PROPERTIES OF PEROXIDE BLEACHED OPEN-END AND RING-SPUN YARNS SCOURED BY NONAQUEOUS, ENZYMATIC, AND CONVENTIONAL METHODS

Gisela Buschle-Diller, Assistant Professor
Textile Engineering Dept.
Auburn University
Auburn, AL
S. Haig Zeronian and Maria K. Inglesby
Professor and Graduate Assistant, Div. Textiles & Clothing
University of California
Davis, CA

Abstract

Solvent extraction with organic solvents and enzymatic scouring with pectinases have been performed on ring- and rotor-spun cotton yarns and compared to the conventional scouring process in aqueous sodium hydroxide solution. The effect of the different scouring methods on the properties of the yarns as well as on further bleaching procedures with hydrogen peroxide have been studied. The influence of specific metal ions on hydrogen peroxide bleaching has also been addressed.

Introduction

Raw, unscoured cotton fibers contain 86 to 90% cellulose based on the dry weight of the fiber. Variations are due to cultivation conditions, such as composition of soil, climate and other factors. After scouring and bleaching the cellulose content of the fiber is approximately 99%.

Noncellulosic compounds in raw cotton (Table 1) comprise pectin, pectoses and other short-chained saccharides, proteins, waxes and oils, mineral salts, and natural coloring matter (pigments). These substances limit the water absorbency of the fiber and give it a yellowish appearance. Scouring and bleaching procedures are therefore essential before any coloration or finishing process can be performed.

Table 1. Noncellulosic materials in unscoured cotton fibers (Batra, 1985; Trotman, 1984, Matthews, 1947).

Compound	Approximate Amount
Pectin, Pectose, Sugars	5-6%
Proteins, Pigments	0.5-2%
Oils, Waxes	0.5-1%
Mineral Matter	1%
Moisture	8-10%

Soluble sodium and potassium salts, phosphates and some sugars can be removed by water (weight loss up to 2.5%). Organic solvents dissolve fats, waxes and certain sugars but leave other impurities on the fiber (weight loss up to 1%). Aqueous sodium hydroxide solution at the boil extracts all noncellulosic matter.

Scouring with 3-6% aqueous sodium hydroxide solution in the presence of sequestering agents and surface active agents has therefore been the conventional method of choice in industrial applications. However, the high caustic concentration causes serious problems with waste water and is very cost-intensive. In addition, scouring with hot sodium hydroxide solution may effect fiber deterioration to some extent, thus reducing fiber quality at an early stage. Milder but equally effective scouring methods therefore need to be developed.

Enzymatic scouring is a novel approach still in the developing stage. It involves the break-down of natural waxes, pectins, and hemicelluloses predominantly on the surface of the cotton fiber by the action of nontoxic enzymes. Pectinases are most suitable for this type of scouring. Small additions of cellulases to the scouring enzymes simultaneously increase yarn softness dramatically by freeing the surface of fine fibrils, thus easing interfiber and interyarn movement. Since the enzymatic reaction takes place mostly on the fiber surface when applied for relatively short treatment times, tensile properties and degree of polymerization of the cellulosic fibers are expected to remain almost unaffected.

Non-polar organic solvents can be used for the extraction of waxes and oils in cotton and cotton/polyester blends. Other impurities are not removed. When applied in a closed system the solvents can be reused and will not pose any environmental problems. However, due to the fact that large-scale closed systems in textile mills are not always easy to maintain, solvent scouring has reached only limited commercial attention.

The most commonly applied solvent is trichloroethylene (Vigo, 1994). Due to its low boiling point, high density, and low surface tension it is very economical and cost-effective. Toxicity and flammability are comparatively low. During the scouring treatment the fibers do not swell. However in further treatments, such as bleaching, the fiber materials seem to be more prone to swelling and easier accessibility.

Scouring and bleaching is generally performed in a continuous process. Hydrogen peroxide is more and more replacing chlorine based bleaching agents in textile preparation. The effectiveness of hydrogen peroxide in regard to whiteness of the textile material is dramatically increased in the presence of certain metal ions. These ions are often introduced into the process in an uncontrolled way and are prone to not only enhance the bleaching effect but also cause fiber damage (Zeronian and Inglesby, 1995).

The reaction with hydrogen peroxide is carried out in alkaline medium at around pH 10-11 at elevated temperature. The mechanism of the reaction is not yet fully

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understood. Both radical and ionic mechanisms have been proposed (Dannacher and Schlenker, 1996).

Ionic mechanism:
$H_2O_2 \rightleftharpoons HO_2^- + H^+$
$HO_2^- \rightleftharpoons O_2^{2-} + H^+$

Radical mechanism:
$HO_2^- + H_2O_2 \rightarrow HO_2\cdot + HO^- + HO\cdot$

Metal ions can act as electron donors in the process, promoting the decomposition of hydrogen peroxide and thus increasing rate and bleaching effect of the reaction. At the same time, however, oxidative fiber damage can occur which is observed as reduction in degree of polymerization and loss in tensile strength.

The objective of this project was to study the influence of different metals on the bleaching effectiveness of hydrogen peroxide and the resulting possible fiber deterioration, using yarn samples which have been scoured in different ways to prepare for the bleaching process. Whether the method of yarn formation (rotor- or ring-spinning) had an influence on the result of the preparatory finishing steps was also investigated.

Methods and Materials

Unscoured open-end and ring-spun cotton yarns, obtained from Southern Regional Research Laboratory USDA, New Orleans, LA, were used for the experiments. Sodium hydroxide scouring was carried out under an atmosphere of nitrogen in 4% aqueous sodium hydroxide solution at the boil for 90 min, followed by rinsing in water and neutralization in dilute acetic acid. Solvent extraction was performed with 1,1,1-trichloroethylene under reflux in a soxhlet. For the enzymatic scouring two different experimental pectinase complexes (Novo Nordisk, Franklinton, NC) were employed at 50°C, pH 4.8-5.0 (acetate buffer), at a concentration of 10 wt.% (conditioned yarn weight) for 3 h. To each batch 5 wt.% Cellusoft (Novo Nordisk, Franklinton, NC) were added. The enzymes were deactivated by boiling water and the samples air-dried.

Bleaching was carried out at a liquor ratio of 1:20 at 90°C, pH 10.8-11, 20 min reaction time, using 0.75% (owf) hydrogen peroxide, 0.5% (owf) sodium silicate, and sodium hydroxide to adjust the pH. Various metal salts for different bleaching series were added in concentrations of 0.05 g/L to 0.1 g/L: $Fe(NO_3)_3$, $CuSO_4$, $FeSO_4$, $MgCO_3$, $Ca(NO_3)_2$. All chemicals used were of reagent grade.

The whiteness of the product samples was measured by using a MacBeth Color Spectrophotometer with D65 standard light source. Breaking load and extension of the samples were tested after each scouring and each bleaching step on an Instron Tensile Tester 1100 at 65% RH and 21 C. Full scale load: 500 g; crosshead speed 20 mm/min, gauge length 76.2 mm. Not less than 30 tests were performed per sample.

The intrinsic viscosity of the scoured and bleached samples was measured at 25 C using FeTNa as a solvent for cellulose. Measurements were done in duplicate and averaged. Intrinsic viscosities were converted to degrees of polymerization using the Mark-Howink-Sakurada equation (Valtasaari, 1965):

$$[\eta] = K M_w^a$$

$[\eta]$ = intrinsic viscosity in [dL/g]; Mw = weight average molecular weight.
The constants K and a for cellulose are 5.31×10^{-4} and 0.78, respectively.

Results and Discussion

Scouring and Hydrogen Peroxide Bleaching in Absence of Metal Ions

Conventional scouring with sodium hydroxide solution yielded the whitest products overall, while solvent scouring with trichloroethylene left the yarns with a yellowish tint. In regard to softness, the best products were obtained after the enzymatic scouring procedure. The addition of a small percentage of cellulase (Cellusoft) can most probably account for this effect. The weight loss after the enzyme treatment was around 3.5%.

The tensile strength of the yarns (see Figure 1) somewhat increased after sodium hydroxide scouring, probably due to a slight compaction of the yarn structure. It remained more or less unchanged after both enzyme treatments. A significant increase in breaking strength, however, was observed after solvent extraction (approx. by 70% and 50%, ring- and rotor-spun yarn, respectively). Single fiber treatments under comparable conditions showed no increase. The reason for the increase in strength must originate again in modified yarn properties. It is speculated that the yarn structure is compacted as a result of the solvent treatment, creating higher friction between the fibers in the yarn and thus increasing tensile strength.

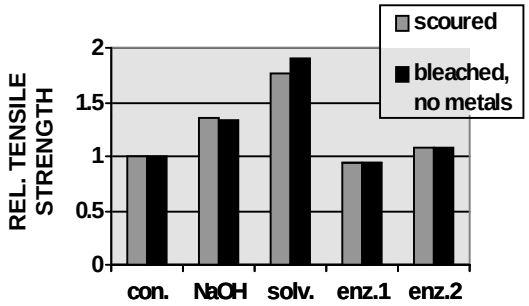

Figure 1. Relative breaking load of scoured and scoured/bleached cotton yarns. Bleaching was carried out in absence of metal ions (con. = control; NaOH = caustic scouring; solv. = solvent extracted; enz.1,2 = enzymatically scoured, batch 1 and 2)

As can be seen from Figure 1, the tensile strength remained mostly unchanged upon bleaching with hydrogen peroxide. For this series of bleaching experiments, deionized water was used. No metal ions were present. The degree of polymerization (DP) of all scoured samples was determined by measuring intrinsic viscosities in FeTNa and compared to those of the scoured/bleached samples. After scouring using any of the scouring procedures no change in DP was observed. However the DP had decreased by 23% and 34% after bleaching in the case of the NaOH scoured ring- and rotor-spun samples, respectively. The DP of the enzymatically scoured samples decreased by approx. 10-12% after bleaching, while the DP of the solvent extracted samples remained unchanged. The high reduction in DP in the case of the alkali scoured samples indicates serious fiber deterioration as a result of the harsh treatment. The effect is not yet visible in the tensile properties of these samples but may become apparent at a later process stage.

The whiteness of this series of bleached samples, bleached absence of metal ions, could be increased dramatically as shown in Table 2.

Table 2. CIEL*a*b* color coordinates of scoured and scoured/bleached cotton yarns (D65 standard light source).

Color Coordinates	Control	NaOH-Scoured	Solvent Extracted	Enz. Batch 1	Enz. Batch 2
Scouring Process Only					
Ring Spun					
Δa*	1.44	-0.1	0.2	0.0	0.0
Δb*	14.44	-6.8	-0.1	-2.7	-3.6
ΔL*	86.96	1.3	-2.5	-0.1	0.4
ΔE*		7.0	2.5	2.7	3.6
Open End Spun					
Δa*	1.60 -	0.3	0.1	0.0	-0.1
Δb*	15.38	-8.1	0.2	-4.2	-3.7
ΔL*	84.99	4.4	0.5	1.2	1.2
ΔE*		9.2	0.6	4.4	3.9
Scouring and Bleaching (No Metals)					
Ring Spun					
Δa*	1.38	-1.1	-1.1	-1.3	-1.3
Δb*	14.61	-11.0	-9.3	-9.5	-9.0
ΔL*	85.28	7.2	7.6	6.9	7.2
ΔE*		13.2	12.1	11.8	11.6
Open End Spun					
Δa*	1.70	-1.4	-1.5	-1.5	-1.6
Δb*	14.90	-13.2	-9.9	-9.9	-9.6
ΔL*	85.64	8.2	7.4	6.4	6.9
ΔE*		15.7	12.5	11.9	12.0

An increase in ΔL* and simultaneous decrease in Δb* indicates a whitening of a sample. The most distinct increase occurred for the sodium hydroxide scoured samples. The other samples showed similar but lower levels of whiteness. The bleaching effect of the solvent extracted yarns was not completely uniform along the fiber length.

The hand of alkali pretreated samples however was rather harsh and felt uncomfortable while the samples after the other treatments were soft. The goal for all further experiments was therefore to achieve a comparable grade of whiteness as in the case of the caustic scoured samples but with less fiber damage and higher levels of softness.

Bleaching in Presence of Metal Ions

In the next two sets of experiments ferric nitrate, $Fe(NO_3)_3$, and cupric sulfate, $CuSO_4$, were added in concentrations of 0.05 g/L to 0.1 g/L bleach liquor. The whitening effect in presence of these salts was only limited. Independent of the concentration, a reduction in the yellowness component (Δb*) by about 5 on the average and an increase in lightness (ΔL*) below 1.0 was measured but was not visually detectable. Tensile tests showed that the breaking load remained unchanged within the limits of experimental error.

A dramatic increase in the whiteness of the yarns, however, could be achieved if the iron(III) salt was replaced by an iron(II) salt ($FeSO_4$). Table 3 shows a comparison of color coordinates for two batches of bleached ring-spun yarns. One set was bleached in presence of 0.1 g/L $Fe(NO_3)_3$ with the amount of sequestering agent reduced by half, the other in presence of $FeSO_4$ with supplementary hard water ions (Ca and Mg ions). The data in Table 3 clearly show the higher efficiency of iron(II), especially under hard water conditions, as compared to iron(III) ions. While the $H_2O_2/FeSO_4$ system rendered the fabric a high level of whiteness, the $H_2O_2/Fe(NO_3)_3$ treated fabric exhibited a grayish tint.

Table 3. CIEL*a*b* color coordinates of scoured and bleached ring-spun cotton yarns (D65 light source) after scouring and bleaching.

Color Coordinates	Control	Solvent Extracted	Enz. Batch 1	Enz. Batch 2
0.1 g/L $Fe(NO_3)_3$ Added; 1/2 the Amount of Silicate				
Δa*	1.55	0.0	0.0	0.0
Δb*	15.45	-5.4	-6.4	-6.0
ΔL*	86.86	-3.6	-3.3	-2.8
ΔE*		6.5	7.2	6.6
0.1 g/L $FeSO_4$ Added				
Δa*	1.38	-1.1	-1.0	-0.9
Δb*	15.20	-9.4	-10.0	-9.4
ΔL*	87.16	5.0	6.3	5.7
ΔE*		10.8	11.9	11.0

Figure 2 shows a comparison of relative breaking loads of ring- and rotor-spun yarns after bleaching with the $H_2O_2/FeSO_4$ system. Here the highest discrepancies in tensile properties between the two types of yarns were found for all the investigated bleaching systems. While all ring-spun yarns maintained the level of tensile strength after bleaching, the enzymatically scoured open-end spun yarns suffered a serious strength reduction after this type of bleaching. The more open structure of the rotor-spun yarn most likely allowed for easier access of the pectinase system and a more excessive scouring result. In this case it is possible that the bleaching time could be drastically reduced to produce the same level of whiteness with less strength reduction.

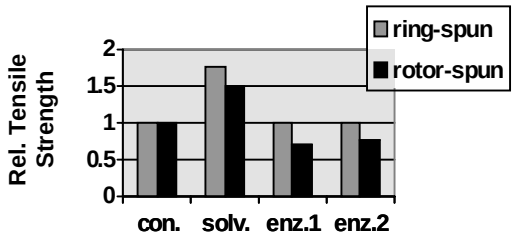

Figure 2. Relative tensile strength of scoured ring- and rotor-spun yarns after bleaching with hydrogen peroxide in presence of Fe(II), Ca(II) and Mg(II) ions (con. = control; solv. = solvent extracted; enz.1,2 = enzymatically scoured, batch 1 and 2).

The hand of enzymatically scoured yarns, especially the open-end spun samples, is very soft and comfortable to touch. Sodium hydroxide and solvent scoured samples, bleached under identical conditions, feel comparatively harsh. In further experiments methods to measure yarn softness will be developed. More experiments will also be necessary to optimize the conditions for scouring and bleaching.

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