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Sequential Oxidative/Reductive Bleaching of Wool in a Single Bath: Woolen Flannel Studies for Bleaching Efficiency and Photostability, and Expansion of the Scope of the Process to Wool/Cotton Blends and All-Cotton Fabric.[1]

ABSTRACT

In a followup to an investigation of the bleaching of worsted challis by the Agricultural Research Service (ARS) two-step, single-bath sequential oxidative/reductive process ("full" bleaching), comparative bleaching studies were carried out on another fabric type, woolen flannel. In the new studies, fabric was bleached in the individual oxidative and reductive steps of full bleaching and results were compared to those from ARS- and traditional full bleaching and to those from conventional bleaching by alkaline hydrogen peroxide. We selected conditions for ARS bleaching that were shown previously to give comparable whiteness to fabrics treated by conventional alkaline peroxide bleaching of the same overall time (85 minutes) and temperature (60C). Thus, results from ARS bleaching using 16g/L of 30% peroxide, followed after 60 minutes by addition of thiourea (@ 70% ow 100% peroxide), were compared to results from peroxide bleaching for the full 85 minutes using 22g/L of 30% peroxide. For traditional full bleaching, the ARS process was modified after the 60-minute oxidative step; in a fresh bath, bleaching was continued using thiourea dioxide in molar amounts equivalent to the thiourea dioxide formed *in situ* by the ARS process. These bleached fabrics then were studied for photoyellowing and phototendering following exposure to artificial sunlight. ARS and conventional peroxide bleaching produced the same levels of yellowness after photoexposure. After photoexposure, the specific stress values of the fabrics from the ARS process were significantly higher than those from conventional peroxide bleaching and those values were not less than the unbleached controls. In full bleaching—ARS or traditional—the reductive step contributed to significant strength loss, which was compensated by the oxidative step so that original strength was retained. As seen for all-wool, the ARS process for bleaching of cotton/wool or 100% cotton fabrics gave equivalent whiteness and yellowness values to that achieved by conventional bleaching. It was surprising that bleached 50/50 union cloth with

worsted wool warp and cotton weft showed significant strength loss when stressed in the warp direction while a 50/50 intimate yarn-blended fabric and a 100% cotton fabric showed no strength losses. This suggests that a yarn blend be recommended over a union cloth.

Introduction

In previous reports (*1,3-7*) and patents (*8-14*) we have described a new process for achieving full bleaching (oxidative followed by reductive) of wool in a single bath. The mechanism of the conversion of the oxidative system to the reductive one by introduction of thiourea involves the transient formation of thiourea dioxide and its subsequent hydrolysis to the reducing species, sulfinate anion (SO_2^{2-}), and byproduct urea (*1*). The ARS process described is a very efficient one for achievement of whiteness; it utilizes unspent peroxide and obviates the need for preparation of a second bleach bath. A typical protocol for achievement of maximum whiteness is outlined in the prior study of worsted challis (*1*).

In the worsted challis study, we found that conditions "22/16T" (Table I) produced maximum whiteness. [22/16T is an abbreviation for the bleaching conditions, as follows: (a) the numbers refer to concentrations of 30% hydrogen peroxide in g/L; (b) the slash (/) separates the first from the second step; *i.e.*, the first 60 minutes from the next 25 minutes; (c) the T stands for thiourea, which is added in an amount equivalent to 70% of the neat weight of peroxide that is used in the second step (here, the neat weight of 16g/L of 30% aqueous peroxide; the change from 22 to 16 indicates that a portion of the first bath was discarded and the residual bath was diluted to 16g/L). (d) the bath temperature is 60C (by default) in all studies discussed herein.]

Conditions 16/16T produced equivalent whiteness to conventional alkaline peroxide bleaching "22/22" [i.e., 22g/L of 30% aqueous peroxide for a full 85 minutes (single bath)]. For the present study with woolen flannel, we focused on the 16/16T and 22/22 conditions, and we also isolated the individual steps (such as "16/-"—16g/L of 30% peroxide for 60 minutes). A complete listing of the various conditions studied is provided in Table I. The resulting sets of bleached fabrics were used for mechanical and physical testing before and following exposure to artificial sunlight.

Recent interest in wool/cotton blended fabrics has led us to incorporate these fabrics into our bleaching studies. Along with the woolen flannel fabrics, we studied 50/50 wool/cotton blended fabrics—intimate yarn-blended and union-blended—and, 100% cotton fabric for reference.

Experimental

Materials

Thiourea[2], thiourea dioxide (formamidinesulfinic acid), and sodium pyrophosphate (TSPP) decahydrate were obtained from Aldrich Chemical Co.[3], 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. Woolen flannel (Carleton Woolen Mills, Inc., Style #188), fabric weight, 11.9oz./linear yd., was processed by carbonizing and alkaline fulling followed by scouring and acetic acid souring to pH 6.5. Also used were the following fabrics: pima cotton/wool yarn blend, 50/50 (Testfabrics Style #5400), 7 1/2-8oz/yd^2, 2 × 2 left-hand twill, scoured, rinsed, dried, but unbleached and not chlorinated; cotton/wool union cloth, 50/50 (Testfabrics Style #4504), 4.3oz/yd^2, plain weave, scoured, without bleaching or chlorination; and

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

[3]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.

100% cotton print cloth (Testfabrics Style #U400), 3.1oz/yd^2, plain weave, desized, scoured, rinsed, dried, unbleached.

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 2854K (CIE Source C illuminant, CIE Standard 2° observer) at a 45° angle from the sample's normal direction, with sample viewing at 0°.

Photoyellowing and Phototendering

Photoyellowing and tendering of bleached woolen flannel was carried out in a Xenon exposure system under controlled irradiance (Atlas Ci65A Weather-Ometer) according to AATCC test method 16-1990, Colorfastness to Light, option E, "Water-Cooled Xenon-Arc Lamp, Continuous Light" with soda lime outer and borosilicate inner filters (full spectral range beginning at 310-320 nm (UV) and into the visible and infrared spectral regions). This illumination simulates outdoor natural sunlight through windowglass. The monitoring point was at 340 nm and exposure time was 80 hours. Relative humidity was maintained at 30-35% ± 5%, black panel temperature at 63 ± 1.0C, and chamber air temperature at 43 ± 2C.

Instron Testing

Fabrics were measured in the wet state for specific stress, elastic modulus, 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). A load cell, Instron 2511-302, 500kg load capacity set at full-range 200kg with crosshead speed 100 mm/sec, was used for these fabrics. Force to break was normalized to the fabric linear density (g/cm) with specific stress reported as Newtons cm/gram.

Results and Discussion

Woolen Flannel

Bleaching: Contributions of Steps 1 and 2

As discussed in the introduction, and as shown in Table I, bleachings are identified by a coded nomenclature that indicates peroxide concentration (e.g., "22") and thiourea ("T"). Thiourea dioxide is abbreviated "TD." Substitution of thiourea and peroxide by an equivalent amount of thiourea dioxide is indicated in brackets; thus, the ARS run 22/16T would be analogous to the traditional full bleaching 22/[16TD].

Table I. Bleaching Conditions, Optimization Runs on Woolen Flannel

Woolen Flannel	Step 1: Oxidative $[H_2O_2]$ (g/L)	Step 1: Oxidative t (min)	Step 2: Reductive $[H_2O_2]$ (g/L)	Step 2: Reductive t (min)	T (C)
0/0 (Control)	0	85	0	25	60
22/22 (Oxidative only, single bath)	22	85	0	25	60
16/16T (ARS full, single bath)	16	60	16	25	60
16/- (ARS, step 1 only)	16	60	0	0	60
22/- (Traditional full, step 1 only)	22	60	0	0	60
-/[16TD]* (Traditional full, step 2 only)	0	0	16	25	60
22/[16TD]* (Traditional full, steps 1 and 2; two baths)	22	60	16	25	60
16/- (Traditional full, step 1 only)	16	60	0	0	60
16/[16TD]* (Traditional full, steps 1 and 2; two baths)	16	60	16	25	60

*Brackets indicate that thiourea dioxide (TD), not peroxide and thiourea (T), was used in these traditional "full" bleaching steps. To compare with the ARS processes, in which thiourea was added only in amounts equivalent to 70% of the residual neat weight of peroxide, thiourea dioxide was added only in molar amounts equivalent to the established 70% weight figures for thiourea. Thus, the ARS run 16/16T (single bath) would be equivalent to the traditional "full" run 16/[16TD] (two baths).

Fig. 1 illustrates bleaching effectiveness in terms of Whiteness Index (WI, ASTM E-313) and Yellowness Index (YI, ASTM D-1925). Note that the minimum significant difference for WI was 4.2 units and for YI, 1.6 units ($p < .05$). In the case of traditional full bleaching (two baths), the fabrics from step 1 were rinsed, dried, and wet out again for step 2 bleaching.

From the wool challis study (*1*), we observed that <u>similar</u> fabric whiteness resulted from conventional runs 22/22 and the ARS runs 16/16T. In the present study on woolen flannel, we therefore used runs 16/16T as the ARS-bleached comparison. This time results of runs 16/16T and 22/22 were similar, but not statistically identical; runs 16/16T's whiteness just surpassed 22/22's by a statistically significant difference. Furthermore, now we can see statistically similar results between traditional full bleaching, runs 16/[16TD], and its parallel protocol, ARS runs 16/16T. The ARS process, of course, offers the added advantage of a single bath for full bleaching.

The WI for runs 22/[16TD] was significantly higher and the YI significantly lower than 22/22; this is not surprising, for in the wool challis study, ARS-bleached runs 22/16T surpassed the whiteness of runs 22/22.

In the examples in which the results from the isolated were considered additive (*i.e.*, steps 1 and 2), those results always indicated less whiteness than what was achieved by the parallel "full" runs (ARS single-bath or traditional dual bath treatment). This apparent synergistic effect was not seen in the yellowness values of Fig. 1.

Photoyellowing and Phototendering

Some of the fabrics of Fig. 1 were subjected to 80 hours of simulated sunlight to determine the effect of bleaching on photoyellowing. The results on the whiteness and yellowness indices are illustrated in Fig. 2. Inspection of the whiteness data shows that all the bleached samples, with the exception of runs -/[16TD], the isolated reductive step 2, experienced a greater loss of whiteness than the unbleached control, 0/0. However, there were no significant differences in the final WI among all the bleached samples. Therefore, the ARS process 16/16T not only was comparable in bleaching efficiency to the conventional peroxide-bleached process 22/22; it also was comparable in its aftereffects of exposure to light.

Inspection of the yellowness data shows a similar pattern. There was a greater increase in yellowness for all bleached samples than the increase for the control sample. Furthermore, the same final YI was achieved for all exposed bleached samples, and slightly (though statistically significant) less than the control.

In general, after 80 hours exposure to simulated sunlight, all the benefits of bleaching were lost. This was the case for all the bleached samples.

The mechanical properties of these same bleached fabrics were investigated before and after exposure to light. Results are illustrated in Fig. 3. Prior to exposure, the ARS-bleached fabric runs (16/16T) showed comparable strength to the conventional alkaline-bleached samples (22/22), and the latter was comparable to the control (0/0). These results differed somewhat from those from the wool challis study (*1*), where 16/16T had shown an 11% loss in strength relative to runs 22/22, and the latter had shown no loss relative to the control 0/0. Whether or not the fabric construction (fulled woolen flannel *vs*. worsted challis) played a role in these differences is just speculation; results in terms of specific stress are normalized for fabric density. Peroxide bleaching at lower concentration and for a shorter time (16/- *vs*. 22/22) led to a strengthening, and reductive bleaching runs (-/16TD) to a weakening. Prior to photoexposure, the strengthening seen in 16/- compensated for the weakening seen in runs -/[16TD], and the results from these individual steps of full bleaching corroborated with results from full bleaching runs (16/16T). This corroboration was maintained in the results that followed photoexposure.

Prior to exposure, extensibility, as measured by % strain at break, was increased by the ARS bleaching (16/16T) relative to the conventional runs (22/22). This followed the pattern seen runs in the wool challis experiments (*1*). The results for the isolated steps, however, are ambiguous, for both steps (16/- and -/[16TD]) led to reductions in strain at break relative to the full process (16/16T).

In all cases, exposure to light led to phototendering—with losses in both strength and extensibility. These results were less severe for the ARS-bleached fabrics than for those bleached conventionally by peroxide.

Wool/Cotton Blended and All-Cotton Fabrics

Bleaching

For all three fabric types tested—the 50% wool/50% cotton fabric of intimately blended yarn (W/C Intimate), the 50% wool/50% cotton fabric of all-wool warp and all-cotton weft ("union blend," W warp/C weft), and the 100% cotton (100% C)—the conventional bleaching runs (22/22) and the ARS bleaching runs (16/16T) gave the same whiteness and yellowness indices (Fig. 4).

Mechanical Testing

With one exception, no differences due to bleaching regimen were seen in either strength loss or strain at break (Fig. 5) in each set of fabrics. The exception was in the specific stress data for the union-blended fabric (W warp/C weft). In this case, both bleachings lessened the fabric's strength, and the ARS-bleaching runs (16/16T) did so more than the conventional runs (22/22). Whatever effect was measured on this fabric was on its wool component, because tension was applied along the wool warp direction. The results seem anomolous, but inasmuch as they were real, we would recommend use of the intimate blend over the union blend.

Conclusions

These studies have focused on properties of fabric—woolen flannel, wool/cotton, and cotton—that result from bleaching to equivalent whiteness using the ARS process (16/16T) or conventional peroxide bleaching (22/22).

Specifically, studies on wool flannel allowed a look at the effect of the individual steps in the ARS two-step process. The cumulative results in whiteness for steps 1 and 2 were more than additive; empirically there seemed to be a synergism in running full (2-step) bleaching, whether by the traditional way runs (22/[16TD] or runs 16/[16TD]) or by the ARS process (16/16T).

These studies also permitted an examination of the propensity of the unbleached and bleached fabrics toward photoyellowing and phototendering. Regardless of the bleaching protocol and the resulting whiteness level thus achieved, subsequent exposure to light reduced whiteness to the same final value. Analogous results were seen for yellowness levels. Light exposure also induced phototendering for all fabrics studied, whether bleached or unbleached, but the final stress and strain values were higher for the ARS-bleached samples (16/16T) than for the peroxide-bleached ones (22/22) of equivalent whiteness.

Studies on the wool/cotton blends and on 100% cotton showed the versatility of the ARS bleaching process toward a cellulosic fiber and its blends with wool. Again, for each fabric type, runs 16/16T and runs 22/22 gave equivalent whiteness and yellowness values. Stress and strain were retained for these fabrics, except for the union blend; that blend, when stress was applied in the wool warp direction, showed an unexplainable loss in strength with the ARS bleaching process.

By these studies we have demonstrated the applicability of the ARS bleaching process to a broader scope of fabrics and fiber types. Based on earlier work *(1)*, the user of the ARS process might select ARS conditions for equivalent whiteness to conventional peroxide bleaching for the resultant softer hand. By analogy, the user could expect to achieve enhanced whiteness and softer hand by applying the modified ARS process 22/16T.

Acknowledgments

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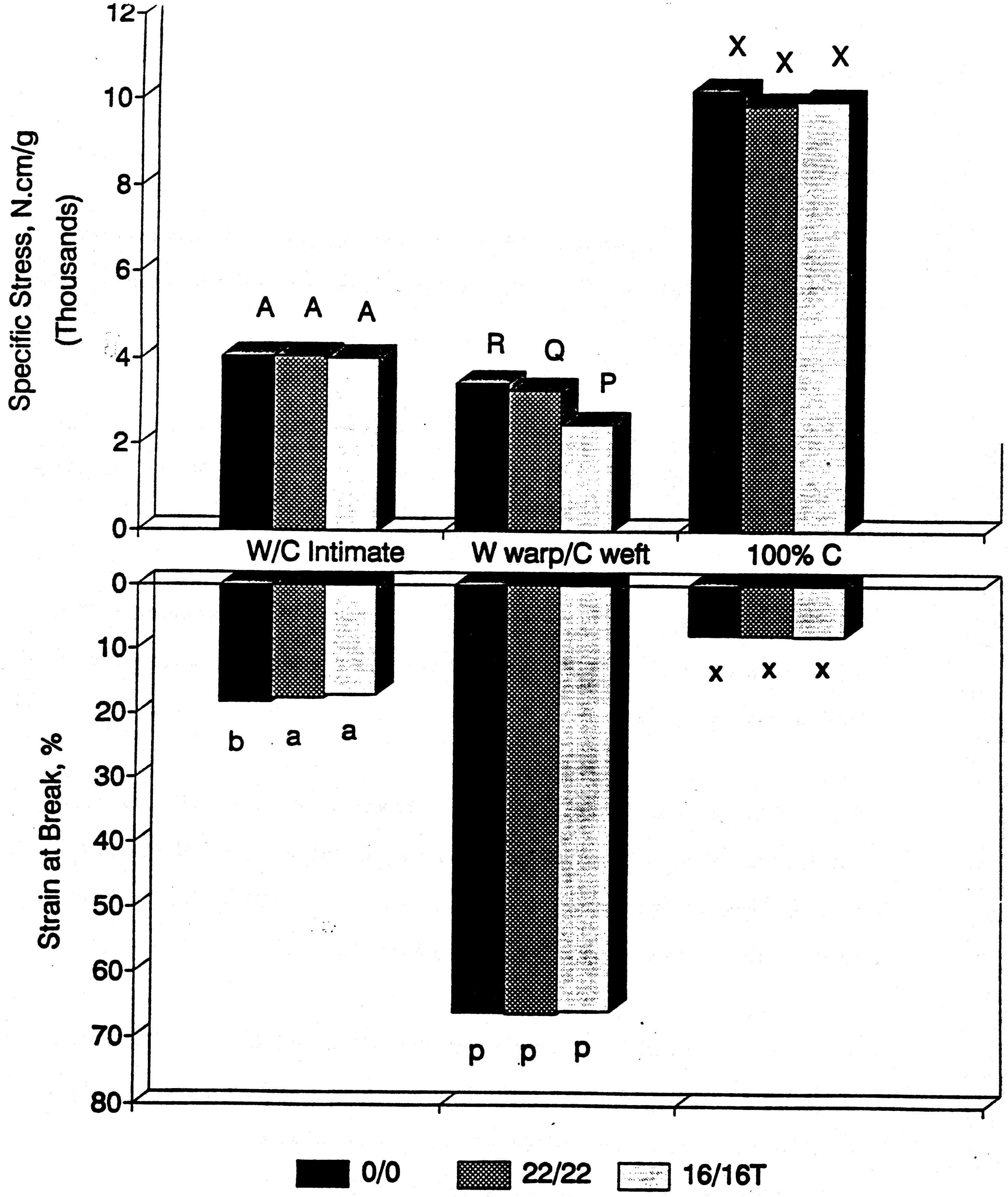
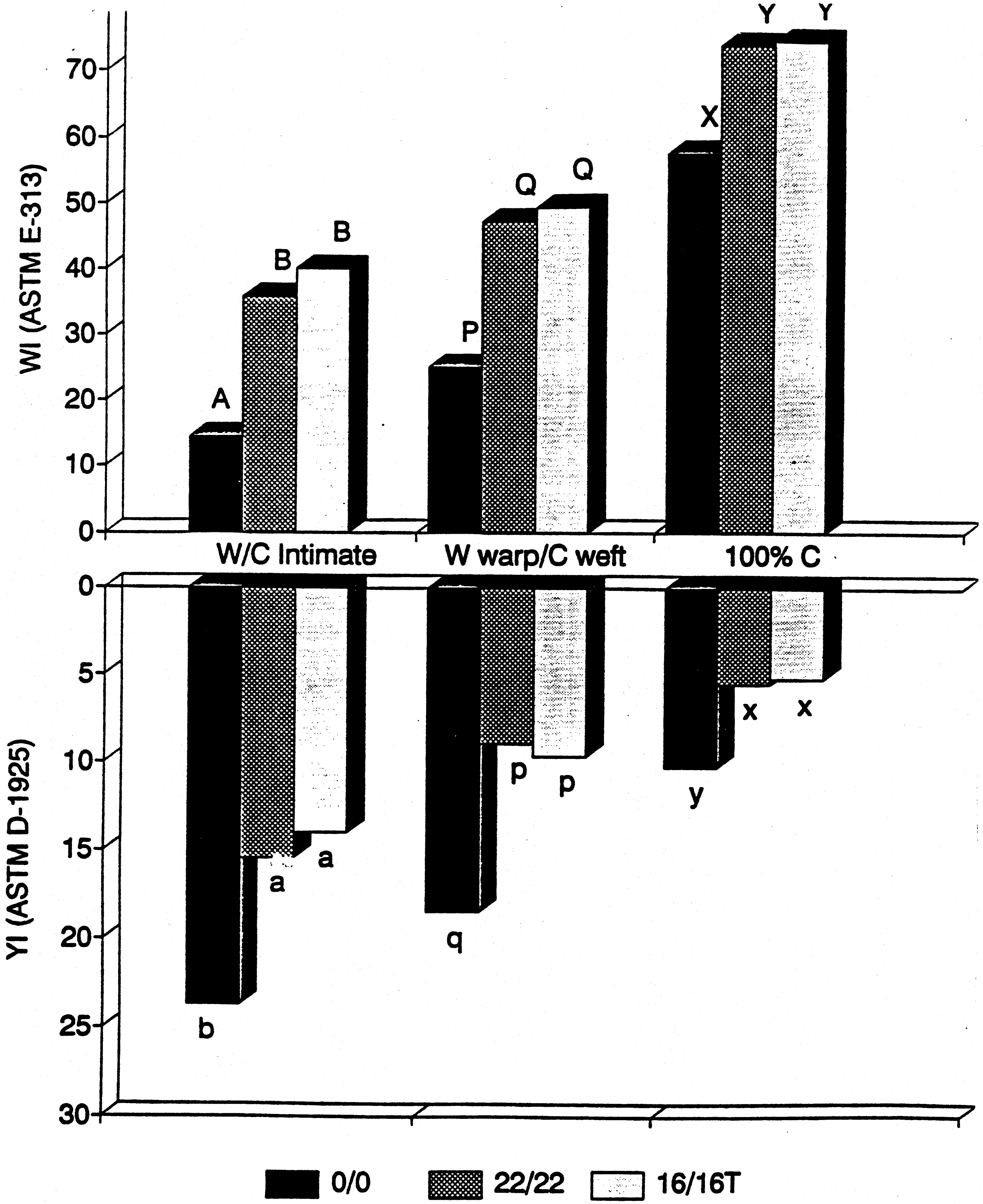
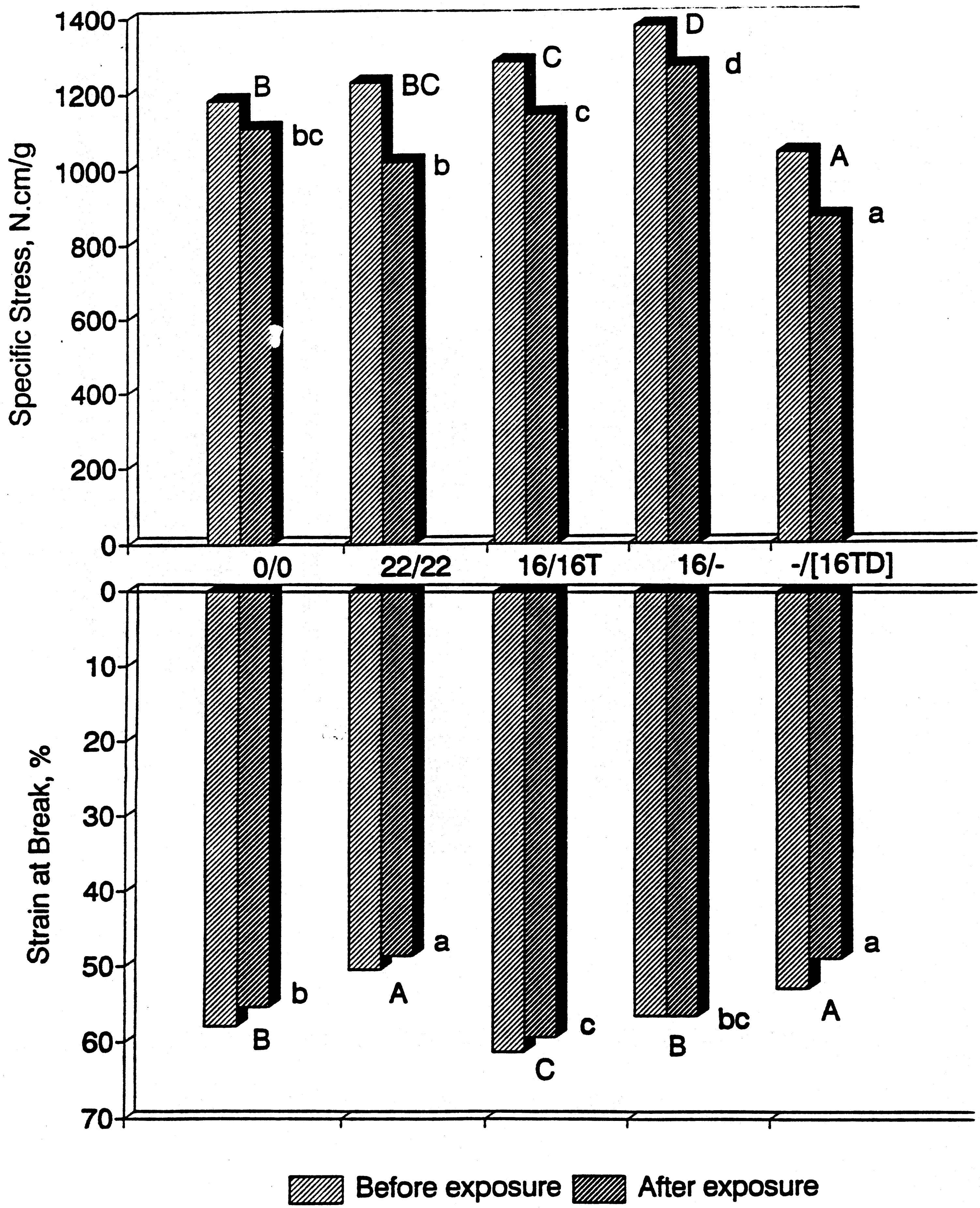
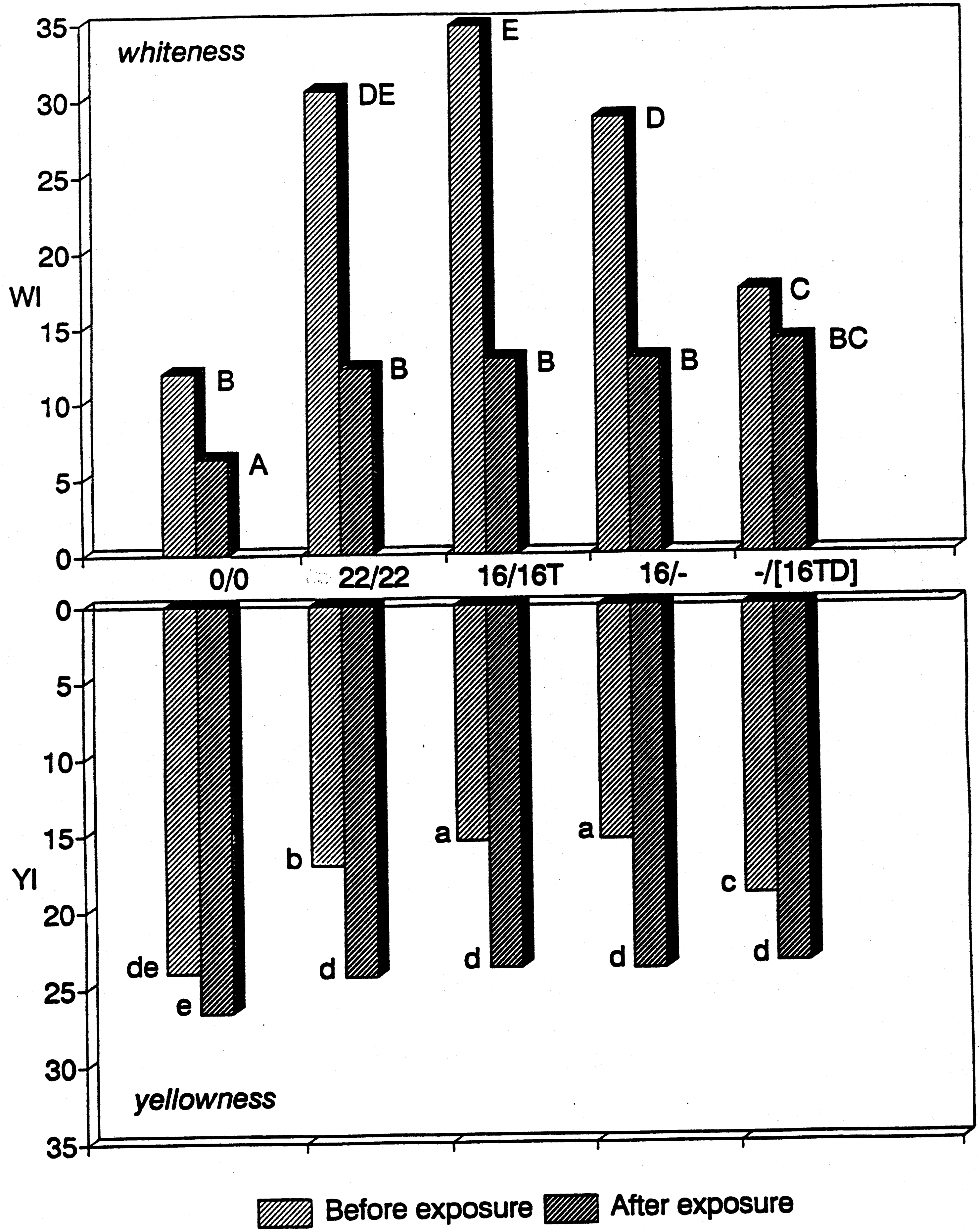
List of Figures



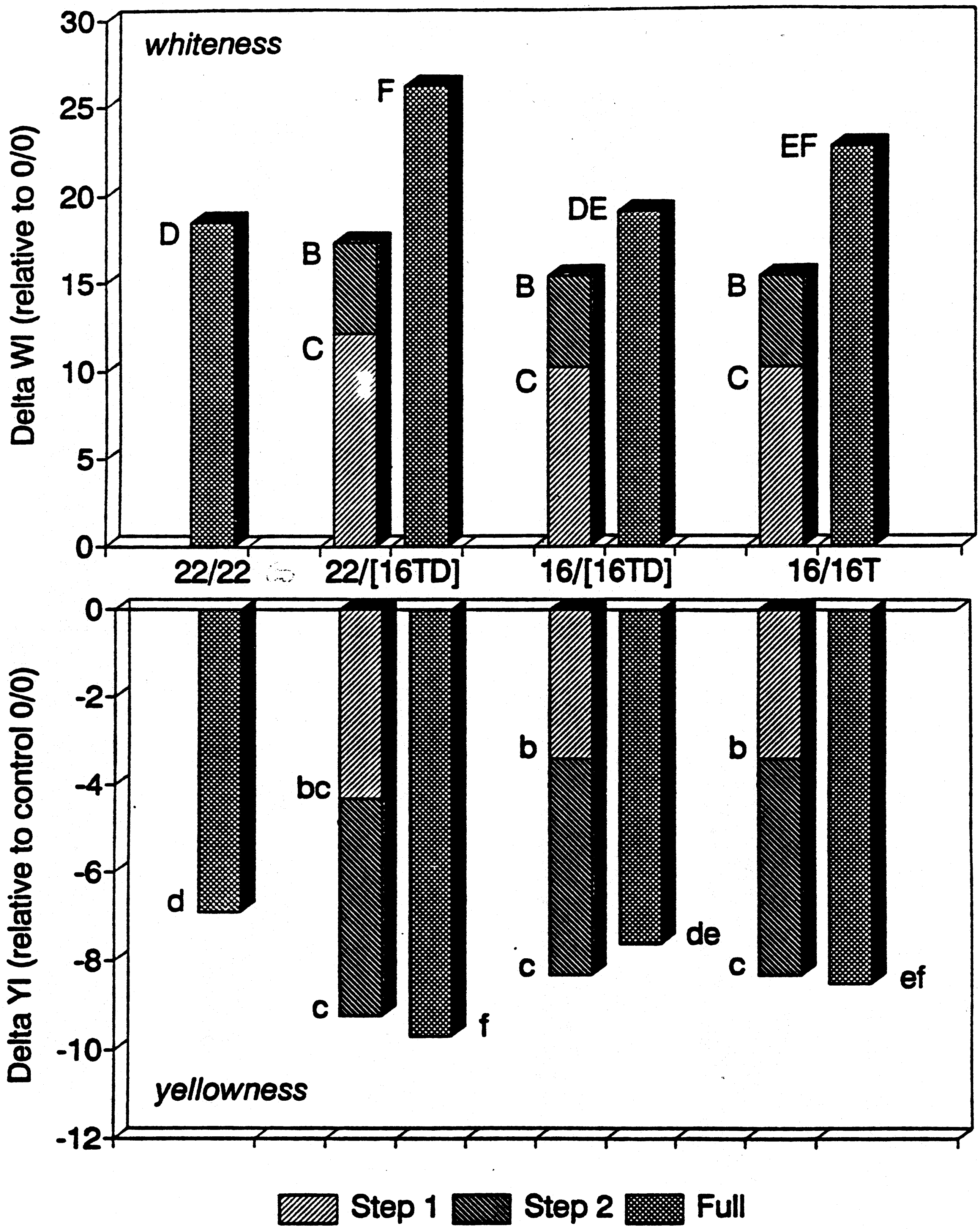
Specific Stress, N.cm/g (Thousands)
12
10
8
6
4
2
0
A A A
R Q P
X X X
W/C Intimate
W warp/C weft
100% C
Strain at Break, %
0
10
20
30
40
50
60
70
80
b a a
p p p
x x x
0/0
22/22
16/16T


WI (ASTM E-313)
0
10
20
30
40
50
60
70
A
B
B
P
Q
Q
X
Y
Y
W/C Intimate
W warp/C weft
100% C
YI (ASTM D-1925)
0
5
10
15
20
25
30
b
a
a
q
p
p
y
x
x
0/0
22/22
16/16T


Specific Stress, N.cm/g
1400
1200
1000
800
600
400
200
0
B
bc
BC
b
C
c
D
d
A
a
0/0
22/22
16/16T
16/-
-/[16TD]
Strain at Break, %
0
10
20
30
40
50
60
70
b
B
a
A
c
C
bc
B
a
A
Before exposure
After exposure



whiteness
WI
35
30
25
20
15
10
5
0
E
DE
D
C
BC
B
B
B
B
A
0/0
22/22
16/16T
16/-
-/[16TD]
YI
yellowness
b
a
a
c
de
e
d
d
d
d
Before exposure
After exposure



whiteness
Delta WI (relative to 0/0)
30
25
20
15
10
5
0
D
B
C
F
B
C
DE
B
C
EF
22/22
22/[16TD]
16/[16TD]
16/16T
Delta YI (relative to control 0/0)
0
-2
-4
-6
-8
-10
-12
d
bc
c
f
b
c
de
b
c
ef
yellowness
Step 1
Step 2
Full