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

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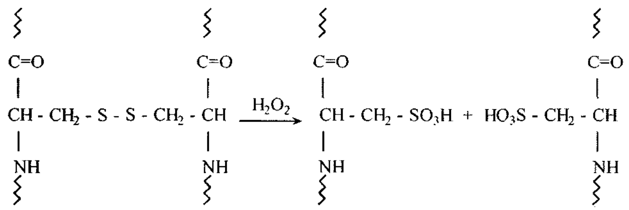
Abstract: This paper reports the effects of bleaching of alpaca tops and dyeing of bleached alpaca tops/yarns on the quality of tops and yarns. A dark brown alpaca top was bleached with hydrogen peroxide. Two bleaching methods were tried for effectiveness of color removal. A portion of each bleached 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 difference of top dyeing versus yarn package dyeing on yarn quality. Fiber diameter, yarn strength, yarn evenness, yarn 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.

Keywords: Bleaching, Dyeing, Alpaca top 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]:



Hydrogen peroxide (H_2O_2) is a widely used agent for the oxidative bleaching of wool and other pigmented animal fibers [1,3-5,7,8]. Under alkaline conditions, H_2O_2 can effectively oxidize cystine to cysteic acid residues [1,3,4], causing a cleavage of the disulfide bond. The breaking of disulfide cross-links of the membrane during bleaching is believed to make it easier for dyes to penetrate the fiber and hence causes an acceleration of dye uptake [4]. In addition to the oxidative treatment the presence of wetting and leveling agents in the dye bath also increases the extent of fiber swelling and so facilitates 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 in Karakul wool than normal wool, 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 [3,4,9-12]. In our previous study two selective bleaching methods were compared in detail for dark brown alpaca tops [13]. 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. Dyeability 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 and they involve chemical reactions taking place amongst bleaching agents, dyes, auxiliaries 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 color variation 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. 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 trends [3].

This paper is to evaluate the effects of two selective bleaching methods on top and yarn properties for colored alpaca fiber. Top qualities such as fiber diameter, color and fiber degradation were measured. Yarn quality including evenness, color, strength and the number of yarn imperfections was analysed. The two bleach methods were selected from conventional and radical selective bleaching systems [13] to assess the

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effectiveness of the radical bleaching system. Bleaching was conducted while the fiber was in the top stage. A parallel study was also conducted with fiber dyed at the top and yarn stages.

Experimental

Bleaching Dark Brown Tops

A dark brown alpaca top was lightened in color by selectively bleaching the colored pigments contained in the fiber. Bleaching was undertaken using two oxidative bleaching methods (*Bleach I - Modified Conventional Ferrous Mordant System, and Bleach II - Radical Ferrous Mordant System* [7]). The methods were fully described by Liu *et al.* [13] with process conditions and chemical concentrations reproduced below. A Theis Ecobloc LFA pressure package dyeing machine was used for bleaching. The liquor ratio was set at 20:1.

Bleach I - Modified Conventional Ferrous Mordant System:

Mordanting was conducted by filling the machine with cold water. 8.0 g/*l* ferrous sulphate ($FeSO_4 \cdot 7H_2O$), 1.0 m*l*/*l* formic acid (HCOOH) and 4.0 g/*l* ascorbic acid ($C_{12}H_{18}O_{11}$) were added. The pH was adjusted to 3.4 with formic acid. The bath was then heated to 80 °C at 3.0 °C/min and held for 60 minutes before being drained.

Rinsing was conducted by refilling the bath and heating to 80 °C at 3.0 °C/min. The bath was held at 80 °C for 20 minutes before being drained. The fiber was then overflow rinsed for 10 minutes.

Bleaching was conducted by filling the machine with cold water. 1.0 g/*l* Imerol XNA (Clariant) and 2.0 g/*l* tetra sodium pyrophosphate (TSPP) were added. The pH was then adjusted to 6.7 with 25 % aqueous ammonia solution. 14.0 g/*l* of 60 % hydrogen peroxide (H_2O_2) was added and the bath heated to 68 °C at 3.0 °C/min and held 80 minutes. After draining the machine was refilled and the fiber rinsed at 50 °C for 10 minutes. The bath was then drained. The machine was filled and heated to 40 °C. 3.0 g/*l* oxalic acid ($HOOCCOOH \cdot 2(H_2O)$) was added and the bath was heated to 70 °C and held for 20 minutes. A warm rinse was then conducted at 50 °C for 10 minutes.

Bleach II - Radical Ferrous Mordant System:

Mordanting was conducted by filling the machine with cold water. 10.0 g/*l* ferrous sulphate, 6.0 m*l*/*l* formic acid and 0.5 g/*l* Cibaflow CIR (Ciba Specialty Chemicals) were added. The pH was adjusted to 2.9 with formic acid. The bath was then heated to 80 °C at 3.0 °C/min and held for 60 minutes before being drained.

Rinsing was conducted by refilling the bath and adding 4.0 m*l*/*l* formic acid. The bath was then heated to 80 °C at 3.0 °C/min. The bath was held at 80 °C for 20 minutes before being drained. The fiber was then rinsed at 50 °C for 10 minutes. The rinse at 50 °C was repeated a second time.

Bleaching was conducted by filling the machine with cold water. 28.0 g/*l* of 60 % hydrogen peroxide solution, 10.0 g/*l* tetra sodium pyrophosphate, 5.0 g/*l* sodium carbonate (Na_2CO_3), 4.0 g/*l* oxalic acid and 0.5 g/*l* Cibaflow CIR were added. The pH was then adjusted to 8.3 with 25 % aqueous ammonia solution. The bath was heated to 70 °C at 3.0 °C/min and held 50 minutes. After draining the machine was refilled and the fiber rinsed at 50 °C for 10 minutes. The bath was then drained. Additional warm rinse was then conducted at 50 °C for 10 minutes.

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 are 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 the top dyed yarn were applied to the yarn dyed after spinning.

Yarn evenness (CV% of mass) and hairiness index were measured on a 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 2000 mm/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 test conditions.

Abbreviations for top and yarn labels are as follows:

1) UnBL: unbleached dark brown 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
8) UnBL-dyed: dyed unbleached top or yarn

Table 1. Yarn specifications

Yarn count (Tex)	Twist (Twists/m)	Twist factor
90.9	273	26
62.5	268	21
62.5	328	26
62.5	390	31
28.6	390	21
28.6	486	26
28.6	586	31

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 320 kg/m^3.

Dyeing Process for Top and Yarn

The dyeing process used for both the yarn and top was the standard dyeing system given in the CIBA Specialty Chemicals-Lanaset pattern card [14]. The pre-metalised dye - Lanaset BORDEAUX B (Ciba Specialty Chemicals) was used for top and yarn dyeing. The dyeing bath contained: 0.5 g/*l* Albegal FFA (Ciba Specialty Chemicals), 2.0 g/*l* Acetic Acid Solution 60 % (CH_3COOH), 1.0 g/*l* Sodium Acetate (CH_3COONa), 5.0 % o.w.f. Sodium Sulphate (Na_2SO_4), 1.0 % o.w.f. Albegal set (Ciba Specialty Chemicals), 3.0 % o.w.f. Ingasol HTW New (Ciba Specialty Chemicals) and 3.0 % o.w.f. Lanaset BORDEAUX B.

The fiber/yarn was put in the machine and the dyebath was set at 40 °C. The auxiliary chemicals were added and the liquor was allowed to equilibrate for 10 minutes. The pH of the dye liquor was adjusted to 4.5-5.0. The dye was added and the machine was run for a further 10 minutes at 40 °C. The bath was then heated to 70 °C at 1.0 °C/min. The bath was held at 70 °C for 15 minutes before being raised to 98 °C at 1.0 °C/min. The bath was held at 98 °C for 30 minutes before being cooled to 50 °C at 3.0 °C/min. The dyed fiber was rinsed for 5 minutes before being softened with 2.0 % o.w.f. Mega soft Jet (Ciba Specialty Chemicals). The bath was held for 20 minutes at 40 °C while the softener was applied.

Color Measurement

The CIE L* (Lightness) and C* (Chromaticity) values of the test fiber and yarns were obtained using a Spectraflash 600 PLUS-CT spectrophotometer. Yarns were wound on a cardboard base to a uniform density before the color measurement. Each sample was measured using a diffuse light source (the standard illumination light D65) and measured at 10 degrees to the sample.

Fiber Degradation Test

A methylene blue staining test was used to determine the level of fiber degradation. Details of the test method originated from Knott's work [15] and have been reproduced below:

A methylene blue solution of pH 3.5 was prepared containing 0.0365 mol/*l* sodium hydroxide (NaOH), 0.210 mol/*l* acetic acid (CH_3COOH), 0.64 g/*l* methylene blue and a drop of Albegal FFA (Ciba Specialty Chemicals). The pH was adjusted to 3.5 with extra sodium hydroxide.

Each unbleached, bleached and dyed alpaca top and yarn was cut into short lengths and weighed to give 0.5 ± 0.005 g test samples. Each sample was treated for 30 minutes in the methylene blue solution at a liquor ratio of 1:10 and at a temperature of 40 °C. The final liquor was set aside, the fibers were squeezed, rinsed in water and dried.

3.0 ± 0.005 m*l* of the exhausted methylene blue treatment liquor was diluted with distilled water to a volume of 500 m*l*. The absorbance was then measured at a wavelength of 664 nm using a Hach DR 4000 spectrophotometer.

Results and Discussion

Fiber Diameter Changes

Table 2 shows that the mean fiber diameter decreases by 4.8 % and 8.0 % for BL-I and BL-II respectively. The reduction of up to 2.3 micron of BL-II was a significant change that could be attributed to the bleaching system. This result is consistent with another trial for alpaca top [13]. Dyeing after bleaching does not affect fiber diameter. Significant diameter change is not seen after dyeing in fiber dyed at either the top or yarn stage. Bleached yarn package-dyed at the yarn stage had better CV (%) of diameter than any of the others.

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

	Un-bleached	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 comparisons of the CIE L* (Lightness) and C* (Chromaticity) values of the alpaca top and yarn at 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 when compared with the unbleached top. The lighter base color of the bleached fiber, achieved by each of the bleaching methods, has less impact on dyed colors. Colors dyed over the bleached fiber are lighter in depth and brighter in chromaticity than the color dyed over

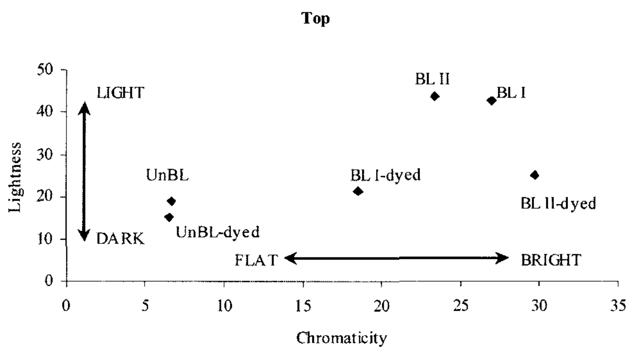

Figure 1. Color differences of unbleached, bleached and bleached/dyed tops.

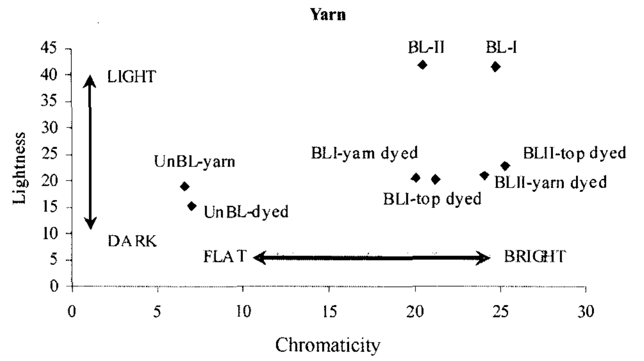

Figure 2. Color differences of unbleached yarn, top bleached and dyed yarn, and top-bleached then package-dyed yarn.

unbleached fiber. Chromaticity values for the dye and fiber are subtractive. Low fiber chromaticity values will result in dull dyed shades so dyeing over an unbleached fiber results in a dull shade. After dyeing BL-II showed better purity of color than that of BL-I.

Figure 2 shows that there is little influence on the dyed color due to the processing path. This allows a processor to leave coloration until further down the processing stage to allow greater flexibility in production. The yarn results show chromaticity values that are slightly flatter than those of the fiber. This reduction is expected as the twist inserted in the yarn reduces the brightness of the measured color.

Comparisons of Yarn Properties

Coarser yarn generally has better evenness (low CV% of mass) than finer yarn where the same fiber diameter is used. As there is a reduction in the diameter of fiber that has undergone BL-II it shows better evenness values than those seen for BL-I and the unbleached fiber (Table 3). This can be explained by the requirement of extra fibers, during spinning, in the cross-section of the yarn to achieve the same count as the other yarns.

Yarn hairiness usually increases with increase in yarn count and the number of fibers in yarn cross section [16]. Shorter fibers also lead to more hairy yarns [16]. The bleaching systems used in this study reduced fibers diameters (Table 2), and caused some fiber damage also [13]. As a result, bleached yarns would have more fibers of shorter length in the cross section, compared with unbleached yarns of similar count. This explains why the bleached samples have significantly higher hairiness results than the unbleached ones (Table 3).

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), 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

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

Yarn count (in tex)/Twist factor	Parameters	UnBL-yarn	BL-I	BL-II	BLI-top dyed	BLII-top dyed	BLI-yarn dyed	BLII-yarn dyed
90.9/26	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
62.5/21	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
62.5/26	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
62.5/31	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
28.6/21	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
28.6/26	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
28.6/31	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

Table 4. Yarn tenacity (cN/tex) and elongation (%)

Yarn count (in tex)/Twist factor	Parameters	UnBL-yarn	BL-I	BL-II	BLI-top dyed	BLII-top dyed	BLI-yarn dyed	BLII-yarn dyed
90.9/26	Tenacity	5.77	5.00	5.97	5.05	5.98	5.54	5.94
	Elongation	9.13	3.1	5.57	2.72	4.61	3.09	6.08
62.5/21	Tenacity	4.15	3.47	4.54	2.07	3.60	4.05	4.73
	Elongation	3.40	2.54	3.12	1.81	2.80	2.52	3.81
62.5/26	Tenacity	5.21	4.35	5.47	4.14	5.07	4.97	5.42
	Elongation	5.56	2.81	4.64	2.45	3.57	2.89	4.63
62.5/ 31	Tenacity	6.40	4.85	5.58	4.72	5.26	5.09	6.01
	Elongation	18.77	3.39	16.00	2.61	6.30	3.22	7.75
28.6/21	Tenacity	2.38	2.57	3.58	2.73	2.12	2.93	3.46
	Elongation	2.89	2.00	2.83	1.75	1.86	1.78	2.49
28.6/26	Tenacity	3.65	3.47	3.98	3.13	3.16	3.91	5.00
	Elongation	3.47	2.49	3.30	2.05	2.65	2.50	4.30
28.6/31	Tenacity	4.69	3.89	4.33	3.22	4.12	4.29	5.14
	Elongation	7.27	2.77	4.73	2.12	4.27	2.71	5.79

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.

Fiber Degradation after Bleaching and Dyeing

Because there is a reverse relationship between absorbance of residual 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 bleaching 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. Although these results show a definite increase in fiber damage the yarns spun from the BL-II fiber were stronger than those of BL-I. This is explained by the reduction of fiber diameter causing an increase during spinning of the number of fibers in the cross-section of the yarn and hence the yarn strength.

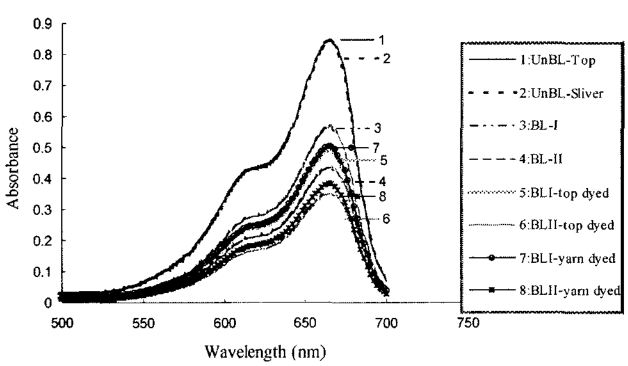

Figure 3. Absorbance of Methylene blue of different treated tops and yarns.

There is no significant difference in fiber damage between bleached/top-dyed and bleached/yarn-dyed for each of the bleaching methods. The practical consequences of damage to fiber during bleaching and dyeing can be seen as difficulties in spinning. These difficulties can include: excessive fly, increased yarn breaks, decreased processing speeds and lower yields. These are problems not uncommon to this style of processing [17].

In summary, both bleaching methods exhibit their own strengths and weaknesses when used in production. BL-I produces a fiber that has little difference in handle properties however it suffers from duller dyed shades, lower yarn strength 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 using BL-II. 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 is still needed to examine the performance of yarn bleaching and dyeing. Unfortunately this processing 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 evaluated the effectiveness of color removal of two bleaching methods, which were developed for colored alpaca fiber, and the dyeing effects after bleaching on top and yarn quality.

Both bleaching methods improved the lightness and purity of color (Chromaticity) of the bleached tops. Bleaching method I (BL-I) led to a reduced lightness and chromaticity improvement than that of bleaching method II (BL-II). Bleaching and dyeing of the alpaca fiber caused fiber damage. Bleaching also reduced fiber diameter, significantly in the case of bleaching method II. The reduction in fiber diameter would increase the average number of fibers in yarn cross section, for a given yarn count. This increases yarn evenness, yarn strength, and also yarn hairiness.

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