NATURALLY COLORED COTTONS – SHADE CHANGES UPON WET TREATMENTS

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Abstract

Conventional caustic and enzymatic scouring, solvent extraction, mercerization and cellulase enzyme treatments were performed on Coyote, Buffalo (brown varieties) and Green naturally pigmented cotton yarns. The effect of these wet treatments on the color shade was evaluated using the CIEL*a*b* color system. It was found that caustic treatments had the highest impact on the hue of these fibers. Further, Coyote and Buffalo plain weave fabrics were treated with metal salt solutions. A dramatic color shift towards darker browns and gray-browns was observed with solutions containing Fe(II) ions while other cations proved to be less effective.

Introduction

Archaeological evidence shows that colored cotton varieties have been known and used for thousands of years in various parts of the world [Vreeland, 1992]. Today they present a relatively small niche for higher-priced specialty products in the international marketplace. In the light of increasing concern for the environment, however, naturally pigmented cotton varieties together with organically grown white cotton have considerably gained interest over the past decades and their market share is increasing [Schwarz, 1996]. Improved fiber quality, such as fiber length and strength, as well as enhanced color consistency have contributed to their successful establishment to the world market [Brighton, 1993].

Naturally colored cottons are currently available in various shades of brown, red and green. The color shade is most likely the product of a variety of pigments that are bound to cellulose by sugar-related links together with lignins, tannins, and other noncellulosic material. The relative percentage and the chemical nature of these compounds vary with growing conditions and location as well as climatic factors. The identification, characterization and quantitization of these colorants is therefore extremely difficult.

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The presence of natural pigments eliminates the need for dyeing processes with synthetic dyes as well as preparatory finishes such as bleaching, thus diminishing the environmental impact of textile processing by reducing waste discharge directly at the source. More color shades, including black and blue, are expected to become available in the near future, either by traditional crossbreeding techniques or by transgenic color alteration [Jividen, 1996]. Wet treatments can also create variations in hue. The objective of this research was to study color changes effected by standard wet processes, such as scouring and mercerizing, as well as by mordanting with mineral salt solutions.

Experimental Procedures

Scouring Methods

Buffalo, Coyote and Green yarns (Naturally Cotton Colours, Inc.) have been scoured in three different ways. Enzymatic scouring was performed with 10% pectinase and 5% cellulase in 0.05M acetate buffer solution of pH 5.0 at 50°C for 3 h. A modified enzymatic scouring process was carried out using 7.5% pectinase and 7.5% hemicellulase under otherwise identical conditions. All enzymes were obtained from Novo Nordisk, Franklinton, NC. For both scouring processes a shaking waterbath was used. The enzymes were deactivated by immersing the samples in boiling water for 5 min. Caustic scouring was performed in 4% aqueous sodium hydroxide solution at 95°C for 90 min under nitrogen atmosphere. The samples were neutralized in 10% acetic acid, washed with water and dried in an air-oven at 50°C. For the solvent extraction 1,1,1-trichloroethylene was used in a soxhlet under reflux for 4 h. The solvent was evaporated and the samples air-dried. The weight losses determined after each scouring procedure were based on the weight of the conditioned sample. The water absorbency was tested after each of the scouring procedures.

Slack Mercerization and Enzyme Treatments

Samples scoured with aqueous sodium hydroxide solution were slack mercerized in 20% sodium hydroxide solution at 0°C for 60 min. They were neutralized in 10% acetic acid, washed until acid-free and dried in an air-oven at 50°C.

Both samples after caustic scouring and solvent extraction were treated with 10% Cellusoft L (Novo Nordisk) in acetate buffer solution of pH 4.8 at 50°C in a Laundrometer (Atlas Corp.) for 90 min. The cellulase enzymes were deactivated in 100% acetone and the samples washed in water and air-dried.

Color Measurement

Untreated and treated yarns were wound onto cardboard and the CIEL*a*b* color coordinates measured with a Bausch & Lomb Color Scan II spectrophotometer, using D6500 standard daylight as the light source.

Metal content

The content of natural metal ions present in the samples was determined by atomic absorption spectroscopy. 100 mg of each sample were dissolved in 10 mL concentrated nitric acid. The samples were tested for Ca, Mg, Fe, Mn and Cu ions. The determination was carried out in duplicate per sample and with 2 independent samples each.

Treatment with Mineral Salt Solutions

Coyote and Buffalo plain-weave fabrics were treated with various salt solutions of concentrations of 0.01 to 0.001M at the boil for 5 minutes. One series of these samples was washed in water and dried, the other was washed in 2.0% AATCC detergent solution at 50°C for 5 min, washed with water until soap-free and air-dried. The following salts were used for these experiments: $FeCl_2$, $FeCl_3$, Fe(III)citrate, $CuSO_4$, $ZnSO_4$, $Na_2Cr_2O_7$, $CoCl_2$, $SnCl_2$, $Al_2(SO_4)_3$. The changes in color were measured with a Bausch & Lomb Color Scan II spectrophotometer and compared to control samples washed in water only.

Results and Discussion

Effect of Scouring

Compared to caustic scouring which resulted in approximately 10% of weight loss on the average (little higher for the Green yarns), observed weight losses for the brown varieties were generally lower than for the Green yarn, irrespective of the method used. The scouring bath was slightly colored after the enzymatic treatment in all cases and colorless after solvent extraction in the case of Coyote and Buffalo while the Green yarns released some coloring matter into the solvent. All scouring methods produced yarns with sufficient water absorbency.

Table 1. Weight loss of Buffalo, Coyote and Green yarns after scouring by different methods.

Method	Weight loss [%]		
	Buffalo	Coyote	Green
Enzymatic scouring (I)	2.2	3.3	5.8
Enzymatic scouring (I)	2.7	2.2	4.6
Solvent extraction	1.0	0.7	4.1

Compared to the untreated control conventional caustic scouring caused the highest color loss in all cases. The values for lightness L* (absolute white: L* = 100) increased considerably and chroma or saturation values C* were reduced (Tables 2-4). The a* (coordinate for redness) of both brown varieties decreased significantly. Similar observations were made for both the yarns after slack mercerization and after a cellulase treatment subsequent to caustic scouring.

Enzymatic scouring slightly intensified the color of both brown varieties but did not influence the shade of the Green to a major extent. After solvent extraction the shade of Coyote seemed unchanged, while Buffalo turned slightly darker and Green slightly lighter. The Green was the only variety that turned to a paler shade when solvent extracted prior to a cellulase treatment (Table 4).

Table 2. CIEL*a*b* color coordinates of Coyote yarn after various wet treatments (L*: lightness; a*: red/green component; b*: yellow/blue component; C*: saturation).

Treatment	L*	a*	b*	C*
untreated	52.46	12.37	25.95	28.74
caustic scouring	61.80	8.82	20.49	22.30
enzymatic scouring (I)	53.49	12.75	27.00	29.86
enzymatic scouring (II)	53.42	12.84	27.00	29.90
solvent extraction	51.84	12.14	25.20	27.98
slack mercerization	56.52	9.30	19.89	21.96
caustic scour., cellulase	61.55	8.37	19.37	21.10
solv. extr., cellulase	51.78	12.72	26.79	29.66

Table 3. CIEL*a*b* color coordinates of Buffalo yarn after various wet treatments (L*: lightness; a*: red/green component; b*: yellow/blue component; C*: saturation).

Treatment	L*	a*	b*	C*
untreated	54.32	10.82	22.26	24.75
caustic scouring	60.21	7.75	16.41	18.15
enzymatic scouring (I)	53.80	11.7	23.44	26.20
enzymatic scouring (II)	54.72	11.94	23.88	26.70
solvent extraction	56.19	11.16	22.85	25.43
slack mercerization	57.05	8.94	19.32	21.29
caustic scour., cellulase	60.45	7.40	16.58	18.15
solv. extr., cellulase	53.14	11.12	23.29	25.81

Any caustic treatment affected the color of the Green variety (Table 4). With dramatically reduced yellowness component b* the color shades of these samples turned to a cooler whitish green after scouring with sodium hydroxide and a grayish shade of green (lower L* value) when additionally mercerized. Solvent extraction had a similar but less pronounced effect.

Table 4. CIEL*a*b* color coordinates of Green yarn after various wet treatments (L*: lightness; a*: red/green component; b*: yellow/blue component; C*: saturation).

Treatment	L*	a*	b*	C*
untreated	67.18	-2.88	21.11	21.31
caustic scouring	70.78	-1.45	13.19	13.27
enzymatic scouring (I)	64.85	-2.17	21.86	22.09
enzymatic scouring (II)	66.11	-2.69	21.33	21.50
solvent extraction	67.51	-2.23	20.16	20.29
slack mercerization	61.14	-1.49	13.63	13.72
caustic scour., cellulase	67.17	-1.03	12.72	12.76
solv. extr., cellulase	63.90	-0.93	18.41	18.43

Caustic treatment of both Coyote and Buffalo fabrics with 2% aqueous sodium hydroxide solution at the boil hardly changed the color coordinates of the samples, while the treatment bath turned dark brown. Caustic treatment of mercerization strength (20%) at 0°C on the other hand slightly increased the red component of the sample shade but left the treatment bath colorless.

Mordanting Treatment with Mineral Salt Solutions

The chemical composition of the natural pigments contained in these cotton varieties is not yet known. It is however clear that each color shade is the product of several different types of colorants with different solubilities in different solvents as observed after scouring. Attempts were made to strip the dyes from the fibers for HPLC analysis, however complete stripping proved to be difficult.

The colored cottons studied in this research had a natural metal ion content of 0.3 to 0.45 ppm Fe, 0.03 ppm Cu and approx. 0.08 ppm Mn as determined by atomic absorption spectroscopy of the nitric acid extract. It was found that boiling with specific mineral salt solutions a shift of the hue to darker shades could be achieved, thus increasing the metal content in the fiber.The reaction occurred instantly after reaching temperature of approximately 60°C. The salt concentration could be reduced to 0.001M for the desired effect.

In Table 5 color differences of the Coyote fabric treated with various salt solutions are displayed. Using solutions containing Fe(II) ions proved to have the most significant effect. The shades obtained were of a warm dark brown to a almost bluish brown-gray (neg. ΔL*, Δa* and Δb* values with simultaneous decrease in chroma). A soaping aftertreatment caused slight additionally darkening. Fe(III) was only effective when accompanied with citrate anion. With Fe(III)chloride a slightly more red-brownish shade was obtained as compared to the untreated sample. However, the intensity of the color shift with Fe(III) ions was clearly less pronounced. All other cations generated only minor color shifts. The hues obtained after these treatments were very similar to the untreated Coyote sample.

Table 5. Color difference after mordanting with salt solution; Coyote fabric, based on untreated sample.

Treatment	ΔL*	Δa*	Δb*	ΔC*	ΔH*
$FeCl_2$	-13.77	-4.55	-8.21	-9.86	1.68
$FeCl_2$, soap	-14.47	-5.71	-7.62	-8.85	0.70
$FeSO_4$	-13.25	-5.48	-7.94	-9.52	1.57
$FeSO_4$, soap	-15.67	-4.31	-7.18	-8.35	0.67
Fe(III)citrate	-10.30	-4.18	-5.03	-6.34	1.63
$FeCl_3$	-8.13	1.72	3.03	3.48	0.14
$ZnSO_4$	-2.68	-0.79	-0.62	-0.91	0.43
$CuSO_4$	-6.77	-0.83	0.26	-0.14	0.86
$CoCl_2$	-3.07	-0.26	0.03	-0.09	0.25
$SnCl_2$	-1.01	-2.29	-4.03	-4.63	0.22
$Na_2Cr_2O_7$	-7.87	-2.03	-0.57	-1.39	1.59
$Al_2(SO_4)_3$	-3.58	-2.17	-1.31	-2.12	1.39

The color shifts observed for treated Buffalo resembled closely those of the treated Coyote samples. Therefore only significant color differences are displayed in Table 6. The effect of all cations other than iron(II) showed to be less than in the case of Coyote.

The fact that permanent washfast color shifts can be created by exposing these naturally colored cottons to mineral salt solutions suggests that some of these pigments are capable of forming stable metal complexes, possibly by chelating similar to metallized acid dyes. It is however not clear at this time why other common mordanting metal ions, such as copper or cobalt, are less effective and why in certain instances the anion also seems to be of influence as it was observed with citrate.

Table 6. Color difference after mordanting with salt solutions; Buffalo fabric, based on untreated sample.

Treatment	ΔL*	Δa*	Δb*	ΔC*	ΔH*
$FeCl_2$	-12.87	-5.41	-8.22	-9.75	1.35
$FeSO_4$	-12.92	-5.41	-8.47	-9.98	1.21
Fe(III)citrate	-9.04	-3.69	-4.74	-5.87	1.28
$FeCl_3$	-3.59	0.37	0.02	0.19	0.31

Conclusions

Caustic scouring procedures caused a considerable shift towards lighter colors of Coyote, Buffalo and Green yarns while the hues did not dramatically change in the case of all the other studied preparatory processes. By immersion in metal salt solutions color shifts towards warm dark brown or gray brown shades, solutions containing Fe(II) ions could be obtained with both Coyote and Buffalo fabrics. The color shift was obtained within very short treatment times and proved to be washfast.

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