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IMPROVEMENT IN BLEACHING AND NONUNIFORMITY OF DYEING OF PAKISTANI INDIGENOUS WOOL

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Dyeing of medullated keratins such as Pakistan's indigenous wools may lead to nonuniformity on account of several factors. Studies have been carried out on overcoming this drawback by subjecting the wool to several pretreatments with such chemicals as bleaching agents. Thus, in addition to certain effective measures for overcoming the nonuniformity of dyeing, bleaching characteristics of these wools have also been studied.

INTRODUCTION

Pakistan's indigenous wool is one of the typical types of carpet wool and is suitable not only for carpet manufacturing, but also for blankets, apparel cloth etc. The dyeing of this wool may, however, result in nonuniform shades on account of various reasons, the major ones having been identified as below: (i) Medullation: The medullated fibres may not dye to the same shades equivalent to those of true fibres. Incidentally, kemps are rare in these wools. (ii) Weathering: Due to excessive heat in the summer, the tips become 'weathered' and take heavier shades of dye.

The phenomenon of 'tippiness'; as known in the art is ascribed to differential dyeing characteristics of the tip versus root. The major reason for this behaviour has recently been identified as weathering [1–3].

The present studies aim at overcoming the non-uniformity by pretreatment with several suitable chemicals. For this purpose, it is well-known in the art that bleaching treatments improve the dye-uptake of the wool fibres. For the present investigations, therefore, the indigenous wolls were first subjected to an investigation of their bleaching characteristics, employing several agents such as those for oxidative and reductive bleaching and their combinations; peracetic and performic acids and chlorinated compounds. The investigation was then followed by an examination of the dyeing characteristics employing samples pretreated with the bleaching agents. The dyes employed belonged to acid (good equalising as well as milling), chrome, premetallised and reactive groups.

One of the objectives of the investigation was to reduce time of treatment required for bleaching operations, at present causing slow progress in processing.

MATERIALS AND METHODS

Wool. A typical fleece of Hashtnagri breed was first skirted and then thoroughly blended. The wool was scoured [4] with nonionic detergent (Neolan salt) at 40–50°.

Hydrogen Peroxide Bleaching. Bleaching [5]: The scoured wool was treated with 2–3 g/l of tetrasodium pyrophosphate ($Na_4P_2O_7$), 20–40 ml, hydrogen peroxide (30% vol), 5–2 ml/l ammonia (25%) at pH 9, 46–49°, for 2 hr, at room temperature for overnight. In all the bleaching experiments the liquor–goods ratio was maintained at 50:1.

Quantitative Determination of Hydrogen Peroxide [6]: The remaining quantity of hydrogen peroxide in the bath was determined with $N/10$ potasium permangnate.

Peracetic Acid Bleaching [7]: Bleaching: The bath consisted of 0.75 ml/l hydrogen peroxide (35%) and 1.05 ml/l acctic anhydride, adjusted to pH 8 with sodium hydroxide. and the treatment was carried out at room temperature for 5 min. Then 1 g/l tetrasodium pyrophosphate was added and pH adjusted to 5.5 with acetic acid. The bleaching was continued at 20° for ½ hr.
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Quantitative Determination of Peracetic Acid [8]: The remaining quantity of peracetic acid in the bath was determined with $N/10$ sodium thiosulphate sol.

Performic Acid Bleaching [9]. 5–30 ml/l hydrogenperoxide (35%), 1–6 g/l Lufibrol W, 0.1 g/l Nekanil LN, heated at 80° for ½ hr.

Reductive Bleaching [10]. The scoured wool was treated with 3 g/l of Blankit II A at 50° for 2 hr.

Combination Bleaching. The wool bleached by the oxidative process as above was treated with 3 g/l Blankit II A at 50° for 2 hr.

Chlorination in Alkali Medium [11]. The wool was treated with 39% sodium hypochlorite (2–3% active chlorine on the wt. of goods) and 0.5 g/l solid sodium hydroxide (pH 9–10). The treatment was started at 20°, raised to 30–35°, and was continued at this temperature for hr.

Chlorination in Acid Medium [12]. Chlorination was carried out with sodium hypochlorite, adjusting pH at 3 with hydrochloric acid.

Dyeing. Acid Dye [13]: The dye bath consisted of 2% dye (Corcein Scarlet 3RS), 4% sulphuric acid (concd) and 10% sodium sulphate based on the wt. of fibre. In order to avoid unevenness in dyeing, the temperature of the dye bath was raised slowly to boiling, which was continued for 1 hr.

Chrome Dye [14]. The dye bath consisted of 2% of Solochrome Green, 4% acetic acid and 10% sodium sulphate. Boiled for 1 hr, squeezed and boiled in fresh bath with 1% potasium dichromate for ½ hr.

Premetallised Acid Dye [12]. The dye bath consisted of 2% Neolan Orange, 5% sulphuric acid, 2% Neolan salt and 20% sodium sulphate. Heated to boiling slowly and the boiling was continued for 1½ hr.

Reactive Dye [16]. The dye bath consisted of 2% dye (Cibalan Brilliant Yellow) and 1% acetic acid (80%) which ensures the maintenance of pH around 6. The bath was heated to about 50° and the material was worked for 10 min. The temperature was raised to boil within 15–45 min and dyeing continued at this temperature for 30 min.

Dye Uptake [17]. The whiteness grade and dye uptake of the dyed fibres were determined with a leukometer (Dr. Burno Lange, GmbH, Berlin) using red, green and blue filters. The dye uptake was claculated from the percentage reflectance of the liquor after dyeing. Normally, measurements were made by comparing a known percentage of standard white for which the reflectance of the measuring instrument was adjusted to the nominal value of the standard. The intensity of colour of the specimen under test was then read off as a percentage of the whiteness of the standard.

Uniformity in Dyeing. A panel of 10 different persons was employed to judge the uniformity of dyeing visually. Each member allotted a score to each sample, the maximum score being 10. Average score of each sample was then worked out.

Alkali Solubility [18]. The damage was determined by the DIN 54281, involving alkali-solubility score.

RESULTS AND DISCUSSION

Hydrogen Peroxide Bleaching. Table 1 gives the results for hydrogen peroxide bleaching of indigenous wools, wherein the quantity of the stabilizer, sodium pyrophosphate, has been changed from 1 to 5 g/l. The Table shows that the 3 g/l concentration of sodium pyrophosphate gives better results as compared to the other two concentrations.

The Table also gives results for combination bleaching for this case, as well as reductive bleaching and the control sample for comparison.

Table 2 gives further results for hydrogen peroxide bleaching, wherein the concentration of sodium pyrophosphate has been kept constant at 3 g/l (based on the results of Table 1) but that of hydrogen peroxide has been varied

Table 1. Effect of tetrasodium pyrophosphate concentration on the whiteness grade, remaining quantity of hydrogen peroxide, and alkali solubility of wool.

Con of tetra-sodium pyrophos-phate (g/l)	Bath I oxidative bleaching			Bath II Combination bleaching (oxidative + reductive)	
	Remaining quantity of H_2O_2 (%)	Whiteness grade (%)	Alkali solubility (%)	Whiteness grade (%)	Alkali solubility (%)
1	75.8	71.45	20.4	73.32	23.5
3	84.9	72.32	21.3	74.15	24.6
5	89.8	72.13	21.5	74.23	24.4
Unbleached scoured wool	–	65.23	12.8	–	–
Reductive Bleaching	–	72.14	13.3	–	–

Table 2. Effect of hydrogen peroxide concentration on the whiteness grade, remaining quantity of hydrogen peroxide and alkali solubility of wool (Concn of sodium pyrophosphate 3 g/l in all cases).

Hydrogen-peroxide concn (ml/l)	Bath I oxidative bleaching			Bath II Combination bleaching (oxidative + reductive)	
	Remaining quantity of H_2O_2 (%)	Whiteness grade (%)	Alkali solubility (%)	Whiteness grade (%)	Alkali solubility (%)
20	89.13	70.30	19.5	73.2	22.5
30	84.6	72.35	21.3	75.23	24.1
40	91.2	71.25	28.7	73.35	31.8
50	90.5	71.30	29.6	74.5	32.6
Unbleached scoured wool	–	65.23	12.8	–	–
Reductive Bleaching	–	72.14	13.3	–	–

Table 3. Effect of hydrogen peroxide and Lufibrol W's concentration on whiteness grade and alkali solubility in the performic acid bleaching at different temperatures and for different intervals.

Concn of hydrogen peroxide (ml/l)	Concn of Lufibrol W (g/l)	Bath I oxidative bleaching				Bath II oxidative + reductive	
		Temp (^oC)	Time hr	Whiteness grade (%)	Alk. Sol. (%)	Whiteness grade (%)	Alk. Sol. (%)
5	1	80	½	69.3	15.3	72.5	17.3
5	2	80	½	71.5	14.9	74.6	16.2
10	1	80	½	71.2	15.7	74.6	16.8
30	6	80	½	72.4	15.6	75.65	16.8
5	1	Room temp	24	70.2	15.98	74.65	17.8
30	6	90	20 min	72.6	16.4	75.8	18.5
30	6	100	10 min	72.3	16.9	75.4	18.3
Unbleached scoured wool				65.23	12.8		
Reductive bleaching				72.14	13.3		

from 20 to 50 ml/l. The results show that the relative concentration of hydrogen peroxide in the given range has little effect on the whiteness grade. Moreover, for concentrations of 30 ml/l or more, the quantity of used up hydrogen peroxide is about the same. On the other hand, the alkali solubility increases from 21.3% for the case of 30 ml/l to 29.6% for the case of 50 ml/l hydrogen peroxide. This shows an excessive damage for concentrations beyond 30 ml/l. Keeping all these factors in view, it may be said that the concentrations of 30 ml/l of hydrogen peroxide is about the optimum, beyond which improvement in whiteness grade is doubtful, rather there is unnecessary wastage of hydrogen peroxide as well as excessive damage to the material.

Performic Acid. Table 3 gives the results for performic acid bleaching under different conditions. The most promising feature of the results is that the alkali damage is the least in comparison to the other bleaching agents, although the whiteness grade obtained is comparable with that of hydrogen peroxide. The method also is the quickest, which is generally carried out for half-an-hour only. In view of the small alkali damage, enhanced conditions, i.e. higher temperatures and shorter periods of treatment were also tried and it was found that the treatment can be carried out even within 10 min employing a temperature of 100^o. However, the combination of 30 ml/l hydrogen peroxide and 6 g/l Lufibrol, at 80^o for ½ hr may be considered to be the optimum treatment. In general, it was observed that while employing higher temperature, time interval should be reduced, otherwise there is increased damage and im-

Table 4. The effect of peracetic acid (by changing the concentration of hydrogen preoxide, acetic anhydride, time and temperature) on whiteness grade and alkali solubility of bleached wool.

Concn of H_2O_2 (ml/l)	Concn of acetic anhy-dride (ml/l)	Remaining quantity of peracetic acid (%)	Temp (°C)	Time (hr)	Bath I. Oxidative bleaching		Bath II Oxidetive + reductive	
					Whiteness grade (%)	Alk. sol. (%)	Whiteness grade (%)	Alk. sol. (%)
1	1.05	80	20	½	69.3	21.3	72.5	22.8
1	2	77	20	½	70.2	23.2	73.3	24.2
2	1.05	68.1	20	½	70.6	21.5	73.8	23.2
1	1.05	–	20	2	70.3	36.3	74.1	38.2
1	2	–	20	2	71.2	39.2	74.2	39.5
1	2	–	20	2	70.8	40.6	73.6	42.6
1	1.05	–	85	½	72.6	53.5	75.8	55.5
Unbleached scoured wool					65.23	12.8		
Reductive bleaching					72.14	13.3		

Table 5. Dyeing of pretreated samples.

Pretreatment	Dye	Dye uptake (%)	Uniformity	Fastness	
				Washing	Light
Without pretreatment	Crocein Scarlet	95	8/10	3–4	5–6
Sodium hypochlorite	,,	98	8/10	3–4	5–6
Performic acid	,,	96	9/10	3–4	5–6
Peracetic acid	,,	97	9/10	3–4	5–6
Without pretreatment	Solochrome Green	90	7/10	4–5	5–6
Sodium hypochlorite	,,	98	6/10	4–5	5–6
Performic acid	,,	95	8/10	4–5	5–6
Peracetic acid	,,	95	8/10	4–5	5–6
Without pretreatment	Neolan Orange	88	6/10	5	6–7
Sodium hypochlorite	,,	97	6/10	5	6–7
Performic acid	,,	92	7/10	5	6–7
Peracetic acid	,,	93	8/10	5	6–7
Without pretreatment	Cibalan	91	7/10	4–5	6–7
Sodium Hypochlorite	Brillant Yellow	98	7/10	4–5	6–7
Performic acid	,,	92	8/10	4–5	6–7
Peracetic acid	,,	93	9/10	4–5	6–7

provement in whiteness grade is negligible.

Peracetic Acid Bleaching. The results for peracetic acid bleaching have been given in Table 4. The treatment yields usual whiteness grades for 20° and short intervals up to ½ hr. However, increments in the temperature or time of treatment result in excessive damage with little or no improvement in the whiteness grade.

Reductive and Combination Bleaching. Results for reductive and combination bleaching have been incorporated in all the above Tables. In each case, whiteness grade was considerably improved when the wool bleached with the oxidative agent was subsequently bleached with the reductive agent as well. In the case of reductive bleaching alone, it was observed that the whiteness obtained was less stable in comparison to the case of combination bleaching. It may be concluded that combination bleaching is the most effective treatment in all the cases and the optimum cases with high whiteness grades and small damage may well be adopted for practical purposes.

Control of Nonuniformity of Dyeing. Table 5 gives the results for the uniformity in dyeing of Pakistani indigenous wool. The good equalising acid dye showed good results. The dye can be used even without pretreatment of the wool but the fastness properties are poor as compared to other classes of wool dyes.

By using other classes of dyes, i.e. Chrome, 1:1 complex dyes and reactive dyes in the case of this wool with large percentage of medullated fibre, there was considerable improvement for the pretreated samples in comparison to the untreated samples in general.

In the case of pretreatment of wool with the chlorinated compound both in the acid and alkali media, the dye uptake increased (Table 5), but the uniformity in dyeing is only slightly improved.

In the case of peracetic acid pretreatment, the uniformity in dyeing was considerably improved at the risk of some damage to wool. At high temperature the wool was considerably damaged as is also the case in Table 4 in which at 85° the alkali solubility is 53.5 as compared to 31.3 at 20°. Increasing the concentration of acetic anhydride in the peracetic acid bleaching, increases wool damage marginally. On the other hand, as pointed out above, increasing the time of treatment seems to cause more extensive damage. Generally, the alkali solubility in bleaching should not increase beyond 30%.

In the case of performic acid pretreatment, the uniformity in dyeing improved to a better level than in the cases for other pretreatments and unpretreated wool, but the improvement was of a smaller order than that in the case of peracetic acid pretreatment. However, the damage was the least in the case of performic acid pretreatment.

In Table 5 the dye uptake considerably improved in the case of all the pretreatments, but the uniformity in dyeing is not directly proportional to the dye uptake.

By pretreatment, the fastness properties, i.e. washing and light fastness were practically not affected.

The non-uniformity in dyeing, the so-called 'tippy dyeing', of carpet wool is due to many reasons. One of the reasons is that the tip of the staple behaves differently to that of the rest of the fibre as regards absorption of the dye. It has been found that tippiness is also caused by the damage due to weathering [1]. It has been recently observed [2] that tippiness increases in the autumn clip in comparison to the spring clip. This may be due to the fact that the autumn clip is subjected to severe conditions, i.e. increased exposure to sunlight etc. Another cause of tippiness is the more rapid rate of growth of the coarse or hairy fibres, which results in the staple having a pointed tip The damaged tips show a deficiency or a total loss of scales [3] and these are more readily wetted out and swell to a greater degree in the dye bath than do the undamaged portions of the fibres, with the result that the tip portions of the fibre are heavily dyed as compared to the rest of the fibre.

Conclusions

Bleaching. A comparison of different methods available for bleaching of wool has revealed that: (i) The combination bleaching (oxidative + reductive) is the most effective method. The whiteness grade is improved by about 3% in comparison to that achieved by oxidative bleaching alone and the damage caused is not excessive. The method may be adopted for high bleaching levels, wherever feasible. (ii) Among the oxidative bleaching agents results with performic acid were the best. The whiteness grade achieved was the highest among this group, the damage was the least and the time of treatment was the shortest (½ hr at 80°). Furthermore, if the treatment is carried out at the boil (100°), the time is reduced to 10 min only. (iii) Peracetic acid bleaching gives a comparable whiteness grade only at the risk of damage. (iv) Hydrogen peroxide bleaching yields average results with a concentration of 3 g/l sodium pyrophosphate and 30 ml/l hydrogen peroxide. The damage in this case is acceptable.

Uniformity. (i) In general, pretreatment with bleaching agents improves uniformity of dyeing of indigenous wools. The best results are obtained with peracetic and performic acid. (ii) It was, however, found that good equalising dyes and 1:2 complex acid dyes yielded reasonably satisfactory results even without any pretreatment. By treatment with chlorinated compounds, the dye uptake increases but the uniformity in dyeing is not necessarily improved.

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