.58</td>
<td>97.21</td>
<td>9.1</td>
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<tr>
<td>500</td>
<td>0.21</td>
<td>-1.45</td>
<td>-1.47</td>
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<td>2.07</td>
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<td>-0.96</td>
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<td>1.58</td>
<td>91.39</td>
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<tr>
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</tr>
<tr>
<td>2000</td>
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<td>-1.48</td>
<td>-0.83</td>
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<td>1.09</td>
<td>2.04</td>
<td>86.37</td>
<td>8.1</td>
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</table>

Figure 5: Effect of Water Hardness on Dyeing with Remazol Yellow RGB

Cotton knitted fabric samples were dyed with Remazol Yellow RGB and the results are shown in Table 6. From Table 6, it was observed that as water hardness increased, the colour strength and K/s values decreased. At water hardness of 2000 ppm, the colour strength decreased to 86%. At higher water hardness, the decrease in colour strength and K/s values may be due to the detrimental effect of heavy metal salts on dyeing. The metal salts may be reacted with the reactive dye and inhibit the exhaustion and fixation of dye on the fabric

Table 6: Colour Strength and K/S values of samples dyed with Turquoise Sky Blue G in presence of water having different hardness.

<table>
<thead>
<tr>
<th>Water Hardness in PPM</th>
<th>DL*</th>
<th>Da*</th>
<th>Db*</th>
<th>Dc*</th>
<th>DH*</th>
<th>DE*</th>
<th>%Strength</th>
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<td>0.23</td>
<td>-0.47</td>
<td>1.45</td>
<td>90.27</td>
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<tr>
<td>1000</td>
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<td>2.58</td>
<td>84.15</td>
<td>10.4</td>
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<tr>
<td>1500</td>
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<td>0.36</td>
<td>-0.26</td>
<td>-1.24</td>
<td>2.79</td>
<td>82.39</td>
<td>10.1</td>
</tr>
<tr>
<td>2000</td>
<td>3.12</td>
<td>-1.04</td>
<td>0.19</td>
<td>-0.13</td>
<td>-1.05</td>
<td>3.30</td>
<td>78.53</td>
<td>9.7</td>
</tr>
</tbody>
</table>
Table 6 shows the effect of water hardness on dyeing of cotton knitted fabric samples with Novacron Orange FNR. From Table 6 and Figure 6, it was observed that the same trend was noticed as earlier dyeing. However, in this case the decrease in colour values are higher than the other shades. This may be due to the higher sensitivity of Turquoise Sky Blue G dye with hard water.

IV. CONCLUSION

Water hardness has detrimental effect on dyeing of textiles. In the case of all shade studied, as the water hardness increases the strength of sample decreases. For different shade, the effect of water hardness was different. This may be due to varying affinity of water the dyes with cotton material. The hardness of water is one the most important factors which affect the dyeing process and cause the shade variation problem. Thus for all the dyeing with reactive dyes, one should use soft water or add sequestering to get better results. The effect of hardness of water varies with the type of reactive dye used for dyeing. Some dyes are more sensitive and some are low sensitive towards the hardness of water.

V. ACKNOWLEDGEMENT

Wish to give my sincere gratitude to PSSGL Dyeing Industries plant situated at Shirpur (Dyeing Unit) for giving me a golden opportunity for this research work, the undersigned is thankful to Centre for Textile Functions, MPSTME, Shirpur, for their invaluable guidance and support throughout the project.

V. REFERENCES

8. R.S. PRAYAG by Bleaching, Mercerising and Dyeing of cotton materials.