Alternative reducing system for dyeing of cotton with sulphur dyes

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An attempt has been made to replace sodium sulphide by reducing sugar, obtained by acid hydrolysis of molasses, in dyeing of cotton with sulphur dyes. The results of dyeing using reducing sugar in alkaline condition have been compared with those of the conventional dyeing with sodium sulphide. It is observed that the depth of shade, expressed as K/S value, is deeper in case of dyeing with reducing sugar than in conventional dyeing.

Keywords: Cotton, Dyeing, Molasses, Reducing sugar, Sulphur dye

1 Introduction

One of the major challenges is the production of textiles using product and application techniques with minimum danger to ecology. Among the various dyes, though the reactive dyes are predominant for cotton dyeing, the sulphur dyes, because of their low dyeing-cost and being free from heavy metals and adsorbable organic halogen, are used considerably, especially for navy blue and black shades. The worldwide consumption of sulphur dyes in terms of quantity is more than 1,00,000 tons per annum.

90% of all the sulphur dyes are still reduced by means of sodium sulphide. A part of the total sodium sulphide is consumed during dyeing and the rest stays in waste water, eventually acting as a contaminant. Sodium sulphide causes no marked odour nuisance above pH 9 but in acidic pH, the gaseous hydrogen sulphide is set free. This is recognizable by its odour of rotten eggs and is toxic when inhaled. Its odour threshold value is 10 ppm (ref. 1).

To eliminate these problems, other reducing agents have been studied and reported in the literature. Sodium hydrosulphite is the most satisfactory reducing agent for vat dyes but it is of minor importance for application of sulphur dyes. It often causes over-reduction, which reduces affinity to fibre, and destruction of certain sulphur dyes. In addition, the dyebaths at temperatures above 80°C lack the necessary stability. Mercaptoethanol can also be used as a reducing agent for sulphur dyeing, for both exhaust as well as one bath-pad-steam process. The yield is slightly poor than that in sulphide but acceptable. However, the dyeing method is costly and does not give complete dissolution for a whole range of dyes².

Hydroxy acetone fails to develop the full colour yield when used in conjunction with pad-steam process. Reducing agents such as sodium borohydride, thiglycolic acid and hydroxymethane sulphonic acid are difficult to use because of the handling problem, inadequate cost effectiveness and poor efficiency¹.

Glucose has long been known as a reducing agent for sulphur dyes. In exhaust dyeing, however, glucose at first gave unsatisfactory result, especially in open dyeing machines like jigger and winch. This is because the dye yield was highly dependent on temperature. Only at a constant temperature (above 90°C), acceptable results were obtained³.

Lokhane et al.² studied dyeing of jute fabric with sulphur dye using laboratory grade glucose. The amounts of sodium sulphide and glucose (along with an equal weight of sodium hydroxide) were taken on the basis of the weight of the dyestuff. In case of 2% shade of C.I. Sulphur Blue 11, it was observed that as the amount of sodium sulphide increased in dyebath, the colour value (in terms of K/S) reached to maximum rather slowly. However, in case of dyeing using glucose, the colour value increased rapidly and the final colour yield was higher as compared to that in sodium sulphide system. In case of C.I. Sulphur Black 1 at 8% shade, both the reducing agents showed increasing trend in the colour value with the increase in the quantity of reducing agent used in dyebath. However, the increase was rapid in case of glucose as compared to that in case of sodium sulphide⁴.

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Laga attempted to replace sodium sulphide by liquid jaggery during dyeing of jute fabric with sulphur dyes. It was found that the liquid jaggery (2.5 times of the weight of the dyestuff) was sufficient to reduce dye completely. Also, it was found that the K/S values of fabric dyed with various sulphur dyes using liquid jaggery were comparable with those obtained using sodium sulphide. Liquid jaggery was prepared by treating commercial jaggery with 0.04% citric acid for 24 h at room temperature.

Among the sulphur dyes, the sulphur black is an important dye on account of its low cost along with its excellent washing and light fastness. But the Central Pollution Control Board prescribes a limit of not more than 2 ppm sulphide in the treated mill effluents. Though glucose gives satisfactory results, the high cost of pure glucose might impose practical constraint. Therefore, the attempts were made in the Century Textiles and Industries Ltd, Mumbai, to substitute sulphide by liquid glucose, a byproduct of starch industry, procured at a competitive price. The commercial trials at Century mill indicated that in sulphur black dyeing, 100 parts of sodium sulphide (50%) can be replaced by 61 parts of liquid glucose (80% solid) plus 26 parts of caustic soda. This option was found to provide a cost-effective substitution of sodium sulphide. Furthermore, no capital expenditure is required in this substitution.

The present study is focussed on the use of reducing sugar obtained by the acid hydrolysis of molasses (a byproduct of sugar industry) as an alternative of sodium sulphide during dyeing of cotton with sulphur dyes.

India is one of the largest producers of sugar in the world. During the last stage of sugar manufacturing process, sugar gets crystallized, leaving behind thick and dark brown syrup known as molasses. It contains about 60% total sugar including glucose, fructose and sucrose. Among these, glucose and fructose are reducing in nature whereas sucrose is non-reducing. Molasses has great industrial importance but in India, only a part of it is utilized for alcohol production, as a cattle feed and as compost in agriculture and the large part is thrown away as waste in effluent. Sucrose from molasses can be hydrolyzed by hydrochloric acid where it gets converted to glucose and fructose.

2 Materials and Methods
2.1 Materials
Commercially available bleached and unfinished cotton poplin fabric having the following specifications was used for the study: weight, 120 g/m²; warp count, 40; weft count, 36; ends/in, 104; and picks/in, 80.

Sulphur Black, Sulphur Dark Crimson, Sulphur Ultramarine Blue, Sulphur Sky Blue and Sulphur Khaki R, obtained from Radiant Dyes, Mumbai, were used.

Molasses as a raw material to obtain reducing sugar, hydrochloric acid, acetic acid, sodium hydroxide flakes, sodium carbonate, sodium sulphide, hydrogen peroxide (30%), copper sulphate, sodium potassium tartrate, common salt and indicator grade methylene blue dye were used for the study.

2.2 Methods
2.2.1 Preparation of Reducing Sugar
The main composition of molasses is sucrose, glucose, fructose and water. The non-reducing sugar (sucrose) was converted into reducing sugar (glucose and fructose) by acid hydrolysis. The molasses sample (25g) was diluted with hydrochloric acid solution (25 ml). The amount of hydrochloric acid in the solution was taken on the basis of percentage of weight of molasses. The hydrolysis of sucrose was carried out at 90°C for 45 min in a water bath. The total reducing sugar content in hydrolyzed molasses was determined by Lane and Eynon method where Fehling's solution is titrated against hydrolyzed molasses using methylene blue as an indicator.

2.2.2 Dyeing
The required amount of dyestuff was mixed with a pinch of soda ash and little water. About 50 ml of warm water was then poured and the required amount of sodium sulphide or reducing sugar was added. The dye solution was kept at 70°C for 15 min for complete reduction of dye.

The sample was introduced into the dye bath at 50°C after diluting the dyebath solution to a required volume by water. The temperature was raised to boil and after 15 min common salt (40 g/L) was added, keeping the material-to-liquor ratio at 1:30. The dyeing was continued for another 45 min at boil. After dyeing, the sample was subjected to cold rinse. Oxidation was carried out with 0.5% H₂O₂ (30% w/v) at 70°C for 15 min at acidic pH using 2 g/L acetic acid. Then cold wash was given followed by soaking with 2 g/L non-ionic soap (Lissapol N) at boil. Finally, the sample was washed thoroughly with cold water and dried.
2.2.3 Tests

Colour yield in terms of the K/S values of dyed samples was determined by using UV-visible spectrophotometer (Perkin-Elmer).

The redox potential of reducing agents was measured using oxidation reduction potential electrode connected to pH meter.

Wash fastness test was carried out according to ISO 3 method. Dry and wet rub fastness tests were carried out by using Shirley Crock Meter for 10 cycles.

3 Results and Discussion

3.1 Hydrolysis of Molasses

Molasses contain water, sugars, non-sugars and inorganic constituents. Among the sugars, glucose and fructose are the reducing sugars whereas sucrose is the non-reducing sugar, which is converted into reducing sugar on acid hydrolysis.

In molasses, there is continuous degradation of sugar, which leads to the formation of organic acids. Because of the degradation of sucrose, there is reduction in the total sugar content in molasses on storage. Table 1 shows the composition of molasses used in present study to obtain reducing sugar for sulphur dyeing and Fig.1 shows the effect of HCl concentration on the extent of hydrolysis of molasses. It is observed that the reducing sugar percentage in molasses increases with the increase in acid concentration up to 2.5 - 3 % and there after it decreases with further increase in acid concentration. At 3 % acid concentration, the maximum reducing sugar was obtained with 98 % conversion. Beyond 3 % acid concentration, the degradation of reducing sugar starts, as indicated by the loss in reducing sugar percentage in hydrolysed syrup and darkening of its colour. Therefore, to get the maximum reducing sugar without the danger of degradation, 2.5% acid concentration was considered optimum. At this concentration, some fluctuation in treatment time and temperature at higher level does not cause any adverse effect.

Fungi and other micro-organism can easily be developed on reducing sugar as it is a food material for them. The growth of micro-organisms can be restricted by using 0.1 % sodium benzoate. As the storage stability of reducing sugar is sensitive to pH, it can be stored for a long time at pH 2-3. At neutral and alkaline or at highly acidic pH levels, it gets degraded into acidic products with darkening of colour.

Table 1 — Composition of molasses

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Content, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Moisture</td>
<td>23</td>
</tr>
<tr>
<td>Original reducing sugar</td>
<td>18</td>
</tr>
<tr>
<td>Original sucrose</td>
<td>24</td>
</tr>
<tr>
<td>Total sugar content</td>
<td>42</td>
</tr>
<tr>
<td>pH</td>
<td>4.65</td>
</tr>
</tbody>
</table>

Fig. 1 — Effect of HCl concentration on hydrolysis of molasses

3.2 Redox Potential of Reducing Agents

In dyeing, the optimized concentration of reducing sugar is 2.5 g/L with an equal amount of sodium hydroxide, as discussed in subsequent section. For a comparative study, the same concentration of sodium sulphide was taken to determine redox potential. It is observed that the redox potential increases with the increase in temperature (Fig. 2)

Redox potential of 2.5 g/L commercial sodium sulphide steadily increases with the increase in temperature and at 70°C it was little above -600 mV which was sufficient to reduce sulphur dye within 20 min. On the contrary, the reducing sugar showed steep rise in reduction potential after 50°C, and at 70°C it gave redox potential more than -700 mV at which sulphur dye is readily reduced.

3.3 Dyeing of Cotton with Sulphur Dyes

Cotton samples were dyed with Sulphur Black in 5% shade. Fig.3 shows a comparison of the dyeings of
Fig. 2—Effect of temperature on redox potential of reducing sugar and sodium sulphide

![Graph showing effect of temperature on redox potential.]

Fig. 3—K/S values of samples dyed with Sulphur Black

![Graph showing K/S values.]

Table 2—Comparative colour yield on cotton

<table>
<thead>
<tr>
<th>Dye</th>
<th>K/S Sodium sulphide</th>
<th>K/S Reducing sugar</th>
<th>Δa*</th>
<th>Δb*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sulphur Black</td>
<td>16.73</td>
<td>17.80</td>
<td>-0.10</td>
<td>0.53</td>
</tr>
<tr>
<td>Radiant Sulphur</td>
<td>12.85</td>
<td>13.18</td>
<td>-0.09</td>
<td>-0.02</td>
</tr>
<tr>
<td>Ultramarine Blue</td>
<td>10.81</td>
<td>11.33</td>
<td>-0.63</td>
<td>0.44</td>
</tr>
<tr>
<td>Radiant Sulphur Sky</td>
<td>5.23</td>
<td>6.02</td>
<td>-0.04</td>
<td>-0.68</td>
</tr>
<tr>
<td>Khaki R</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Radiant Sulphur Dark</td>
<td>6.47</td>
<td>6.57</td>
<td>-0.64</td>
<td>-0.12</td>
</tr>
</tbody>
</table>

Sulphur Black using sodium sulphide and reducing sugar as reducing agents. The amounts of sodium sulphide and reducing sugar were taken on the basis of multiple of weight of dyestuff. In case of reducing sugar, an equal amount of sodium hydroxide was used. It is observed that as the amount of sodium sulphide increases in dyebath, the colour value (K/S) increases rather slowly and it gives maximum dye uptake when the amount is 2.5 times the weight of dyestuff. However, in the case of reducing sugar, the colour value increases rapidly giving maximum dark shades when 1.5 times reducing sugar is used. For both the reducing agents, as the amount increases beyond the optimum, the colour value decreases. It may be due to the over reduction of dye.

By using the above optimized conditions for the amount of reducing agents in Sulphur Black dyeing, the cotton samples were dyed with few more sulphur dyes in 5% shade. The dyed samples were tested for colour value in terms of K/S, and for tonal difference in terms of Δa* and Δb*, keeping the samples dyed with sodium sulphide as standard. It can be seen from Table 2 that the dye uptake for reducing sugar is comparable to that for sodium sulphide. However, the samples show little tonal variation. The Δa* values for all the samples were found to be negative which indicates that the non-conventional reducing system gives greener tone when compared to conventional system. The negative Δb* values indicate tonal shift towards bluer side, except for Sulphur Black and Radiant Sulphur Sky Blue dyes which have yellower tone, as indicated by their positive Δb* values, when dyed with reducing sugar.

3.4 Fastness Properties of Dyed Cotton

Wash fastness test was carried out according to ISO 3 test and the samples were assessed for change in colour and staining. Dry and wet rub fastness tests were carried out by using Shirley Crock meter for 10 cycles and the samples were assessed for change in colour and staining using grey scale.

It has been observed that the use of hydrolyzied molasses for reduction of sulphur dye did not alter the wash fastness and crock fastness values of dyed samples.
4 Conclusion

Sodium sulphide, hazardous to health and to environment, can be successfully replaced by reducing sugar, obtained by acid hydrolysis of sucrose present in molasses, in dyeing of cotton. Reducing sugar gives higher dye uptake than sodium sulphide when used as a reducing agent for sulphur dyeing. The fastness properties of the sample dyed with reducing sugar are comparable with those of the sample dyed using sodium sulphide.

References