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Optimum Conditions for Sequential Oxidative/Reductive Bleaching of Wool in a Single Bath

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ABSTRACT

Conventional bleaching of wool with alkaline H_2O_2 was compared to variations of the ARS single-bath sequential oxidation/reduction bleaching process. The ARS process involves peroxide bleaching (Step 1), then *in-situ* formation of thiourea dioxide from the reaction of thiourea with unspent peroxide (Step 2). Subsequent hydrolysis of thiourea dioxide forms the reducing agent, sulfinate ion, with urea as by-product, and reductive bleaching ensues.

Mechanistic studies for this reaction, using ^{13}C solution NMR in the absence of wool, showed the appearance of urea as a marker for the conversion of thiourea dioxide to sulfinate. In all but the mildest bleaching conditions, the conversion of thiourea dioxide was immediate and complete. Only under the mildest conditions (50°C, 8 g/L peroxide, pH 7.8 for the reductive bleaching step) did a stable thiourea dioxide signal appear, and this disappeared upon the addition of wool.

In bleaching studies on wool challis, we compared conventional peroxide bleaching using 22 g/L (20 mL/L) 30% hydrogen peroxide at 50°C and 60°C with various ARS single-bath compositions: (a) 16 g/L; or (b) 8 g/L in Step 1 followed by the addition of thiourea (70% of the weight of peroxide) in Step 2; or (c) 22 g/L peroxide in Step 1 followed by modifying the bath to reach an effective peroxide level of 16 g/L and 8 g/L before the addition of thiourea.

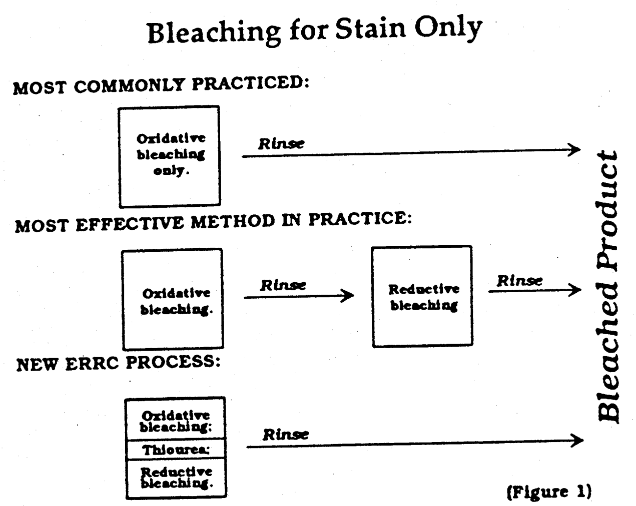
Results indicated that various levels of whiteness can be achieved that equal or surpass conventional alkaline bleaching carried out within the same time and temperature limits. Physical testing of the ARS-bleached fabrics showed them to have achieved comparable or improved whiteness (up to 8 WI units) over the conventionally bleached fabrics. By Instron testing, the whiter ARS-bleached samples have no more than an 11% loss in specific stress, with only slight changes in elastic moduli and % strain at peak stress.

These fabrics were also analyzed by the KES system. The ARS-bleached challis showed measurable decreases in shear stiffness and in bending and shear hystereses, as well as increases in maximum extension. These factors contribute to the overall fabric-handle expression "Shinayakasa," the values of which indicated greater softness, flexibility and smooth feeling for the ARS-bleached fabrics.

INTRODUCTION

The processing of wool most often includes its bleaching to remove stain and, occasionally, black hair contamination. The most effective bleaching regimens for stain incorporate both an oxidative and a reductive bleaching step and are referred to as "full" bleaching. Such full bleaching is normally a two- or three-step process carried out in separate baths. Initial oxidative bleaching normally makes use of hydrogen peroxide. Subsequent reductive bleaching uses such agents as dithionite, sodium formaldehyde sulfoxylate or thiourea dioxide (1).

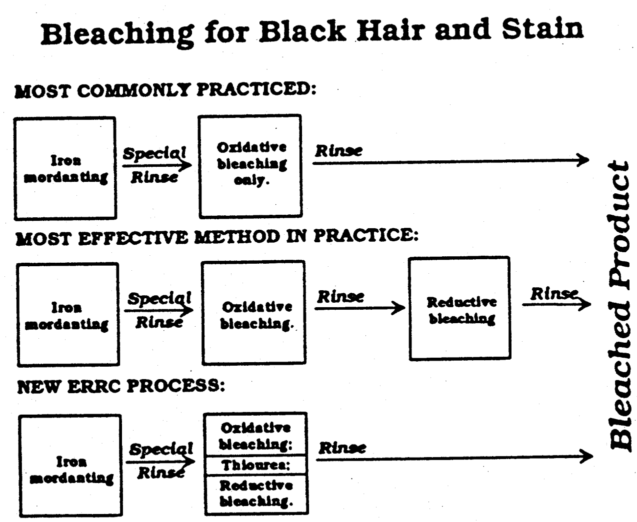
In a series of recent reports (2-6), patents and patent applications (7-13), we have reported on the development of new approaches to full bleaching that integrate the processes into single-bath procedures (Figure 1).



(Figure 1)

By conventional processes, initial bleaching with hydrogen peroxide is interrupted by quenching. Residual peroxide can simply be destroyed catalytically and a subsequent reductive bleaching carried out by addition of reducing bleach. In the ERRC ARS process, residual peroxide is best utilized in a quick chemical reaction that converts the bath into a reductive medium. When thiourea is added under controlled conditions to the peroxide bath, thiourea dioxide is produced. It then hydrolyzes to sulfinate — the reductive bleaching species (2, 4-8, 11, 13).

Bleaching for black-hair removal typically is done by initial mordanting with ferrous sulfate, then controlled rinsing to eliminate all iron except that which is selectively adsorbed onto the black fibers. Then, hydrogen peroxide is added, black hairs are bleached by a radical mechanism induced by adsorbed iron, and overall stain is bleached concomitantly (14). Here again, we have found that residual peroxide may be utilized by conversion of the bleach bath to a reducing medium by controlled addition of thiourea (Figure 2).



This process is more effective for bleaching stain that could have been obscured by the pigmentation. It also eliminates traces of any orange-colored ferric species (from the mordanting) by reduction to soluble ferrous ion (3, 4, 9-11, 13).

A study (6) by ^{13}C NMR of the chemistry of the reductive bleaching process shows that thiourea reacts initially with hydrogen peroxide to form thiourea dioxide (Equation 1):

$$H_2N\text{-}C(=NH)\text{-}SH + 2\,H_2O_2 \longrightarrow H_2N\text{-}C(=NH)\text{-}SO_2H + 2\,H_2O \qquad \text{EQ. 1}$$

thiourea *thiourea dioxide*

Thiourea dioxide in turn undergoes hydrolysis when the pH of the bath is adjusted to 7-8. It is at this step that the redox potential becomes negative, indicating formation of a reductive medium. NMR shows that thiourea dioxide is converted to urea and presumably sulfinate ion, the true reductive species (Equation 2):

$$H_2N\text{-}C(=NH)\text{-}SO_2H + 2\,OH^- \longrightarrow H_2N\text{-}C(=NH)\text{-}OH + SO_2{}^{2-} \qquad \text{EQ. 2}$$

thiourea dioxide *urea* *sulfinate*

Sulfinate in turn acts on the wool and is oxidized to sulfate during the bleaching period (Equation 3):

$$SO_2{}^{2-} + 2\,[O] \longrightarrow SO_4{}^{2-} \qquad \text{EQ. 3}$$

sulfinate *sulfate*

Any residual reductive activity may be quenched at the end of bleaching by addition of a small amount of hydrogen peroxide.

We have developed an extension of the single-bath bleaching process to allow subsequent dyeing in the same bath. This is advantageous not only due to the dissipation of all bleaching activity at the end of the ARS process (thus not jeopardizing the dye species), but also because the products of the bleaching step, urea and sulfate, are themselves dye assists (5).

The procedure for ARS wool bleaching minimizes the amount of thiourea needed without sacrificing resulting whiteness. Thiourea is added in amounts equivalent to the weight of residual peroxide. ^{13}C NMR studies (6) and empirical testing showed that this 3:2 molar ratio of peroxide to thiourea produces a strong reducing medium of high negative potential (-630mV) and an exclusive urea signal. This indicates the complete conversion of thiourea dioxide to urea and sulfinate.

A typical protocol for ARS full bleaching is outlined below under Experimental.

PREVIOUS WORK

Woolen flannel (8.3 oz/yd^2) was bleached by the ARS process—a single-bath, two-step sequential oxidative-reductive system. In the individual steps, time, temperature and peroxide concentration were varied. The bath for Step 1 consisted of H_2O_2 (22.2 g/L; 30% aqueous), tetrasodium pyrophosphate decahydrate (TSPP, 10 g/L), and Triton X-100 (1.0 g/L) at pH 9.5. In Step 2 the concentration of thiourea varied from 3.07 g/L to 7.69 g/L (46% to 100% o.w. neat peroxide).
These prior results showed:

(a) By varying the thiourea concentration and bleaching times, maximum reduction potential and whiteness could be achieved—after one hour at 60°C in Step 1— by the addition of either 4.61 g/L (-663 mV) or 5.38 g/L (-698 mV) of thiourea in Step 2 with a pH adjustment to 7.4 and 25 min of subsequent reductive bleaching.

(b) By varying the time of oxidative bleaching in Step 1 from 40 to 60 min, followed by 25 min of reductive bleaching in Step 2 with 6.15 g/L thiourea, an improved whiteness of 8-14 WI units could be achieved over the results from 65 to 85 min of oxidative bleaching (Step 1) alone.

(c) By increasing the bath temperature from 55 to 70°C, increased whiteness was observed as follows:

55 to 60°C, +2 WI; 55 to 70°C, +5 WI (2).

We extended these studies to investigate the efficiency of bleaching when the initial peroxide concentration in Step 1 is reduced from 22 g/L to 8 g/L, 16 g/L, or 12 g/L. We also investigated corresponding "modified" bleach baths where the original 22 g/L peroxide was decreased to 8 g/L or 16 g/L at the end of Step 1 by discarding a portion of the bleach bath. This allowed a lesser amount of thiourea to be needed for running Step 2. We carried out these reactions at 50°C and 60°C (and 55°C in the case of 12 g/L).

Further mechanistic studies also were carried out using ^{13}C NMR solution spectroscopy and ^{13}C-labelled thiourea to follow the conversion of the oxidative bath to the reductive bath.

EXPERIMENTAL

Materials

Thiourea[1] and sodium pyrophosphate (TSPP) decahydrate were obtained from Aldrich Chemical Co.[2], Milwaukee, WI. Hydrogen peroxide was a 30% (w/w) aqueous solution obtained from Mallinckrodt, Inc., Paris, KY. Avolan UL-75 amphoteric wetting agent was provided by Mobay Corp., Pittsburgh, PA.

Worsted wool challis, weight 3.7 oz/yd^2, fabric thickness 0.78 mm (at 0.5 gf/cm^2) was purchased as 530NC from Test fabrics, Middlesex, NJ. It was received already mildly scoured with nonionic rinsing, decatized, and without having been carbonized.

ARS Full Bleaching Technique

Step 1, Oxidative Bleaching: Bleaching was carried out at a liquor ratio of 30:1, typically using 10 g of woolen fabric and 300 mL of bleaching medium for each of six beakers in an Ahiba Texomat apparatus (Ahiba A.G., Dietlikon, Zurich, Switzerland). Wool was added at ambient temperature to an alkaline bleach bath of the following composition: 30% aqueous hydrogen peroxide (8.0 g/L, equivalent to 2.4 g/L neat hydrogen peroxide), tetrasodium pyrophosphate decahydrate (TSPP; 2.0 g/L), Avolan UL-75 (0.167 g/L). The pH of the bleach bath initially was 9.1. The bath temperature was increased at a rate of 1°C/min to 60°C (140°F), and oxidative bleaching was allowed to proceed for 1 hr from the addition of wool to the bath. At the end of this stage, the pH of the bleach bath had decreased somewhat (to 8.2-8.7).

Step 2, Reductive Bleaching: The bath, while still 60°C, was acidified to a pH of 5.0-5.5 with acetic acid (56%; approximately 3 mL/L). Then thiourea was added; 1.68 g/L would be equivalent to 70% of the initial hydrogen peroxide, but titration of residual peroxide would probably show about a 10% loss by this time, and a concomitant adjustment in the amount of thiourea would be appropriate (though not necessary). Ten min was allowed for reaction with residual hydrogen peroxide in the bath (to form thiourea dioxide). Then sufficient aqueous ammonia was added to adjust the pH to 6.8-7.2 to obtain the surge in potential to -640 mV to carry out reductive bleaching. Reductive bleaching was allowed to proceed for an additional 25 min at 60°C.

For bleaching with 12 g/L and 16 g/L peroxide levels, the bath amounts were proportional quantities. For modified ARS bleach baths, Step 1 with 22 g/L peroxide was completed and a proportional volume of the bath was discarded and replaced with water to lower the concentration to 8, 12, or 16 g/L before Step 2.

Variations in Bleaching for Optimum Conditions

The various conditions for ARS bleaching are found in Table I. The standard fabrics (STD, unbleached) were carried through both steps, but without contact with any bleaching medium.

[1] Although thiourea is a cancer-suspect agent, it is easily handled with care and is completely consumed upon reaction with hydrogen peroxide.

[2] Reference to a particular brand or firm name does not constitute endorsement by the U.S. Department of Agriculture over others of a similar nature not mentioned.

TABLE I. Conditions for ARS Bleaching, Optimization Runs

SAMPLE NAME	Step 1 $[H_2O_2]$ (g/L)	Step 1 t (min)	Step 2 $[H_2O_2]$ (g/L)	Step 2 t (min)	T (°C)
STD6000	0	85	(no Step 2)		60
STD5000	0	85	(no Step 2)		50
CON6022	22	85	(no Step 2)		60
CON5022	22	85	(no Step 2)		50
ARS6016	16	60	16	25	60
ARS5016	16	60	16	25	50
ARS6008	8	60	8	25	60
ARS5008	8	60	8	25	50
ARS5512	12	60	12	25	55
MOD6016	22	60	16	25	60
MOD5016	22	60	16	25	50
MOD6008	22	60	8	25	60
MOD5008	22	60	8	25	50

Measurements of Fabric Properties

Whiteness Index (WI; ASTM E-313; 3.387Z - 3Y) and Yellowness Index (YI; ASTM D-1925; 100 [1.277X - 1.06Z)/Y]) were measured on The Color Machine spectrophotometer (BYK Gardner). Measurements were made using 360° circumferential illumination by a quartz halogen lamp at a color temperature of 2854 K (CIE Source C illuminant, CIE Standard 2° observer) at a 45° angle from the sample's normal direction, with sample viewing at 0°.

Fabric Handle

The Kawabata Evaluation System (KES) was used to examine the fabric's physical and mechanical properties, using weight, thickness, and tensile bending, shearing, and compression data.

Instron Testing

Fabrics were measured for specific stress, elastic moduli, and percentage strain at peak stress on an Instron Model 1122 analyzer. Analyses were carried out according to ASTM 1682-64, Raveled Strip method for wet specimens (Section 17.2) with 23 kg (50 pound) load cell (Instron 2511-103) and full range switch setting 50 for 50-pound full-scale load deflection. Crosshead speed was 200 mm/sec to allow the fabric strip to break within 23 sec during the test. Force to break was normalized to the fabric linear density (g/cm) with specific stress reported as N•cm/g.

NMR Spectroscopy

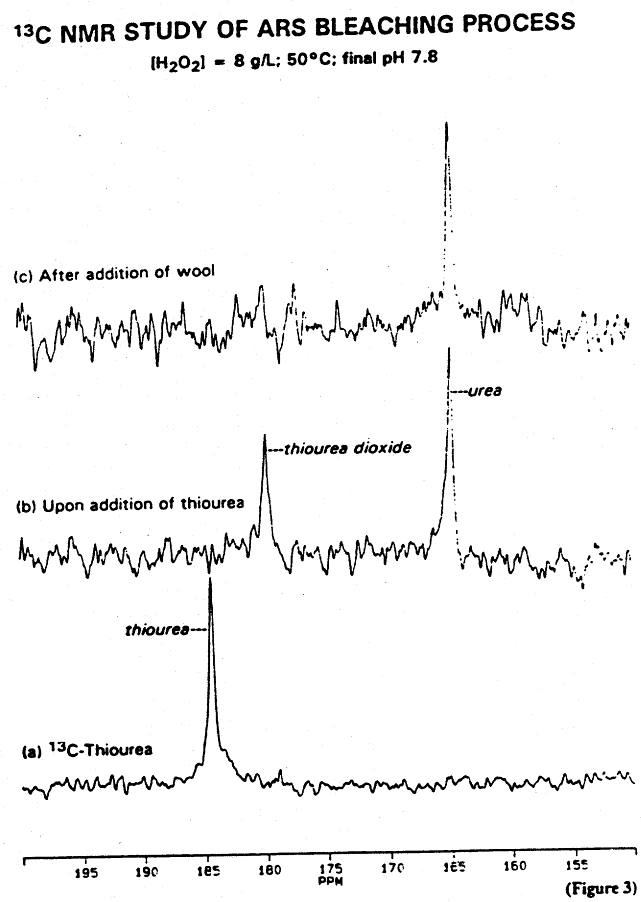
All ^{13}C-NMR spectra were obtained on a Bruker MSL-300 instrument operating at 75.5 MHz. All spectra were obtained with a 9 microsec (80°) pulse with a recycle time of 10 sec. Each spectrum was obtained from 66 8K-data-point scans. Temperature was controlled to within ± 1°C.

We examined the 8 and 16 g/L (Step 2) reactions at 50°C and 60°C and at pH ranges of 7.1-7.8 and 8.4-8.9. The procedure involved preparing 15 mL stock solutions of 8 g/L (1.07×10^{-3} mol) peroxide and 16 g/L (2.14×10^{-3} mol) peroxide. The corresponding amounts of thiourea required were 3.3×10^{-4} mol and 6.6×10^{-4} mol, respectively, wherein the peroxide to thiourea molar ratio was 3:2 in each case. Aliquots (3 mL) were taken for each NMR analysis.

RESULTS

Reaction Mechanism

The NMR spectrum of ^{13}C-thiourea (Figure 3a) was not stable in the presence of hydrogen peroxide at pH 4.5-5.5, but changed instead to the signal for thiourea dioxide (179.8 ppm). When the pH then was raised to >7, complete reaction of the thiourea dioxide was seen, leaving only a signal for the reaction product urea (164.7 ppm). Under the mildest bleaching conditions (8 g/L, 50°C, pH 7.8), however, the thiourea dioxide signal remained pronounced along with the new signal for urea (Figure 3b). Complete conversion to urea in that case was observed (Figure 3c) only after wool was added and stirred into the bleaching solution.



(Figure 3)

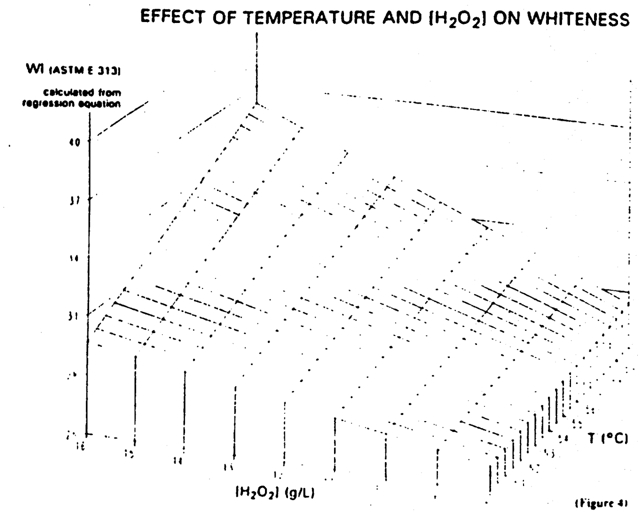
These findings support the work of others who found that the decomposition of thiourea dioxide is controlled by the effect of temperature and time with higher temperature causing greater decrease in thiourea dioxide in the absence of wool. In the presence of wool there was an obvious acceleration of the rate of decomposition of thiourea dioxide (15).

Whiteness and Yellowness

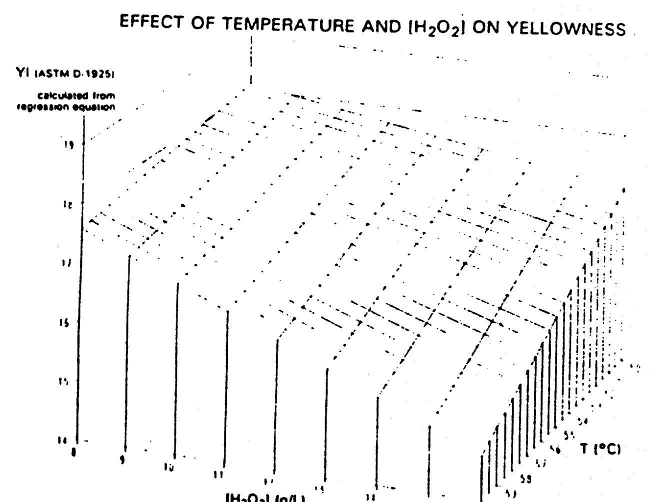
The average values for whiteness index WI and yellowness index YI for 18 replications for each bleaching condition are reported as observed values and have been analyzed for statistical differences. The estimated values used to formulate the graphs in Figures 4 and 5 were derived from the method of least squares from the multiple regression equations 4 and 5 to describe the influence of temperature (T), peroxide concentration $[H_2O_2]$, and the combined effects:

$$WI = 43.745 - 0.42T - 2.89\,[H_2O_2] + 0.066T\,[H_2O_2] \quad \text{EQ. 4} \; (R^2 = 0.918)$$

$$YI = 13.04 + 0.123T + 0.973\,[H_2O_2] - 0.022\,T\,[H_2O_2] \quad \text{EQ. 5} \; (R^2 = 0.900)$$



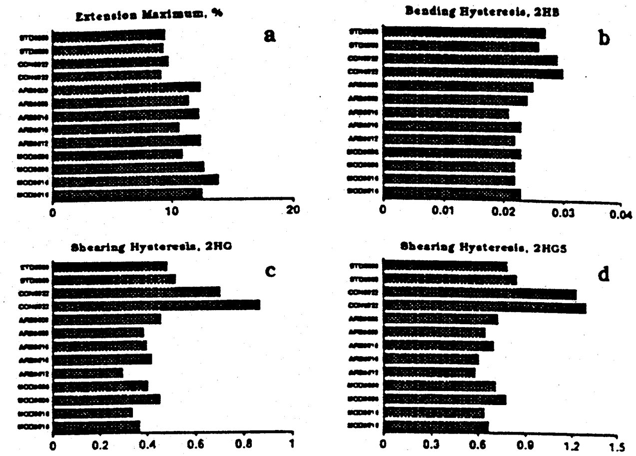
(Figure 4)



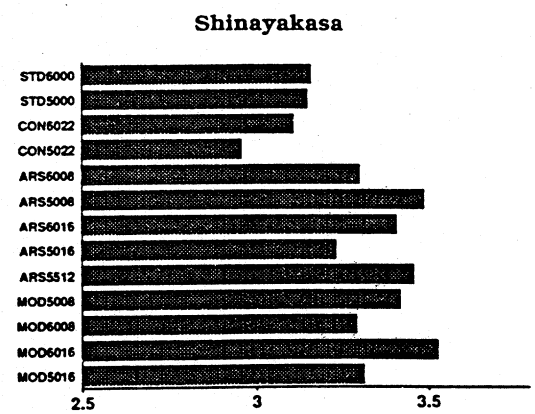
(Figure 5)

Fabric Handle

Evaluation of fabric handle by the Kawabata Evaluation System (KES-F) was made on three fabrics selected randomly from the 18 replications per bleaching condition. Each fabric was tested three times in the warp and three times in the weft directions for a total of 6 evaluations. The most pronounced differences (Figure 6, a-d) when conventional and ARS fabrics are compared are in the parameters EM% (extension maximum at 500 g/cm) in (a), 2HB (Bending Hysteresis) in (b), 2HG (Shearing Hysteresis at 0.5° shear angle) in (c), and in 2HG5 (Shearing Hysteresis at 5° shear angle) in (d). The hand expression suitable for thin fabrics, in particular for women's thin dress fabric is the Kawabata term, "Shinayakasa" (16), which indicates softness, flexibility, and smooth feeling. Shinayakasa results are shown in Figure 7.

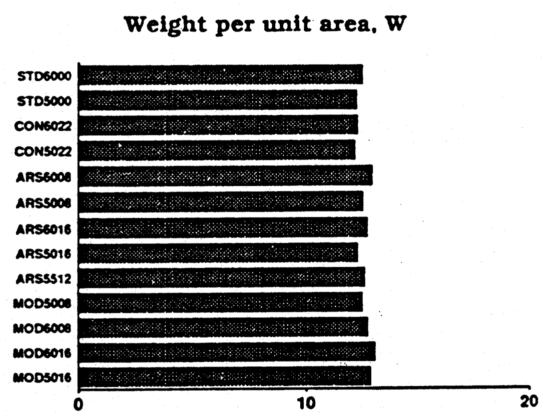


(Figure 6)



(Figure 7)

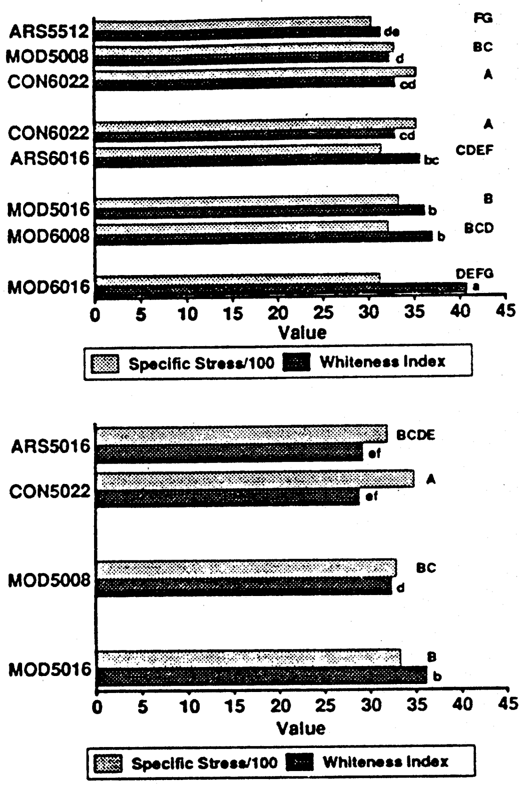
The KES system also provides the "W" parameter for weight per unit area in mg/cm^2 in Figure 8. It can be used in reference to chemical damage for comparing the after-effects of wool bleaching.



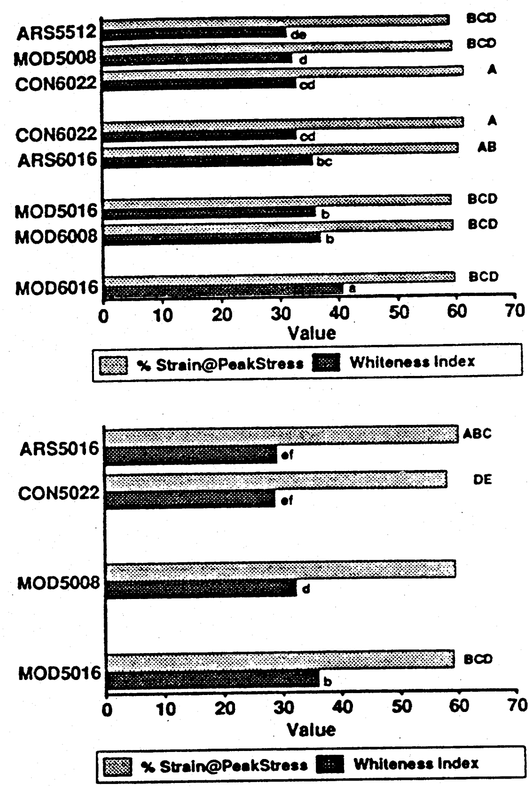
(Figure 8)

Mechanical Property Testing

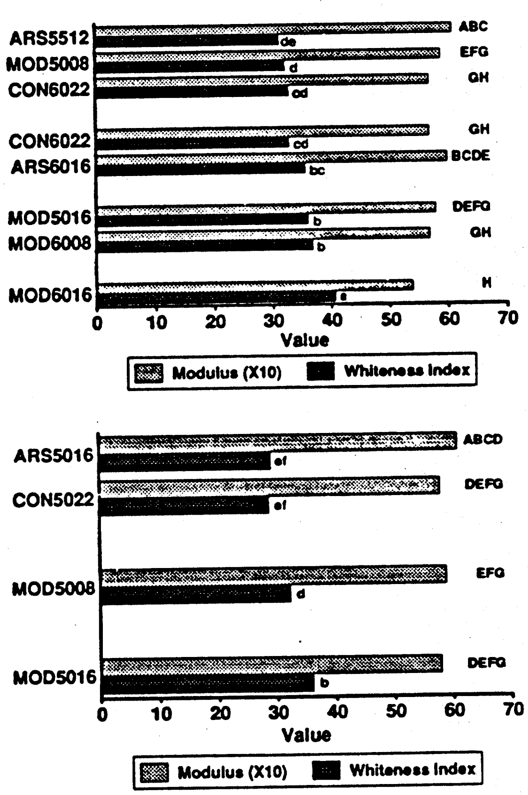
Results from Instron testing are given in Figures 9-11. Solid bars indicate whiteness (WI) and shaded bars indicate the mechanical property (specific stress, elastic modulus, and percent strain at peak stress, respectively). In each figure, the top set compares all bleachings (50 and 60°C) shown to give equivalent or better whiteness than the conventionally bleached sample CON6022. The bottom set compares all 50°C bleachings that gave equivalent or better whiteness than CON5022 (itself a 50° bleaching). All bars labelled with a common letter are not statistically different ($p<.005$).



(Figure 9)



(Figure 11)



(Figure 10)

DISCUSSION

Relative to <u>conventional bleaching at 60°C</u> (CON6022; 85 min oxidative bleaching only; $[H_2O_2]$ = 22 g/L, WI = 33), the following observations were made: (Note that bold entries are statistically different; *italicized are not* [p<.005].)

To achieve the <u>same degree of whiteness</u>, use the conditions of ARS5512 (drop T to 55°C; use only 12 g/L H_2O_2 (*WI = 31*)). This results in the following mechanical and KES properties:

14% loss in specific stress.
7% increase in elastic modulus.
4% reduction in % strain at peak stress.
KES Shinayakasa: 111%
KES Bending Hysteresis 2HB: 75%
KES Shear Stiffness G: 80%
KES Shearing Hysteresis (0.5 deg) 2HG: 43%
KES Shearing Hysteresis (5.0 deg) 2HG5: 48%
KES Maximum Extension @500 g/cm, EM%: 128%

or use the conditions of MOD5008 (drop T to 50°C; start at 22 g/L H_2O_2, but reduce to 8 g/L (*WI = 32*):
7% loss in specific stress.
No change in elastic modulus.
3% reduction in % strain at peak stress.
KES Shinayakasa: 110%
KES Bending Hysteresis 2HB: 78%
KES Shear Stiffness G: 88%
KES Shearing Hysteresis (0.5 deg) 2HG: 58%
KES Shearing Hysteresis (5.0 deg) 2HG5: 58%
KES Maximum Extension @500 g/cm, EM%: 112%

or use the conditions of ARS6016 (keep T at 60°C; use only 16 g/L H_2O_2 (*WI = 36*):
11% loss in specific stress.
5% increase in elastic modulus.
No change in % strain at peak stress.
KES Shinayakasa: 110%
KES Bending Hysteresis 2HB: 73%
KES Shear Stiffness G: 85%
KES Shearing Hysteresis (0.5 deg) 2HG: 57%
KES Shearing Hysteresis (5.0 deg) 2HG5: 57%
KES Maximum Extension @500 g/cm, EM%: 126%

To achieve better whiteness using an ARS process, use the conditions of MOD5016 (drop T to 50°C; start at 22 g/L H_2O_2, but reduce to 16 g/L for Step 2 (*WI = 36*):

6% loss in specific stress.
No change in elastic modulus.
4% reduction in % strain at peak stress.
KES Shinayakasa: 106%
KES Bending Hysteresis 2HB: 78%
KES Shear Stiffness G: 86%
KES Shearing Hysteresis (0.5 deg) 2HG: 53%
KES Shearing Hysteresis (5.0 deg) 2HG5: 54%
KES Maximum Extension @500 g/cm, EM%: 129%

or use the conditions of MOD6008 (keep T at 60°C; start at 22 g/L H_2O_2, but reduce to 8 g/L for Step 2 (*WI = 37*):

9% loss in specific stress.
No change in elastic modulus.
3% reduction in % strain at peak stress.
KES Shinayakasa: 106%
KES Bending Hysteresis 2HB: 75%
KES Shear Stiffness G: 87%
KES Shearing Hysteresis (0.5 deg) 2HG: 65%
KES Shearing Hysteresis (5.0 deg) 2HG5: 63%
KES Maximum Extension @500 g/cm, EM%: 130%

To achieve the best whiteness using an ARS process, use the conditions of MOD6016 (keep T at 60°C; start at 22 g/L H_2O_2, but reduce to 16 g/L for Step 2 (*WI = 41*):

11% loss in specific stress.
No change in elastic modulus.
3% reduction in % strain at peak stress.
KES Shinayakasa: 114%
KES Bending Hysteresis 2HB: 77%
KES Shear Stiffness G: 83%
KES Shearing Hysteresis (0.5 deg) 2HG: 48%
KES Shearing Hysteresis (5.0 deg) 2HG5: 52%
KES Maximum Extension @500 g/cm, EM%: 142%

We may also compare the conventional bleaching run at 50°C (CON5022, 85 min oxidative bleaching only, (*WI = 29*)) to the ARS bleaching runs done at 50°C:

To achieve the same degree of whiteness, use the conditions of ARS50 16 (16 mL/L H_2O_2 (*WI = 29*):

8% loss in specific stress.
No change in elastic modulus.
3% increase in % strain at peak stress.
KES Shinayakasa: 109% of CON5022
KES Bending Hysteresis 2HB: 76%
KES Shear Stiffness G: 85%
KES Shearing Hysteresis (0.5 deg) 2HG: 48%
KES Shearing Hysteresis (5.0 deg) 2HG5: 47%
KES Maximum Extension @500 g/cm, EM%: 116%

For better whiteness, use the conditions of MOD5008 (start at 22 mL/L H_2O_2, but reduce to 8 mL/L for Step 2 (*WI = 32*):

6% loss in specific stress.
No change in elastic modulus.
2% increase in % strain at peak stress.
KES Shinayakasa: 116% of CON5022
KES Bending Hysteresis 2HB: 76%
KES Shear Stiffness G: 88%
KES Shearing Hysteresis (0.5 deg) 2HG: 47%
KES Shearing Hysteresis (5.0 deg) 2HG5: 55%
KES Maximum Extension @500 g/cm, EM%: 120%

For the best whiteness at 50°C, use the conditions of MOD5016 (start at 22 g/L H_2O_2, but reduce to 16 g/L for Step 2 (*WI = 36*):

4% loss in specific stress.
No change in elastic modulus.
No change in % strain at peak stress.
KES Shinayakasa: 112% of CON5022
KES Bending Hysteresis 2HB: 76%
KES Shear Stiffness G: 85%
KES Shearing Hysteresis (0.5 deg) 2HG: 43%
KES Shearing Hysteresis (5.0 deg) 2HG5: 51%
KES Maximum Extension @500 g/cm, EM%: 137%

CONCLUSION

The most pronounced property changes were in whiteness, strength, and fabric handle. We have shown that the whiteness indices (WI) for ARS-bleached fabrics using less peroxide compare to or surpass the WI for fabrics bleached by the conventional process.

All ARS-bleached samples were up to 11% weaker than conventionally bleached fabrics CON6022 and CON5022 at 60° and 50°C. Statistically, there were no differences in specific stress among all ARS-bleached fabrics at 50°C, but all were weaker yet whiter than the conventionally bleached CON5022. Statistically, ARS fabrics bleached at the higher temperature, 60°C, were except for MOD6008 weaker than fabrics bleached at 50°C, and they were weaker than conventionally bleached CON6022.

Regarding determinations of elastic modulus, run on the Instron analyzer, only two of the ARS bleachings showed significant changes (slight increases, ≤7%) from the conventional bleachings. Regarding percent strain at peak stress, also run on the Instron analyzer, most ARS samples broke at a slightly lower extension (≤5%) than the conventional runs.

The KES studies provide a better examination of mechanical properties under slight deformation, which correlate better to fabric handle than the Instron-derived values. Figures for maximum extension @500 g/cm indicate markedly higher extensions (up to 142%) for the ARS samples. These differences and those seen for shearing and bending properties all contribute to the KES expression "Shinayakasa," for improved softness, flexibility and smooth feeling. The ARS samples fell in a range of 109 to 116% of the CON6022 value.

Although there is a slight trade-off in strength loss of 6 to 11%, the advantage to using ARS bleaching is better whiteness, softer handle and a savings in energy. Energy is conserved, of course, when the process is run at 50°C. However, if we compare the ARS single-bath process to "full" conventional bleaching (oxidative in one bath and reductive in another), further energy savings are obvious. An added bonus is that the spent ARS bath contains sulfate from oxidized sulfinate and urea from reacted thiourea dioxide; these products are dye-assists for subsequent dyeing when the ARS-bleaching technology is expanded to include dyeing in the same bath (5).

Although chemical analysis for protein damage to wool has not been completed for the latest study, earlier studies of alkali solubility indicated no deterioration (2). Furthermore, the KES fabric weight determinations (W) for all samples presented here appear to be the same (Figure 8), supportive of minimal damage by alkali.

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