

# USE OF AN ELASTOMER FORMED IN SITU FOR SOFTENING LEATHER\*

by

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## ABSTRACT

Poly (vinyl oleate) was used as a model compound in a continuing study of polymeric fatliquoring agents. It was emulsion-polymerized in-situ in retanned, non-fatliquored blue stock. The products showed appreciable improvements in mechanical properties, including increased elongation at failure and increased energy to break with no loss in tensile strength. Lower levels of acoustic emission were observed in treated samples, indicating reduction in fiber adhesion. X-ray probe (EDX) microanalysis with the aid of osmium tetroxide was used to locate sites of unsaturation and polymerized vinyl oleate in the interior of the treated leather.

## INTRODUCTION

In a recent study of leather lubricating agents obtained from polymerizable fatty acid derivatives, we have reported the use of poly (vinyl stearate).<sup>1</sup> The resulting product after drying showed a 65% increase in elongation as well as a 75% increase in energy to break. Improved water repellency and resistance to water penetration were noted as the amount of vinyl stearate was increased.

In the work presented here, vinyl oleate was used instead of the waxy vinyl stearate. After polymerization of the vinyl group, it was expected that the internal unsaturated oleate group would remain unaffected and thus furnish a means for locating the elastomeric polymer within the leather. Also, vinyl oleate is a liquid monomer and is emulsified

more readily than solid vinyl stearate. Because polymers usually tend to stiffen leather, we wished to see if a polymer with a low glass temperature could lead to a softer leather when formed in situ.

## EXPERIMENTAL

### Materials

Blue stock was purchased from Prime Tanning Company\*\* and was washed, neutralized and retanned with acrylic syntan and wattle powder before fatliquoring experiments. Vinyl oleate was purchased from GAF Corporation but is not currently commercially available. Triton X-100 was from Union Carbide Chemicals Company. Osmium tetroxide was obtained from E. M. Sciences and imidazole hydrochloride from Sigma Chemical Company.

### Experimental

The procedures were carried out in one-quart mason jars containing 100 g of retanned blue stock, 300 mL deionized water, 12.0 g vinyl oleate and 3.0 g each of sodium persulfate, sodium bisulfite and Triton X-100. Sufficient dry ice was added to displace the air; the jars were sealed and their contents were mixed in a Gyrotor Shaker (New Brunswick Scientific Co., NJ) for 4 hours at 40-45° C. The control samples were treated in similar fashion, but no monomer was added.

After polymerization, the samples were cooled, and the hide was washed thoroughly in cold water. The samples were toggled and dried at room temperature. They were then conditioned for 24-48 hours at 70° F and 50 percent

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\*\* Reference of brand or firm names does not constitute an endorsement by the U.S. Department of Agriculture over others of a similar nature not mentioned.

relative humidity before testing for tensile strength and percent elongation at 20%/min. on 100 mm x 20 mm "dog-bone" samples with an Instron Universal Tester, Model 1122. Acoustic-emission spectroscopy was performed with a Physical Acoustics LOCAN-AT spectrometer as described earlier<sup>2</sup>.

### X-Ray Microanalysis and Element Maps

Rectangular samples (ca. 5 mm wide, 10 mm long and 0.5 mm thick) were cut from the treated leather with a stainless steel razor blade. The slabs were immersed in a solution of 2 percent osmium tetroxide in 0.1 M imidazole hydrochloride (pH 7.0) for two hours at room temperature. By use of this procedure, initially described by Greyer<sup>3</sup> and modified by us for use with leather, osmium reacts with and remains bound by unsaturated functions present in the leather and can be detected by X-ray microanalysis. The samples were subsequently washed in distilled water and air-dried for 24 hours before mounting with Leit-c-plast adhesive (E. M. Sciences). The X-ray microanalysis was carried out with a model 840A scanning electron microscope (JEOL USA, Peabody, MA) integrated with an Imix workstation (Princeton Gamma-Tech, Princeton, NJ). Digital maps of osmium ( $M\alpha$  1 line) and chromium ( $K\alpha$  1 line) were collected at 15 KV at an instrumental magnification of 40X.

## RESULTS AND DISCUSSION

Table I shows the effects of polymerization of vinyl oleate onto leather. In this table the mechanical properties of a control sample containing no vinyl oleate are contrasted with those of a sample treated with vinyl oleate but uncatalyzed and a sample which has the benefits of polymerized vinyl oleate. Prior to testing, all samples were extracted with isopropanol to remove unreacted vinyl oleate, then soaked in water and air dried. No staking was carried out. In each instance, the leather containing polymerized vinyl oleate showed the best properties such as increased percent strain at break or energy to break. The vinyl oleate treated samples were appreciably softer and more flexible than the untreated control. No water repellency was observed, in contrast to previous results with poly (vinyl stearate).

Each row in Table I shows the means of the data from four similar preparations, each of which was evaluated with five or six mechanical tests. The total number of tests for each preparation was 24. The standard deviations for each preparation were pooled. The lowering of the modulus due to the monomer or polymer is obvious. The extraction with isopropyl alcohol removed monomer but not polymer.

Rewetting and drying does not return the monomer-softened leather to its previous high-modulus (6.98 MPa) state.

The moduli of the samples containing polymer were found by paired student's t-tests to be significantly different from those that were uncatalyzed (calculations not shown), even though the overall pooled variances are large.

In a separate study, after polymerization had occurred, the float was extracted several times with hexane to recover any vinyl oleate which had not entered the leather. After drying with magnesium sulfate and removal of the hexane, 3.9 g (32.5 percent of the original 12.0 g vinyl oleate) was isolated. Subsequent extraction of the treated leather with isopropanol to remove unreacted monomer led to recovery of 5.7 g (45.5% of the original). It was thus obvious that only 20 % of the offered vinyl oleate had effected the improvement in physical properties of the treated leather.

Table II summarizes the results obtained in a material balance study from a series of 4 similar polymerizations with vinyl oleate. In each case, after polymerization, the float was extracted with hexane, and the leather was first extracted with isopropanol to recover monomer and then with hexane to remove the polymer. The results are in accord with those discussed above showing that approximately 20 % of the vinyl oleate offered had led to the improved properties.

Figure 1A shows the correlation between the stress and the acoustic activity during elongation of a sample of cattlehide that was dried after chrome tanning with no softening additive of any kind — no retan or fatliquor<sup>2</sup>. The initial slope of the stress-strain curve is rather large, and the sample fails at a small elongation. The bottom curve is the rate of acoustic-pulse emission; it reveals considerable acoustic activity over the whole elongation. As failure is approached, the upper curve shows the emission of a few large-energy pulses, signalling the breaking of fibers.

Figure 1B, on the other hand, shows results from a similar leather sample that contains poly (vinyl oleate). The material examined here had not been extracted with isopropyl alcohol, so it contains monomer and polymer in the ratio 54:20. The initial slope of the stress-strain curve is smaller, and the elongation at break is larger, showing its effect. There is almost no acoustic activity over the first part of the stretch. We conclude that the inclusion of the solid polymer does not negate the effect of the oil in reducing the strength of the adhesions between fibers, which are pulled apart only near the end of the test, but with little fiber breakage<sup>2</sup>.

**TABLE I**  
**Mechanical Properties of Leather After Vinyl Oleate Treatment**  
**and Extraction with Isopropyl Alcohol**

Instron Properties at Peak (n=24)				
Addition to Leather	% Strain	Stress (MPa)	Energy to Break (MPa)	Secant Modulus (MPa)
No Addition	84.3 ± 19.0	5.51 ± 1.43	22.5 ± 7.9	6.98 ± 1.58
Vinyl oleate monomer	95.0 ± 14.0	7.24 ± 0.88	28.7 ± 5.3	4.57 ± 1.05
Vinyl oleate polymer	109.5 ± 20.0	7.65 ± 0.57	35.3 ± 9.0	4.12 ± 0.80

**TABLE II**  
**Material Balance Study After Polymerization of Vinyl Oleate**

Experiment	Vinyl Oleate Offered (g)	Recovered from float		Extracted with Isopropanol		Extracted with Hexane		Total Extracted	
		(g)	(%)	(g)	(%)	(g)	(%)	(g)	(%)
1	12.0	2.5	20.8	6.6	55.0	2.7	22.5	11.8	98.3
2	12.0	3.0	25.0	6.8	56.7	2.5	20.8	12.3	102.5
3	12.0	3.8	31.7	5.3	44.2	2.4	20.0	11.5	95.9
4	12.0	13.1	25.8	7.4	61.7	1.8	15.0	12.3	102.5
Average	12.0	3.1 ± 0.5	28.8 ± 4.5	6.5 ± 0.9	54.4 ± 7.4	19.6 ± 3.2	2.4 ± 0.4	12.0 ± 0.4	99.8 ± 3.3

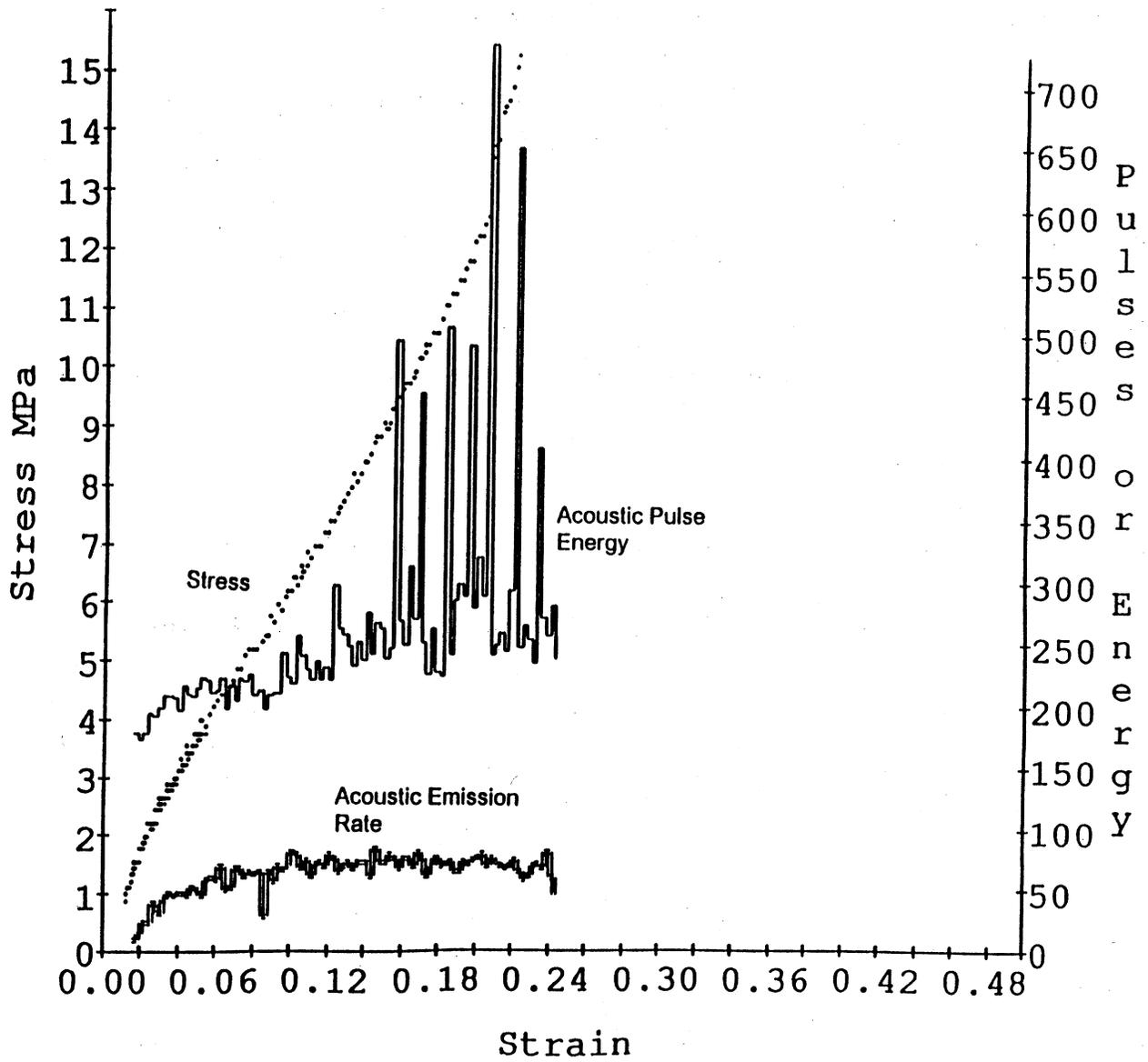


FIGURE 1A. — When leather is stretched, it emits sound pulses (acoustic emission) that report on the pulling apart and breaking of fibers that are adhering to each other. These pulses are especially emitted frequently even at small elongations in leather that contains no fatliquor; the rate increases sharply until failure.

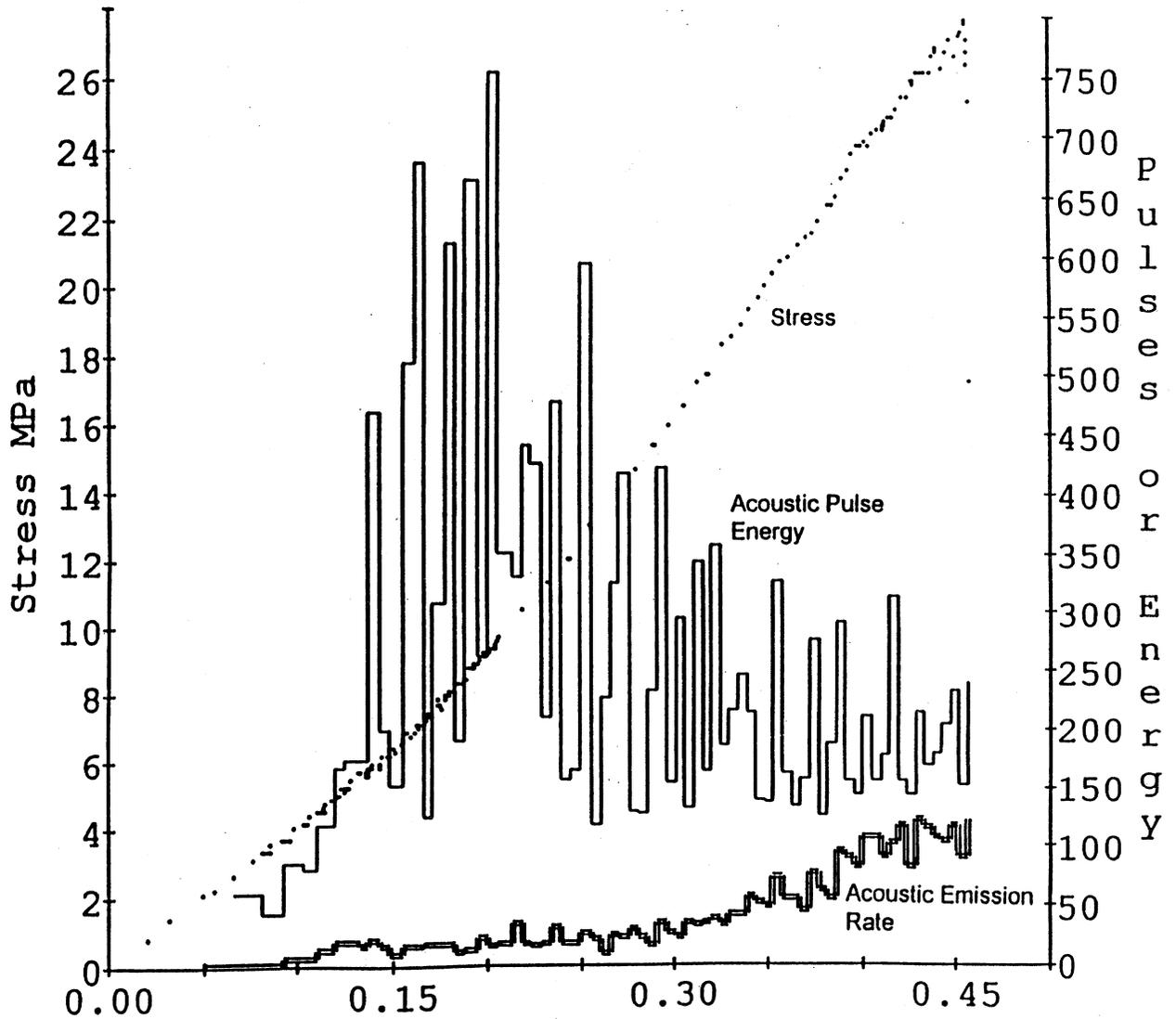


FIGURE 1B. — When the leather has fatiquor, there is almost no acoustic activity when it is stretched until the elongation approaches the failure point. Here, this is shown also for leather treated with poly (vinyl oleate) which reduces the acoustic activity at the beginning of the stress.

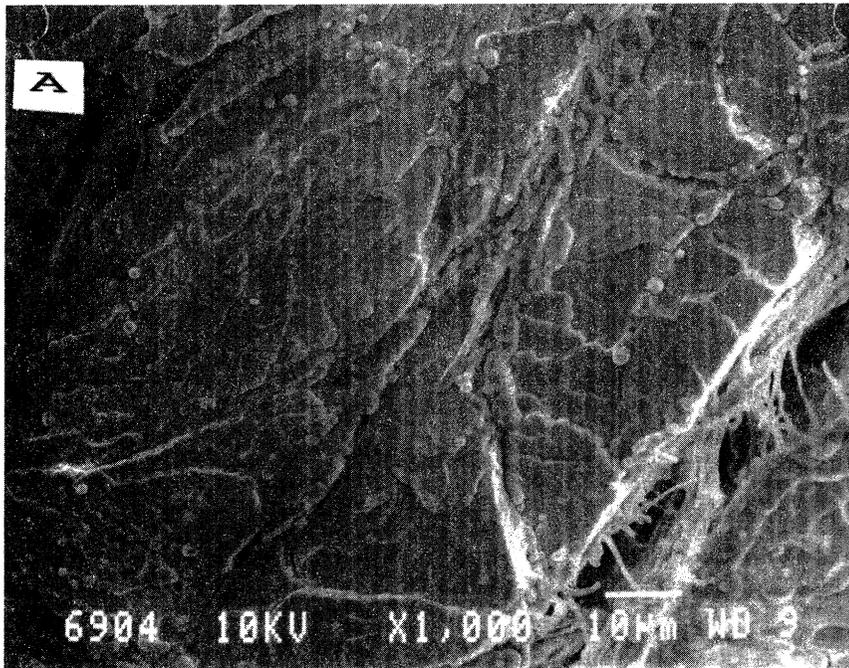


FIGURE 2A. — When the retanned leather was dried without polymer, it formed thick fibers with cross-sectional dimensions of about 100  $\mu\text{m}$ . This is usual for leather without fatliquor. Such leather is, as expected, stiff.

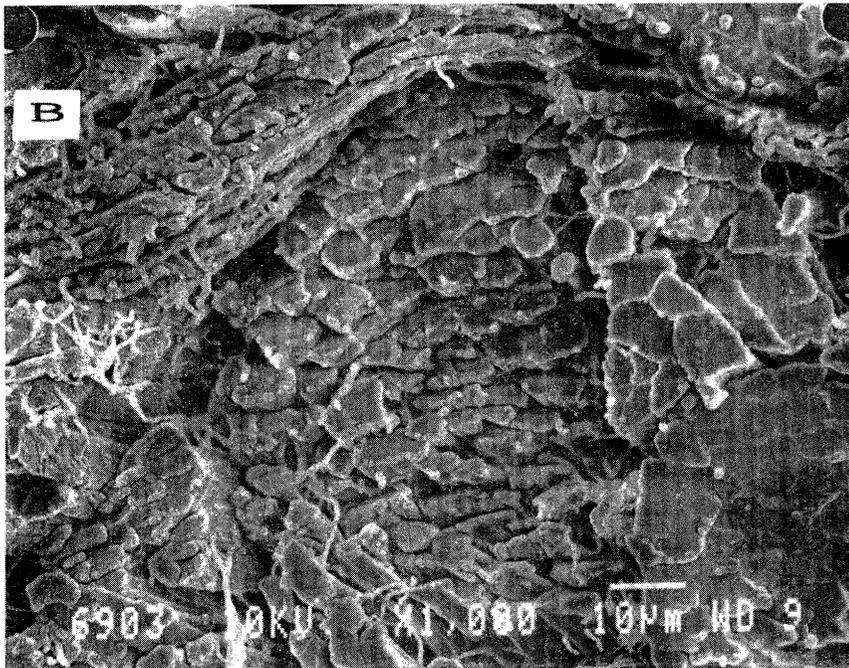


FIGURE 2B. — The fibers in the dried leather that contained the polymer were small fragments, about 5  $\mu\text{m}$  in cross-sectional dimension. These are usually found in leather that has been treated with fatliquor, and explain why such leather is soft.

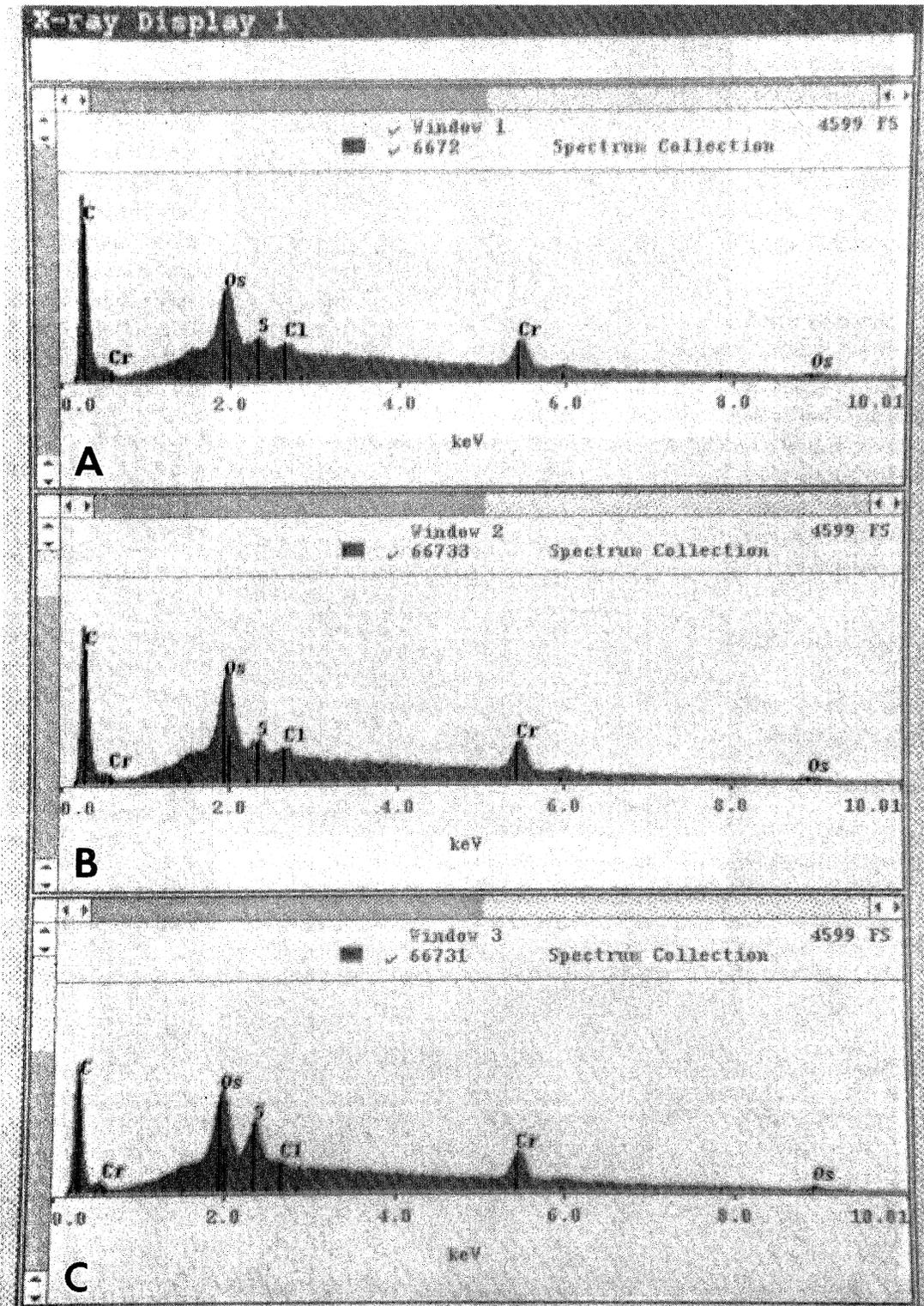


FIGURE 3. — X-ray spectra of leather samples after osmium tetroxide treatment.  
 (A) CONTROL  
 (B) VINYL OLEATE (UNCATALYZED)  
 (C) VINYL OLEATE (CATALYZED)

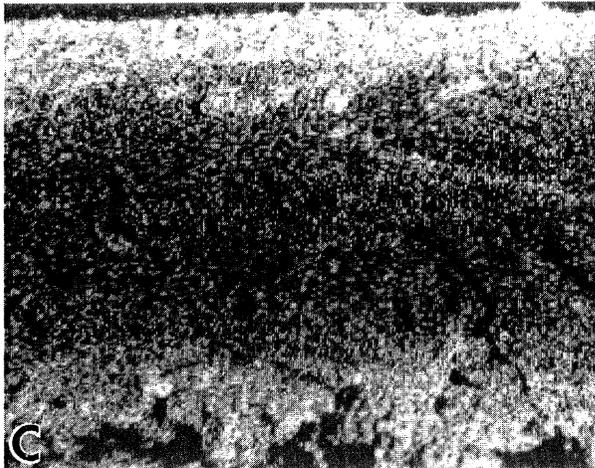
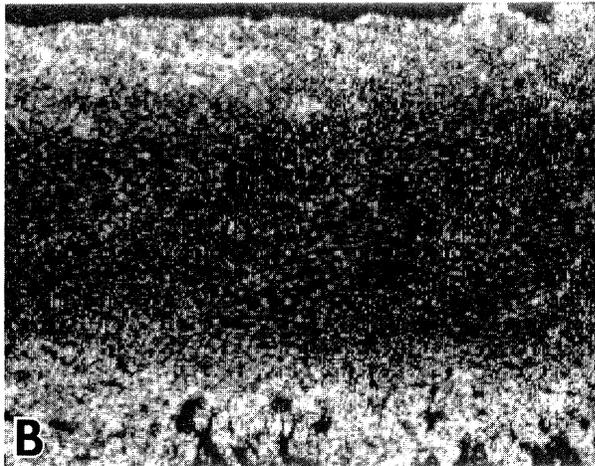
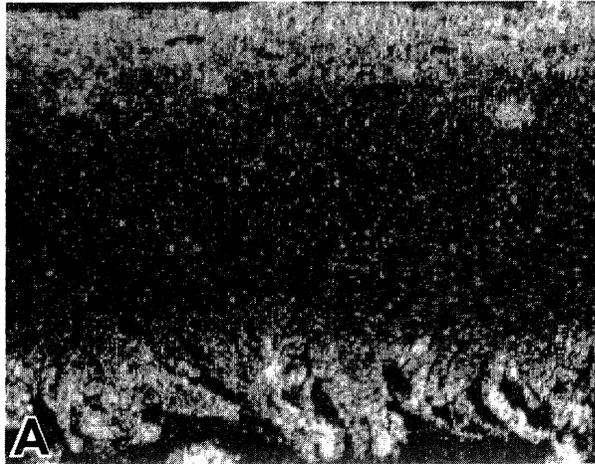


FIGURE 4. — X-ray maps showing presence of unsaturation (bright areas) after osmium tetroxide treatment. These are side views of cut surfaces, with grain at top, flesh side at bottom of each panel.

- (A) CONTROL
- (B) VINYL OLEATE (UNCATALYZED)
- (C) VINYL OLEATE (CATALYZED)

Acoustic-emission data show that fatliquor softens leather by diminishing the adhesions among fibers<sup>2</sup>, but it is difficult to visualize without microscopic examination. Figure 2a shows a cross-section of a fiber in a cattlehide tanned and dried without fatliquor. One sees that these fibers are cohesive units about 100  $\mu\text{m}$  thick. In the usual model for the action of fatliquor, the 100-nm collagen fibrils are coated with the oil, which serves as a "lubricant", allowing them to slide over each other when leather is deformed. However, the actual texture of the leather with poly (vinyl oleate) in Figure 2b shows no direct evidence of separated fibrils. Instead, the thick fibers are divided into many smaller ones about 5  $\mu\text{m}$  thick. We hold that this explains the softening effect of the added softener, not lubrication. The leather becomes more like that from a smaller animal.

The results of energy dispersive X-ray microanalysis are shown in Figures 3 and 4. Samples were analyzed after treatment of the leather with osmium tetroxide solution to label covalently sites of unsaturated bonds and locate the polymerized vinyl oleate.

Figure 3 displays the X-ray spectra of each of the leather samples: control (A), uncatalyzed (B), and catalyzed (C). Peaks represent X-ray counts over a selected range that includes C, Os and Cr. The ratios of peak heights, C/Os or Cr/Os, provide the best indices for measuring the amount of Os in the samples. The catalyzed sample has almost equal numbers of counts from carbon and osmium, indicating that it contains the largest amount of added unsaturation due to poly (vinyl oleate).

The location of osmium in the X-ray maps, indicating the presence of unsaturation including the vinyl oleate, is indi-

cated by the bright areas in Figure 4, which compares the distribution of osmium of the control (A), non-catalyzed vinyl oleate-treated (B), and the catalyzed vinyl oleate sample (C). The most extensive distribution of osmium, indicating the presence of unsaturation, occurs in the catalyzed sample, mainly near the grain and flesh edges of the leather, but also extending into the middle area, where the control and non-catalyzed samples have little or no osmium label. It is expected that methods that increase the amount of bound polymer will result in increases in fixed osmium.

## CONCLUSIONS

Although solid polymers added to leather usually make it stiffer, an elastomer such as poly (vinyl oleate), formed in situ from an oil, acts as a leather softener like a fatliquor. Softening is generally achieved by replacing large, 100- $\mu\text{m}$  fibers by small, 5- $\mu\text{m}$  fibers. Softening accomplished in this way is accompanied by diminished interfiber adhesion, measured by smaller levels of acoustic emission.

## REFERENCES

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