# THE MOISTURE SORPTION PROPERTIES OF GLUTARALDEHYDE-CHROME-TANNED SHEARLINGS*

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## ABSTRACT

Data on the water vapor sorption properties of shearlings tanned with glutaraldehyde, with chrome, and with glutaraldehyde in combination with chrome are presented. The quantity and rate of absorption and desorption of water vapor by the leather and by the wool and the effects of chemical modification by glutaraldehyde on these properties are also given. The water vapor sorption of shearlings is compared to that of two synthetic polymeric materials now being used for bed pads.

## INTRODUCTION

It has been reported previously that a more washable and perspiration-resistant shearling could be produced by using glutaraldehyde in the tanning process and that the glutaraldehyde-modified leather and wool have enhanced chemical stability, especially to alkaline solutions (1, 2). These properties have been utilized for the production of more durable medical pads and paint rollers.

The absorption and transmission of moisture by the wool and dissipation through the wool and leather are important properties of shearlings. These properties are desirable for the prevention and treatment of decubitus ulcers, commonly known as bed sores.

The absorption of moisture by wool and by leather is well known. Grassman and Zeschitz (3) made a comprehensive study of the moisture absorption of leathers tanned with various materials including glutaraldehyde as well as that of other natural and synthetic fibers. However, no data were available on the moisture sorption properties of shearlings tanned with various tanning agents or of glutaraldehyde-modified wool.

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This paper reports studies of the absorption and desorption of water vapor by chemically modified or tanned shearlings, leather, and wool, and by two synthetic polymeric materials now being used for bed pads.

## EXPERIMENTAL

The glutaraldehyde-tanned shearling was selected from an experimental, 84-skin production pack tanned with 15 percent glutaraldehyde (25 percent solution) for 24 hours. The processed shrinkage temperature (Ts) was 81°C. The glutaraldehyde-chrome-tanned shearling was selected from another pack of the same size tanned with 10 percent glutaraldehyde (25 percent solution) for 24 hours, acidified, then retanned with four percent basic chromium sulfate in the presence of one percent sodium formate for 24 hours. The processed Ts was 85°C. The chrome-tanned shearling was selected from an experimental, three-skin laboratory pack tanned with eight percent basic chromium sulfate in the presence of two percent sodium formate for 24 hours. The processed Ts was 78°C. The percent of the chemicals is based on the drained, pickled weight of the shearlings.

Two-inch-square samples of processed shearlings, leathers and synthetic products were used for these studies. The samples of leather and wool were prepared by clipping the wool from the shearlings. For control purposes, wool clipped from a scoured, pickled shearling was neutralized to pH 5.3, washed and dried at room temperature.

All samples, previously at ambient room condition, were brought to equilibrium in a conditioning room at 50 percent relative humidity and 73°F. for one week prior to testing. The water vapor absorption apparatus is shown in Figure 1. The samples were suspended from stainless-steel hooks, one in each desiccator, at a constant temperature of 73° ± 1.0°F. The samples of wool were placed in baskets made in the Instrument Shop of 1.5 mm.-mesh, stainless-steel screen, 33 mm. diameter, 57 mm. height, with stainless-steel wire handles, to fit into ground-glass-covered weighing bottles.

Preliminary experiments with a saturated atmosphere produced erratic results from moisture condensation on the samples due to the 2°F. fluctuation in room temperature. Since the temperature could not be controlled within the limits required to avoid condensation at relative humidities of 95 percent to 100 percent, a lower relative humidity was used.

A saturated solution of sodium tartrate was selected since its vapor pressure, in the presence of an excess of the salt, produces a nearly constant relative humidity of 91.5 ± 1.2 percent in a closed container over the wide temperature range of 14.4° to 39.6°C., as shown in Figure 2. The relative humidities were calculated by dividing the values of the vapor pressure of a saturated solution

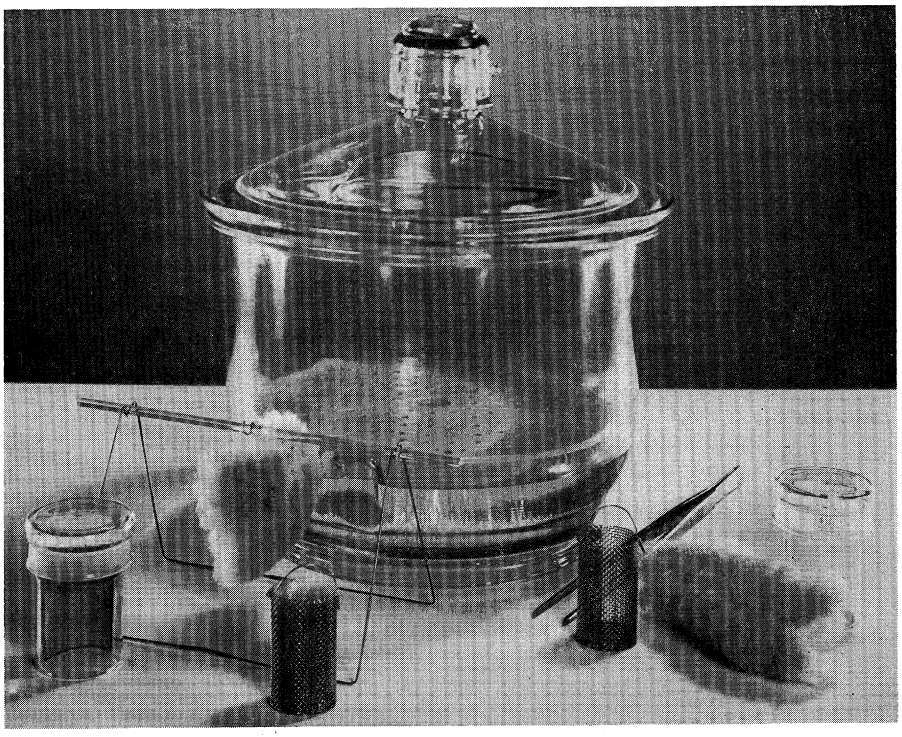

FIGURE 1.—Water vapor absorption apparatus.

of sodium tartrate at various temperatures, as reported by Lowry and Morgan (4), by the vapor pressure of water at the same temperatures. The fact that the two curves are nearly parallel indicates the nearly constant relative humidity. The calculated relative humidity at 22.8°C. (73°F.) was 91.4 percent. An average value of 90.7 percent was obtained when checked with the Honeywell Relative Humidity Sensor,‡ an electrical resistance instrument. One liter of a saturated solution of sodium tartrate and an excess of solid sodium tartrate were placed in each desiccator to provide a large quantity of available moisture for each sample. The samples were weighed in ground-glass-covered weighing bottles after 0.5, 1, 2, 4, 8, 24 and 48 hour exposures, to determine water vapor absorption. Between weighings the bottles were covered to retain any moisture accumulated on the inside surfaces by contact with the samples and placed in a desiccator containing a desiccant, to maintain a dry outside surface.

‡Mention 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.

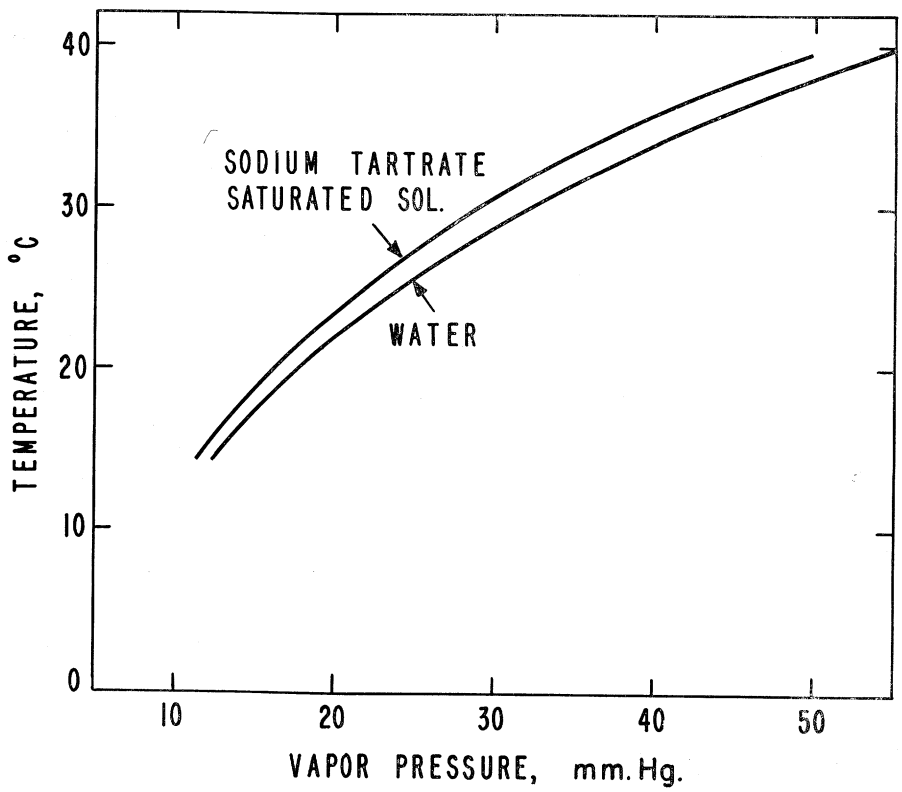


FIGURE 2.—Vapor pressures of a saturated solution of sodium tartrate and water at various temperatures.

The water vapor absorption of a glutaraldehyde-chrome-tanned shearling was also determined at 98.6°F. (37.0°C.) by placing the desiccator containing the sodium tartrate solution in an incubator-type oven.

The moisture desorptions were determined after the above time intervals by exposing the samples to the atmosphere of the conditioning room at a constant 50 percent relative humidity and a constant temperature of 73° ± 1.0°F. All absorptions and desorptions were run in duplicate.

The dry weights of the samples were determined later by drying to constant weight in a vacuum oven continuously swept with zero humidity air at 50°C.

## RESULTS AND DISCUSSION

The water contents of the samples during water vapor absorption, starting with the equilibrium water content at 50 percent relative humidity, and during

water vapor desorption were plotted against time. The percent water at each time interval during absorption and desorption, calculated from the vacuum-dried weight, is the average of two determinations. The word "absorption" includes the water vapor adsorbed on the surface as well as the water absorbed within the fibers.

## Glutaraldehyde-Tanned and Glutaraldehyde-Chrome-Tanned Shearlings

*Absorption.*—The water vapor absorption rates and capacities of the leathers of both tannages are considerably greater than those of the wool (Figure 3). The absorption by the shearling is between that of the leather and the wool. It is closer to the wool than to the leather since the rate of water vapor penetration into the leather is decreased by the presence of the one-inch-long layer of wool on the grain surface. The weight proportion of leather to wool, approximately 45 percent to 55 percent respectively in these samples, and the thickness of the leather also influence the quantity of water vapor absorbed. To compare

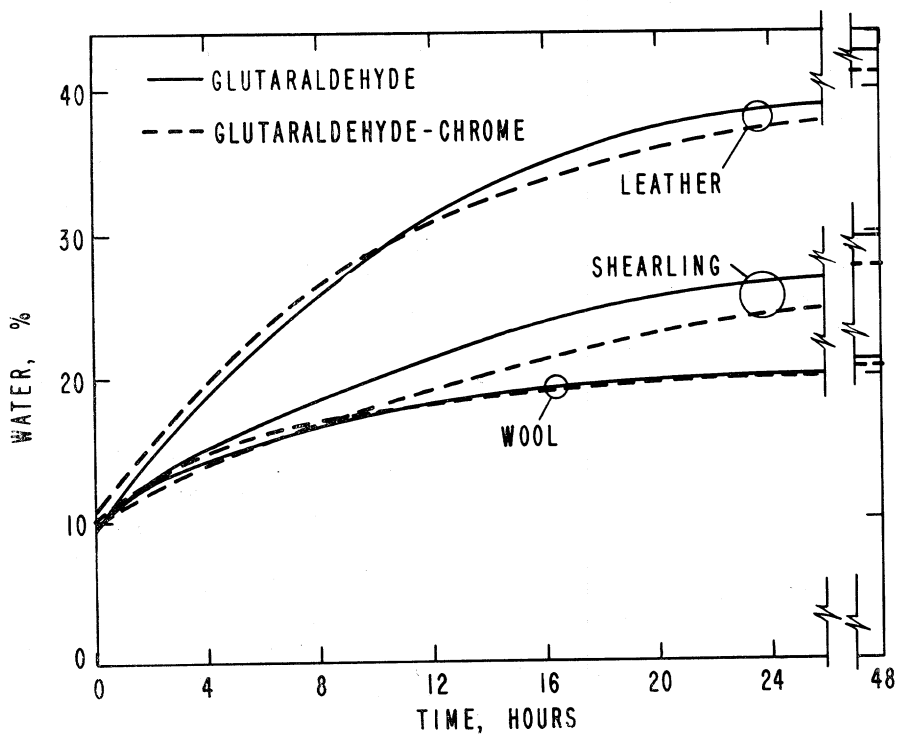


FIGURE 3.—Water vapor absorption of glutaraldehyde-tanned and glutaraldehyde-chrome-tanned shearlings at 91 percent R.H. and 73° ± 1°F.

two tannages it was necessary to sample the same skin areas and to select test pieces of approximately equal weights.

The addition of chrome to the glutaraldehyde tannage caused a moderate decrease in water vapor absorption by the shearling and leather, but had no effect on the wool since only a small quantity of chrome, equivalent to 0.06 percent $Cr_2O_3$, is combined with the wool. After 48 hours the glutaraldehyde-tanned leather had a water content of 43 percent, the glutaraldehyde-chrome-tanned leather 41 percent. The water content of the glutaraldehyde-tanned shearling was 30 percent, the glutaraldehyde-chrome-tanned shearling 28 percent. The wool of both tannages had 21 percent water after 48 hours.

*Desorption.*—The shearlings, leathers and wool of both tannages lost water vapor at a rapid rate (Figure 4). The leathers lost water vapor more rapidly than the shearlings. The shearlings lost water vapor more rapidly than the wool. There were no significant differences between the two tannages. In general, the desorption rate varied directly with the amount of water vapor previously absorbed. The water contents of the shearlings, leathers and wool, after 48 hours

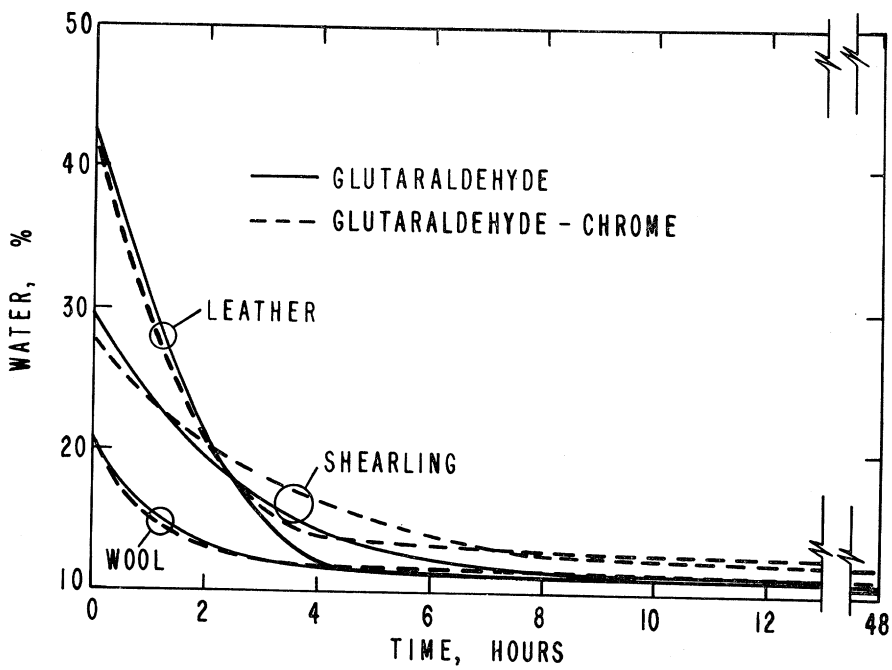


FIGURE 4.—Water vapor desorption of glutaraldehyde-tanned and glutaraldehyde-chrome-tanned shearlings at 50 percent R.H. and 73° ± 1°F.

desorption, were one to two percent higher than at the start of water vapor absorption.

## Chrome-Tanned and Glutaraldehyde-Chrome-Tanned Shearlings

*Absorption.*—The chrome-tanned leather absorbed slightly less water vapor than the glutaraldehyde-chrome-tanned leather, its water content after 48 hours was 39 percent compared to 41 percent for the glutaraldehyde-chrome (Figure 5). The absorption capacities of both shearlings were the same, 28 percent water. After 48 hours the wool of the chrome-tanned shearling contained 22 percent water, the wool of the glutaraldehyde-chrome-tanned shearling 21 percent.

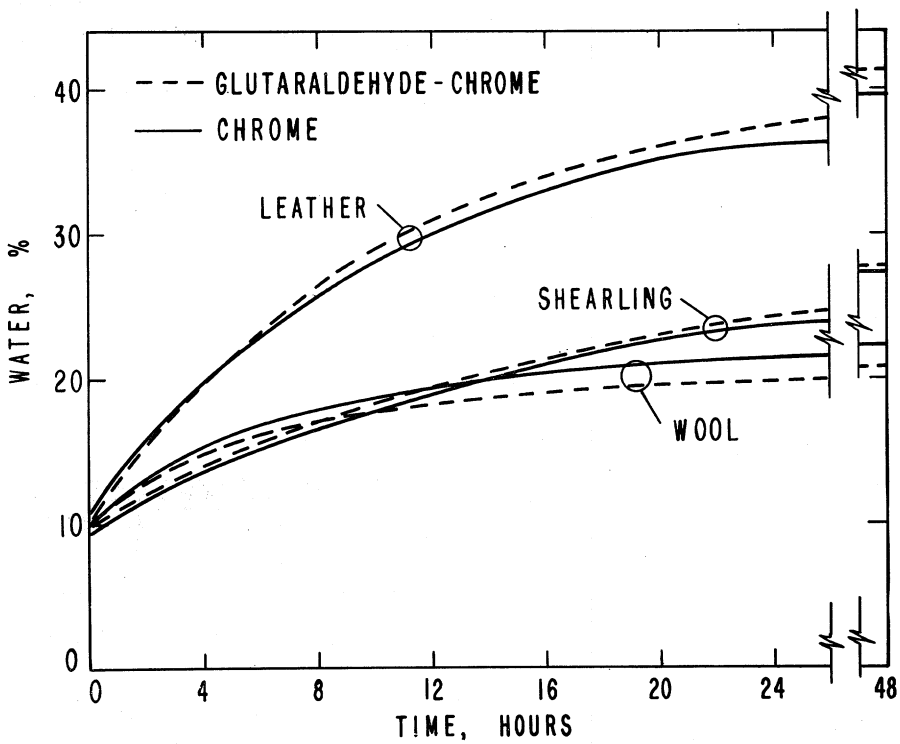


FIGURE 5.—Water vapor absorption of chrome-tanned and glutaraldehyde-chrome-tanned shearlings at 91 percent R.H. and 73° ± 1°F.

*Desorption.*—The desorption rates of the leathers were greater than those of the shearlings and the rates of the shearlings were greater than those of the wool (Figure 6). Starting with different water contents, the samples had approximately the same percent water after eight hours. Again, the water content of the shear-

lings, leathers and wool, after 48 hours desorption, were one to two percent higher than at the start of water vapor absorption. There were no significant differences in desorption rates between the two tannages.

## Glutaraldehyde-Chrome-Tanned Shearling

*Absorption-Desorption.*—These curves are plotted on the same graph to aid in the direct visual comparison of the rates of absorption and desorption of water vapor by the glutaraldehyde-chrome-tanned shearling (Figure 7). Water vapor was absorbed rapidly and continuously during the entire 48 hours. The desorp-

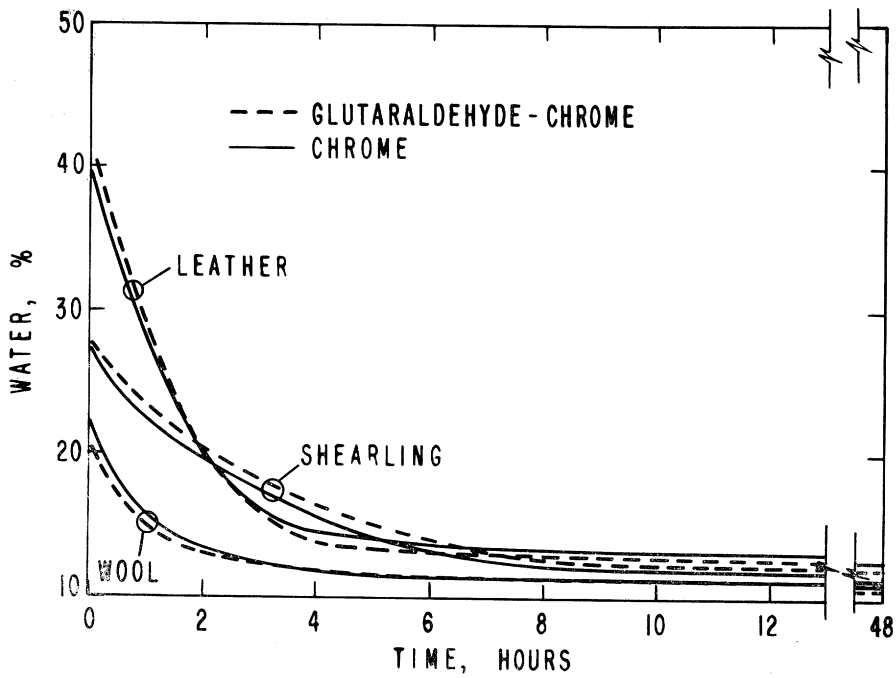


FIGURE 6.—Water vapor desorption of chrome-tanned and glutaraldehyde-chrome-tanned shearlings at 50 percent R.H. and 73° ± 1°F.

tion rate, particularly during the first eight hours was considerably greater than the absorption rate, then it leveled off after 16 hours. The hysteresis described previously (Figures 4 and 6) is shown by the shearling as it approached, but did not quite reach, its original equilibrium water content after 48 hours of desorption at 50 percent relative humidity.

## Glutaraldehyde-Modified and Unmodified Wool

*Absorption-Desorption.*—The wool from the shearling tanned with 15 percent glutaraldehyde was used for this study. We have reported previously (2)

that glutaraldehyde combines chemically with wool keratin with an uptake of as much as four percent glutaraldehyde (100 percent), based on the dry weight of the wool.

The rate of water vapor absorption of the glutaraldehyde-modified wool was approximately the same as that of the unmodified wool for the first 12 hours (Figure 8). Then the rate of the glutaraldehyde-modified wool did not decrease as rapidly so that at the end of 48 hours its water content reached 21 percent (a total increase of 12 percent) compared to 20 percent (a total increase of nine percent) for the unmodified wool.

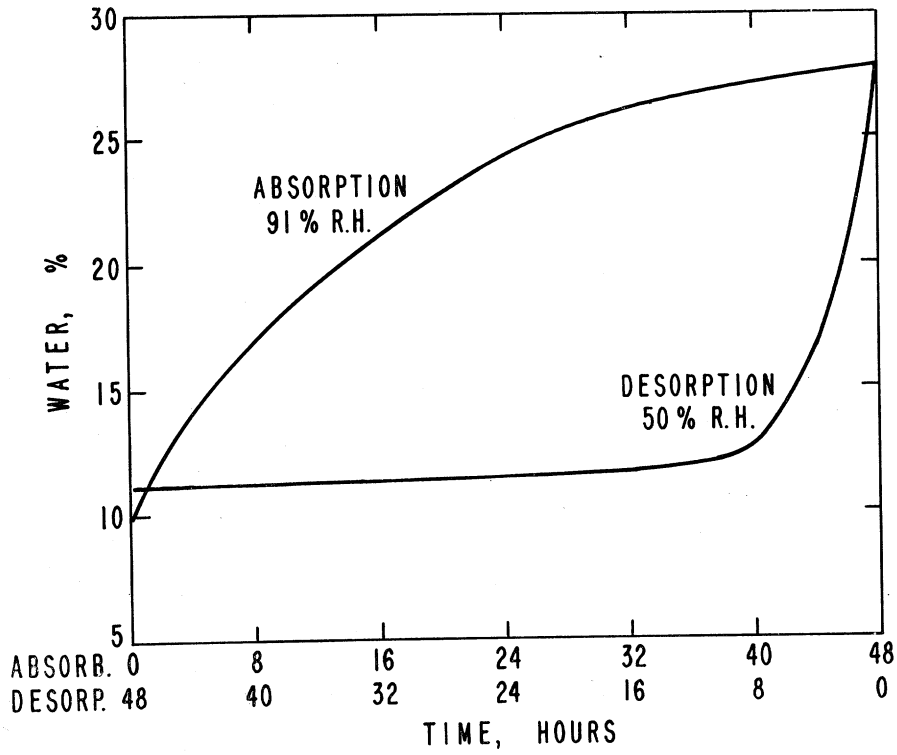


FIGURE 7.—Water vapor absorption-desorption curve of a glutaraldehyde-chrome-tanned shearling.

Watt (5) has shown, in reacting keratin with formaldehyde, that the extent of water swelling of the keratin at the time of cross-link formation influences its subsequent moisture sorption properties. Glutaraldehyde may react with keratin in a similar manner, thus allowing the wool fiber to absorb moisture to the volume existing at the time of combination. The wool is probably maintained in a swollen and hydrophilic state.

The glutaraldehyde-modified wool desorbed water vapor at a greater rate than the unmodified wool during the first four hours, then the rates of both samples leveled off. The hysteresis effect is again shown since both samples of wool, after 48 hours desorption, had approximately one percent higher water content than at the start of water vapor absorption.

## Effect of Temperature on Water Vapor Absorption

This experiment was run to determine the effect of body temperature on the water vapor absorption of a glutaraldehyde-chrome-tanned shearling.

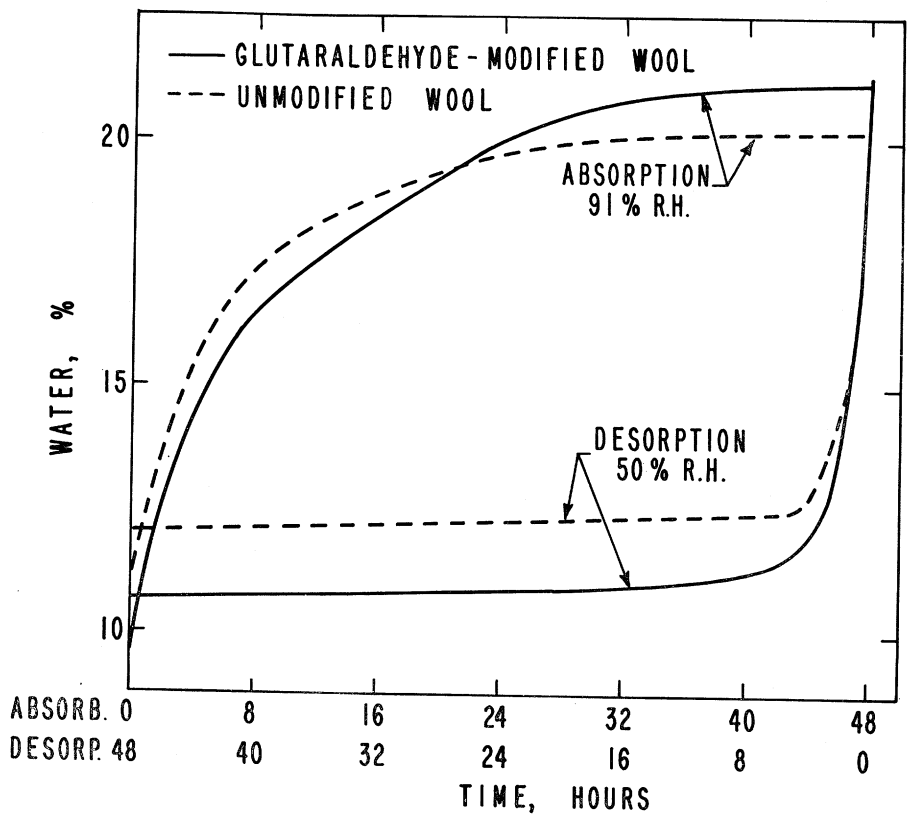


FIGURE 8.—Water vapor absorption-desorption curves of glutaraldehyde-modified wool and unmodified wool at 73° ± 1°F.

The absorption rate and capacity at 98.6°F. are considerably greater than at 73°F. (Figure 9). After eight hours the water content was five percent higher, then the difference decreased to three percent at the end of the test. After 48

hours the water content at 98.6°F. was 31 percent; at 73°F. it was 28 percent. The sodium tartrate solution has a higher vapor pressure at the higher temperature and more water vapor is available. Therefore the shearling absorbs a greater quantity of water vapor at the higher temperature.

## Shearling, Polyurethane Foam Pad and Polyester Fiber Pad

*Absorption.*—The water vapor absorption rate and capacity of shearlings are many times greater than those of the two synthetic polymeric materials, polyurethane foam and polyester fiber (Figure 10). The shearling absorbed water vapor rapidly from the start and after 48 hours had absorbed approximately ten to 20 times as much as the synthetics. The shearling had a water content of 28 percent, the polyurethane foam 2.7 percent, and the polyester fiber 1.4 per-

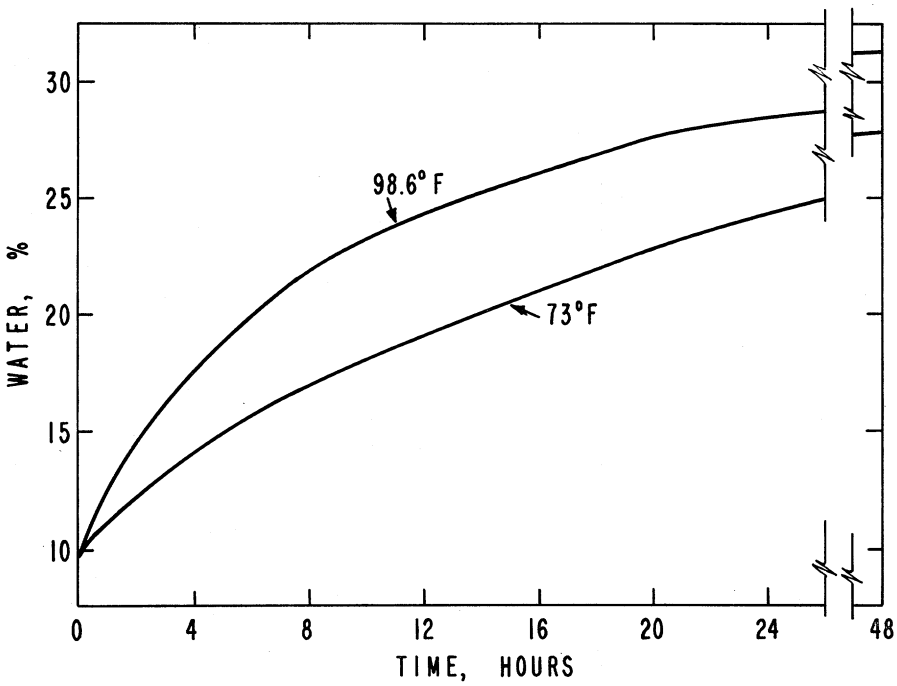


FIGURE 9.—Effect of temperature on the water vapor absorption of a glutaraldehyde-chrome-tanned shearling at 91 percent R.H.

cent. While there is a small advantage in water vapor absorption of the glutaraldehyde-chrome-tanned leather and shearling over the corresponding chrome tannage (Figure 5), both are so much superior to the synthetics that this alone would not justify changing the tannage from chrome. The principal advantages

of the glutaraldehyde-chrome tannage are stability to washing and perspiration, as reported previously (1).

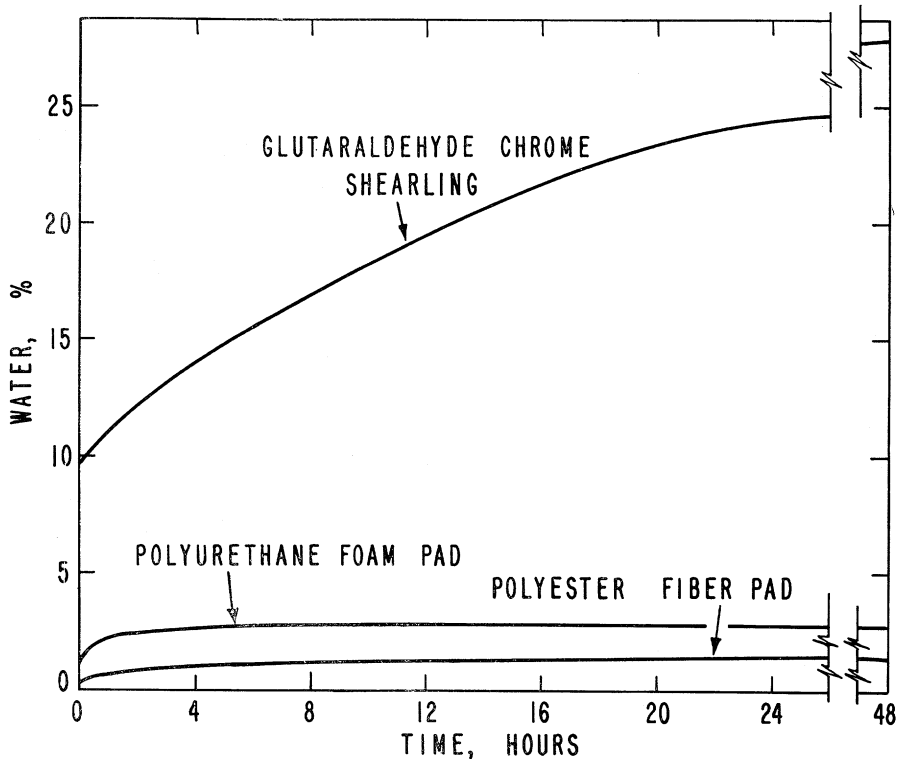


FIGURE 10.—Water vapor absorption of a glutaraldehyde-chrome-tanned shearling, polyurethane foam pad and polyester fiber pad at 91 percent R.H. and 73° ± 1°F.

*Desorption.*—The shearling desorbed the large quantity of water vapor rapidly and effectively (Figure 11). The synthetic products, having only small amounts of water, gave them up quickly and exhibited no hysteresis.

## SUMMARY

Data on the water vapor sorption properties of shearlings, leather, wool and two synthetic polymeric materials and the effects of chemical modification by glutaraldehyde on water vapor sorption are presented.

Shearlings rapidly absorb and desorb significant quantities of water vapor. The leather with the wool removed absorbs more than the wool alone. The shearlings are intermediate. Glutaraldehyde-tanned leather absorbs more water vapor than chrome-tanned leather. The glutaraldehyde-chrome-tanned leather is intermediate.

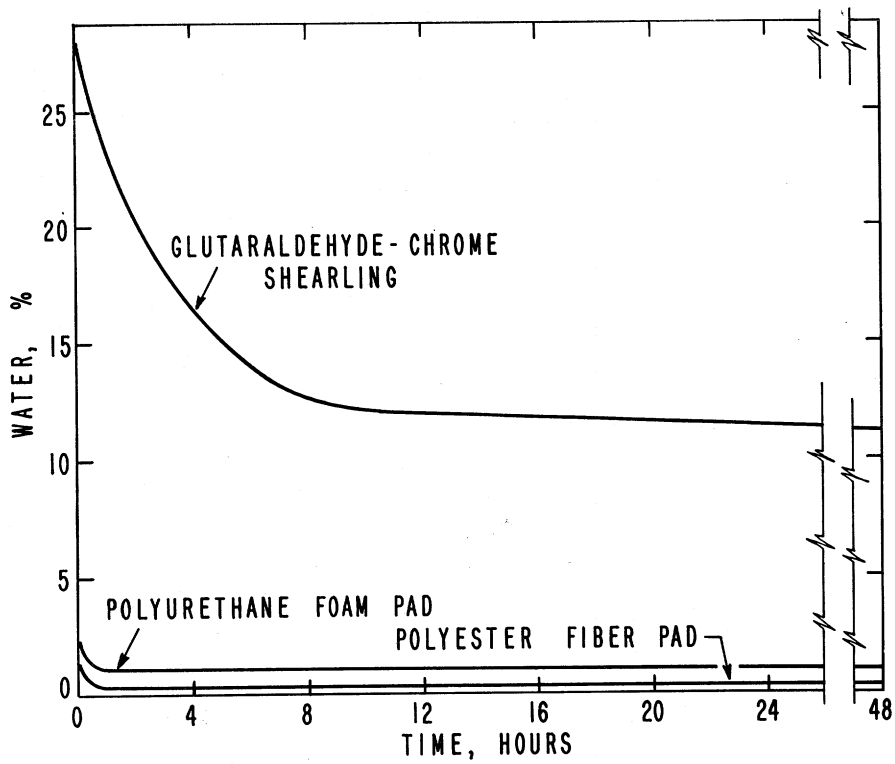


FIGURE 11.—Water vapor desorption of a glutaraldehyde-chrome-tanned shearling, polyurethane foam pad and polyester fiber pad at 50 percent R.H. and 73° ± 1°F.

Raising the temperature of the shearling to that of the body increases its water vapor absorption rate and capacity. Glutaraldehyde modification of wool slightly increases its water vapor absorption capacity in comparison with untreated wool.

The shearlings absorb ten to 20 times as much water vapor as the polyurethane foam and the polyester fiber after 48 hours in an atmosphere of 91 percent relative humidity at 73°F.

Leather alone desorbs water vapor more rapidly than wool alone and shearlings are intermediate. The type of tannage has no significant effect on the desorption rate. The natural fibers, leather and wool, exhibit hysteresis in their water vapor absorption-desorption curves but the synthetic materials, polyurethane foam and polyester fiber, do not.

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## DISCUSSION

MR. RODDY: The discussion leader for this paper is Merton A. Bell of the A. C. Lawrence Leather Co.

MR. BELL: We've heard another fine paper concerning the work done at Eastern Regional. There is no doubt that their research on glutaraldehyde has been beneficial to the leather industry.

Until the use of glutaraldehyde in the tanning of shearlings, shearlings where exposed to alkali and numerous washings were losing out to synthetics. This trend has been reversed.

This research helps to show why the wool of a shearling helps to prevent and to treat bed sores. The skin of the patient is kept dry by having the perspiration absorbed, reducing the chances for irritation.

The comparison between a natural product, shearling, and the synthetic polymeric material is of extreme interest. This is another bit of evidence that the natural product can out-perform a man-made material under certain conditions.

Mr. Happich, what was the moisture content at the start of your water absorption tests?

MR. HAPPICH: The equilibrium moisture contents at 50 percent relative humidity at the start of the water-vapor absorption tests were determined later by drying to constant weight in a vacuum oven at 50°C. The glutaraldehyde-chrome-tanned shearling had 9.7 percent moisture, the leather from this shearling had 10.3 percent moisture, and the wool from this shearling had 9.8 percent moisture.

MR. BELL: Are there any questions from the floor?

DR. GEORGE VON FUCHS, Consultant: I could put this in the form of a question, but I think it's simpler to put it in the form of a statement. You discussed water vapor absorption. You probably remember the paper Dr. Seligsberger presented two years ago and which was published in the August 1965 issue of the *Journal.*

In the December 1965 issue of *Das Leder* I found a wonderful comparison of water vapor absorption of synthetic materials, such as corfam and perlon, with natural products like silk, cotton, wool, vegetable-tanned leather, and chrome leather. This appears on page 279 of the December issue. I thought maybe it would be of interest to those who hadn't seen this article to look at it. It certainly gives leather a clean bill of health.

MR. BELL: Anyone else? If not, I'll ask the second and last. How is the perspiration absorbed and dissipated when the shearling medical pad is in use?

MR. HAPPICH: We think the perspiration is absorbed near the ends of the wool fibers, then transmitted towards the skin end of the fibers where it evaporates. The wool fibers are resilient and do not mat down, thus allowing air to circulate under the patient.

MR. BELL: Anyone else? If not, that will conclude this discussion. Thank you.