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## NEW PROCESS EXPANDS USES FOR WOOLSKINS

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### SYNOPSIS

This paper summarizes the results of investigations on shearlings (woolskins) stabilized with glutaraldehyde. Shearlings can be fully tanned with 15% glutaraldehyde (25% commercial solution) in a 24-hr process, to produce leather with a shrink temperature (resistance to hot water) of 85° to 86°C. This can be increased by retanning with basic chromium sulfate (chrome). Glutaraldehyde also combines chemically with the wool, turning it yellow and increasing its stability to alkaline solutions. Analysis of the glutaraldehyde-stabilized wool indicated that lysine was the only amino acid that reacted with glutaraldehyde. Shearlings tanned with glutaraldehyde alone or in combination with chrome have increased resistance to deterioration by warm soap solutions and by artificial perspiration, rapidly absorb and desorb significant quantities of water vapor, are non-toxic, and retain their natural fire resistance. However, their moth-resistance is not improved. The shearlings can be disinfected by laundering with a quaternary ammonium compound, a phenolic compound or with alkalinized glutaraldehyde, the latter being most effective. Amphoteric surfactants, added to the final rinse water, counteract the felting tendency of the wool and aid in maintaining the shearling in a soft condition.

### INTRODUCTION

Shearlings (woolskins) have been used for many years as bedpads for the prevention and treatment of bedsores (decubitus ulcers) [1-5] and as paint-roller covers. However, their use for these purposes was limited by the special care previously required to prevent shrinkage and hardening of the leather during washing and by their short service life. Basic aluminum sulfate (alum) and basic chromium sulfate (chrome) have been the conventional tanning agents for shearlings.

The tanning property of glutaraldehyde was discovered by Filachione and co-workers [6-8]. The washability of glutaraldehyde-tanned leather [9] suggested the use of this tanning agent for the production of "easy-care" shearlings.

## GLUTARALDEHYDE MODIFICATION

### Tanning of Shearlings

Special tanning procedures with relatively large solution to skin ratios (10:1 or greater) and a minimum of agitation are used to prevent matting and felting of the wool [10]. Using the following typical procedure, the rate of tanning was determined under practical conditions on three shearlings:

Shearlings, scoured, pickled*	100%
Water, 35°C	920%
Sodium sulfate, anhydrous	3%
Sodium formate	3%
Glutaraldehyde (25% solution)	10%

The percent of chemicals is based on the drained weight of the scoured, pickled shearlings, with the exception of the sodium sulfate, which is on a solution basis. Tanning was started at pH 4.0 to avoid too rapid reaction with the glutaraldehyde. The pH was raised gradually by three additions of sodium carbonate (dissolved in the remainder of the water) to approximately 6.5, then to 7.6, and finally to 8.2 to complete the tanning. Tanning was rapid during the first 6 hr, increasing as the pH was raised (Figure 1). After 24 hr the shrink temperature (Ts) of the leather was 85° to 86°C, the maximum obtainable with glutaraldehyde. After tanning, the shearlings were washed, acidified with sulfuric acid to a skin pH of approximately 4, then washed again and drained.

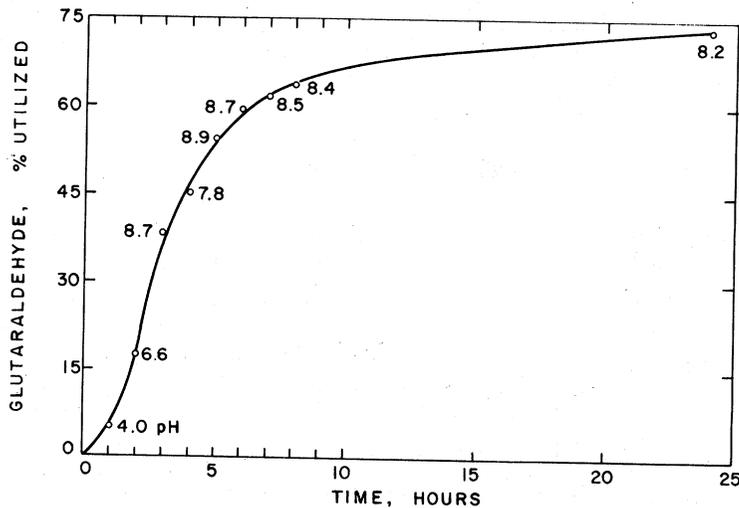


FIG. 1. Reaction of glutaraldehyde with shearlings during tanning, as the pH was gradually increased. (Reprinted by permission [10]).

\*Woolskins preserved at a pH of approximately 2 by the use of a sodium chloride-sulfuric acid solution.

The effect of time and concentration on glutaraldehyde utilization was determined (Table I). Although the maximum  $T_s$  was obtained in 7 hr by use of at least 20% glutaraldehyde, the aldehyde continued to react and a more fully tanned product of greater durability was produced by a 24-hr procedure. Glutaraldehyde utilization was efficient at all but the two highest concentrations. A full tannage can be obtained with 15% glutaraldehyde.

TABLE I  
Effect of Time and Concentration on the Utilization  
of Glutaraldehyde in Tanning Shearlings

Added* (%)	7-hr Tannage			24-hr Tannage		
	Uptake* (%)	Utilized (%)	$T_s$ (°C)	Uptake* (%)	Utilized (%)	$T_s$ (°C)
5	3.6	71	73	4.7	95	71
10	7.0	70	70	8.5	85	85
15	9.8	65	73	10.8	72	85
20	12.1	61	85	13.1	65	86
25	11.1	44	85	14.8	59	86

\*25% solution on pickled shearling weight. (Reprinted by permission [10]).

The  $T_s$  of the glutaraldehyde-tanned shearlings can be raised to over 100°C by retanning with a sufficient quantity of basic chromium sulfate (chrome) in the presence of sodium formate at a pH of 3.6 to 3.8, in a 24-hr procedure. A higher hydrothermal stability helps to prevent possible accidental heat damage to the leather during laundering.

#### Reaction with Wool

Glutaraldehyde also combines chemically with the wool to produce a stable, golden-yellow product [11, 12]. To obtain quantitative data, samples of purified wool and wool cloth were modified with various amounts of glutaraldehyde by the 24-hr procedure described above. The amount of glutaraldehyde combined increased with increasing concentration to a maximum of approximately 4%, based on the dry weight of the wool (Table II). However, larger amounts of aldehyde were combined and utilized when both wool and skin (shearlings) were present.

A dewooled skin, a shearling, and the wool from a whole shearling, tanned separately under identical conditions, with 10% glutaraldehyde (25% solution) for 24 hr, showed a glutaraldehyde utilization of 81%, 73%, and 64%, respectively. The data indicate that glutaraldehyde has a greater affinity for collagen than for keratin, and that there is a competing reaction when both are present.

The mechanism is presumably the same as in the tanning of the skin

TABLE II

## Glutaraldehyde Uptake by Shearlings and Wool

Added* (%)	Combined*		Utilized	
	Shearling (%)	Wool (%)	Shearling (%)	Wool (%)
1.25	1.18	—	95	—
2.50	2.13	1.9	85	76
3.75	2.70	—	72	—
5.00	3.28	2.8	65	56
6.25	3.70	—	59	—
7.50	—	4.2**	—	56**
10.00	—	4.1	—	41

\*Glutaraldehyde (100%); shearlings on pickled weight; wool and wool cloth on air-dried weight.

\*\*Wool cloth.

collagen, i.e., by cross linking, as evidenced by the markedly enhanced chemical stability of the glutaraldehyde-modified wool, especially to alkaline solutions. The strong cross links help to stabilize the structure of the fiber even after scission of the disulfide bonds by sodium sulfide (Table III).

TABLE III

## Stability of Glutaraldehyde-Modified Wool to Attack by Sodium Sulfide

Concentration of $\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$ (%)	pH	Solubility of Wool*	
		Unmodified (%)	Glutaraldehyde Modified (%)
1	12.4	62.4	5.7
		61.7	5.2
3	12.6	88.8	21.1
		88.9	22.7

\*1.0 g wool immersed in 100 ml solution at  $65 \pm 0.05^\circ\text{C}$  for 1 hr; data are the results of duplicate analyses. (Reprinted by permission [11]).

A determination of the amino acid composition of the above three samples of stabilized wool indicated that of the 17 amino acids measured, lysine was the only one that showed any evidence of having reacted with glutaraldehyde [13].

As the amount of added glutaraldehyde increased, the lysine showed a continual and smooth decrease to 55% of its original value. Lysine in other proteins usually reacts with glutaraldehyde to a much greater extent. The dense, compact structure of the keratin may limit the accessibility of the lysine.

The modified wool showed no resistance to attack by larvae of the black carpet beetle [14]. Wool stabilized with glutaraldehyde retains its natural fire-resistance. Like unmodified wool, it will char in an open flame but will not ignite or support combustion. Toxicity patch tests of glutaraldehyde-modified wool showed no evidence of any irritation of rabbit and human skin after 98 hr and 48 hr exposures, respectively.

## PROPERTIES OF GLUTARALDEHYDE-CHROME-TANNED SHEARLINGS

### Durability

Shearlings tanned with glutaraldehyde alone or in combination with chrome have increased resistance to deterioration by warm soap solutions. In "Launder-Ometer" tests the shearlings withstood long continued washing at 120° F very well (Table IV) [10]. The best skins in regard to both Ts and area stability were those tanned with 20% glutaraldehyde and 10% glutaraldehyde-4% chrome.

TABLE IV

Effect of Repeated Laundering on the Stability of Glutaraldehyde  
and Glutaraldehyde-Chrome-Tanned Shearlings

Glutaraldehyde (%)	Chrome (%)	Tanned Ts (°C)	Six 15-min cycles at 120°F*			Twelve 15-min cycles at 120°F		
			Ts (°C)	ΔTs** (°C)	Area Loss (%)	Ts (°C)	ΔTs† (°C)	Area Loss (%)
10	—	83	75	-8	14	74	-9	17
20	—	86	76	-10	12	74	-12	12
10	4	92	81	-11	9	79	-13	9
5	8	99	84	-15	9	83	-16	12

\*0.5% Ivory soap solution.

\*\*ΔTs refers to the change from the tanned Ts after 6 washes.

†ΔTs refers to the change from the tanned Ts after 12 washes (Reprinted by permission [10]).

The increased durability indicated by the laboratory tests and by a preliminary hospital trial was confirmed by a full-scale hospital service test [15, 16]. Two hundred and sixty-two shearlings were tanned commercially with alum, chrome, and glutaraldehyde individually and with glutaraldehyde in combination with various amounts of chrome. The wool was clipped to one inch length during processing. The bedpads were distributed to eight hospitals, a

nursing home and an outpatient clinic, used under various clinical conditions during a three-year period, and removed from service after various periods of use for laboratory evaluation.

The shearlings were washed for 10 min with a mild soap or a detergent at a temperature of not over 120°F to prevent shrinkage of the wool or hardening of the leather. An initial rinse was used if the bedpads were heavily soiled. A disinfectant was added either in the wash cycle or in the final rinse. The pads were soured with a commercial sour to a skin pH of near neutrality, spun dried, then tumble dried at a stack temperature of not over 130°F; or the shearlings were hung to air-dry. Excessive matting of the wool and overheating should be avoided. One hospital sterilized the shearlings by exposing them to ethylene oxide after each laundering. However, ethylene oxide is expensive, and routine use of this gas has been reported to detan shearlings and shorten their useful life [17].

A few pads became stiff or hard when the recommended laundering and/or drying temperatures were exceeded or when tanned with alum or small amounts of chrome. Pads with high chrome had increased durability, but they did not last as long as the pads containing glutaraldehyde and they became stiff sooner.

Glutaraldehyde aided in maintaining the shearlings in a soft, flexible condition whether or not chrome was present. However, it was found advantageous to have sufficient chrome present with the glutaraldehyde to maintain the shrink temperature well above the washing-drying temperature range. The shearlings tanned with glutaraldehyde alone or in combination with various amounts of chrome had commercially acceptable strength and excellent durability. They were serviceable for as long as 28 months with as many as 54 launderings. This was considerably longer than the six-month service period and/or 10 launderings that one large hospital stated was required to make the use of the pads economically feasible.

The experimental shearlings prepared for this hospital test were tanned with glutaraldehyde, then retanned with chrome. However, shearlings of equal durability can be obtained by tanning with glutaraldehyde and chrome simultaneously under conditions of conventional chrome tannage or the aldehyde may be applied as a retannage to chrome-tanned skins.

With repeated laundering the wool of the shearlings tends to felt but this is not detrimental in any way to its use as a bedpad. The wool continues to support the patient and remains comfortable. However, for decorative uses such as throw-rugs, maintenance of the original, combed-wool appearance is desirable. Laboratory experiments have shown that the addition of an amphoteric surfactant to the final rinse of the laundering process will prevent the wool from forming into bundles and will also prevent the leather from developing a "dry-surface-feel" [18,19]. Long chain amino acid derivatives of coconut oil, commercially available from General Mills\* under the trade name Deriphath 151 C, added to the final rinse water each time, prevented the wool from forming into bundles. The substantivity of the Deriphaths appears to be an important factor in imparting desirable properties to the wool and leather.

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

### Moisture Sorption

The rapid absorption and dissipation of perspiration is important in the prevention of decubitus ulcers. The absorption of water vapor by shearlings, wool, and synthetic products was measured in an atmosphere of 91% relative humidity and desorption was determined by exposure to 50% relative humidity [20]. The glutaraldehyde-chrome-tanned shearling rapidly absorbed and desorbed significant quantities of water vapor (Figure 2). Glutaraldehyde modifi-

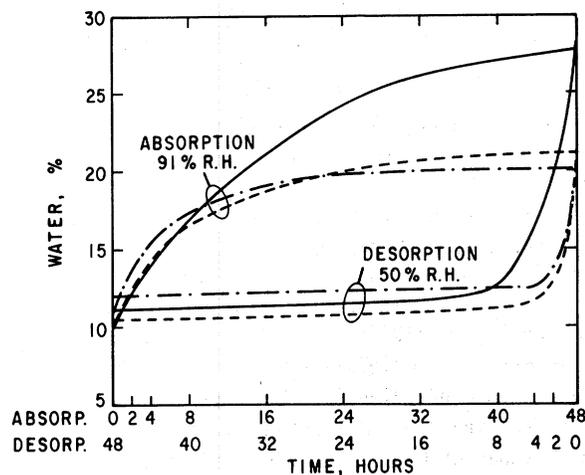


FIG. 2. Water vapor absorption-desorption curves of glutaraldehyde-modified wool (- - -), unmodified wool (- · - · -), and a glutaraldehyde-chrome-tanned shearling (—) at  $73^{\circ} \pm 1^{\circ}\text{F}$ .

cation of the wool slightly increased its water vapor absorption capacity in comparison with untreated wool. It is also of interest to note that shearlings absorbed 10 to 20 times more water vapor than pads made from polyurethane foam or from polyester fiber. These data indicate that wool is a much more effective material than synthetics in keeping the skin dry.

### DISINFECTION OF GLUTARALDEHYDE-CHROME-TANNED SHEARLINGS

Hospitals and nursing homes use a variety of disinfectants and disinfecting procedures to minimize the possibility of cross infection. Laundering shearlings contaminated with vaccinia virus, polio virus, *Staphylococcus aureus* or *Pseudomonas aeruginosa*, in warm water solutions of a quaternary ammonium compound (Hyamine 3500), a phenolic compound (Santophen 1), or alkalized glutaraldehyde at the recommended concentrations produced a substantial reduction in the vaccinia virus and *Staphylococcus aureus*, but had less effect against the

more resistant polio virus and *Pseudomonas aeruginosa* [21, 22]. Glutaraldehyde, even at 0.5% concentration (one-fourth of the recommended amount), was the most effective of the disinfectants tested.

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