Non-Bleaching Heather Method for Improved Whiteness of Greige Cotton

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ABSTRACT
In accordance with the color space theory known as additive light mixing, the presence of dispersed blue-dyed fiber reduced the overall yellowness of a blended greige fiber and they were perceived as "whiter". Various intimate blends of blue-dyed cotton fiber in greige cotton fiber were analyzed for color properties using a L*a*b* color space chromameter and a Ultraviolet-Visible (UV-Vis) spectrophotometer. A design of experiments (DOE) matrix approach provided a statistically-based mathematical means to predict the color properties of the intimate blends. The predictive accuracy of the mathematical model was confirmed in a follow-up experiment, and the blend resulting in the lowest yellowness and highest whiteness was determined. For fiber end uses which are too cost sensitive to support comprehensive wet chemical treatment of all of the fiber, such as nonwovens, intimate blending with low amounts of dyed fiber could produce visible effects at lower cost.

Keywords: Additive color mixing, additive light mixing, cotton, chromameter, whiteness, intimate blend, heather, nonwoven, DOE

INTRODUCTION

Greige cotton is typically off-white to slightly yellow in color [1]. The majority of cotton spinning, weaving or knitting employs greige cotton which is subsequently scoured and bleached prior to use in white goods or prior to dyeing in an even and predictable manner before use in colored goods. However, some specialty end uses, such as nonwovens where dyeing is uncommon, could use greige cotton in the final product if not for the negative consumer perception of yellowness. Many nonwoven end uses such as wipes, diapers or personal care items have difficulty supporting increased fiber costs introduced by scouring and bleaching cotton, and thus incorporate synthetic fibers instead.

To resolve the yellow color issue in finished goods, as early as 1883, commercially available bluing formulations containing a blue-dyed pigment were used in the laundry rinse cycle to whiten fabrics. The solution contained a colloidal suspension of iron particles which did not covalently bind to textile fibers and gradually washed out after repeated laundry cycles, allowing the fabric's yellow appearance to return [2]. A more modern approach used optical brightening agents (OBAs), whose fluorophores whitened textiles by absorbing light in the ultraviolet region of the spectra and re-emitting light in the blue-dyed region (400 – 450 nm) by fluorescence [3]. Many OBAs were stilbene derivatives and their fluorescent properties were enhanced by the addition of polyols such as polyethylene glycol and polyvinyl alcohol [4]. OBAs gradually washed out after laundering or became ineffective due to their susceptibility to photolytic degradation [5].

As a potential alternative to wet chemical treatment of greige cotton to reduce yellowness such as bleaching, bluing, or optical brighteners, this study investigated a mainly mechanical approach, involving low level intimate blending of blue-dyed fiber into a slightly yellow greige cotton base fiber. In accordance with the color space theory known as additive light mixing (also called additive color mixing), close physical or overlapping association of yellow and blue sources of light will appear white to light grey to the observer, such as in an LED television monitor producing white from red, blue, and green LED pixels. This is different from the more intuitive observation of subtractive color mixing like mixing dyes or pigments where blue mixed with yellow appears green (*Figure 1*) [6].

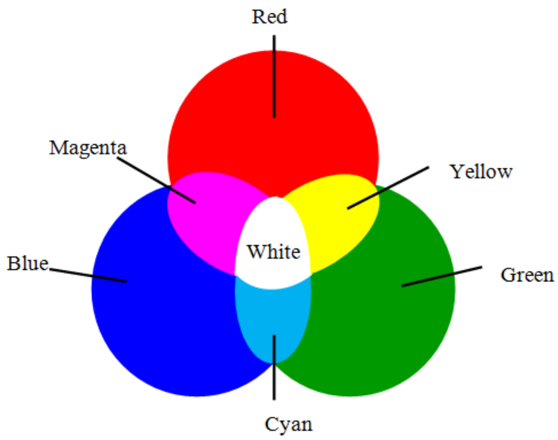

FIGURE 1. Additive Light Mixing scheme.

In this study samples of one bale of off-white greige cotton which was mechanically cleaned of foreign matter were dyed with three different reactive blue dyes, each having a slightly different color spectrum. Guided by a statistically designed blending experiment, these three different blue-dyed fiber samples were then blended back into the original greige cotton in various ratios to each other and at varying levels up to 5% by mass of total blue-dyed fiber in the overall blend. L*a*b* color measurements and UV-Vis spectral analyses confirmed a variation of yellowness with the blended blue fiber and a low yellowness, high whiteness optimum was found.

EXPERIMENTAL

All chemicals were purchased from commercial sources and used without further purification. Greige cotton (G) was received from TJ Beall and used as received. Three shades of blue-dyed fibers (B1, B2, B3) were prepared from the greige cotton, according to the procedure outlined in *Table I*. The blue-dyed fiber was hand distributed onto the surface of the greige fiber matt (11” x 15”), which was then mechanically blended on a minicard (Hollingsworth Lab Card) as follows: Hollingsworth Lab Card - 3 cardmaster plates; Main cylinder -155 to 160 rpm; Doffer -7.8 to 8.0 rpm; Feed Roll -1.9 to 2.0 rpm. The blend was carded twice and the web turned 90^{o} the second time through to achieve optimal blending.

After carding the optimized intimate blend and greige starting material were separately hydroentangled using a low water pressure of 30 bars at the consolidating, pre-wetting jet head and a high water pressure of 80 bars at the two fabric-forming jet heads of the Fleissner (Truetzschler) N1056 hydroentangling system. The line production speed was 5 meters per minute and the jet strip hole size diameter was 0.12 mm (40 holes/inch).

TABLE I. Dyeing procedures for blue-dyed fiber (B1, B2, B3) preparation

Dyeing process of Greige cotton 10 grams of fiber (B1).	Liquor ratio: 25 : 1	1) Place fibers in Jet and fill with 1.4 L of distilled H_2O
	1.0% on fiber – Reactive Blue 198 (Standard Colors Inc.) – 0.1 grams	2) Circulate at room temp for 20 minutes.
	60 g/L Sodium chloride	3) Dissolved the dye in warm water.
	15 g/L Soda ash	4) Added the dye solns over 10 minutes at room temperature.
Dyeing process of Greige cotton 10 grams of fiber (B2).	Liquor ratio: 25 : 1	5) Raised temperature to 80°C.
	0.25% on fiber – Reactive Blue 198 (Standard Colors Inc.) – 0.25 grams	6) Added salt over 10 minutes.
	0.08% on fiber – Reactive Red 231 (Standard Colors Inc.) – 0.08 grams	7) Circulated for 45 minutes
	60g/L Sodium chloride	8) Rinsing – 4 times at 95°C.
	15g/L Soda ash	9) Remove and dry fiber
Dyeing process of Greige cotton 60 grams of fiber (B3).		1) Place fibers in Jet and fill with 8.4 L of distilled H_2O
	Liquor ratio: 25 : 1	2) Add 1.5% Triton X-100 per liter of H_2O
		3) Circulate at room temp for 20 minutes.
	1.5 % on fiber - Triton x100 – 0.9grams	4) Dissolved the dye in warm water.
		5) Added the dye solns over 10 minutes at room temperature.
	0.5 % on fiber - Permabril Blue R Special 160% (Standard Colors, Inc.) – 0.3 grams	6) Raised temperature to 60°C.
		7) Added salt over 10 minutes.
	0.5 % on fiber- Intracon Brill Violet U5-5R (Crompton & Knowles.) – 0.3 grams	8) Circulated for 45 minutes & Cool to 60°C.
		9) Rinsing – 3 to 5 times.
	60.0 g/L Sodium Sulfate	10) Fill the Jet with 8.4 L of distilled H_2O – raise temp to boil and circulate for 20 minutes.
	8.0 g/L Soda ash	11) Cool to 60°C; drain and rinse 3 times.
		12) Extract and dry fiber

The HE drum had a 24 mesh embossing pattern. The fabrics were dried at 180^{o}C using an inline gas-fired, hot-air dryer containing a rotating drum and subsequently wound onto fabric rolls for spectroscopic testing.

The carded and hydroentangled fiber blend samples were analyzed for spectroscopic properties using a Konica Minolta CR-410 chromameter and a Varian Cary 100 spectrophotometer.

The chromameter analyzed samples for color space properties in terms of CIELAB color coordinates (*L**, *a** and *b**) using the 2^{o} observer and the CIE standard illuminant C. *L** represents lightness and can be measured independently of color hue. A decrease in lightness is associated with a decrease in fabric reflectance. Normal to the *L** axis (lightness) are the +*b** to – *b** axis and the perpendicular +*a** to –*a** axis, where *b** represents the color yellow (90^{o}),–*b** blue (270^{o}), +*a** red (360^{o}) and –*a** green (180^{o}) as shown in *Figure 2*. Each recorded L*a*b* measurement was the average of three reflectance readings obtained by rotating the samples after each measurement.

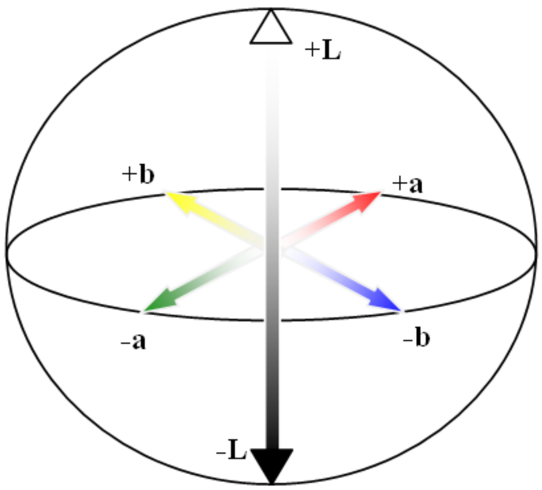

FIGURE 2. L*a*b* color space scheme.

The Varian Cary 100 spectrophotometer, fitted with a Labsphere integrating sphere diffuse reflectance accessory, was used for percent reflectance measurements of the greige cotton (G), the blue-dyed cotton (B1, B2, B3), and the intimately blended products. The diffuse reflectance accessory was run inside the sample compartment holder of the spectrophotometer and the instrument and computer were controlled using a Varian Scan software program. The spectrophotometer also used a photomultiplier tube detector with a spectral wavelength range of 400 to 700 nm. To perform a baseline correction, a Spectralon (PTFE) certified reflectance disk was placed over the open 70 mm port of the accessory, followed by scanning the specified wavelength range in reflectance mode. Similarly, to collect spectral data on the cotton fibers, the Spectralon disk was replaced with the individual cotton fiber sample over the open port, followed by scanning the same wavelength range in reflectance mode.

A design of experiments (DOE) matrix approach using Design Expert® (version 9.0.3.1, Stat Ease, Inc.) was constructed to determine the optimal fiber ratio to blend from a mixture of three blue-dyed fiber samples (B1, B2, B3) and the control greige fiber (G). After determining the optimal ratio of fibers from the DOE, a final experimental carding of fibers confirmed the predicted optimal fiber ratios and color space values.

RESULTS AND DISCUSSION

In order to determine the optimal fiber blend with the least yellowness, a matrix of twenty intimate fiber blends was constructed from the DOE based on four independent factors (the three blue-dyed fiber samples – B1, B2 and B3 and the original greige fiber - G) and three output responses (L*, a* and b* color measurements). *Figure 3* and *Table II* contain the UV-Vis spectra and L*a*b* color space properties of the four fibers (G, B1, B2, B3) used in this series of experiments.

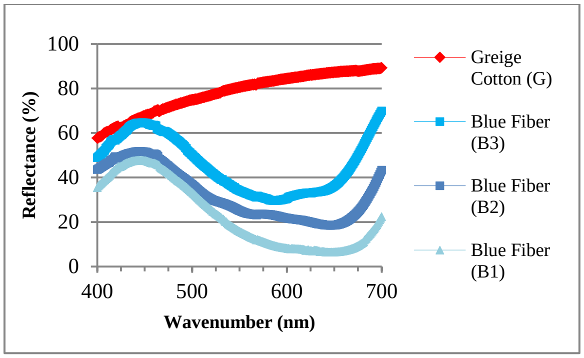

FIGURE 3. Comparison of UV-Vis spectra of Greige Cotton (G) and blue-dyed fibers (B1, B2, B3).

TABLE II. L*a*b* color space values for Greige Cotton (G) and blue-dyed fibers (B1, B2, B3).

Fiber Name	L*-value	a*-value	b*-value
Greige Control (G)	93.16	0.14	9.03
B1	46.73	4.77	-41.63
B2	58.77	7.31	-30.77
B3	66.41	8.35	-27.95

In all blends, the greige fiber (G) amounted to no less than 95% of the total weight of the mixed fiber sample. The three blue-dyed fibers (B1, B2 and B3) were dyed to different shades of blue based on different dyes. The various blends contained varying ratios of B1, B2, B3 and G, but the total percentage of blue-dyed fiber(s) never exceeded a 5% maximum. In order to properly account for residual errors, five of the twenty experiments are replicates. The experimental parameters and results from the twenty experiments are shown in *Table III*.

TABLE III. Results from Design of Experiments (DOE).

Run	B1 (%)	B2 (%)	B3 (%)	G (%)	L-value	a-value	b-value
1	0.63	0.63	0.63	98.13	90.27	-1.04	5.68
2	0	5	0	95	87.88	-1.1	1.96
3	3.13	0.63	0.63	95.61	87.03	-2.88	0.05
4	2.5	2.5	0	95	86.1	-2.68	-0.3
5	1.27	1.27	1.27	96.19	88.83	-1.68	2.33
6	0	0	5	95	88.6	-0.06	3.77
7	0	0	2.5	97.5	90.74	-0.03	5.92
8	0	5	0	95	88.06	-1.07	2.85
9	0.63	0.63	3.13	95.61	88.81	-0.85	3.28
10	0	0	0	100	92.99	0.12	8.99
11	0	2.5	2.5	95	88.43	-0.57	2.94
12	2.5	0	0	97.5	88.55	-2.82	2.28
13	0.63	3.13	0.63	95.61	88.31	-1.4	2.88
14	0	0	5	95	89.87	0.05	3.63
15	2.5	0	2.5	95	86.92	-2.25	0.72
16	5	0	0	95	85.19	-3.74	-2.23
17	2.5	2.5	0	95	86	-2.66	-0.36
18	0	0	0	100	93.32	0.16	9.07
19	5	0	0	95	85.2	-3.53	-1.27
20	0	2.5	0	97.5	90.78	-0.73	5.47

The experiment sought to obtain an intimate blend that maximized the L*-value and minimized the a*- and b*- values as defined in the L*a*b* color space, leading to a whiter appearance. L*a*b* color space results from experiments 10 and 18 which used 100% control greige cotton fiber (G) averaged L* = 93.16, a* = 0.14, and b* = 9.03. This meant that the control L*-value was slightly less than bleached samples; the control a*-value was slightly on the red side; the control b*-value was strongly on the yellow side. In experiments 2-5 as many as three shades of blue-dyed fibers were blended together with the control greige fiber. From the results of L*a*b* color space measurements, both the L*- and b*-values ranged from 86.1 to 88.83 and -0.3 to 2.33, respectively, but note that the a*-value ranged from -1.to -2.88, meaning the mixed fibers appeared green. However, note the result from experiment 7 which used a single blue-dyed fiber (B3) to blend with the control fiber: L* = 90.74, a* = -0.03, b* = 5.92. By using just 2.50% of blue-dyed fiber (B3), the yellow appearance of the greige control (G) cotton fiber was reduced from an average of 9.03 to 5.92. Note experiments 6 and 14: In these two replicate experiments which both used 5.00% of blue-dyed fiber (B3), the average L*a*b* values were L* = 89.24, a* = -0.01, and b* = 3.7. From the results in *Table III*, it was apparent that the optimal intimate blending of fibers would be between 2.5% to 5.0% of fiber (B3) with 95% to 97.5% of control greige fiber (G).

After processing the experimental data, it was concluded that the L*-value response followed a linear model and the a*- and b*-value responses followed a quadratic model. There was a 0.01% chance that the model selections were due to experimental noise. For the L*-, a*-, and b*-value responses, all four fiber samples significantly influenced all three responses, with the exception that fiber (B3) did not influence the a*-value response. All models passed diagnostic evaluations for normal plot of residuals, predicted versus actual values, and Box-Cox analysis. Most importantly, all three models predicted a single, identical, optimized solution as shown in *Table IV*. In a confirmation experiment, using the fiber amounts prescribed by the optimized solution in *Table III*, 1.43 grams (4.77%) of blue-dyed fiber (B3) were carded with 28.57 grams (95.23%) of greige fiber (G). The L*a*b* color space measurements for the confirmation experiment were consistent with those predicted from the DOE. A close up view of the greige fibers (G) and the optimized blend is shown in *Figure 4*.

TABLE IV. Predicted solution from DOE and confirmational experimental results.

Optimized Solution (predicted from statistical software)

Run	B1 (%)	B2 (%)	B3 (%)	G (%)	L*-value	a*-value	b*-value
1	0.000	0.000	4.77	95.23	89.275	-0.028	3.817

Confirmational Experiment (using optimized parameters from statistical software)

Run	B1 (%)	B2 (%)	B3 (%)	G (%)	L*-value	a*-value	b*-value
1	0.000	0.000	4.77	95.23	89.010	-0.090	3.970

A comparative UV-Vis reflectance analysis of cotton fibers is shown in *Figure 5* and further illustrates the additive light mixing effect from blending fibers. The reflectance spectra of the control greige cotton (G), the blue-dyed fiber (B3), and the optimized blend of fibers (G) and (B3) are shown. It is evident from the spectra of the optimized fiber blend that the intimate blending of the blue-dyed fiber (B3) and the greige fiber (G) resulted in a leveling of the spectra in the visible range between 485 – 600 nm. This is the blue-green range of human color perception. Additionally, there is a red color contribution from the blue-dyed fiber (B3) in the 650 – 700 nm range. With the addition of the blue-dyed fiber (B3) to the control greige cotton (G), instead of the greige cotton appearing yellow, the optimized final product blend appears whiter.

FIGURE 4. Close up view of control greige cotton (G) and optimized blend.

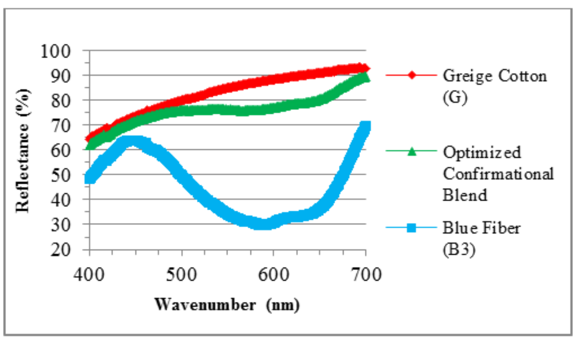

FIGURE 5. UV-Vis Spectra of greige control (IV) fiber (red), optimized fiber blend from the confirmation experiment (green), and the blue-dyed (III) fiber (blue).

Although many textile colorists scour and bleach greige fibers prior to dyeing, it is important to mention that none the blue-dyed fibers used in this series of experiments were bleached or scoured. This will significantly reduce cost and shorten processing time. Additionally, while durability testing was not performed on the carded fiber blends, it is believed that the blue-dyed fibers will be more durable than those prepared using bluing solutions or OBAs. While single use, disposable, nonwoven applications do not usually depend on laundering durability, many applications are packaged in aqueous medium in which case chemical leaching becomes a factor. It is also important to mention that further optimization is possible by varying the intensity of blue color of the blue-dyed blending stock. By doing this the percentage of blue-dyed fiber needed for intimate blending with the control greige cotton fiber can be further reduced, resulting in less blue-dyed fiber demand and lower cost but with increased potential that the individual blue-dyed fibers would be visible in the intimate blend. In one such experiment a blue-dyed sample with greater color intensity was blended at 1% in greige cotton but a blue tint and some blue-dyed fibers were observed in the carded blend.

Samples of the greige cotton (G) and the optimized intimate blend were separately hydroentangled. The L*a*b* chromametric analyses of the two products are reported in *Table V* and indicate that the hydroentanglement process removes some of the yellow color from the cotton fibers. Before the 100% greige cotton (G) was hydroentanglement the b*-value is 8.99; after hydroentanglement the b* value is 3.42. Similarly, the b*-value of the optimized intimate blend changes from 3.97 before hydroentanglement to -4.36 after hydroentanglement. There are other slight variations before and after hydroentanglement in the L*- and a*-values of 100% greige cotton (G) and the optimized intimate blend as well. In the case of the intimately blended fibers, the hydroentanglement process resulted in a slightly blue appearance afterwards. A change in color appearance after hydroentangling cotton fiber was previously reported by Sawhney et al [7]. The present result indicates, however, that a further refinement of the intimate blend may be necessary in order to achieve optimal whiteness, if downstream processing involves hydroentanglement.

TABLE V. Comparison of L*a*b* measurements *before* / *after* hydroentanglement.

	Fabric Type	L*-value	a*-value	b*-value
Average L*a*b* measurement *before/after* hydroentanglement	Greige Cotton (G)	92.99	0.12	8.99
		94.05	-0.66	3.42
	Optimized Intimate Blend	89.01	-0.09	3.97
		89.02	-0.5	-4.36

CONCLUSION

Using the principles of additive light mixing, a process method was developed in which carded blue-dyed cotton fibers were intimately blended with greige cotton fibers to produce a product which appeared whiter than the starting greige material. Neither the greige cotton nor the blue-dyed fibers were bleached or scoured prior to dyeing or blending, which significantly reduced cost and process time in the preparation of whiter cotton blends. The optimal ratio of blue-dyed cotton fibers and greige cotton was 4.77% fiber (B3) to 95.23% fiber (G), respectively. This primarily mechanical process presents an alternative to whole-batch wet chemical treatments such as bluing, optical brighteners or bleaching to achieve reduced yellowness and greater whiteness. Preliminary hydroentanglement experiments showed the greige cotton's natural yellow color was partially removed in the hydroentanglement process, increasing the blue appearance of the intimately blended product.

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