

Wool Shrinkage Control and Surface Modification by Ozone

W. J. THORSEN, W. H. WARD, and M. M. MILLARD, *Western Regional Research Laboratory, Science and Education Administration, U.S. Department of Agriculture, Berkeley, California 94710*

Synopsis

In treating fine wool top, more ozone is needed to achieve a given level of felting shrinkage control than with coarse wool. Treatment that allows no more than about 20% top shrinkage in three successive washes is usually satisfactory for controlling fabric shrinkage. A detergent rinse after treatment markedly decreases top and fabric shrinkage. Ozonization decreases fiber strength and wet friction against glass but increases fiber-to-fiber adhesion enough to increase yarn strength. Scanning electron microscopy (SEM) of fibers before and after treatment and laundering indicates that ozone makes the fiber surface more plastic (presumably when wet) but more liable to mechanical damage and erosion, which increase with the severity of treatment and with laundering. However, treatments most effective for shrinkage control are not distinguished from less effective treatments by the degree and character of surface changes shown by SEM. Ring dyeing of fiber cross sections shows that effects of ozone are greatest near the surface. X-ray photoelectron spectroscopy (XPS) and amino acid analysis show that cystine is oxidized to cysteic acid and that carbon is also oxidized at the surface. The increased dyeability (rate and uptake) is attributed to increased wettability, changed ionic balance, and crosslink scission, which, with cuticle damage, allow greater swelling and easier penetration. As found earlier with coarse wools, acid milling (leveling) dyestuffs further decrease shrinkage of treated fine wool. The position of wool in the triboelectric series is shifted toward the negative end by ozone treatment, expressing the higher electron work function of the added sulfonic acid groups. This shift is not simply related to shrinkage. Decreased feltability is attributed to softening of the wet cuticle layer and to increased surface charge, but the mechanism needs further study.

INTRODUCTION

Several benefits can be achieved by treating wool with ozone. These include a high resistance to felting shrinkage, improved dyeability, increased yarn strength, and altered electrostatic behavior.¹⁻³ After treatment the fibers exhibit increased acid and alkali solubility¹⁻³ and decreased friction.^{1,3} Other physical and chemical changes occur, too. For example, cystine residues in wool are known to be readily oxidized by other oxidizing agents.⁴ The detection, measurement, and evaluation of such changes, particularly as they occur at the fiber surface or in the cuticular region, have important implications in (a) formulating mechanical processing or chemical finishing procedures, (b) developing new approaches to such operations, (c) measuring the degree or level of ozone treatment in order to optimize the resistance to felting shrinkage that will occur in various knitted and woven fabric structures, and (d) refining theories of wool shrinkage or developing new ones.

In an earlier study³ various levels of ozone treatment were applied to coarse wool top. Yarns and fabrics were produced and relevant fiber, top, yarn, and fabric properties evaluated. Several of the knit fabrics were effectively stabilized

against shrinkage in repeated launderings. In the present study, fine wool fibers were similarly treated and evaluated. Therefore, data from the two experiments provide an opportunity to compare effects of ozone on the physical and chemical properties of coarse and fine wool. Also, the availability of ozone-treated fibers from the two studies made possible a thorough evaluation of the interaction of fiber fineness and conditions of treatment in determining yarn and fabric properties. In particular, the surfaces of wool fibers treated with ozone under various conditions were examined by available instrumental and chemical techniques. The changes observed are described and related, where possible, to changes in textile properties. Mechanisms are suggested by which observed fiber changes are related to the observed changes in yarn strength, dyeability, wettability, electrostatic properties, and resistance to felting.

EXPERIMENTAL

Materials and Treatments

The coarse $\frac{1}{4}$ -blood wool top (T-1817) has been described.³ The fine wool top (T-1001) was of 64s grade, 6.9 cm staple length, and weighed 18 g/m.

The methods and equipment used to generate and measure ozone and apply it to wool have been described.³ The fine top was ozonized, damp, at three different levels by the same procedures used for coarse top. An additional lot, given the intermediate treatment, was specially rinsed afterward, exactly as before treatment, between wire screen belting in the first bowl of a laboratory scouring train. The bowl contained 0.05% of a nonionic surfactant, Igepal CO-710, a nonylphenoxy poly(ethoxy)ethanol, at 120°F (50°C). Residence time in the bowl was about 15 sec. Squeeze rolls reduced wet pickup to about 50%. The various treated tops were air dried at room temperature or in a raw stock drier at 170°F (77°C).

Treated and corresponding untreated tops were spun into 1/20s, 4.1 turns per cm, Z-twist yarns. The yarns were then two-ply, S-twist, 1.8 turns per cm. Parts of each lot, including untreated lots, were dyed in skeins with acid leveling dyes and knitted into single jersey fabrics.

Test Methods

Standard textile tests were applied to treated and untreated materials as previously described.³ These tests included measuring oil repellency by AATCC Test Method 118-1972⁵ and water absorbency by AATCC Test Method 79-1972.⁶ A modified JEOLCO JSM-1 scanning electron microscope was used to record differences in surface structure. For this purpose, about 20 fibers from each of variously treated and untreated samples were mounted side by side and coated in groups to minimize possible differences due to coating technique. Composition and oxidation state of the fiber surfaces were determined by x-ray photoelectron spectroscopy.^{7,8} Wagner's sensitivity factors⁹ were used to get quantitative estimates.

Uptake of acid and basic dyes by fiber cross sections were used to confirm preferential change near the fiber surfaces. McIlvaine's buffers,¹⁰ mixtures of 0.2M disodium hydrogen phosphate and 0.1M citric acid, were used, diluted to

about 0.0005M, to control pH in these dyeing tests. Electrification and the position of samples in the triboelectric series were determined as described by Landwehr.¹¹

RESULTS, INCLUDING COMPARISON OF FINE AND COARSE WOOL

Feltability, Fiber Friction and Strength, and Yarn Strength

Table I summarizes shrinkage tests of untreated and the variously treated tops and fabrics. For fine wool, a decrease in top shrinkage to about 20% appears sufficient to assume good fabric stability. Laundering increased the fuzziness of some fabrics; these may need more severe treatment. With coarse wool, a decrease of top shrinkage to about 15% appears sufficient for good fabric stability and low pilling through ten launderings.³

The best results were obtained with the intermediate treatment time, 115 sec, and an afterrinse as described. The rinse markedly decreased the shrinkage of both top and fabric. The reasons for this effect are being further studied.

Comparing the shrinkage of coarse³ and fine (Table I) wools at equivalent treatments shows that fine wool needs relatively more ozone for a given degree of shrinkage control. Fine wools usually felt more readily than coarse. To be effective, therefore, extra ozone may be needed so that the fibers will be sufficiently treated. On the other hand, fine wools have a greater specific surface (surface area per unit mass). To be specific, our fine wool has about one third more surface than the same weight of the coarse wool. More ozone would therefore be needed to modify the greater surface to a given depth.

Table I shows also that the dyed fabrics shrank less than corresponding undyed

TABLE I
Fine Top^a Shrinkage, Knit^b Fabric Shrinkage Before and After Dyeing, and Fabric Fuzziness

Treatment time, sec	Sample no.	Top length shrinkage, ^c %	Fabric area shrinkage, ^d %	Fabric fuzziness	Dyed fabric area shrinkage, ^e %	Dyed fabric fuzziness
Untreated controls	T-1001	f	g	none	g	none
80	P-2522	40.9	45.4	(felted) ⁱ	6.9	little
115	P-2523	29.0	18.5	(felted)	-5.7 ^h	none
150	P-2524	21.2	9.5	(felted)	-4.2 ^h	none
115 ^j	P-2525	20.0	-1.6 ^h	medium	-10.6 ^h	none

^a 250-260 grains/yard.

^b Single jersey, 2/20s yarn.

^c Third wash.

^d Tenth wash.

^e Fifth wash. Dyed with Acid Light Scarlet GL, an acid leveling dye (Colour Index Acid Red 145).

^f First wash shrinkage was 45%.

^g First wash shrinkage was 25%.

^h Minus sign indicates that the fabric expanded rather than contracted.

ⁱ Because of felting, comparison of fuzziness is difficult.

^j Rinsed with Igepal CO-710 after treatment.

fabrics. Although the undyed pieces were washed only five times, our experience indicates that little further shrinkage will occur in the next five washes and that those fabrics that are expanding (minus sign) will continue to expand. The beneficial effect of this type of dye, a milling color, on resistance to felting shrinkage was noted earlier for coarse wool.³

Table II summarizes wet friction properties of the fine wools. All treatments decrease friction, both against scale and with scale, and also the directional difference. Nevertheless, the differences among treated lots are not statistically significant. No clear relationship is established with either treatment level or shrinkage control.

Friction measurements, shown in Table III, were also obtained for coarse wools that had been ozone treated under widely varied conditions in the earlier study.³ In this series, treatment usually produced greater friction changes; but, as with fine wools, the changes are not clearly related to feltability. For instance, the sample with the least frictional change, P-2477, has excellent shrinkage resistance, while P-2473 does not, even though its frictional properties have been more affected.

TABLE II
Fine Wool Fiber^a Friction^b Before and After Ozone Treatments

Treatment Time, sec	Sample No.	Against scale		With scale		Difference	
		μ_a	S.D.	μ_w	S.D.	$\Delta\mu$	S.D.
Untreated	T-1001	0.27	0.05	0.13	0.05	0.14	0.02
80	P-2522	0.23	0.04	0.11	0.02	0.12	0.06
115	P-2523	0.20	0.03	0.09	0.02	0.11	0.02
150	P-2524	0.19	0.05	0.11	0.03	0.08	0.03
115 ^c	P-2525	0.25	0.06	0.12	0.07	0.13	0.04

^a 64s grade.

^b Capstan method, over glass, in water. μ_a = Coefficient of friction against scale direction (fiber tip-to-base); μ_w coefficient of friction with scales, i.e., fiber base to tip; $\Delta\mu$ = friction difference $\mu_a - \mu_w$; S.D. = standard deviation.

^c Rinsed with Igepal CO-710 after treatment.

TABLE III
Coarse Wool Fiber^b Friction^c Before and After Ozone Treatments

Treatment conditions Ocftrm ^a	Sample No.	Against scale		With scale		Difference	
		μ_a	S.D.	μ_w	S.D.	$\Delta\mu$	
Untreated control	T-1817	0.28	0.05	0.18	0.06	0.10	
13-74-1.5-100-117-44	P-2473	0.16	0.02	0.09	0.01	0.07	
13-74-1.5-100-117-44		0.20	0.03	0.09	0.01	0.11	
10.8-72-1.5-100-100-43	P-2477	0.20	0.07	0.13	0.03	0.07	
10.3-69-1.5-100-100-27		0.15	0.03	0.09	0.01	0.06	
10.8-72-1.5-100-100-18.7		0.12	0.02	0.08	0.02	0.04	
8.3-69-1.5-100-80-17.3		0.11	0.03	0.09	0.02	0.02	
6.4-71-1.5-100-60-20.6		0.19	0.06	0.10	0.02	0.09	
13.3-76-1.5-115-117-19.6		0.11	0.02	0.07	0.01	0.04	
9.1-76-1.5-123-80-23.1		0.20	0.09	0.12	0.05	0.08	

^a O = Total ozone (cfr $\times 10^{-3}$), c = ozone concentration (mg/l.), f = flow rate (scfm), t = temp. ($^{\circ}$ C), r = residence time (sec), m = moisture content (%).

^b 54s grade, 7.4 cm (2.9 in.) staple length.

^c Capstan method, over glass, in water. For more information about these samples, see ref. 3, especially its Table I.

TABLE IV
Fine Wool Fiber^a and Yarn^b Strength Before and After Ozone Treatments

Treatment time sec	Sample no.	Fiber strength ^c		Yarn strength ^d	
		g/tex	S.D.	lb	Confidence limit, 95%
Untreated (off ball ^e)	T-1001	10.98	0.18		
Untreated (wetted out ^f)	T-1001	11.47	0.29	889.1	15
	(average)	11.22			
80	P-2522	11.42	0.40	997.3	22
		9.86	0.62		
	(average)	10.64			
115	P-2523	10.21	0.37	989.3	18
		9.48	0.22		
	(average)	9.84			
150	P-2524	10.07	0.36	916.6	16
		9.99	0.32		
	(average)	10.03			
115 (after-rinsed ^g)	P-2525	9.82	0.20	903.8	12
		10.43	0.53		
	(average)	10.12			

^a 64s grade.

^b Single 20s, 4.1 average turns per cm (10.4 average turns per in.), Z twist.

^c Clemson bundle test.

^d Skein break product.

^e Fibers were taken from top as received and conditioned at 21°C (70°F) and 65% relative humidity.

^f Top was wetted with 0.05% Igepal CO-710 at 49°C (120°F) and air dried. Fibers were then conditioned as above.

^g Top was rinsed with Igepal CO-710 after treatment.

Table IV shows breaking strengths of fine wool fibers and yarns. Ozonization diminishes fiber strength by 5% to 12%, but yarn strength is increased by 2% to 12%. Yarn strength was actually increased most by the shortest, 80-sec, treatment. With longer treatment, yarn strength decreased as shrinkage decreased (Table I). Satisfactory shrinkage control was realized with a treatment that gave yarn that was slightly (perhaps not significantly) stronger than the original.

Fiber strengths of coarse wool samples treated in the earlier study³ are shown in Table V. In these instances, treatment decreased fiber strength by 7% to 25%; yarn strengths, not shown, increased very slightly.

Microscopic Surface Structure

Ozonization progressively changes the wool surface. Scanning electron microscopy was used to record possible surface changes related to the severity of treatment as well as after-rinsing, dyeing, and laundering. Fine and coarse wools were studied. Ozonized lots with good shrinkage resistance were compared with untreated material and also with treated lots that were not effectively shrink proofed. Comparisons were made before and after laundering.

TABLE V
Coarse Fiber^b Strength Before and After Ozone Treatments

Treatment conditions Ocftrm ^a	Sample No.	Fiber strength ^c	
		g/tex	S.D.
Untreated control	T-1817	12.85	0.60
13-74-1.5-100-117-44	P-2473	11.10	0.61
13-74-1.5-100-117-44		10.28	0.71
10.8-72-1.5-100-100-43	P-2477	11.88	0.39
10.3-69-1.5-100-100-27		11.16	0.89
10.8-72-1.5-100-100-18.7		10.86	0.32
8.3-69-1.5-100-80-17.3		11.62	0.65
6.4-71-1.5-100-60-20.6		10.33	1.27
13.3-76-1.5-115-117-19.6		11.78	0.38
9.1-76-1.5-123-80-23.1		11.77	0.80

^a O = Total ozone (cfr $\times 10^{-3}$), c = ozone concentration (mg/l.), f = flow rate (scfm), t = temp. ($^{\circ}$ C), r = residence time (sec), m = moisture content (%).

^b 54s grade, 7.4 cm (2.9 in.) staple length.

^c Clemson bundle test. Fibers were conditioned at 21 $^{\circ}$ C (70 $^{\circ}$ F) and 65% relative humidity. For more information about these samples see ref. 3, especially Table I.

Surface Structure of Native Wool

The fine structure of ordinary wool fiber surfaces has been widely observed and used for comparison to show effects of chemical and mechanical treatment. Effects of oxidants, in particular, have been studied by Swerdlow and Seeman,¹² Bradbury, Rogers, and Filshie,¹³ Hepworth and associates,¹⁴ Anderson and associates,^{15,16} and Coe.¹⁷

Intact wool ideally has sharply defined scale edges (replicas may exaggerate the sharpness). At escarpments, the surface drops (ideally) in one step approximately perpendicularly to the surface of the underlying scale. The joint between the upper and lower scales is distinct but small compared to the scale thickness. Margins are continuous. Scale patterns are strongly related to fiber diameter. They have been classified qualitatively by Wildman.¹⁸ Scale surfaces often have ridges that are superficially like edges but are molded impressions at the site of cell boundaries in the adjoining root sheath during growth. Except for such marks, scale surfaces seen at magnifications of a few hundred times appear smoothly rounded. Minor debris, which may include skin flakes and residual grease, is sometimes conspicuous. Fibers from top, and especially from cloth, often show chipped scale edges attributed to mechanical processing and finishing.^{15,16} Clean surfaces at high magnification commonly show fine, lengthwise corrugations with a periodicity¹⁹ of the order of 0.2 micrometer that may be accentuated by tension²⁰ or chemical treatment.^{13,14,21} Such wrinkles may result from patterned erosion, as sometimes suggested. They are not evidence of ordered fibrous components in the cuticle.²⁰ They may result from incompletely reversible circumferential stretching of the outer surface layer during swelling and subsequent drying or to solubilization and loss of underlying material, so that a given circumference is conformed to a smaller cross section. In practice, fibers from a given fleece and especially from ordinary tops and fabrics vary considerably. Examples from untreated fine (T-1001) and (T-1817) coarse tops as taken for ozonization in this study are shown in Figures 1 and 2 for comparison with their ozonized counterparts.

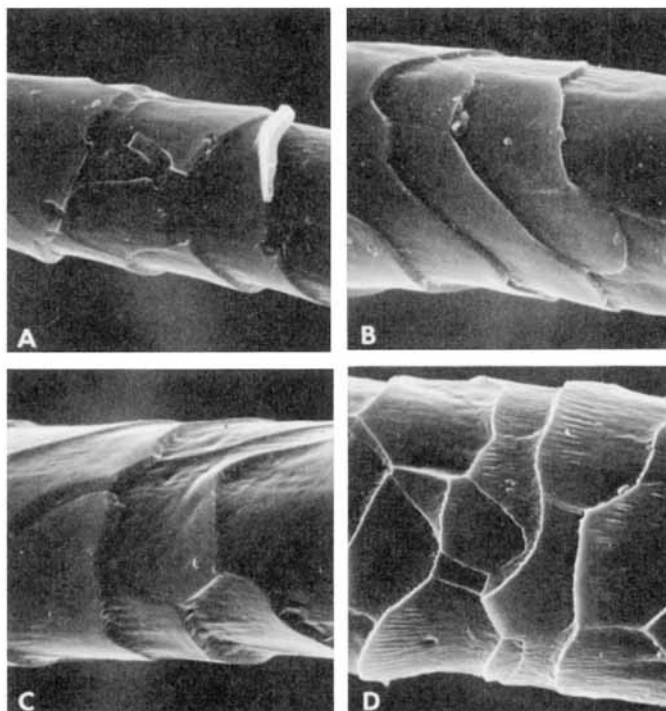


Fig. 1. Scanning electron micrographs (SEMs) of wool fibers from fine top T-1001, not ozone treated, to compare with ozonized fibers shown in Figs. 3(a), 3(b), 5, 6, and 7. (a) Diameter 13 to 14 μm ; raised and torn scale edges show mechanical damage, possibly from mechanical processing. (b) Diameter 17 to 19 μm ; relatively undamaged surface. (c) Diameter 17 to 18 μm ; the surface is distorted from an unknown cause. (d) Diameter 22 to 23 μm ; lengthwise corrugations with spacing roughly 0.5 μm appear to be more common on the coarser fibers. A few scale edges have been torn.

Surface Effects of ozonization

Fibers from ozonized wool have been found to differ from the original wool in the several ways illustrated in Figures 3 and 4. Fibers from ozonized wool often show scale tips that have been bent backward as if they had become pliable, with decreased elasticity, at some stage during treatment, Figure 3(a). On the other hand, transverse cracks, commonly in groups, are evidence that the surface has become more fragile or less extensible than normal, so that it appears to have failed when the fiber was bent or stretched, Figure 3(b). Again, fibers often show lengthwise cracks that suggest that the surface may have broken during a process of radial swelling, Figure 3(c). Some treated surfaces are irregularly wrinkled as if either the surface layer had stretched or underlying material had been removed, so that the remaining surface layer then appears too large to fit closely, Figure 3(d). These wrinkles are larger and less regular than the lengthwise corrugations often seen on untreated fibers. Finally, ozonization, very likely assisted by abrasion, can erode fiber surfaces to remove scales partly, Figure 4(a), or extensively, Figure 4(b).

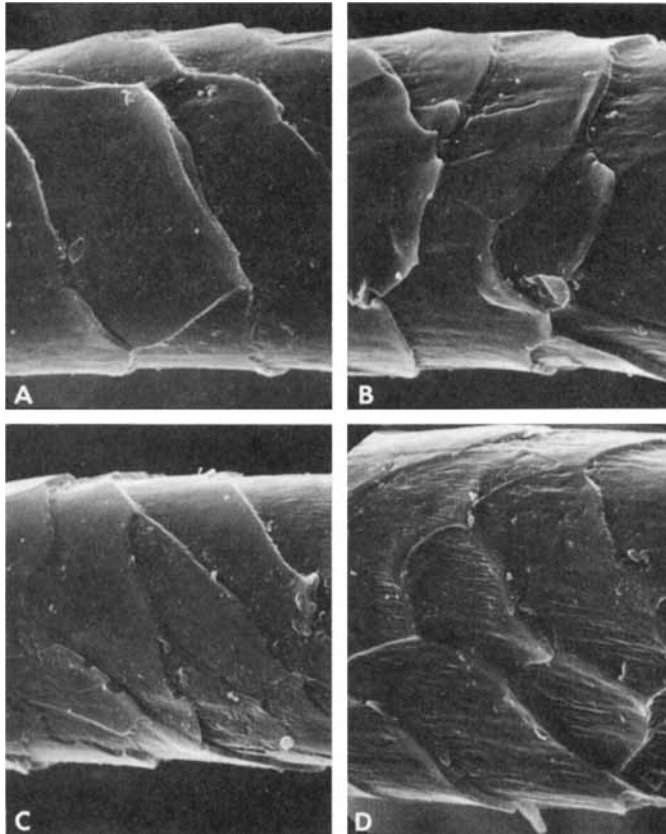


Fig. 2. SEMs of wool fibers from coarse top T-1817, not ozone treated, to compare with ozonized fibers in Figs. 3(c), 3(d), and 4. (a) Diameter 24 to 25 μm ; some scale edges are raised and show mechanical damage as ragged edges and short cracks. (b) Diameter 24 to 26 μm ; this fiber shows traces of lengthwise corrugations; damage appears as raised scale edges, surface flaws, and a roughened surface possibly due to loss of outer part of scale. (c) Diameter 21 to 22 μm ; a relatively dirty surface with corrugations and loss of parts of scales. (d) Diameter 27 to 28 μm ; a fiber with conspicuous lengthwise corrugations as in Fig. 1(d) and very prominent scale edges, two of which are lifted and partly broken.

Surface Changes Due to Particular Treatments

Ozonized wools, like the original materials, show great variety even among adjoining fibers within a given sample. This variation hinders inferring a relationship between surface appearance and shrinkage behavior. For instance, the coarse wool top that provided the treated fibers (P-2477) shown in Figures 3(c), 3(d), 4(a) and 4(b) was made up into a knit fabric with good shrinkage resistance and low fuzziness after washing. Nevertheless, fibers from another treated lot (P-2473) from the same original top gave fibers, shown in Figures 4(c) [cf. 4(a)] and 4(d) [cf. 3(d)], that seem fundamentally similar even though fabric from this lot (ozonized slightly longer than the other) shrank slightly more and was much more fuzzy. Other instances will be apparent. Such comparisons show that the degree of surface damage is not a useful means of estimating shrinkage behavior.

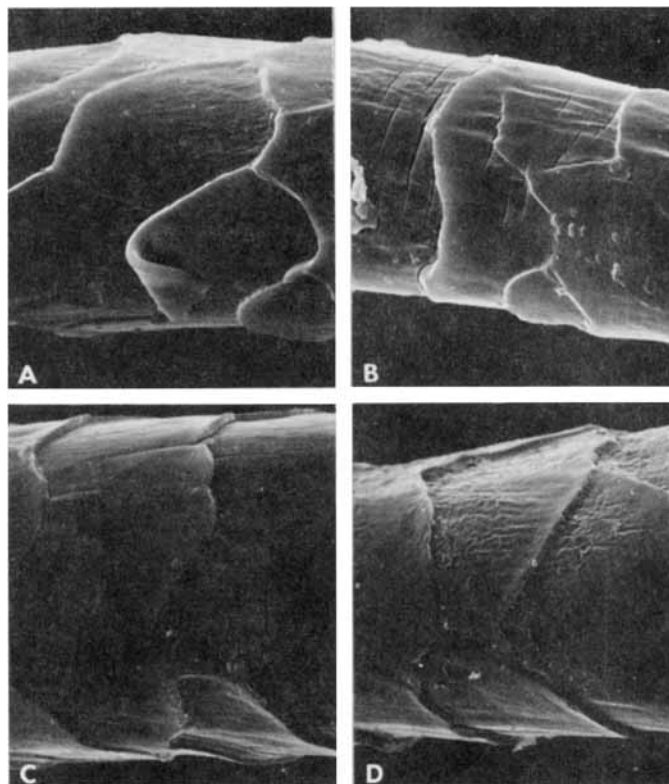


Fig. 3. SEMs of ozonized wool fibers (not rinsed with Igepal after treatment). (a) Diameter 21 to 22 μm ; fiber from fine top P-2523 shows scale tip bent back as if plastic when deformed; surfaces are slightly wrinkled and roughened, especially near bases of scales; the knit fabric shrinkage was 19% in 10 washes. (b) Diameter 18 to 19 μm ; fiber from the same top shown in 3(a); Transverse cracks suggest that a weakened, inextensible surface layer broke when the fiber was stretched or bent. (c) Diameter 25 to 26 μm ; fiber from coarse top P-2477 shows lengthwise cracks spaced roughly 3 μm apart, as if an inextensible surface split when fiber swelled radially; the knit fabric shrinkage was less than 1% after 10 washes. (d) Diameter 21 to 23 μm ; another fiber from the same top shown in 3(c); the irregularly wrinkled surface suggests that it has become inelastic and too large to fit the underlying fiber closely, either because it has been stretched or because underlying material has dissolved away.

Effects of Rinsing with Igepal CO-710

In this study a fine top given a moderate ozonization treatment was found to have only fair shrinkage resistance (19% in 10 washes) but excellent resistance (1% shrinkage in 10 washes) if the top was rinsed with 0.05% of Igepal CO-710 before further processing. Figures 5(a), 5(b), and 5(c) show rinsed fibers (P-2525) corresponding to the lot shown unrinsed (P-2523) in Figure 3(a) and 3(b). The partly removed, limp-appearing scale in Figure 5(a) may possibly have lost internal substance from an earlier state more like that in Figure 3(a). A similar process may account for the difference in appearance of the transverse cracks in Figures 3(b) and 5(b). Figure 5(c) shows extensive, predominantly lengthwise wrinkling in another, perhaps less damaged, fiber from the same rinsed lot. Such differences are not clearly consistent nor are they clearly related to the shrinkage differences. Incidentally, the amount of Igepal used is estimated to be only enough to give a surface coating about 30 Å thick if it were all adsorbed. Igepal is therefore unlikely to be directly visible in these pictures.

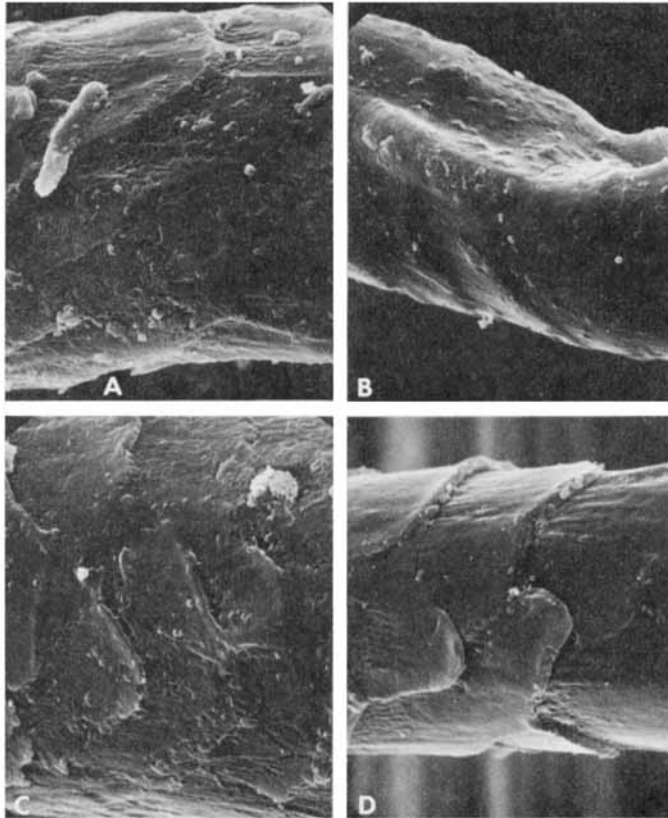


Fig. 4. SEMs of ozonized wool fibers (not rinsed with Igepal after treatment). (a) Diameter to about $27\ \mu\text{m}$; fiber from same coarse top P-2477 shown in Fig. 3(c) and 3(d); the surface is wrinkled and eroded; in some places the scale layer is completely removed. (b) Diameter 18 to $19\ \mu\text{m}$; fiber from same coarse top shown in Figs 3(c), 3(d), and 4(a); traces of the scale pattern persist in spite of extensive loss of scales; the rough, pitted surface is cracked both lengthwise and crosswise; this group illustrates the wide range in appearance found in a single, effectively treated lot. (c) Diameter about $30\ \mu\text{m}$; fiber from a similar but slightly less effectively treated coarse top P-2473 shows a rough, wrinkled surface and prominent scale edges not unlike 4(a); knit fabric shrinkage was 1% to 7% after 10 washes. (d) Diameter 27 to $29\ \mu\text{m}$; another fiber from the same top shown in 4c has prominent raised scale edges; surfaces are especially wrinkled near the bases of scales, cf. 3(d).

Effects of Laundering

Laundering, with accompanying swelling, solvent action, agitation, and abrasion, might be expected to remove scales, perhaps especially from material effectively protected from shrinkage. Furthermore, the initial laundering would seem to be equivalent to a detergent rinse before the ozonized top was processed further into fabric. Figure 5(d) shows two fibers in place in a fabric (P-2522) made from lightly ozonized top after the fabric had been laundered five times, during which it shrank 45%. The fiber surfaces are very wrinkled, but scales have not been lost. In contrast, the fiber in Figure 6(a), from the same specimen, has no scales and a very irregular surface. Figure 6(b), also from this specimen, has lengthwise, slightly zigzag cracks somewhat regularly spaced on the scale surfaces. Lengthwise cracks are common on surfaces of laundered ozonized fibers. They may be characteristic of a weakened, inelastic surface layer fractured by swelling.

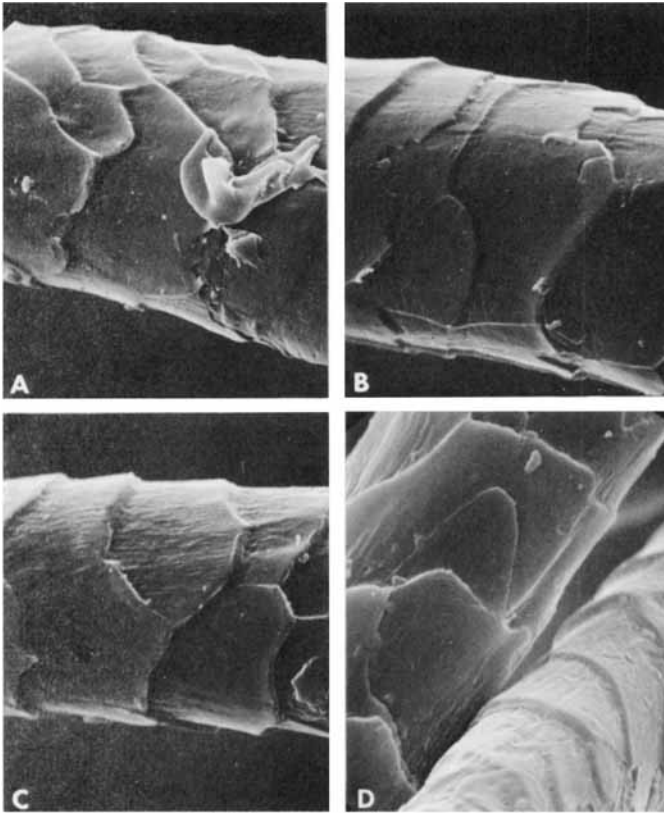


Fig. 5. SEMs of ozonized wool fibers from fine top (a, b, c) and laundered fabric (d). (a) Diameter 20 to 22 μm ; this fiber is from ozonized fine top P-2525, like that shown in Fig. 3(a) and 3(b) but rinsed with 0.05% Igepal CO-710; an evidently plasticized scale remnant has been partly stripped from the surface; shrinkage in 10 launderings was 1%. (b) Diameter 21 to 22 μm ; a fiber from the same rinsed top shown in 5(a) has transverse cracks, rounded scale edges, and partial loss of scales. (c) Diameter 17 to 19 μm ; a fiber from the same rinsed top shown in Fig. 5(a) and 5(b) has lengthwise corrugations and prominent scale edges, cf. Fig. 1(d). (d) Diameter about 15 to 19 μm ; two fibers in a knit fabric made from a lightly ozonized fine top P-2522; the fabric has shrunk 45% in five launderings; scales persist, but edges are rounded and surfaces, wrinkled, cf. Fig. 6(a).

Figure 6(c) and 6(d) compare fibers from fabrics, 10 times laundered, from, respectively, the “rinsed” and “unrinsed” tops of Figures 5(a), 5(b), 5(c), 3(a), and 3(b). In these examples, scales are present, surfaces are rough, and both show sites of local mechanical damage where a patch of cuticle has been removed. Both laundered samples however have many fibers with scales damaged or removed. Figure 7(a) and 7(b) show examples from the “rinsed” sample. In 7(a), scale edges are clearly present, but much rounded, and the surfaces are wrinkled. Parts of scales have been lost. In 7(b), loss of scales and rounding of contours has gone further. Both 7(a) and 7(b) have the lengthwise cracks noted in 6(b) and common in our laundered samples. In addition, 7(b) has rounded, transverse wrinkles that suggest lengthwise contraction.

Finally, Figure 7(c) and 7(d) show fibers from a laundered fabric (P-2524) from the most severely treated top in this series. In spite of the fact that most fibers show greatly damaged surfaces as in 7(c), for instance, this fabric shrank 14%

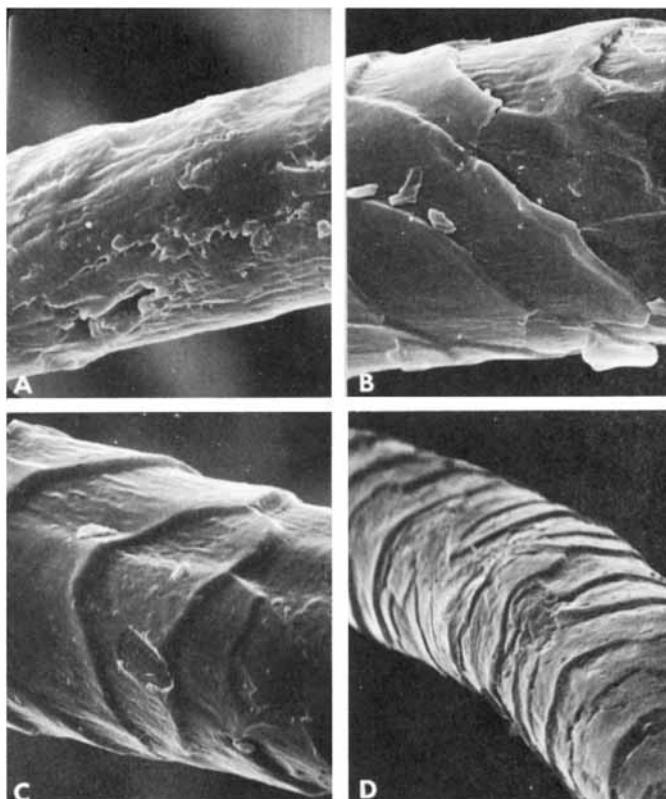


Fig. 6. SEMs of ozonized fine wool fibers from laundered fabrics. (a) Diameter about $17\ \mu\text{m}$; fiber from same laundered lightly ozonized fabric P-2522 shown in Fig. 5(d); loci of scale edges are still visible although scales have been removed from the rough, damaged surface. (b) Diameter about $24\ \mu\text{m}$; another fiber from the same laundered lightly ozonized fabric has rounded, raised scale edges, lengthwise cracks, and wrinkles; the wide variation in surface damage in this sample may indicate the difficulty of getting uniform treatment with restricted amounts of reagent. (c) Diameter 21 to $22\ \mu\text{m}$; fiber from fabric from the treated, unrinsed top P-2523 shown in Fig. 3(a) and 3(b), but after 10 launderings (19% shrinkage); scale edges are rounded and surfaces are wrinkled and mechanically damaged. (d) Diameter 15 to $16\ \mu\text{m}$; fiber from fabric from the treated and rinsed top P-2525 shown in Fig. 5(a), 5(b), and 5(c), but after 10 launderings (1% shrinkage); although the surface is rough and mechanically damaged, scale edges are relatively sharp, cf. Fig. 6(c); the basis for better shrinkage control is not evident.

in ten launderings. Figure 7(d) shows an unusual pattern of grooves intersecting at an acute angle of about 41° ; corrected for the 30° tilt of the specimen, this becomes about 47.6° (standard deviation roughly 3°). This pattern is unexplained.

In short, ozonization produces certain described changes in the microscopic appearance of fiber surfaces seen after drying. The changes are interpreted as showing that the wet fiber surface layer loses elasticity during ozone treatment, becoming plastic at first and afterwards increasingly fragile, so that the surface cracks when the fiber bends or swells. The changes are expressed by deformed scales, wrinkles, cracks, and erosion and culminate in loss of scales. The changes are accentuated by laundering and perhaps marginally by rinsing with a nonionic wetting agent. Extensive scale removal appears neither necessary nor sufficient for good control of shrinkage.

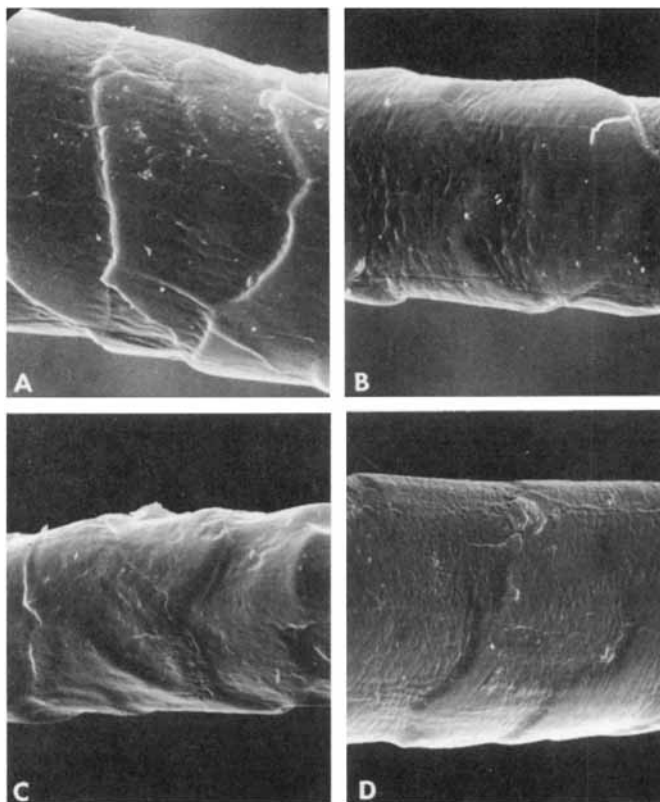


Fig. 7. SEMs of ozonized fine wool fibers from laundered fabrics. (a) Diameter 23 to 24 μm ; fiber from the treated, rinsed, and laundered fabric P-2525 shown in 6(d) and, before laundering, in Fig. 5(a), 5(b), and 5(c); the wrinkled surface has lengthwise cracks; scale edges are rounded; some scales have been broken and partly removed. (b) Diameter 16 to 18 μm ; fiber from the same treated, rinsed, and laundered fabric shown in Figs. 6(d) and 7(a); the scales are much rounded. Transverse wrinkles suggested that the fiber has contracted but that the outer layer did not (or contracted less); lengthwise cracks, rarely deflected by the wrinkles, may have formed afterward. (c) Diameter 14 to 15 μm ; fiber from laundered fabric made from severely ozonized top P-2524 (not rinsed with Igepal); the fabric shrank 14% in 10 laundings; scale edges are rounded; scales are partly torn away; surfaces are rough. (d) Diameter 28 to 30 μm ; fiber from same severely ozonized, laundered fabric; rounded residual scale escarpments are still visible; the surface is remarkable for two sets of grooves intersecting at angles (corrected for tilt of specimen) near 49° ; the appearance suggests that the fiber has contracted in length and expanded in thickness.

In interpreting these findings, we note that a small proportion of feltable fibers in a lot has been reported²² to produce a highly shrinkable fabric. Makinson²³ has concluded from studies of wet fibers that effective degradative shrinkproofing treatments attack material inside the cuticle cells so that the scales are softened, easily deformed, slow to recover their initial shape, and are easily torn and detached.

Surface Analysis by X-Ray Photoelectron Spectroscopy (XPS)

Equipment and techniques described earlier^{7,8} were used to analyze, by XPS, the surface (to a depth of about 50 \AA or less) of several of the ozone-treated fine tops. In XPS, core electrons are ejected from surface atoms by x-rays, and from

their energy and count the identity and concentration of various atom species as well as their valence state can be determined. Thus, in comparing the spectra of untreated and treated fiber samples, chemical and structural changes at the surface can be measured. In Figure 8, the carbon 1s electron spectra for untreated (T-1001) and ozone-treated fine wool (150 sec, P-2524) are shown. For the treated sample, the shoulder in the curve at the higher-energy side indicates that some of the carbon atoms are combined with oxygen, perhaps as C=O. In

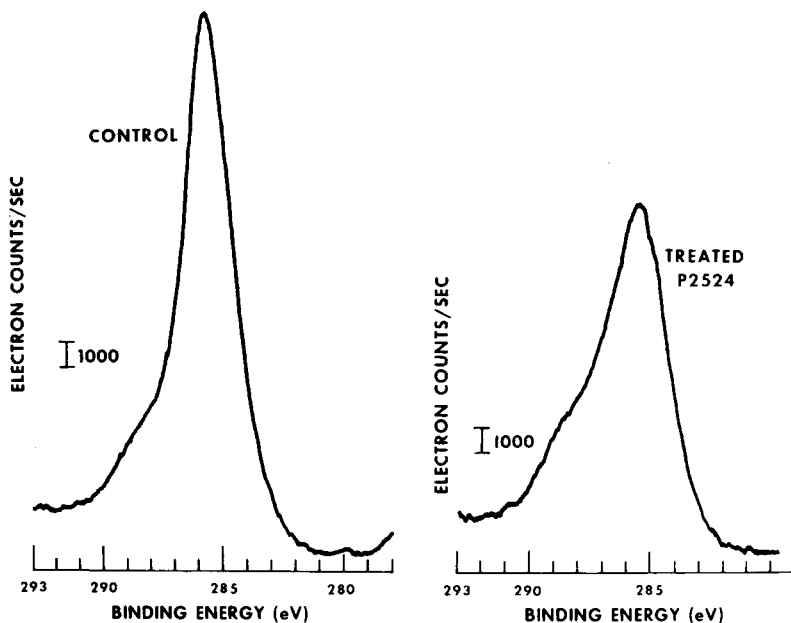


Fig. 8. Carbon 1s XPS spectra for untreated (T-1001) and 150-sec ozone-treated wool (P-2524).

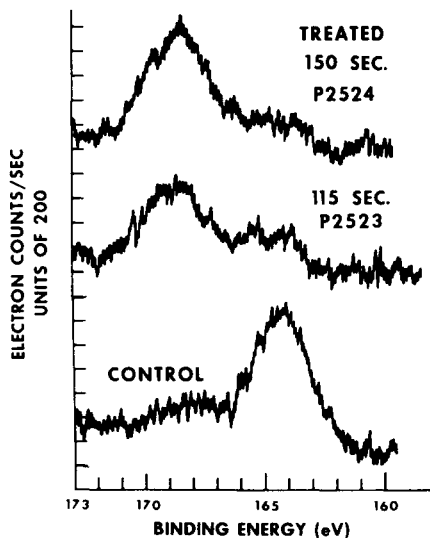


Fig. 9. Sulfur 2p XPS spectra for untreated (T-1001), 115-s (P-2523), and 150-sec (P-2524) ozone-treated wool. Records are arbitrarily displaced vertically to avoid overlapping.

Figure 9, the sulfur $2p$ spectra are shown for untreated (T-1001), 115-sec (T-2523), and 150-sec (P2524) ozone-treated fibers. The shift in the sulfur peak to the higher binding energy indicates that most of the cystine disulfide sulfur at the surface has been converted to S^{6+} , that is, to either sulfone or sulfonic acid. The presence of sulfonic acid groups is confirmed by amino acid analyses (Table VI), which show large increases in cysteic acid for the 115-, 150-, and 115-sec after-rinsed samples. Methionine sulfone was not found. Methionine near the surface may have been oxidized to unrecognized products, possibly to homocysteic acid, for example. The oxygen $1s$ line intensity is increased in the ozonized samples, again indicating surface oxidation. The binding energies of oxygen in carbonyl and carboxyl groups, etc., are so close, however, that the various oxygen species could not be resolved. Table VII gives carbon/oxygen/nitrogen/sulfur ratios (integrating all species of each element) for untreated (replicated), 115-, 150- (replicated), and 115-sec after-rinsed samples. The ratios calculated are referred to carbon (1.0), the assumption being that it has changed the least.

None of the N/C ratios changes much, but the 150-sec sample shows a slight, possibly significant, increase. From the O/C ratios, however, the proportion of oxygen near the surface has clearly approximately doubled in all treated samples.

TABLE VI
Amino Acid Analyses of Untreated and Ozone-Treated Fine Wools

Treatment time, sec, sample No.	Untreated	115	150	115 ^a
	T-1001	P-2523	P-2524	P-2525
Amino acid	Millimoles per 100 g wool			
Lysine	22.9	21.7	21.8	20.7
Histidine	6.4	6.0	5.8	6.3
Ammonia	82.1	90.3	77.3	94.5
Arginine	54.7	50.4	53.4	54.7
Aspartic acid	46.2	50.0	49.3	44.4
Threonine	50.3	48.9	48.8	44.3
Serine	79.8	80.6	79.5	73.1
Glutamic acid	89.7	88.4	90.2	82.2
Proline	52.2	48.9	51.5	44.1
Cysteic acid	1.5	6.6	6.4	8.4
Glycine	65.1	62.1	64.6	55.6
Alanine	44.0	40.4	42.7	36.9
Half-cystine	85.0	73.6	78.8	61.4
Valine	43.6	40.1	43.1	35.9
Methionine	4.6	3.5	4.5	3.6
Isoleucine	23.6	21.5	23.1	20.0
Leucine	57.5	53.8	55.9	48.7
Tyrosine	29.4	25.8	26.3	21.1
Phenylalanine	20.9	19.6	20.0	17.7
Weight accounted for, %	84.1	80.3	82.9	74.1
Weight accounted for, %, adjusted to give leucine = 63 mmole per 100 g sample	92.1	94.0	93.4	95.9
Nitrogen in material accounted for, %	17.6	17.7	17.5	18.4
Sulfur in material accounted for, %	3.4	3.4	3.5	3.2

^a Rinsed with nonionic surfactant after ozonization.

TABLE VII
Surface Electron Line Intensities and Atom Ratios from Untreated and Ozone-Treated Fine Wools

Sample	Core level	Intensity cps/1000 ^a	Corrected intensity ^b	Atom ratio to carbon (= 1)
Control T-1001	C 1s	29.8	110	C 1
	O 1s	9.5	18.3	O 0.167
	N 1s	4.5	10.7	N 0.097
	S 2p	1.5	3.3	S 0.030
Control (replicated) T-1001	C 1s	25.8	95.7	C 1
	O 1s	7.5	14.4	O 0.15
	N 1s	3.0	7.15	N 0.075
	S 2p	1.1	2.4	S 0.025
115 sec P-2523	C 1s	21.4	79.4	C 1
	O 1s	12.5	24	O 0.31
	N 1s	3.75	8.9	N 0.112
	S 2p	1.0	2.17	S 0.027
150 sec P-2524	C 1s	20	74.1	C 1
	O 1s	14.5	27.9	O 0.378
	N 1s	5.0	11.9	N 0.16
	S 2p	1.3	2.8	S 0.038
150 sec (replicated) P-2524	C 1s	20.8	77	C 1
	O 1s	13	25	O 0.325
	N 1s	3.9	9.3	N 0.12
	S 2p	1.1	2.4	S 0.031
115 sec (after-rinsed) P-2525	C 1s	22.3	82.5	C 1
	O 1s	12	23.1	O 0.28
	N 1s	3.9	9.5	N 0.115
	S 2p	1.2	2.6	S 0.032

^a Thousands of counts per sec in x-ray photoelectron spectroscopy.

^b Electron line intensities divided by Wagner's sensitivity factors.⁹

Depth of Ozone Penetration Into the Fiber

The increased number of sulfonic acid groups at the surface (see above) and the increased amount of cysteic acid in the bulk of ozone treated wool (Table VI) suggest that fiber cross-sectioning and differential staining could confirm to what extent ozone reaction is confined to the fiber surface. The very high concentration of sulfonic acid groups at the surface (Fig. 9), coupled with loss of cystine in the whole fiber by about 8% to 28% (Table VI), suggests that ozone reacts in the cuticular region. This highly crosslinked region with more than the average cystine content^{24,25} is, presumably, especially susceptible to oxidation. Moreover, ozone must cross this region before it can react with underlying parts. A basic dyestuff is expected to dye such an acidic region preferentially. Therefore, the cationic dyestuff Sevron Brilliant Red 2B (Fig. 10) was selected as a differentiating stain. Sections of the 80- and 150-sec treated and untreated fibers were stained 5 min at room temperature in 0.0005M McIlvaine-buffered solutions¹⁰ at pH 4.1. The cuticular region of most treated fibers was highly stained (Fig. 11). When the treatment temperature was raised to 85°C and time increased to 1 hr, no differential staining occurred; staining was then uniform throughout the cross sections. Sections of untreated fibers never showed strong differen-

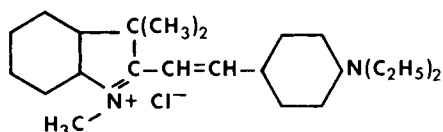


Fig. 10. Sevron Brilliant Red 2B cationic dyestuff (Colour Index Basic Violet 16).

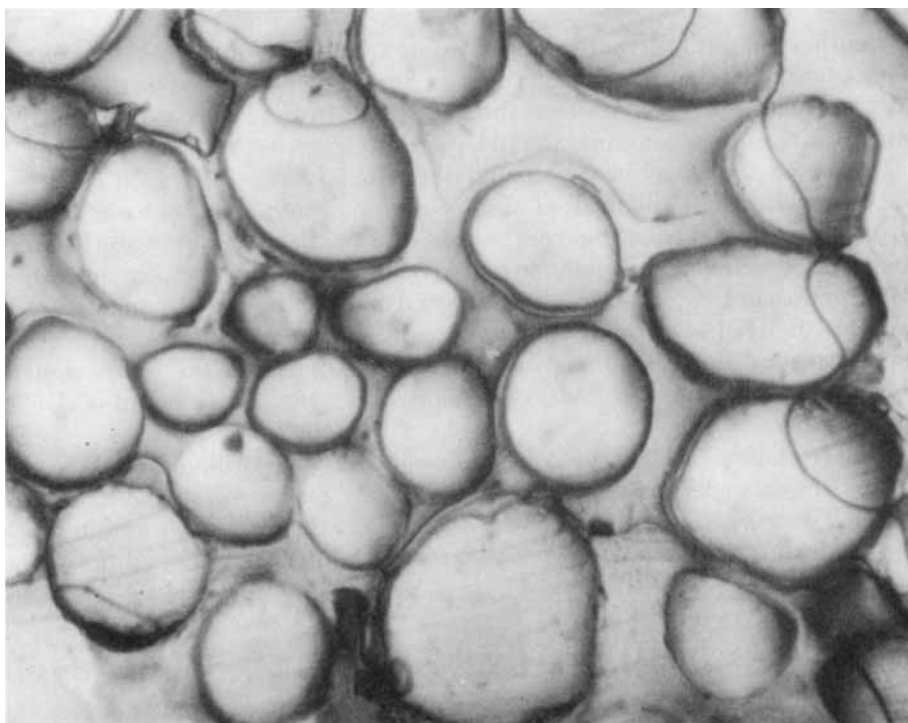


Fig. 11. Cross section of 80-sec ozone-treated wool P-2522 stained in cross section with Sevron Brilliant Red 2B, imbedded in cellulose nitrate and cross-sectioned with Schwarz fiber microtome, slice thickness ca. $50\ \mu\text{m}$.

tiation. Because all samples were dyed as sections, ring dyeing is not due to delayed penetration radially from the original surface.

In order to determine whether the basic nature of the Sevron dye or some other factor causes these rate differences, dyeing with the acid dye Sulfonine Brilliant Red B (Fig. 12) was compared. Cross sections treated under the same conditions as before (5 min at R.T. and 60 min at 85°C) were stained fairly uniformly, as

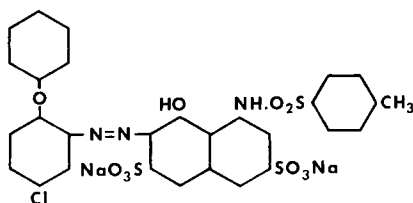


Fig. 12. Sulfonine Brilliant Red B (also Brilliant Milling Red B) anionic dyestuff (Colour Index Acid Red 249).

were sections of unozonized fibers. This clearly demonstrates the strong influence of ionic charge on dyeing rate in the anionic (acid) regions of ozonized fibers.

Effect of Molecular Structure, Time, Temperature, and pH on the Dyeing Rate of Ozone-Treated Fabric

Depth of shade differences between ozone-treated and untreated fabrics can be demonstrated that accord with the mechanisms just discussed for differential cross section staining. As before, time, temperature, and the nature of the dye affect the dyeing rate, as does the pH during dyeing.

Untreated and 80-sec ozone-treated fine wool fabrics were dyed at pH 4.1 as above with Sevron Brilliant Red 2B, one pair for 5 min, another for 60 min at 85°C. As expected from the cross section results, the cationic dyestuff strikes the ozonized fabric more rapidly, so that in 5 min a darker shade is obtained (Fig. 13) than with untreated fabric. With longer dyeing, untreated and ozone-treated samples are dyed to virtually the same shade. The explanation of this is that rate effects are most prominent in the first stages of dyeing; but where enough time is allowed, untreated fibers can absorb about the same amount of dye as treated fibers.

The effect of molecular type is evident when Sulfonine Brilliant Red B is used in an identical experiment. Because of the anionic nature of this dye, the rate at which it strikes (Fig. 14) is much less than that of the Sevron dye so that much less shade difference is obtained between ozonized and untreated fabrics. The

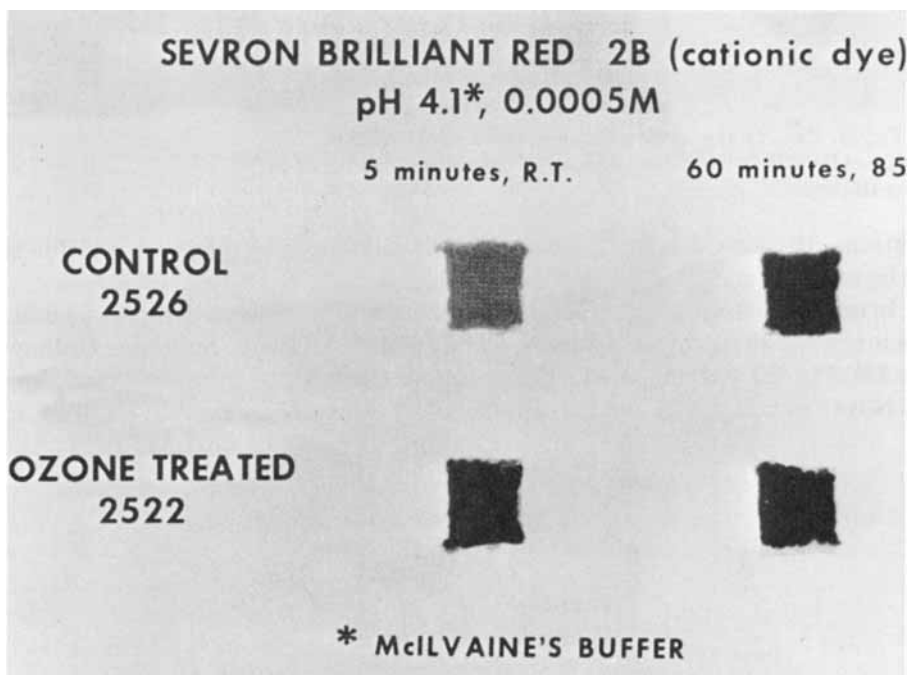


Fig. 13. Effect of 80-sec ozone treatment on rate of cationic dye strike into fine wool fabric P-2522 during 5-min and 60-min dyeings at pH 4.1.

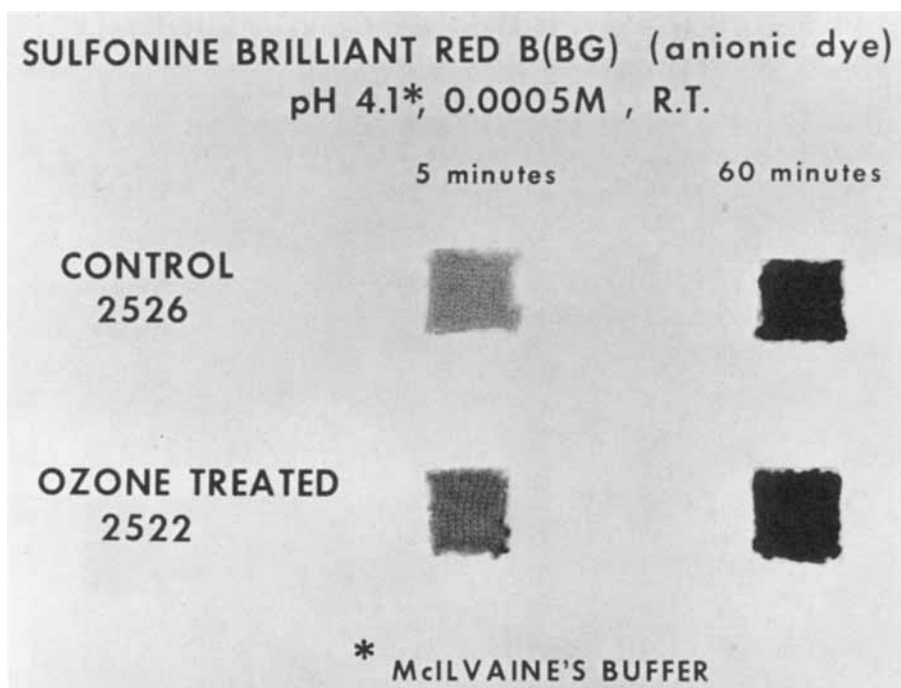


Fig. 14. Effect of 80-sec ozone treatment on rate of anionic dye strike into fine wool fabric P-2522 during 5-min and 60-min dyeings at pH 4.1.

actual slightly increased rate is probably due to other factors: increased cuticular swellability, hydrophilicity, etc. Like the Sevron dye, the Sulfonine dye will dye untreated fabric and ozonized fabric to about the same shade if a longer dyeing time is used (Fig. 14).

If dyeing with Sevron is done at the lower pH, 2.3, suppression of ionization of the weakly ionized $-\text{COOH}$ groups markedly reduces the dye uptake of untreated fabric (Fig. 15) in a 5-min dyeing. With the ozone-treated fabric, however, since pH does not appreciably affect the ionization of sulfonic acid groups, lowering the pH to 2.3 makes little difference in dye uptake.

This research thus, like earlier work, shows that ozone increases the rate^{1,2} of dyeing. Ozone also increases levelness.³ In contrast to some other oxidative shrinkproofing processes, ozonization in our studies does not impair dyefastness.³ The increased dyeing rate is very likely due to several causes. First, since the stabilizing disulfide bonds are broken in the cuticle, this region of the fiber is more easily swelled by aqueous systems. Thus, diffusion of dye molecules into and through this region to the interior can be more rapid. Also, the normal hydrophobicity of the cuticle (in which residues of proline and valine are relatively abundant, while those of aspartic acid, glutamic acid, and arginine are less common than in the fiber as a whole²⁴) is reduced. Its increased hydrophilic nature after treatment makes it more compatible with polar dyestuffs. Peptide bond cleavage will also produce more of the polar groups $-\text{NH}_2$ and $-\text{COOH}$.

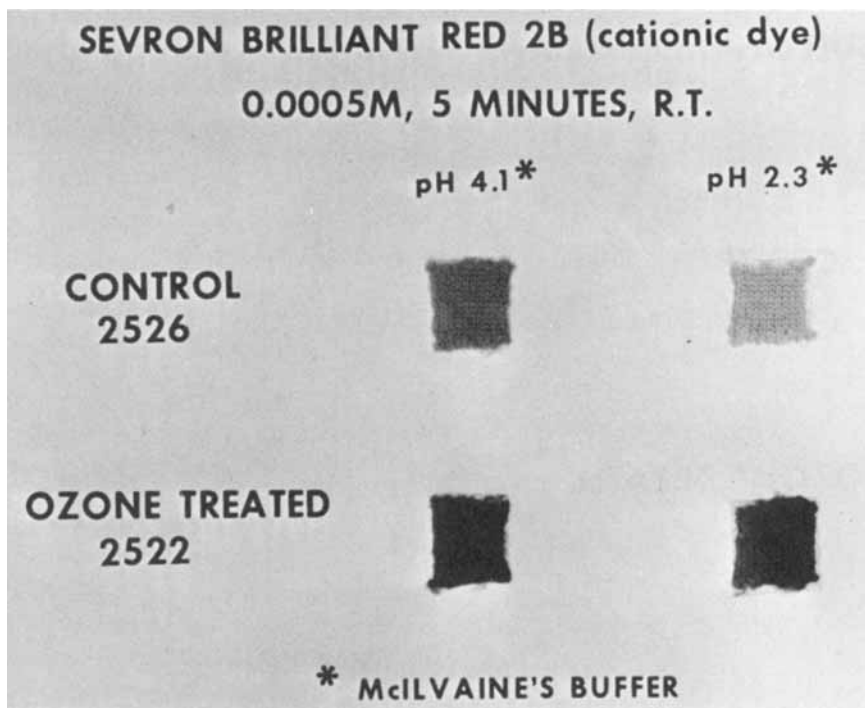


Fig. 15. Effect of 80-sec ozone treatment on rate of cationic dye uptake into fine wool fabric P-2522 at pH 4.1 and 2.3.

Oil, Soil, and Water Repellency

Oil repellency and soil repellency are not improved by any of the ozone treatments given to the fine and coarse wools of this study. On the other hand, the water repellency of both wools is decreased by ozone treatment. Wettability of the fine wool fabric was evaluated by measuring the time required for a drop of a water to be absorbed into the fabric. Untreated fabric, with antistatic processing oil still present, wets very rapidly (Fig. 16). If this oil is removed, however (along with wool wax), by a soap solution wash, the drop of water never penetrates—it evaporates. The same occurs with this fabric if it is dyed, because in dyeing most of the ionic or polar impurities (along with the wool wax) are removed in the final rinses. Both processes expose the hydrophobic wool fiber surface.

Ozone-treated fabrics absorb water at a rate that depends on the level of ozone treatment. The 80-sec treated fabric (P-2522) absorbs the drop in about 100 min, whereas the 115-sec (P-2523), 115-sec after-rinsed (P-2525), and 150-sec (P-2524) treated fabrics absorb the drop in about 70, 30, and 10 min, respectively. The reason for increased wettability is that the increased number of $-\text{SO}_3^-$ and other oxidized groups at the surface increases its polar nature or hydrophilicity. If the ozone-treated fabrics are washed in soap solution, the effect is opposite that of washing the untreated wool containing the antistatic oil. With the ozonized fabrics, washing removes residual wool wax so that the oxidized surface containing sulfonic acid groups is more completely exposed. Thus, with all ozonized wools a further increase in wettability by water is obtained (Fig. 16)

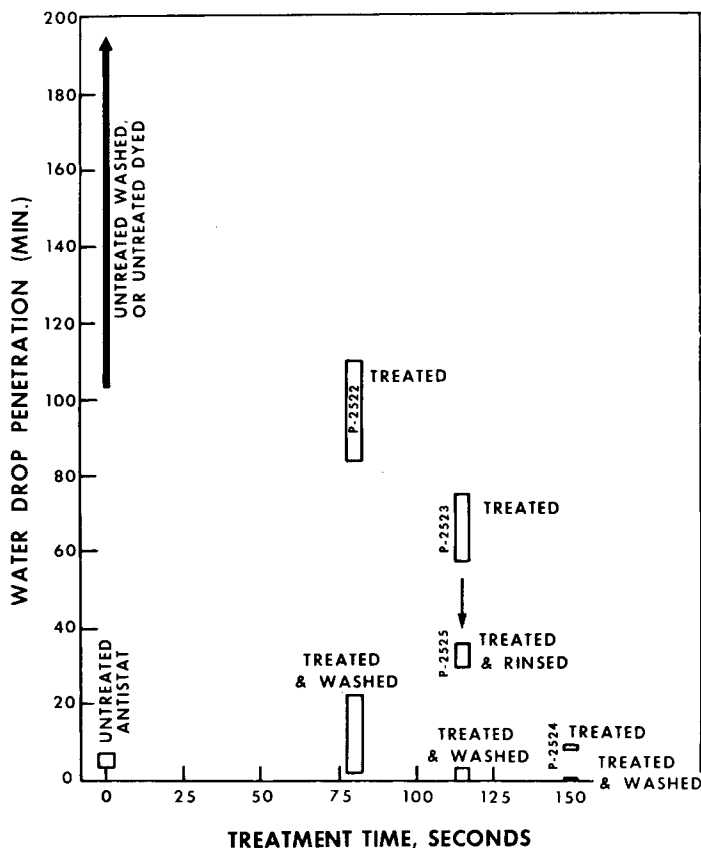


Fig. 16. Water wettability of untreated and ozone-treated fine wool fabrics (P-2522-5) with and without oil removal.

by washing. The decrease in wetting time is not simply related to shrink resistance (Table I).

Change in Electrostatic Behavior

When two insulators are rubbed together, one will acquire a negative charge if its removable surface electrons have the higher average work function.²⁶ The more negative material will be ranked below the other in the triboelectric series; the top of the series is the plus end and the bottom the negative end. The creation of more $-\text{SO}_3^-$ groups at the surface of wool by ozone or corona treatment shifts it from its positive position in the table to lower, more negative positions.¹¹

The fine wool and two coarse wool fabrics of this study (Tables III and V) were also tested and ranked in the triboelectric series (Table VIII). The untreated fine wool fabric was washed before testing to remove antistatic processing oil. A steamed, fine wool, ozone-treated fabric was also tested. One of the ozonized coarse wool fabrics (P-2477 dyed light red with the reactive dye Lanazol Red G), which had excellent resistance to felting shrinkage combined with low pilling,³ and the best fine wool fabric are at the negative end of the fabric series. On the other hand, the 80-sec ozonized fine wool fabric (P-2522) with low shrink resis-

TABLE VIII
Trielectronic Series^a of Selected Materials Including Ozone-Treated Fabrics

Material		Fabric ^b
Untreated wool and mohair	T-1001	untreated fine wool ^c
Nylon		
Cotton		
Silk		
Shoe leather (sole)		
Steel	P-2523	115 sec ^c (steamed)
Rubber (heel)	P-2477 ^d	(dyed dark red)
Orlon	P-2524	150 sec ^c
	P-2523	115 sec ^c
	P-2522	80 sec ^c
	P-2525	115 sec after rinsed ^c
	P-2477 ^e	(dyed light red)
Polyethylene		
Teflon		

^a Each substance becomes positively charged in contact with materials below it in the table, but negatively charged in contact with those preceding it. Thus, untreated wool loses electrons more easily (has a smaller electron work function) than the other materials shown and Teflon, with a very large electron work function, takes up electrons from most other substances.

^b Single jersey.

^c 64s grade, 2/20s yarn; all samples (except the first) ozonized as indicated.

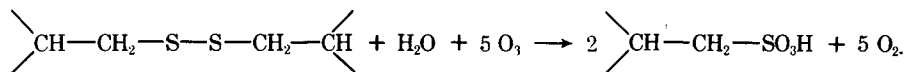
^d 50s grade, 4/8s yarn, acid milling dye Brilliant Milling Red B (Colour Index Acid Red 249).

^e 50s grade, 4/8s yarn, reactive dye Lanazol Red G (Colour Index Reactive Red 83). More information about the (undyed) fabric P-2477 used to make these dyed samples is given in Tables III and V.

tance is also near this position. Moreover, the P-2477 fabric dyed dark red with Brilliant Milling Red B, which had excellent shrink resistance, is near the positive end of the fabric series. Therefore, shrinkage resistance can not be reliably predicted from the position in the triboelectric series.

Stoichiometry and Efficiency of Cystine Ozonization

Reaction of ozone with cystine is probably similar to that of other oxidizing agents⁴ so that it can be represented by the equation



In this case, five moles ozone are required for every mole cystine. Amino acid analyses (Table VI), uncorrected for loss of cystine in the usual hydrolysis, show about 42.5 mmole cystine per 100 g untreated wool. In the three treated samples, the average reduction in cystine content is about 16.5%, or 7 mmole per 100 g. In this work, about 3.5 g, or 73 mmole ozone was used on the average per 100 g wool, and since 5 moles ozone are required to oxidize one mole cystine, about 14.6 mmole cystine theoretically could have been oxidized. Some of this extra ozone not used to oxidize cystine was consumed in oxidizing carbon (see above). Most of the remainder may have been decomposed either because of the high temperature of the reaction or by catalysis by the substrate.

CONCLUSIONS

Ozone reacts primarily in the cuticular region of wool fibers. Substantial, progressive changes occur in topography. The main reaction observed is oxidation of cystine to sulfonic acid, although carbon is also oxidized. Many physical properties of the fibers, yarns, and fabrics can be related to the scission of cystine disulfide by ozone and the formation of sulfonic acid groups at the fiber surface. The reduction in feltability that occurs is compatible with the theory offered by Makinson²³ for other oxidizing agents that also oxidize cystine and soften the (wet) cuticle. The charged sulfonic acid groups may also provide an ionic antifelting mechanism, as they can, according to Stigter,²⁷ decrease fiber interaction. Cuticular softening by disulfide scission can also explain increased fiber adhesion, which would be favored by increased areas of contact.

The authors are gratefully indebted to many colleagues for help in this work. Those who have helped produce technical data cited include Frederick J. Ahrens and Gunter Bendix (spinning yarn and knitting fabric), Lona M. Christopher and Buenafe T. Molyneux (measuring fiber friction, yarn strength, and shrinkage), Francis T. Jones (optical microscopy and photographs of dyed fiber sections), Eddie C. Marshall and Amy T. Noma (hydrolyzing and analyzing samples for amino acid content), and Thomas L. Hayes of the Lawrence Berkeley Laboratory, who arranged for use of the scanning electron microscope. Reference to a company or product is only for information and does not imply recommendation by the U.S. Department of Agriculture to the exclusion of other products that may be suitable.

References

1. W. J. Thorsen, *Text. Res. J.*, **35**, 638 (1965).
2. W. J. Thorsen and R. Y. Kodani, *Text. Res. J.*, **37**, 975 (1967).
3. W. J. Thorsen and R. C. Landwehr, in *Proc. 5th Int. Wool Text. Res. Conf. III*, 1975, K. Ziegler, Ed., Deutsches Wollforschungsinstitut, Aachen, 1976, pp. 295-304.
4. F. O. Howitt and WIRA, *Wool Sci. Rev.*, **24**, 16 (1964).
5. AATCC Test Method 118-1972, *Oil Repellency: Hydrocarbon Resistance Test*, AATCC Technical Manual 50, 1974, p. 205.
6. AATCC Test Method 79-1972, *Absorbency of Bleached Woven Cloth*, AATCC Technical Manual 50, 1974, p. 161.
7. M. M. Millard, *Anal. Chem.*, **44**, 828 (1972).
8. M. M. Millard, in *Proc. 5th Int. Wool Textile Res. Conf. II*, 1975, K. Ziegler, Ed., Deutsches Wollforschungsinstitut, Aachen, 1976, pp. 44-53.
9. C. D. Wagner, *Anal. Chem.*, **44**, 1050 (1972).
10. T. C. McIlvaine, *J. Biol. Chem.*, **49**, 183 (1921).
11. R. C. Landwehr, *Text. Res. J.*, **39**, 729 (1969).
12. M. Swerdlow and G. S. Seeman, *J. Res. Nat. Bur. Stand.*, **41**, 231 (1948).
13. J. H. Bradbury, G. E. Rogers, and B. K. Filshie, *Text. Res. J.*, **33**, 617 (1963).
14. A. Hepworth, J. Sikorski, D. J. Tucker, and C. S. Whewell, *J. Text. Inst.*, **60**, 513 (1969).
15. C. A. Anderson, H. J. Katz, M. Lipson, and G. F. Wood, *Text. Res. J.*, **40**, 29 (1970).
16. C. A. Anderson, M. T. Goldsmith, H. J. Katz, and G. F. Wood, *Appl. Polym. Symp.*, **18**, 715 (1971).
17. A. B. Coe, in *Scanning Electron Microscopy Studies of the Surface Structure of Wool and Mohair*, Summary Report, Contract No. 12-14-100-9558 (74) ARS, USDA, 1972.
18. A. B. Wildman, *The Microscopy of Animal Textile Fibres*, WIRA, Leeds, 1954, pp. 53-59, 72-81.
19. N. Ramanathan, J. Sikorski, and H. J. Woods, *Biochim. Biophys. Acta*, **18**, 323 (1955).
20. L. J. Wolfram, *Text. Res. J.*, **42**, 252 (1972).
21. G. Mazingue and P. Kassenbeck, *Bull. Inst. Text. Fr.*, **23**, 161 (1969).
22. K. Baird and R. A. Foulds, *J. Text. Inst.*, **66**, 138 (1975).
23. K. R. Makinson, *Appl. Polym. Symp.*, **18**, 1083 (1971).
24. J. H. Bradbury, *Adv. Protein Chem.*, **27**, 111 (1973).

25. P. Kassenbeck, H. Marfels, and H. Meichelbeck, in *Proc. 5th Int. Wool Textile Res. Conf. II*, 1975, K. Ziegler, Ed., Deutsches Wollforschungsinstitut, Aachen, 1976, pp. 162-172.
26. S. P. Hersh and D. J. Montgomery, *Text. Res. J.*, **25**, 279 (1955).
27. D. Stigter, E. Menefee, and R. C. Landwehr, *Text. Res. J.*, **44**, 454 (1974).

Received September 9, 1978

Revised November 28, 1978