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Effects of Bleaching and Dyeing on the Quality of Alpaca Tops and Yarns

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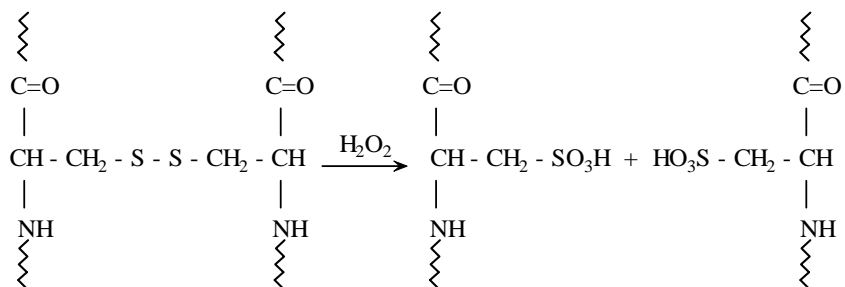
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Abstract: This paper reports the effects of bleaching of alpaca tops and dyeing of bleached alpaca tops/yarns on the quality of tops and yarns. A dark brown alpaca top was bleached with hydrogen peroxide. Two bleaching methods were trialled for effectiveness of color removal. A portion of each bleached top was dyed after bleaching. Color parameters were examined for unbleached, bleached and bleached/dyed tops, these tops were then converted into yarns of different twist levels and counts using a worsted spinning system. Some of the bleached yarn from each bleaching method was dyed in a package dye vat to compare the effects of top dyeing and package dyeing on the yarn quality. Fiber diameter, yarn strength, yarn evenness and hairiness and fiber degradation were tested to examine the effects of bleaching and dyeing on these properties at top and yarn stages. A processing route for bleaching and dyeing alpaca fiber was recommended.

Keyword: Bleach, Dyeing, Alpaca fiber and yarn, Color, Fiber degradation or damage

Introduction

Alpaca fiber, like wool and other animal hair, contains a high amount of the amino-acid cystine, which provides disulfide crosslinks within and between the polypeptide chains [1-3]. The mechanical properties of fibers are highly dependent upon the number of disulfide crosslink present and their distribution [4]. The disulfide bonds or polypeptide chains are easily attacked by wet processing conditions such as: the bleaching reagents (either oxidative or reductive), high temperature and alkali treatment. For example, one cystine unit can be oxidized to form two cysteic acid residues [1, 5, 6]:



Methylene blue is a kind of basic dye containing three heterocyclic rings [2, 7]. It forms a salt with cysteic acid under weak acidic conditions. As the amount of cysteic acid of fiber increases, the absorbtion of methylene blue will also increase. Due to this the amount of cysteic acid present can be measured by treating the fiber samples in a solution of methylene blue. The absorbance of the finished liquor has a negative linear

relationship to the percentage of cysteic acid present [8]. Since the cysteic acid is the residue of cystine disintegration when the disulphide bond is broken under oxidation, high temperature or other chemical treatment, this index (Absorbance value) can be used to identify the fiber damage after bleaching and dyeing.

Fine animal fibers including alpaca consist of inner cortical cells and outer cuticle cells [3, 4]. Of particular interest to the dyer is the shape and nature of the outer layer (namely scale) of the fiber [2]. There are three sub-grouped layers of each cuticle: exocuticle, endocuticle and epicuticle [3, 4, 9, 10]. Exocuticle cells contain the major part of cystine amino-acids of the cuticle. The cystine acid present in the exocuticle is highly crosslinked to protect the fiber. The crosslinking also reduces dye penetration into the cortical cell. Endocuticle cells contain low cystine amino-acid. These cells are enzyme-digestible. The low cystine content makes the endocuticle more susceptible than the exocuticle to chemical attack. Epicuticle cells have a thin hydrophobic membrane, which is relatively chemically inert. This resistant membrane is the last part of the fiber to dissolve during treatment with reagents such as acids, alkalis, proteolytic enzymes and oxidizing or reducing agents[3].

Hydrogen peroxide (H_2O_2) is a widely used agent for the oxidative bleaching of wool and other pigmented animal fibers [1, 3-5, 11, 12]. Under alkaline conditions, H_2O_2 can effectively oxidizes cystine to cysteic acid residues [1, 3, 4], causing a cleavage of the disulfide bond. The exocuticle or epicuticle of each cuticle scale is an effective barrier to dye penetration. The breaking of disulfide crosslinks of the membrane during bleaching is believed to make it easier for dyes to penetrate the fiber and hence cause an accelerate dye uptake [4]. In addition to the oxidative treatment the presence of wetting and leveling agents in the dye bath also increase the extent of fiber swelling and so facilitate dye penetration. Some researchers have reported that the dyeing properties of mordant-bleached fiber such as Karakul wool are different from those of normal wool. In particular the uptake of acid dyes is slower, indicating the presence of a relatively large number of sulphonic acid groups in the modified wools [3].

Bleaching is chemically damaging to the fibers. Choosing optimum process conditions is essential to minimize damage [3, 4, 13-16]. In our previous study two selective bleaching methods were compared in detail for dark brown alpaca tops [17]. Results from the Radical Ferrous Mordant System (Bleach method II: BL-II) showed radical changes to the fiber surface morphology and inner protein matrix, and moderate losses of fiber strength. By comparison, the modified conventional bleaching system (Bleach method I: BL-I) resulted in less fiber damage and a better retention of fiber properties. Dye-ability was also different for the two bleached tops. BL-I top showed better dye exhaustion and wash fastness than BL-II top. Dyeing also further affects the quality of the bleached tops. Both bleaching and dyeing processes are complex, they involve the chemical reactions taken place between bleach agents, dyes, chemicals and fibers [2, 3, 5]. The chemical compounds generated from these reactions could affect the fiber properties, particularly mechanical properties.

There is a large degree of variation of color existing in the pigmented fibers, such as alpaca fiber, Karakul wool etc. Bleached and bleached/top dyed slivers need to have increased gillings before spinning to remove this variation of color. There was a change in the structure of the wool-dyeing industry during 1980-90s, with a trend away from the loose stock dye and worsted top dye to the late-stage coloration [3]. Yarn package dyeing provides the textile industry with an opportunity to color yarn at the latest

possible stage prior to fabric manufacture. This is of prime importance if the dyer is to respond rapidly to changes in fashion and consumer demands [3].

This paper is to further evaluate the bleaching methods developed for colored alpaca fiber. Yarn quality including evenness, strength and the number of yarn imperfections is important to the end-product quality. To investigate the effects of bleaching and dyeing on further processing and their end products, two selective bleaching methods [17] were used to bleach dark brown alpaca tops. Tops were processed into yarns, using a worsted spinning system, with different yarn counts and twist settings. The bleaching and dyeing effectiveness of the bleached fiber at top and yarn stages were also presented in this study.

Experimental

Bleaching dark brown tops

A dark brown alpaca top was selective bleached using two bleaching methods (*Bleach I - Modified Conventional Ferrous Mordant System [17], and Bleach II - Radical Ferrous Mordant System [11]*). The methods were fully described by Liu et al [17]. The main differences between the two bleach systems are the concentration of Hydrogen peroxide (H₂O₂) (The concentration of H₂O₂ of bleach method I is half of that in Method II), bleach chemicals, bleach time, bleach pH and rinsing process.

Yarn specifications and yarn and fiber property measurements

Dark brown alpaca top, two bleached tops and two bleached/top dyed tops were processed into yarns using a worsted spinning system. The yarn counts and twists have been listed in Table 1. A portion of each of the bleached yarns was yarn dyed after spinning. The same dyeing system and yarn parameters as top dyed yarn were applied to the yarn dyed after spinning.

Table 1. Yarn specifications

Yarn count (Tex)	Twist (Turns/m, tpm)	Twist factor ($\frac{tpm \times \sqrt{tex}}{100}$)
90.9	273	26.0
62.5	268	21.2
62.5	328	25.9
62.5	390	30.8
28.6	390	20.9
28.6	486	26.0
28.6	586	31.3

Yarn evenness (CV% of mass) and hairiness index were measured by a Zellweiger USTER[®] Tester 4 system. Results of yarn tenacity (cN/tex) and elongation (%) were obtained using an USTER[®] Tensorapid 3 according to ISO 2062 (1993). The testing clamp speed was set at 2000mm/min. Fiber diameter of each set of top and yarn was measured using an OFDA 100 according to AS 4492.5-2000. All tests above were carried out under the standard ambient conditions.

Abbreviations for top and yarn labels are as follows:

- 1) UnBL: unbleached top or yarn
- 2) BL-I: top or yarn from Bleach (method) I
- 3) BL-II: top or yarn from Bleach (method) II
- 4) BLI-top dyed: dyed top or yarn from BL-I at top stage
- 5) BLII-top dyed: dyed top or yarn from BL-II at top stage
- 6) BLI-yarn dyed: dyed yarn after spinning from BL-I top
- 7) BLII-yarn dyed: dyed yarn after spinning from BL-II top

Yarn preparation for dyeing

Yarns from BL-I and BL-II were package wound on disposable plastic dye centers ready for package dyeing. The packages were wound in a cheese form to a density of 320g/l.

Dyeing process for top and yarn

The pre-metallised dye - Lanaset BORDEAUX B (Ciba Specialty Chemicals) was used for top and yarn dyeing. The standard dyeing system given in the CIBA Specialty Chemicals- Lanaset pattern card [18] was adopted. The dyeing bath contained: 0.5% w/w Albeval FFA (Ciba Specialty Chemicals), 2.0g/l Acetic Acid Solution 60% (CH₃COOH), 1.0g/l Sodium Acetate (CH₃COONa), 5.0% w/w Sodium Sulphate (Na₂SO₄), 1.0% Albeval set (Ciba Specialty Chemicals), 3.0% Ingasol HTW New (Ciba Specialty Chemicals) and 3.0% Lanaset BORDEAUX B. The pH of the dye liquor was adjusted to 4.5-5.0. The bath was then heated to 70°C at 1°C/min. The bath was held at 70°C for 15 minutes before being raised to 98°C at 1°C/min. The bath was held at 98°C for 30 minutes before being cooled to 50°C at 1°C/min. The dyeing was rinsed for 5 minutes before being softened with 2.0% Mega soft Jet (Ciba Specialty Chemicals). The bath was held for 20 minutes at 40°C while the softener was applied.

The recipe and process were kept the same for both top and yarn dyeing.

Color measurement

The CIE L* (Lightness) and C* (Chromaticity) values of treated and unbleached tops and yarns were obtained using a Spectraflash 600 PLUS-CT spectrophotometer, under the standard illumination light D65. Yarns were wound on a cardboard base to a uniform density before the color was measured.

Fiber degradation test

A simple method for fiber degradation test was applied in this study. Details originated from Knott's work [8] are as follows:

Preparation of methylene blue solution

The pH 3.5 methylene blue solution contained 0.0365 mol/l sodium hydroxide (NaOH), 0.210 mol/l acetic acid (CH₃COOH), 0.64 g/l methylene blue and a drop of Albeval FFA (Ciba Specialty Chemicals). The pH was adjusted to 3.5 with extra sodium hydroxide.

Fiber treatment

Each unbleached, bleached and dyed alpaca top and yarn was cut into short lengths and weighed 0.5g as a test sample. Each sample was treated in a 5ml of methylene blue solution at a liquor ratio of 1:10 for 30 minutes at 40°C. The final liquor was set aside, the fibers were squeezed, rinsed in water and dried.

Measurement of absorbance

A bath was made up to a total volume of 500ml with 3ml of the methylene blue treatment and distilled water. The absorbance of remained methylene blue was then measured at a wavelength of 664nm using a Hach DR 4000 spectrophotometer.

Results and discussions

Fiber diameter changes

Table 2 shows that the mean fiber diameter decreases 4.8% and 8.0% for BL-I and BL-II respectively. Reduction up to 2.3 microns of BL-II was significant. This result is consistent with another trial for alpaca top [17]. Dyeing after bleaching does not affect fiber diameter for both bleach methods dyed at top or yarn stage. Bleached yarn package dyed at the yarn stage had better CV (%) of diameter than the others.

Table 2. Effect of bleaching and dyeing on fiber diameter (FD) of top and yarn

Fiber Properties	Untreated	Bleached top		Dyed yarn			
				Top Dyeing		Package dyeing	
		I	II	I	II	I	II
FD (µm)	28.9	27.5	26.6	27.8	26.5	27.4	26.6
CV (%)	27.7	28.9	28.2	28.2	28.1	26.6	26.1

Color differences of unbleached, bleached and dyed tops and yarns

Figures 1 and 2 show a comparison of the CIE L* and C* values of the alpaca top and yarn before and after bleaching, bleaching/top dyeing and bleaching/yarn dyeing stages. It can be seen that the lightness and purity of color (Chromaticity) of both bleached tops have been improved. As the base color of the bleached fiber is lighter, it has less impact on the dyed color. This allows for lighter shades to be obtained from the dark fiber without greatly affecting the hue of the dye. An improvement of the chromaticity of the BL-I fiber gives less influence on the chromaticity of the dyed product. As chromaticity values of the dye and fiber are subtractive, a low chromaticity value for the fiber will result in a dull dyed shade.

After dyeing BL-I had a reduced lightness and chromaticity improvement than that of BL-II. This can be explained by the deeper brown color of the base fiber having an influence on the depth and purity of shade. Alternatively, chemical modification during bleaching, which alters the number of basic groups in fibers, will also alter the level of dye uptake at saturation [4].

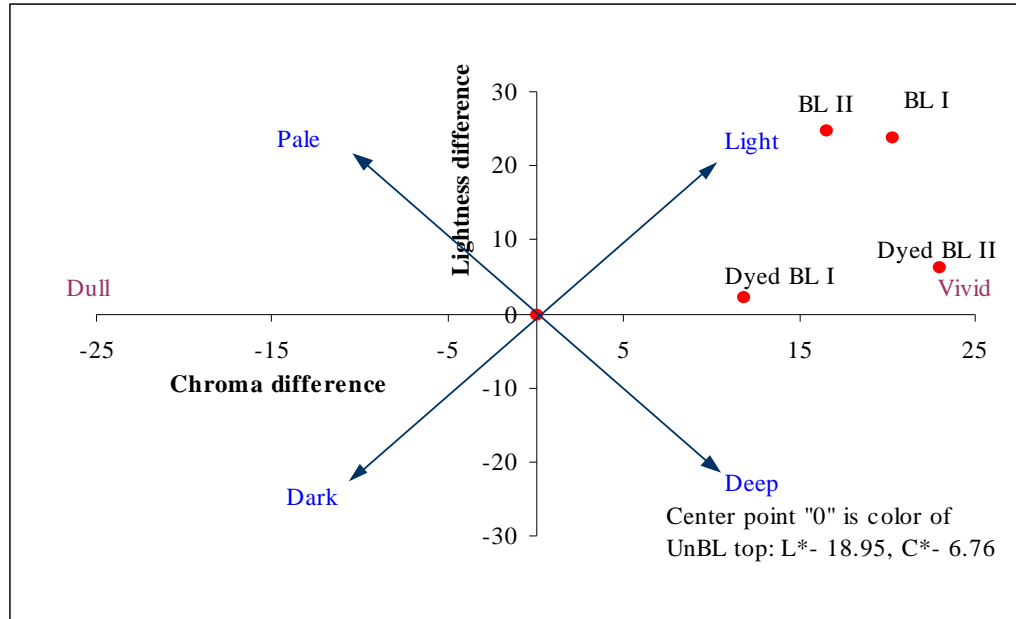


Figure 1. Color differences of unbleached, bleached and bleached/dyed tops

Figure 2 shows that there is little influence on the dyed color due to the processing path compared with Figure 1. Results were similar between the top dyed and yarn dyed routes. This allows the process to leave coloration until further down the processing stage to allow greater flexibility in production. BL-II top provides a lighter color base for dyeing both top and yarn to a more vivid extent than BL-I.

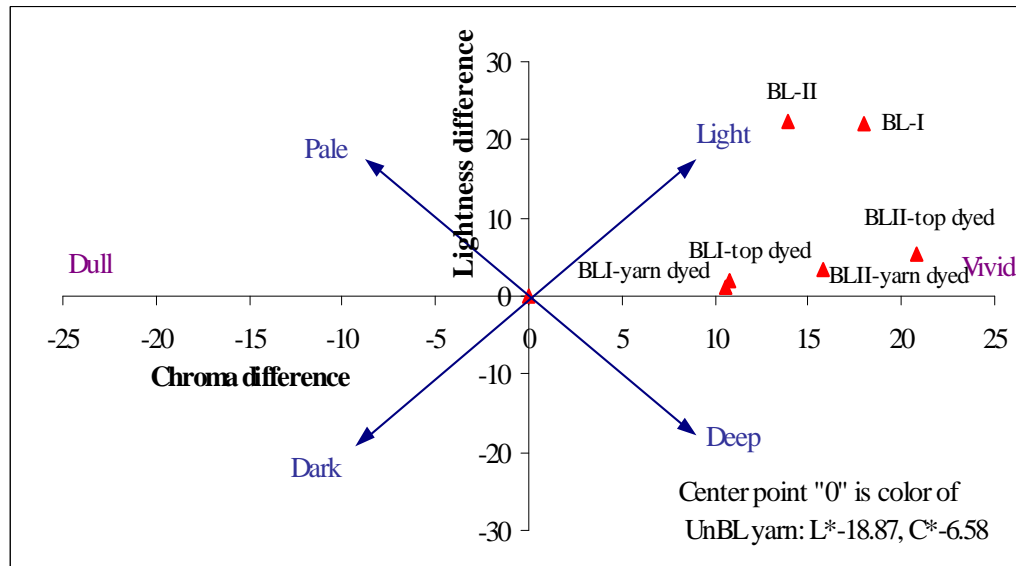


Figure 2. Color differences of unbleached yarn, top bleached and dyed yarn, and bleached top then package dyed yarn

Comparisons of yarn properties

Coarser yarn generally has better evenness (low CV% of mass) than finer yarn where the same fiber diameter is used (Table 3). There are slight differences of evenness between yarns from two bleached tops and two bleached/dyed tops respectively. There are no significant evenness differences found between the two bleach systems for yarns dyed at the yarn stage. Some yarns dyed at the yarn stage were more even than yarn dyed at the top stage. This is because top dyeing tends to increase the degree of fiber entanglement in the top. Entangled top leads to greater fiber breakage and unevenness of top during further processing. Strength loss also occurs during dyeing which results in an increase in fiber breakage during further processing.

Hairiness decreased from coarse yarn to fine yarn (Table 3). Hairiness values of the yarn from BL-II system are higher than that of BL-I for bleached, top-dyed yarn and bleached yarn-dyed yarn. This may be due to the reduced mean fiber diameter for the BL-II yarn which increases the average number of fibers in the yarn cross section. Previous studies have shown that the number of 'hairy ends' is closely related to the number of fibers in the yarn cross section [19, 20]. In addition, the increased fiber damage for the BL-II system may lead to increased fiber breakage during processing and reduced fiber length in the yarn, resulting in further increase in yarn hairiness. Hairiness of treated yarn either bleached or bleached/dyed increases significantly compared with untreated dark-brown yarn.

Table 3. Evenness and hairiness of dark-brown alpaca yarn comparing with bleached and bleached dyed yarns

Yarn count (in tex) / Twist (turns/m)	Parameters	DKBR-untreated	BL-I	BL-II	BLI-Top Dyed	BLII-Top Dyed	BLI-Yarn Dyed	BLII-Yarn Dyed
90.9 / 273	CV %	13.52	12.55	11.94	13.52	11.99	12.37	13.52
	Hairiness	3.90	6.66	8.53	4.79	8.36	5.60	8.14
62.5 / 268	CV %	15.64	14.36	14.93	17.80	15.16	15.28	15.20
	Hairiness	3.86	5.72	8.63	5.13	8.73	6.39	8.75
62.5 / 328	CV %	16.66	15.31	14.67	17.26	15.11	15.02	15.32
	Hairiness	3.52	5.91	7.28	4.42	7.47	5.01	7.14
62.5 / 390	CV %	16.23	16.08	15.03	16.48	15.21	14.49	14.84
	Hairiness	3.09	4.93	6.79	3.98	6.82	5.26	6.54
28.6 / 390	CV %	22.16	21.07	19.58	20.09	20.42	21.55	23.27
	Hairiness	2.82	4.25	5.90	3.28	6.13	4.54	6.46
28.6 / 486	CV %	21.8	22.26	21.17	20.90	21.50	21.39	19.95
	Hairiness	2.32	4.02	5.53	3.09	5.63	3.92	5.26
28.6 / 586	CV %	21.81	21.22	21.31	22.51	20.46	21.05	19.99
	Hairiness	2.28	3.81	5.08	2.84	5.26	3.48	4.77

For yarns with the same yarn count, the yarn tenacity and elongation increase with increasing twist (Table 4). With the same or similar twist factor (i.e. 26.0), tenacity decreases with a decrease of yarn count. Elongation also trends in the same direction. For yarns with the same count and twist, tenacity decreases after bleaching and dyeing

in most cases. Yarns from the bleach-II system have higher yarn strength and elongation than yarns from bleach-I system. The strength increase is mainly due to the reduction of fiber diameter of BL-II during bleaching (See Table 2). A reduction in fiber diameter causes an increase in the number of fibers in the yarn cross section. Such change causes an increase in the yarn strength.

After top bleaching, spinning and yarn dyeing, tenacity and elongation are higher than that of yarn spun from fiber that was bleached and dyed at the top stage. This result may be due to less fiber damage during the yarn package dyeing. Alternatively, low tenacity and elongation of top-dyed yarn may be caused by a reduction in length from fiber breakage during gillings before spinning. The differences in yarn tensile properties also resulted from the fiber degradation after bleaching and top dyeing.

Table 4. Yarn tenacity(cN/tex), break work (N.cm) and elongation (%)

Yarn count (in tex)- Twist (turns/m)	Parameters	DKBR- untreated	BL-I	BL-II	BLI- Top Dyed	BLII- Top Dyed	BLI- Yarn Dyed	BLII- Yarn Dyed
90.9 / 273	Tenacity	5.77	5.00	5.97	5.05	5.98	5.54	5.94
	B-work	20.77	5.04	12.52	3.59	9.73	4.68	13.44
	Elongation	9.13	3.1	5.57	2.72	4.61	3.09	6.08
62.5 / 268	Tenacity	4.15	3.47	4.54	2.07	3.60	4.05	4.73
	B-work	2.99	1.91	3.06	0.88	2.19	1.87	3.83
	Elongation	3.40	2.54	3.12	1.81	2.80	2.52	3.81
62.5 / 328	Tenacity	5.21	4.35	5.47	4.14	5.07	4.97	5.42
	B-work	6.89	2.59	6.06	1.99	3.88	2.73	5.61
	Elongation	5.56	2.81	4.64	2.45	3.57	2.89	4.63
62.5 / 390	Tenacity	6.40	4.85	5.58	4.72	5.26	5.09	6.01
	B-work	32.58	3.53	26.34	2.24	7.73	3.13	11.89
	Elongation	18.77	3.39	16.00	2.61	6.30	3.22	7.75
28.6 / 390	Tenacity	2.38	2.57	3.58	2.73	2.12	2.93	3.46
	B-work	0.59	0.56	1.14	0.48	0.43	0.51	0.86
	Elongation	2.89	2.00	2.83	1.75	1.86	1.78	2.49
28.6 / 486	Tenacity	3.65	3.47	3.98	3.13	3.16	3.91	5.00
	B-work	1.39	0.82	1.36	0.60	0.86	0.85	2.32
	Elongation	3.47	2.49	3.30	2.05	2.65	2.50	4.30
28.6 / 586	Tenacity	4.69	3.89	4.33	3.22	4.12	4.29	5.14
	B-work	4.22	1.07	2.26	0.67	1.89	1.05	3.53
	Elongation	7.27	2.77	4.73	2.12	4.27	2.71	5.79

Fiber degradation after bleaching and dyeing

Because there is a reverse relationship between absorbance of Methylene blue and the amount of Cysteic acid present in the fiber, the lower the absorbance value, the higher the degradation of the fiber. Bleaching and dyeing of the fiber using either bleach

method results in a degradation of the fiber (Figure 3). It can be seen that all the samples from BL-II had a higher level of fiber damage than BL-I. This is due to higher temperatures and chemical concentrations used in the bleaching step of the method [17]. There is no significant difference in fiber damage between bleached/top-dyed and bleached/yarn-dyed for each of the bleach methods. The practical consequences of damage to fiber during bleaching and dyeing can be seen as difficulties in spinning, such as excessive fly, increased end-breaks in spinning, decreased processing speeds, and lower yields, and /or as deleterious changes in strength, which are agreed with the previous study [21].

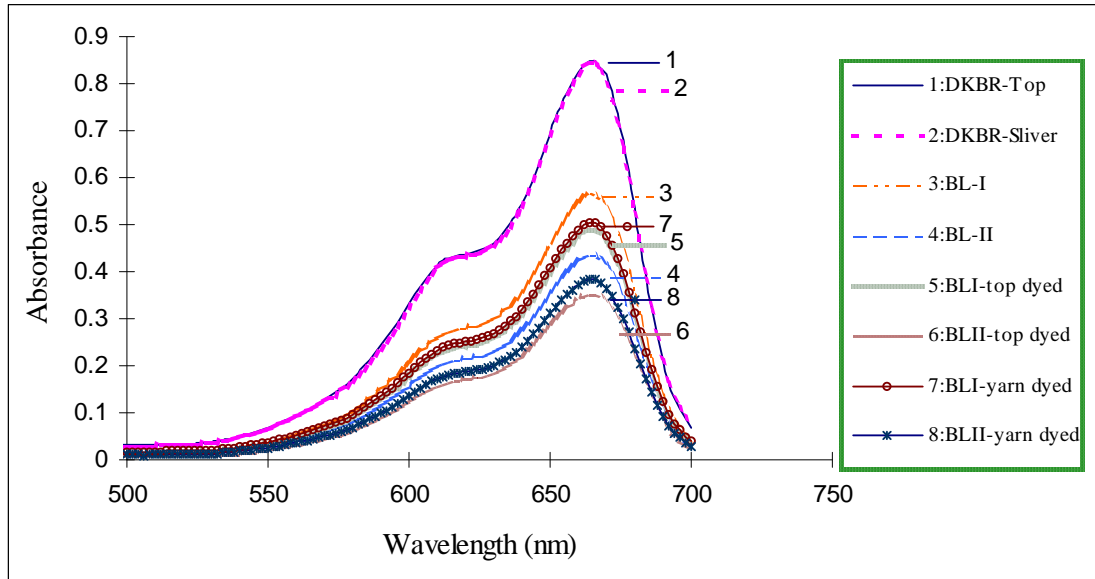


Figure 3. Absorbance of Methylene blue of different treated tops and yarns

Both of the bleach methods exhibit their own strengths and weaknesses when used in production. BL-I produces a fiber that has good yarn strength and handle properties however it suffers from duller dyed shades and poorer yarn evenness than that of BL-II. BL-II produces yarns with good evenness, strength and purity of color however hairiness and handle are sacrificed.

The best processing route is for a top bleached/yarn dyed product. Top bleaching/dyeing results in yarns of increased hairiness, decreased tenacity, decreased evenness and reduced elongation. All of these property changes are due to a reduction in fiber strength and an increase in fiber entanglement during the wet top processing stage. Further work needs to be investigated into the ability to yarn bleach and dye. This should remove the yarn property changes associated with wet processing and bleaching of tops. Unfortunately this process route would remove the benefits of yarn evenness produced by the fiber reduction of BL-II as the reduction would occur after spinning.

Conclusions

This study further evaluated the effectiveness of color removal of two bleaching methods, which were developed for colored alpaca fiber, and dyeing effects after bleaching on top and yarn quality.

Both bleaching methods improve the lightness and purity of color (Chromaticity) of the bleached tops. BL-I has a reduced lightness and chromaticity improvement than that of BL-II. Fibers of BL-I have less damage than BL-II. Bleaching and dyeing of the alpaca fiber causes a reduction in yarn tenacity and elongation. A 2.3 μ m reduction in fiber diameter after bleaching with BL-II caused an increase in the number of fibers in the cross section of the yarn. This resulted in an increase in the yarn strength and hairiness. The increased fiber damage recorded for BL-II also contributed to the higher level of hairiness of the bleached and bleached/ top dyed yarns. It is recommended from this study that a lower concentration of Hydrogen Peroxide (such as that used in BL-I) can be used to minimize fiber damage but still achieve a light color base for dyeing pigmented alpaca fiber. A top bleached/yarn dyed processing approach is recommended to reduce yarn strength and evenness problems associated with the top bleached/top dyed fiber.

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References

- 1 J. Cegarra and J. Gacén, *Wool Science Review*, **59** (9), 1-44 (1983).
- 2 J. Rivlin, *The Dyeing of Textile Fibres: Theory and Practice*, Copyright: Joseph Rivlin (1992)
- 3 D. M. Lewis ed., *Wool Dyeing*, Society of Dyers and Colourists (1992)
- 4 J. A. Maclaren and B. Milligan, *Wool Science: The Chemical Reactivity of the Wool Fibre*, Science Press (1981)
- 5 P. A. Duffield, *Review of Bleaching*, Textile Technology Group, IWS Development Centre (1986)
- 6 E. R. Trotman, *Textile Scouring and Bleaching*, Charles Griffin & Company Ltd. (1968)
- 7 T. Miyamoto, H. Sakabe, H. Ito and H. Inagaki, *Proceedings of the 7th International Wool Textile Research Conference*, Tokyo, Japan (1985)
- 8 J. Knott, *Fine Animal Fibres and Their Depigmentation Process*, COMETT EUROTEx (1990)
- 9 F. C. Kong, S. L. Lu and B. G. Yuan, *Theory and Practice of Wool Fabric Dyeing and Finishing*, Textile Industry Press (1989)
- 10 K. R. Makinson, *Shrinkproofing of Wool*, Marcel Dekker Inc. New York and Basel (1979)
- 11 W. G. Chen, D. Z. Chen and X. G. Wang, *Textile Research Journal*, **71** (5), 441-445 (2001).
- 12 J. T. Marsh, *An Introduction to Textile Bleaching (Forth impression)*, Chapman & Hall Ltd. (1956)
- 13 P. R. Brady, *Proceedings of the 7th International Wool Textile Research Conference*, Tokyo, Japan (1985)
- 14 R. Convert, L. Schacher and P. Viallier, *Textile Science 1998: Textile Chemistry and Finishing section*, (1998)
- 15 D. P. Collins, *American Dyestuff Report*, **53** (16), 218-221 (1964).

- 16 J. Gacen, J. Cegarra, M. Caro and L. Aizpurua, *Journal of Society of Dyers and Colourists*, **95** (11), 389-395 (1979).
- 17 X. Liu, C. J. Hurren and X. Wang, *Fibers and Polymers (submitted)*, (2003).
- 18 CIBA-GEIGY, *Lanaset Dyes on Wool (Pattern Card) 3440, Edition 1992*, (1992)
- 19 A. Barella, *Journal of the Textile Institute*, **48**, 268-280 (1957).
- 20 A. Barella, *Textile Progress*, **13** (1), 61 (1983).
- 21 D. S. Taylor, *Proceedings of the 7th International Wool Textile Research Conference*, Tokyo, Japan (1985)