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### **Abstract**

Vinyl stearate, a commercially available monomer, was used as a model compound for studying polymeric fatliquoring agents. It was readily polymerized in emulsion by free radical initiation in the presence of retanned, non-fatliquored blue stock. The product showed improvement in mechanical properties such as a 65% increase in elongation at failure and a 75% increase in energy to break with no loss in tensile strength. In addition, improved water repellency and resistance to water penetration were noted as the amount of vinyl stearate offered was increased.

### **Introduction**

One of the aims of our investigations at ERRC is to develop novel lubricating agents for leather from polymerizable surface active agents. We plan to base these agents on long chain fatty acid derivatives currently used in synthetic membrane systems. It is believed that incorporation of polymerizable groups within a fatliquoring agent can provide a means for furnishing improved lubrication properties to leather. The polymerizable groups will include vinyl or acrylic or methacrylic moieties which can be polymerized after application to leather. The effect of these products on the structures and properties of the resulting leathers will be studied.

In recent work carried out in this laboratory<sup>1,2</sup>, acylation of collagen was studied to see the effect of reaction of amino groups in collagen with fatty acid-based acylating agents. In the presently reported research, however, no attempt was made to affect the collagen chemically, but only to fix the fat-based polymer physically because of its molecular size.

Vinyl stearate was chosen as a model compound in our polymerization studies. This compound was initially reported and described by Swern and coworkers and found extensive use as a plasticizer<sup>3,4</sup>. The information derived from its use as a leather lubricant will be subsequently applied to other polymerizable fatty derivatives.

## Experimental

### MATERIALS

Vinyl stearate was obtained from CasChem, Inc., Bayonne, NJ\*\*. Triton X-100 was from Rohm & Haas Co. Blue stock purchased from Prime Tanning Company was washed, neutralized and retanned by standard methods with syntan and mimosa powder before fatliquoring experiments.

Typical fatliquoring experiments: The procedures were carried out in one-quart Mason jars containing 100 g of retanned blue stock, 300 mL deionized water, 3.0 g each of sodium persulfate, sodium bisulfite and Triton X-100 and 2.0 g vinyl stearate. Sufficient dry ice was added to displace the air, the jars were sealed and tumbled end-over-end for 4 hours at 40°C. The samples were cooled and the hide washed thoroughly in cold water before toggling, drying and staking at room temperature.

A portion of the fatliquoring mixture was lyophilized, and when dry was extracted with a small amount of water to remove inorganic salts. The remaining material was filtered and redried and its infrared spectrum was obtained. Inspection of the absorbance at 1650 cm<sup>-1</sup> was used to follow the presence of vinyl groups. As polymerization proceeded at 40°C, the intensity of the bands ascribable to vinyl groups decreased. In an additional experiment run at a higher temperature (58°C), the presence of a new absorption band at 1700 cm<sup>-1</sup> indicated that hydrolysis to the free carboxylic acid had occurred. Optimum results were obtained when polymerizations were run at 40°C for 4-6 hours in an anaerobic atmosphere with a "redox" initiation system of sodium persulfate and sodium bisulfite. Larger amounts of initiator were used to circumvent the loss of free radicals by their transfer to the collagen. Triton X-100 (3% by weight of the hide) was used as emulsifying agent. A typical formulation appears below.

### FORMULATION FOR EMULSION POLYMERIZATION OF VINYL STEARATE

LEATHER	100 g
FLOAT	300 g
VINYL STEARATE	2 g
SODIUM PERSULFATE	3 g
SODIUM BISULFITE	3 g
TRITON X-100	3 g

The fatliquored samples were conditioned for 24-48 hours at 70°F and 50% relative humidity. They were then tested for tensile strength and percent elongation with an Instron Universal Tester, Model 1122. Acoustic-emission data were determined as described by Kronick and Thayer<sup>5</sup> on Physical Acoustic equipment (Princeton, NJ), comprising a Local AT-2 analyzer with a Model 1220A preamplifier, LA/DAQ software, and a 150 KHz Transducer clipped to the center of the sample through silicone grease for acoustic coupling. The amplitude window was set between 25 and 75 dB.

## Results and Discussion

A summary of the effects of polymerizing vinyl stearate onto leather is shown in Figures 1 and 2. It can be seen readily in Figure 1 that as the amount of vinyl stearate originally present is increased, the percent elongation rises, indicating that lubrication is occurring. This is further

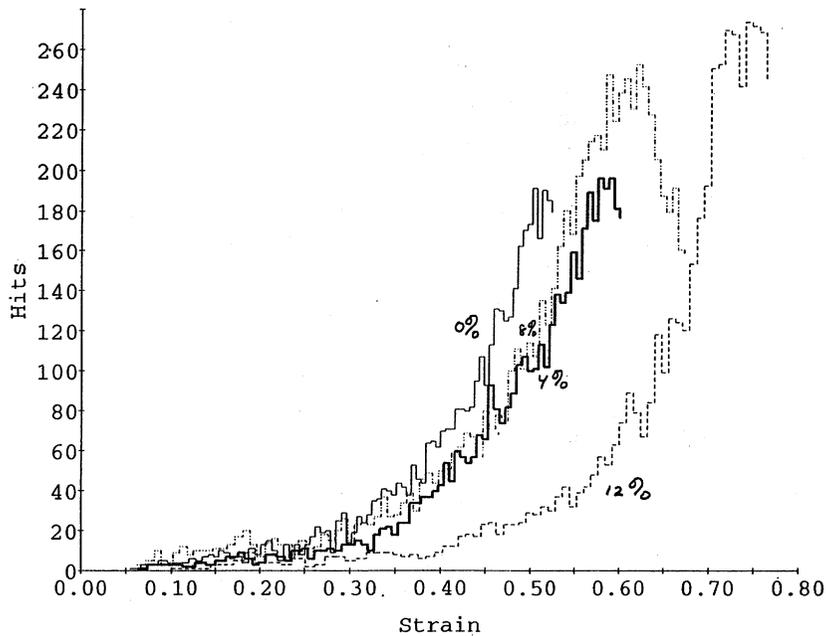


FIG. 1. — Effect of vinyl stearate on extensibility of leather.

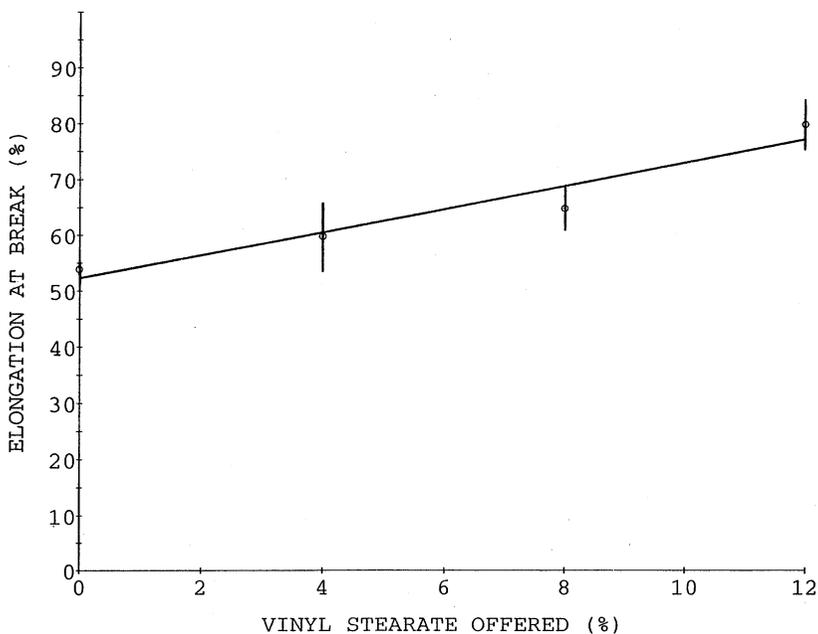


FIG. 2. — Acoustic emission of leather treated with varying amounts of vinyl stearate.

borne out with the acoustic emission results in Figure 2, which indicate that the detected fiber breakages occur later with increases in the amount of vinyl stearate added.

Kjeldahl nitrogen analyses were carried out to determine the effect of addition of varying amounts of vinyl stearate. Comparison of the percent nitrogen content of the untreated hide with

that of the treated samples showed an appreciable decrease (13.2% in control sample vs 12.5% after 2% vinyl stearate treatment). A further drop in nitrogen content to an average of 11.8% was found after the vinyl stearate offered was increased to 4, 8 and 12 percent. The leveling off of the nitrogen content might be due to the non-uniform distribution (see below), with most of the polymer tending to saturate the superficial regions of the leather.

Of particular interest was the fact that as the amount of vinyl stearate was increased to 4% and above, the resulting leather became more water repellent, as evidenced by formation of beads of water with contact angles greater than 90° on the leather surface. In additional experiments, no water repellency was noted at the 4% vinyl stearate level when the redox initiating system was omitted, indicating that polymerization was necessary before the phenomenon could be observed.

The penetration of vinyl stearate into the leather was examined by determining the effect on water repellency. Water was readily absorbed into the untreated leather. When the offer was 4% or 8% vinyl stearate, both the grain and the flesh surfaces became water repellent, with contact angles greater than 90°, but the grain-corium interface, made accessible by splitting the sample, did not. Therefore, the 2% emulsion did not penetrate into the leather enough to coat the interior fibers. When the offer was 12%, however, penetration was sufficient to render the interior water repellent. Since the treatment times for the various monomer contents were the same, it is clear that the distribution was not uniform for any. More prolonged treatments would have achieved better uniformity, but might have led to hydrolysis of the monomer, as previously demonstrated when the temperature was raised to 58°C. Prolonged Soxhlet extraction of the treated leather with hexane or acetone led to a marked decrease in water repellence, showing that no chemical binding had occurred.

The effect of poly (vinyl stearate) on the mechanical properties of leather is shown in Fig. 1. The elongation at break was increased by 65% when the offer was 12% fatliquor. The lack of statistical significance of the apparent upward trend of intermediate points is very likely due to the nonuniform distribution of the polymer described above. Only when the concentration was high enough to deposit significant amounts of poly (vinyl stearate) in the interior of the leather was the elongation greatly increased. The lubricating effect, however, is clear.

Table I shows the effect of additional of vinyl stearate on the tensile properties of the treated leather. No significant effect on the initial modulus or stress at break was observed at the 4, 8, or 12% offer of vinyl stearate. The energy to break, however, was significantly increased — the leather became tougher.

**TABLE I**  
**Effect of Vinyl Stearate on Mechanical Properties**

	Initial Modulus (kg/mm <sup>2</sup> )	Energy to Break (kg x mm)	Stress at Break (kg/mm <sup>2</sup> )
Control	1.29 ± 0.21	459 ± 13	1.05 ± 0.27
4% Vinyl Stearate	1.45 ± 0.05	540 ± 30	0.80 ± 0.20
8% Vinyl Stearate	2.65 ± 0.35	609 ± 80	1.55 ± 0.05
12% Vinyl Stearate	1.65 ± 0.05	798 ± 38	1.10 ± 0.20

Further evidence for the effect of poly (vinyl stearate) on the fiber adhesion of leather is shown by the change in acoustic emission from the dry material (Fig. 2) during the elongations reported by Fig. 1. All of the materials had a low level of acoustic activity during the initial part of the deformation, showing the effect of the retan treatment. (Had this treatment been omitted,

the control [0% offer] would have had a large constant acoustic pulse rate over the whole deformation, due to rupture of fiber adhesions.) At about 30% elongation, the pulse rate begins to increase rather sharply. We have shown earlier that this rise of activity is correlated with an increase in the energy of the pulses due to the contribution of breaking fibers<sup>5,6</sup>.

This rise in acoustic activity in the sample with the 12% offer is delayed until about 45% elongation, where the control sample is already failing. The concentration of the activity near the failure point indicates that fibers have had the freedom to reorient maximally during the deformation, so that they all would fail close together.

We conclude that poly (vinyl stearate) is a lubricant for leather that improves the mechanical properties with increased elongation at failure and no loss in tensile modulus. That it lubricates leather might be due to its ability to coat the fibers, preventing them from adhering to each other during drying. A softer product might result from use of vinyl esters of mixed chain lengths (vinyl tallowate, e.g.) to prevent crystallization.