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Comparative Analysis of Two Selective Bleaching Methods on Alpaca Fibers

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Abstract: Dark brown Alpaca fiber was reduced in shade via selective bleaching with peroxide. Two selective oxidative bleaching methods were tested on alpaca top to assess their effectiveness for color removal and fiber quality properties. Color change, bundle strength, weight loss, fiber diameter, surface modification, dye-ability and dye wash fastness were assessed for both methods and compared with the original brown top. Bleach method 1 (BL-I) showed little surface modification, 5.8 % weight loss and 2.4 % strength loss. D1925 yellowness index was reduced to 74.3 from 83.1 and provided a good base for the dyeing of medium to deep shades. Bleach method 2 (BL-II) displayed considerable surface modification, 7.8 % weight loss and 18 % strength loss. BL-II also resulted in a mean diameter reduction of 1.9 micron during bleaching. Yellowness was reduced to 64.5 from 83.1 and provided a very good base for the dyeing of medium to deep shades. BL-I showed better exhaustion of the pre-metallised dye Lanaset Violet B than BL-II. Wash fastness for BL-II was 1 grey scale unit poorer than BL-I. BL-II showed far better color clarity at pale depths however the wash fastness of the finished product was not good enough to maintain the depth or clarity of the color. BL-I showed poorer clarity of color but exhibited better wash fastness results.

Keywords: Bleaching, Dyeing, Alpaca fiber, Color, Yellowness, Hydrogen peroxide

Introduction

Alpaca fibers are produced in a wide range of natural colors, which may provide a natural alternative to dyed fibers [1]. However, the uneven color varieties and limited fiber quantity have been the major barriers to the development of an alpaca fiber industry in Australia. Textile manufacturers pay a premium for white or non-colored alpaca fibers while the colored alpaca fibers attract a large discount in the market place. The bulk of the Australian alpaca clip has a brown to dark brown color, which attracts discount at present. White fiber provides processors with dyeing flexibility and allows for pastel shade dyeing however dark pigmented fibers restrict the dyeing of bright pale or medium shades. Bleaching is a potential solution to 'lighten' the color so that bright colored textile articles can be produced from these brown alpaca fibers.

The bleaching agent commonly used is Hydrogen peroxide (H_2O_2). Its oxidation mechanism is reviewed in detail in literature [2,3]. During oxidizing reaction, H_2O_2 is converted into the perhydroxy species (HO_2^-), which is responsible for bleaching. Since the HO_2^- ion is relatively unstable and easily forms molecular oxygen (O_2), which escapes from the bleach solution reducing the bleaching effect [4], a stabilizer is often added to the bleaching bath. A stabilizer, such as tetra sodium pyrophosphate (TSPP), enhances the stability of the bleaching species in the bleach bath and inhibits the wasteful breakdown of perhydroxy ion to yield molecular oxygen [2,3]. Additionally, the rate of decomposition of H_2O_2 rises with increases in temperature and pH, as does the rate of bleaching [2].

Hydrogen peroxide is commonly used because it is a liquid, odorless, easily manageable and available in convenient and safe forms [3]. However, it does cause damage to the fiber [3,5]. The damage arises from attack on amino acids in the keratin fiber, particularly cystine which is converted into cysteic acid [2]. Thereby oxidative bleach reagents rupture the disulphide bonds [2], crosslinking components of proteins and possibly the polypeptide chains [3]. This damage can lead to adverse effects on the fibers mechanical properties.

The pigmented fibers, such as alpaca and karakul wool, require a specific mordant bleaching process, if the dark melanin pigment is to be removed [2]. An efficient pigment bleaching with minimum fiber damage is provided by the use of metal catalysts in mordanting step preceding peroxide bleaching [5]. Because the electron density of native melanin is higher than that of keratin, the metal cations are preferably absorbed by the melanin. Iron (II) salts are commonly used as a mordant. The presence of iron II ions in the melanin pigment causes hydrogen peroxide to undergo radical conversion to form the perhydroxy anions. This increase in the number of radicals and their location, next to the melanin, brings about a more complete disruption of the melanin polymer [2].

Rinsing following the mordanting step proved to be critical with regard to fiber damage [2,5]. The rinsing step is to remove excess iron from the keratin fiber matrix which is not bound to a melanin pigment. If excess iron is present in the fiber then over bleaching occurs throughout the whole fiber rather than at the pigment source causing a reduction in fiber strength.

A wetting agent added to the bleach bath will help with the

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penetration of the bleach chemicals into fiber structure. Penetration is essential as the pigment is contained inside the fiber structure as well as on the fiber surface [5,6]. The wetting agent also assists in the removal of air from the fiber bundle so that water penetrates into all fibers in the fiber bundle. The benefit of detergents in the bleach bath is to maintain any particles and /or soiling, removed from the fiber, in suspension. Detergents also assist in the wetting of the fiber as its structure is similar to that of a wetting agent.

Research has been carried out on bleaching effects on karakul cashmere and colored wool [2,5,7]. However reference for bleaching alpaca fiber is currently inadequate. In this study, we selected two oxidative bleaching methods for trial on alpaca top to assess their effectiveness in color removal and effect on fiber properties.

Experimental

Bleaching

A Theis Ecobloc LFA pressure package dyeing machine (capacity of 20 liters) was used for bleaching. The liquor ratio was set at 20:1. A dark brown alpaca top was selected as the trial fiber. The fiber was split up into three groups. One group remained as a control (Unbleached) while the other two groups (1.0 kg for each) were treated using two selective oxidative bleaching methods respectively. Process methods and recipes for bleach methods I and II are listed as follows:

Bleach I - Modified Conventional Ferrous Mordant System

Mordanting: Fill the bath with cold water and add: ferrous sulphate ($FeSO_4 \cdot 7H_2O$) –8.0 g/*l*, formic acid (HCOOH) –1.0 m*l*/*l* and ascorbic acid ($C_{12}H_{18}O_{11}$) –4.0 g/*l*, check bath pH of 3.4. The bath is then heated to 80 °C at 3.0 °C/min and held for 60 minutes before being drained.

Rinsing: Refill the bath and heat to 80 °C at 3.0 °C/min, hold for 20 minutes; drain and refill again, overflow rinse for 10 minutes and drain.

Bleaching: Refill the bath and add: Imerol XNA (Clariant) –1.0 g/*l*, tetra sodium pyrophosphate (TSPP) –2.0 g/*l*, then check bath pH of 6.7. Add hydrogen peroxide (H_2O_2) –14.0 g/*l* and heat bath to 68 °C at 3.0 °C/min and hold 80 minutes then drain. Refill and rinse at 50 °C for 10 minutes and drain. Fill and heat the bath to 40 °C, and add oxalic acid (HOOCCOOH $\cdot$ 2(H_2O)) –3.0 g/*l*; then heat bath to 70 °C and hold for 20 minutes. Warm rinse at 50 °C for 10minutes.

Bleach II - Radical Ferrous Mordant System [7]

Mordanting: Fill the bath with cold water and add: ferrous sulphate ($FeSO_4 \cdot 7H_2O$) –10.0 g/*l*, formic acid (HCOOH) –6.0 m*l*/*l* and Cibaflow CIR (Ciba Specialty Chemicals) –0.5 g/*l*, check bath pH of 2.9. The bath was then heated to 80 °C at 3.0 °C/min and held for 60 minutes before being drained.

Rinsing: Refill the bath and add formic acid (HCOOH) –4 g/*l*, and heat to 80 °C at 3.0 °C/min, hold for 20 minutes and cool to 70 °C; drain and fill again, rinse at 50 °C for 10 minutes and repeat rinse at same condition once.

Bleaching: Fill the bath and add: hydrogen peroxide (H_2O_2) –28.0 g/*l*, tetra sodium pyrophosphate (TSPP) –10.0 g/*l*, oxalic acid (HOOCCOOH $\cdot$ 2(H_2O)) –4 g/*l*, sodium carbonate (Na_2CO_3) –5 g/*l*, and Cibaflow CIR –0.5 g/*l*. Adjust pH for above solution to 8.3 with ammonia solution, then heat bath to 70 °C at 3.0 °C/min and hold 50 minutes. Fill and rinse at 50 °C for 10 minutes and drain, and repeat rinse.

(Note: BL-I, BL-II and UnBL will be short for Bleach method I, Bleach method II and Unbleached respectively.)

Top Dyeing and Wash Fastness Testing

To compare the dyeing ability of bleached alpaca tops, the standard dyeing system given in the CIBA Specialty Chemicals- Lanaset pattern card [8] was used. The pre-metallised dye - Lanaset Violet B was dyed at three different concentrations given below (Table 1). Dye exhaustion was calculated based on a calibration line obtained from dye solutions of known concentrations. Wash fastness was assessed after dyeing according to the IWS standard TM 193.

Fiber Physical Properties Measurement

Moisture regain analysis was conducted on the bleached and unbleached alpaca tops using a CSIRO direct reading regain tester. Five tests were conducted within 24 hours. Each of the groups was sub-sampled and measured for fiber diameter using an Optical Fiber Diameter Analyser (OFDA 100) according to AS 4492.5-2000. Fiber weight loss was calculated by weighing oven dried samples before and after bleaching.

Bundle strength testing was performed according to ASTM standard 1294 using a Lloyd LR30K tensile tester. The Color Index was obtained for the treated and untreated top with a spectrophotometer- Spectraflash 600 PLUS-CT. A field

Table 1. Different dyeing levels of Violet B

Color depth	Bleach I	Bleach II	Violet B
	Sample No.		
Pale	1	2	+ 0.1 %
Medium	3	4	+ 0.8 %
Deep	5	6	+ 3.0 %

emission gun scanning electron microscope (LEO-1530) was used to examine the fiber surface profiles of the bleached and unbleached tops.

Results and Discussion

Differences of Bleach Method I and II

Differences between the two bleaching methods are listed in Table 2. The concentration of H_2O_2 of bleach method I is half of that in Method II. Therefore, the level of perhydroxy species in the bleaching bath of system I is less than that in system II. The differences of time and pH setting in the two bleaching baths have caused a portion of the difference in bleach results. The main areas that have been affected are the fiber properties such as strength, color and diameter.

Table 2. Differences between two bleach methods

Process		BL-I	BL-II
Mordant		√	√
Rinse	+ HCOOH	√	√ +
Bleach-	Stabiliser	÷	÷
	pH control	÷	÷
	Detergent	÷	×
	Wetting agent	×	÷
	H_2O_2	√ (1/2)	√ (1)
	Oxalic Acid	×	÷
After rinse	+ Oxalic Acid	√	×
Bleach temperature		68 °C	70 °C
pH		6.7	8.3
Relative chemical cost (at liquor ratio of 20:1)		1	1.4

× chemical or step not included, √ chemical or step included

Color Change after Bleaching

The hydrogen peroxide bleaching of the brown alpaca fiber reduced the depth of shade and improved the chromaticity of the fiber. As shown in Table 3, the D1925 yellowness index is reduced to 74.3 and 64.5 from 83.1 in the case of BL-I and BL-II respectively. These results indicate that both bleached tops provide a good base for the dyeing of medium to deep shades. The lower the yellowness or whiteness index, the better the color of the dyed fabric [2,9].

Changes of Fiber Mechanical Properties

Since the volume of H_2O_2 used in bleach method II was double that in method I, the more severe bleaching can lead to more damage to the fibers. Table 4 shows that the bundle strength of BL-II top was reduced significantly by 18.0 % whereas BL-I was only reduced by 2.4 %. Fiber extension is reduced more for BL-II than that of BL-I. These results

Table 3. Whiteness, yellowness index and tristimulus values

Top	Whiteness CIE	Yellowness D1925	X	Y	Z
UnBL	−148.9	83.1	5.95	5.34	3.00
BL-I	−140.5	74.3	18.98	18.48	9.96
BL-II	−117.5	64.5	32.65	32.80	19.48

Table 4. Bundle strengths of bleached and unbleached alpaca top

Top	Stress (N/Ktex)	Strain %	Weight loss %
UnBL	88.9^a	38.0^a	
BL-I	86.7^a	18.4^b	5.8
BL-II	72.9^b	11.9^c	7.8

-Means with different superscripts in columns are significantly different

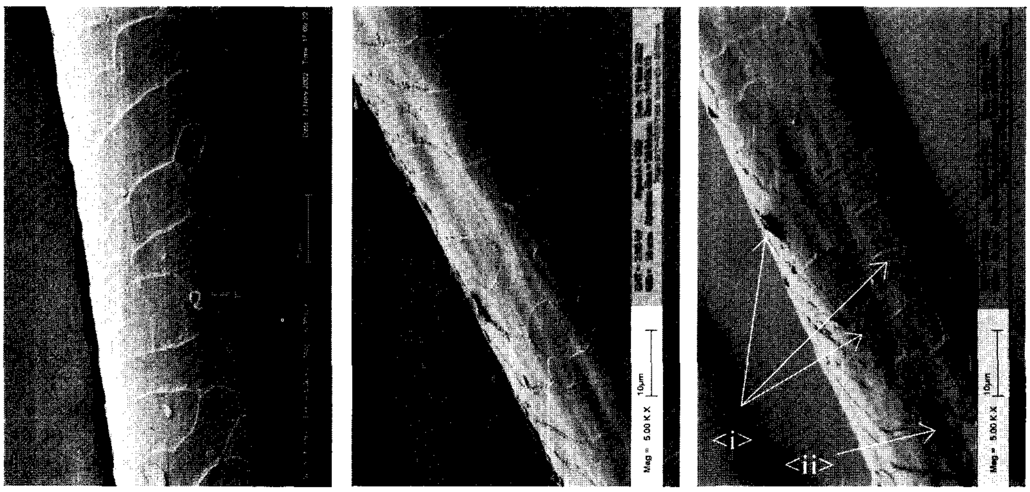

Figure 1. Surface modification after bleaching (UnBL → BL-I → BL-II).

should be attributable to damage/changes of the keratin matrix. Fiber weight is also reduced during bleaching, the more severe the bleaching, the higher the loss of fiber weight. Oxalic Acid was used in the final rinse bath of BL-I to remove any iron deposits that are still present in the fiber. Iron still present in the fiber before dyeing can reduce the wet and rub fastness properties of the dyed fiber.

Modification of Fiber Surface and Fiber Diameter

BL-I showed little surface modification (Figure 1), scales mostly remained. However, considerable surface modification can be seen in the BL-II fiber image. Scales were stripping off from the fiber trunk and edges were removed (Figure 1 <i>). Such changes may result in a smooth surface, but may also affect fiber cohesion during yarn processing. The fiber is also shriveled as shown in Figure 1 <ii>. BL-II resulted in a mean diameter reduction of 1.9 microns during bleaching, while BL-I only gave a 0.5 micron reduction (Table 5). Prickle factor of two bleached tops is remarkably improved. If the strength losses are within the tolerances of the fiber diameter change then the reduction of fiber diameter would be a benefit of method BL-II. A reduction in fiber diameter allows for the production of a finer yarn or a coarse yarn with improved evenness.

Dyeing Ability and Wash Fastness after Bleaching

In the comparison of dye-ability, BL-II displayed a far better color clarity at pale to deep depths (Figure 2). However the subsequent wash fastness of the finished product was 1 grey scale unit on average poorer than BL-I (Table 6), and the dyed top did not maintain the depth or clarity of the color after laundering. Scale removal may also improve dyeing rate because of the reduction of the surface barrier effect [10], however the dye can easily migrate out of the fiber during subsequent laundering. BL-II also had reduced dye exhaustion (Table 7), which may be due to more cysteic acid residues formed when the fiber disulphide bond was broken during oxidizing [3,7]. The cysteic acid may repel the negative ions of the dye and reducing dye exhaustion. BL-I showed better exhaustion of pre-metallised dye CI Violet blue than BL-II. BL-I also showed poorer clarity of color but exhibited better wash fastness results.

Table 5. Fiber diameter (FD) measurement for bleached and unbleached top

Top	Mean FD (μm)	SD of FD (μm)	CV of FD (%)	Prickle factor (%)
UnBL	29.0^{a}	8.2^{a}	28.2^{a}	41.4^{a}
BL-I	28.5^{b}	7.9^{b}	27.8^{b}	38.9^{b}
BL-II	27.1^{c}	7.6^{c}	27.9^{ab}	30.3^{c}

-Means with different superscripts in columns are significantly different.

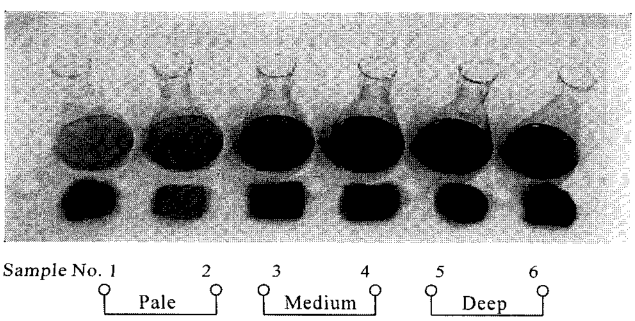

Figure 2. Comparisons of dyeing ability after bleaching.

Table 6. Wash fastness testing for bleached/dyed samples (Color change and staining were assessed separately after dyeing using grey scales)

Color depth	Pale		Medium		Deep	
Sample No.	1	2	3	4	5	6
	BL-I	BL-II	BL-I	BL-II	BL-I	BL-II
Color change: Grey scale	3	2	4	3	4	4
Stain fabric	BL-I	BL-II	BL-I	BL-II	BL-I	BL-II
Acetate	5	5	4/5	4/5	5	4
Cotton	5	5	5	4/5	4/5	4
Nylon 6.6	5	4/5	4	3/4	4	4
Polyester	5	4/5	4/5	4/5	4	3/4
Acrylic	5	4/5	5	4/5	4/5	4
Wool	4/5	4/5	4/5	4/5	4	3/4

Table 7. Dye exhaustion (%) calculation

Treatment	Violet B	Absorbance	Dye concentration in treated liquor (%w/w)	Dye exhaustion (%)
BL I	+ 0.1 %	0.384	0.052	48.4
	+ 0.8 %	0.606	0.128	84.0
	+ 3.0 %	1.166	0.322	89.3
BL-II	+ 0.1 %	0.308	0.058	41.8
	+ 0.8 %	0.534	0.136	83.0
	+ 3.0 %	1.293	0.398	86.7

Differences of Moisture Regain between Bleached and Unbleached Top

Fiber surface modification and scale removal can also result in changes of fiber moisture regain. Figure 3 shows that the bleached fiber is quicker to absorb water from the air in the first few hours after drying. The regain saturation values of the bleached fiber after 24 hours were not as large as that of the unbleached fiber. The changes in moisture concentration with time, $\partial c/\partial t$, is governed by Fick's Second Law [11].

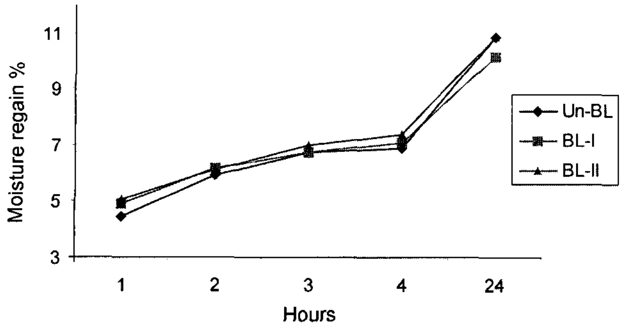

Figure 3. Moisture regain differences between bleached and unbleached top.

$$\frac{\partial c}{\partial t} = \partial\left(\frac{D\partial c}{\partial x}\right)\partial x \tag{1}$$

Where ∂x is the thickness of the fiber, and D is the diffusion coefficient of the water through the fiber materials. In the case of animal fibers with scales, the diffusion coefficient will be different from the fibre surface to the fiber interior, and any modifications to the fiber surface and interior will change the diffusion coefficient, and hence the moisture concentration in the fiber. A removal or break down of the scale structure by the bleaching process could aid this change. The reduced regain saturation values could be attributed to a reduction of the polar groups in the bleached fibers. Moisture is attracted to the polar groups present in the alpaca fiber. A reduction of these groups would result in a reduction of the regain saturation value for the fiber. This phenomenon would affect moisture content of the top during further processing and handling of finished products. By subjectively assessing the tactile sensation, using multiple assessors, the effect of static electricity was observed to be noticeably reduced in the bleached top. It is supported by the research work of Johari *et al.* [12], that the increase in moisture regain causes a reduction in electrical resistance of fibers, hence static electricity.

Conclusions

Both bleach methods provide a good base for dyeing alpaca fiber into a more attractive medium or deep shades. These shades will enhance the value of dark colored alpaca. Modified conventional bleaching (BL-I) led to a good finished product that retained the handle and strength of the untreated brown alpaca fibers. This method resulted in less damage and should be used where retaining the properties of the alpaca fiber is important. The radical selective bleaching (BL-II) gave some quite radical changes to the handle and lustre. This led to a significant reduction in both color depth and fiber micron resulting in a whiter and finer alpaca fiber. Due to the reduced use of chemicals and energy in BL-I the cost of processing should be lower than that of BL-II. Color reduction in pigmented fibers may be more important than fiber damage [2], moderate losses in strength can be offset by the advantages the bleached fiber attributes to the yarn. To make BL-II more attractive future work needs to be conducted to investigate dye fixation.

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