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ABSTRACT

Procedures are given for the tanning of shearlings with glutaraldehyde as the only tanning agent and for retanning with basic chromium sulfate. Data are presented on the utilization of the glutaraldehyde and on the properties of the leather. The shearlings were processed for possible use as bed pads and were evaluated for resistance to deterioration from washing and perspiration. Acceptable area stability and hydrothermal resistance were obtained when the shearlings were tanned with 15% glutaraldehyde alone or with a combination of 10% glutaraldehyde and 4% chrome in a 24-hr. process.

INTRODUCTION

The prevention of bed sores on hospital patients is a serious problem. The use of shearlings as pads is known to reduce the incidence of decubitus ulcers (1). However, shearlings require special care in cleaning to avoid damage to the leather.

Pressley (2) has reported on the stability of chrome-tanned shearlings containing the equivalent of 3.0% Cr_2O_3 and recommended the presence of a much higher amount of chrome tanning agent. Ewing, Garrow, and McHugh (3) have described the use and washing of chrome-tanned shearlings.

The washability of glutaraldehyde-tanned leather (4) suggested the use of this tanning agent, alone or in combination with other tanning agents, for the production of "easy-care" shearlings. This paper reports the initial studies on the methods of conducting this tannage and on the properties of the shearlings.

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†Eastern Utilization Research and Development Division, Agricultural Research Service, U. S. Department of Agriculture.

EXPERIMENTAL

The raw stock for these studies consisted of scoured, pickled shearlings. Three tanning procedures will be described, two using glutaraldehyde as the only tanning agent, and the third, a glutaraldehyde tannage followed by a chrome retannage.

Glutaraldehyde tannage.—The following procedures were run using one shearling at a time. An Evans churn,* equivalent to a small drum, was used, since no paddle was available.

Twenty-four hour procedure.—The percent of chemicals is based on the drained pickled weight of the skin, including the wool, with the exception of the sodium sulfate, which is on a solution basis.

Pickled shearling, scoured	100%
Water, 35°C.	920%
Sodium sulfate, anhydrous	3%
Sodium formate	3%
Glutaraldehyde (25% solution)	10%
Tan 1 hr.; pH 4.0; temp. 29°C.	
Sodium carbonate	2%
Water	30%
Tan 1 hr.; pH 6.5; temp. 28°C.	
Sodium carbonate	2%
Water	30%
Tan 2 hr.; pH 7.6; temp. 27°C.	
Sodium carbonate	1%
Water	20%
Tan 20 hr.; pH 8.6–7.7; temp. 26°C.; Ts 83°C.	
Wash — two 1-min. soakings	
Sulfuric acid, 95%	2%
Water	1000%
Acidify 2 hr. to skin pH 4.0; Ts 82°C.	
Wash — one 1-min. soaking.	

The churn was warmed to about 35°C. by steaming for 5 min. Most of the water and all of the initial chemicals were added at one time. A total liquor ratio of 1000% and a minimum of agitation were used in all tannages and

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

acidifications to prevent matting and felting of the wool. The churn was run for 1 min. every 30 min. during the day and allowed to stand overnight. Part of the water was withheld to dissolve the sodium carbonate and rinse it into the churn through the gudgeon. The pH was raised gradually. Tanning was started at pH 4.0 to avoid too rapid combination of the glutaraldehyde. The pH was then raised to approximately 6.5 and then to 7.6 to increase the rate of tanning. Tanning was completed at a pH of 8.6. The pH dropped slowly overnight to 7.7. The final shrinkage temperature was 83°C.

After tanning, the shearling was washed in the drum twice by running the drum half full of water for 1 min. each time. It was then acidified for 2 hr. by drumming 1 min. every 30 min. to a skin pH of approximately 4. It was then washed once and horsed.

Seven-hour procedure.—This shorter tanning method is essentially the same as the 24-hr. procedure. After tanning for 7 hr., the shearling was acidified for 35 min., then horsed out of the acid solution overnight without washing. The next morning it was acidified in the same solution for 2 hr. to a skin pH of approximately 4 and washed.

Glutaraldehyde tannage of wool.—The golden-yellow color of the wool indicated that there was a significant amount of fixation of the glutaraldehyde by the keratin. To determine this and to distinguish it from the amount taken up by the skin the wool was removed from a shearling by painting.* The wool was washed, acidified, and tanned with 10% glutaraldehyde (25% solution), based on the drained wet weight, by the 24-hr. procedure already described. The spent tanning solution was analyzed for glutaraldehyde.

Glutaraldehyde tannage – chrome retannage.—To study the effect of a higher shrinkage temperature on the washability of the leather a number of chrome retannages were run, varying the amounts of glutaraldehyde and basic chromium sulfate. A typical example is the following:

A shearling, tanned with 10% glutaraldehyde for 24 hr., had a shrink temperature of 85°C. The shearling was acidified to a skin pH of 3.6 and retanned, in the presence of 1% sodium formate, with 4% of basic chromium sulfate for 24 hr. The pH was adjusted from 3.6 to 3.8 with sodium bicarbonate for the last 3 hr. of the retannage. The final shrink temperature was 98°C.

Chrome tannage.—For comparative purposes several shearlings were tanned with 8% of basic chromium sulfate for 24 hr. in the presence of 2% sodium formate. Tanning was started with 880% of the water at 35°C. and at a pH of 3.4. The remaining 120% water was used to dissolve the chrome and sodium bicarbonate used in neutralization. The churn was run 1 min. every 30 min. during the day and allowed to stand overnight. Tanning was finished at a pH of 4.1 with a Ts of 88°C.

*The process of applying a depilatory consisting of sodium sulfide and other minor ingredients.

CHEMICAL AND PHYSICAL TESTS

Glutaraldehyde analysis.—In the tanning rate study 50-ml. portions of tanning liquor were removed at 1-hr. intervals for analysis. In the other tanning studies the spent tanning liquors were analyzed at the end of the 7-hr. or 24-hr. periods. Glutaraldehyde was determined by the iodometric method of Fein and Harris (5). The glutaraldehyde uptake was calculated by subtracting the amount remaining in the tanning liquor from the amount present at the start of tanning and dividing by the drained pickled shearling weight.

Chrome analysis.—The wool was closely clipped from the shearling samples, and the chromium content of the leather and of the wool was determined as chromic oxide by the ALCA alkaline fusion method (6).

Washability.—Washing tests were run in a "Launder-Ometer"* by a modification of the ALCA-ASTM "Method of Test for Colorfastness and Transfer of Color in the Washing of Leather" (7). All samples were cut from the butt area. Each 2″ x 3″ shearling sample was washed in 150 ml. of 0.5% Ivory* soap solution (pH about 10) together with 20 stainless-steel balls for mechanical agitation at a speed of 60 r.p.m. The washing cycles were 15 min. and 45 min. Washing temperatures of 120°, 140°, and 160°F. were used. The shearlings were not dried between washes. After completion of the washing, the swatches were dried, and the stiffness, area loss, and shrink temperature were determined.

The area was estimated by use of a 2″ x 3″ gauge made in our shops of clear, 1/16″ Plexiglas.* Lines were engraved at 0.05″ intervals on one face, in 1″ bands parallel to both the short and long sides. The percent area loss due to shrinkage was calculated by the equation:

$$\%\ area\ loss = \frac{10x + 15y - 0.25xy}{6}$$

where x = number of lines on gauge protruding beyond edge of leather on the 2″ (short) side; and

y = number of lines on gauge protruding beyond edge of leather on the 3″ (long) side.

Slit tear resistance.—The ALCA-ASTM "Tentative Method for the Measurement of Slit Tear Resistance" was used to determine the slit tear strength of the shearlings (8). Samples were cut from an area 5″ from the butt end and 2″ on either side of the backbone.

Perspiration resistance.—The ALCA-ASTM "Proposed Method of Measuring Resistance of Chrome-Tanned Shoe Upper Leather to Artificial Perspiration" was used to determine the perspiration resistance (9). All samples were cut from the butt end.

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RESULTS AND DISCUSSION

The utilization of glutaraldehyde is shown in Table I. In the 7-hr. tannage glutaraldehyde uptake increases with increasing concentration and levels off when 20% to 25% is used. It can be seen from the data that 7 hr. is insufficient time to produce optimum results at any glutaraldehyde concentration. To reach the maximum shrink temperature of 85°–86°C. it was necessary to use high quantities of glutaraldehyde, and as a consequence the utilization was poor. This is undoubtedly due to the long float and minimum agitation.

TABLE I

EFFECT OF TIME AND CONCENTRATION ON THE UTILIZATION OF GLUTARALDEHYDE IN TANNING SHEARLINGS

Added %	7-hr. Tannage			24-hr. Tannage		
	Uptake* %	Utilized %	Ts °C.	Uptake* %	Utilized %	Ts °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.

In the 24-hr. tannage glutaraldehyde uptake again increases with increasing concentration (Table I). Although the maximum Ts is obtained at 10% concentration, glutaraldehyde continues to combine at the higher concentrations. Utilization is efficient at all but the two highest concentrations. However, a comparison of the data shows that utilization in the 24-hr. tannage is considerably greater than in the 7-hr. tannage at all concentrations. A 24-hr. glutaraldehyde tannage appears to be necessary for obtaining a high-quality product under the above conditions.

The rate of tanning with glutaraldehyde was determined under practical conditions using three shearlings and 10% glutaraldehyde. Tanning was quite rapid during the first 6 hr., increasing as the pH was raised, as shown in Fig. 1. Glutaraldehyde continued to combine overnight even though the drum was not run. After 24 hr. the utilization was 73%, and the Ts was 85° to 86°C.

The wool alone reacted with glutaraldehyde with an uptake of 6.4% out of the 10% used, in 24 hr. This is a utilization of 64%, indicating that there is a substantial reaction between the glutaraldehyde and the wool keratin. The fixation of glutaraldehyde by the wool is lower in the presence of the skin be-

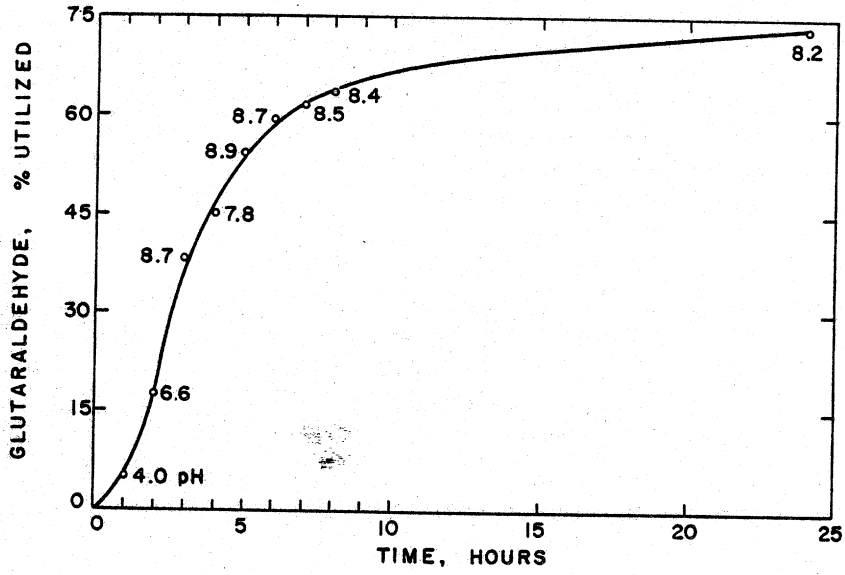

FIGURE 1.—Uptake of glutaraldehyde by shearlings during tanning.

cause of the competing reaction. The dewooled skin when tanned alone utilized 81% of the glutaraldehyde under the same conditions. This indicates that glutaraldehyde has a greater affinity for skin collagen than for wool keratin. However, chrome reacts more slowly than glutaraldehyde in combining with keratin. Analysis of the wool from a shearling tanned for 24 hr. in a solution of basic chromium sulfate containing the equivalent of 1.9 g. Cr_2O_3 per liter showed 0.06% combined Cr_2O_3 (Table V). Gustavson, using more concentrated chrome solutions, showed that wool keratin tanned with solutions of 67%-acid chromium sulfate containing the equivalent of 20 g. Cr_2O_3 per liter combined with 1% Cr_2O_3 in 1 day and with 4% to 5% Cr_2O_3 in 28 days (10).

The effects of concentration and masking of chrome on the shrink temperature of retanned shearlings are shown in Table II. The last column, $\triangle$Ts, shows the increase in shrink temperature by retannage. The first run, namely, 10% glutaraldehyde and 4% chrome in the absence of formate, shows a $\triangle$Ts of only 7°C. The same quantities plus 1% formate show a $\triangle$Ts of 13°C. The next three runs, with 5% glutaraldehyde, 8% chrome, and 1%, 2%, and 3% formate, respectively, produced optimum results with 2% formate; the Ts was over 100°C. (shrank after boiling 30 sec.), and the $\triangle$Ts was over 27°C. The chrome-tanned control using 8% chrome and 2% formate had a Ts of 88°C.

Analyses of the leathers showed that approximately 40–50% of the chrome added was utilized in the majority of the tannages (Table V). The utilization of glutaraldehyde is significantly greater than that of chrome under the above tanning conditions.

TABLE II

EFFECT OF CONCENTRATION AND MASKING OF CHROME ON THE SHRINK TEMPERATURE OF RETANNED SHEARLINGS

Glutar-* aldehyde %	Chrome† %	Sodium‡ Formate %	Ts, after: Glutar-aldehyde °C.	Ts, after: Chrome °C.	ΔTs** °C.
10	4	—	82	89	7
10	4	1	85	98	13
5	8	1	72	85	13
5	8	2	73	>100	27+
5	8	3	77	99	22
—	8	2	—	88	—

*25% solution on pickled shearling weight.
†33% basic chromium sulfate on pickled shearling weight.
‡Amount used with chrome on pickled shearling weight.
**ΔTs refers to the increase in Ts after chrome retanning.

Critical experiments in the above glutaraldehyde and glutaraldehyde-chrome tanning procedures were repeated using three shearlings for each test. In most cases the Ts and percent glutaraldehyde utilized were greater than in the one-skin runs.

An extensive study was made of the washability of glutaraldehyde and glutaraldehyde-chrome–tanned shearlings. The results of washing shearling swatches under various conditions of time and temperature are presented in Table III. The Ts was lowered by processing and usually raised by washing. The ΔTs columns are the changes from the tanned Ts's after three washing cycles. Area measurements are approximate. An area loss of 10% or less is considered to be acceptable in this accelerated test. Differences between tannages are accentuated in the more severe 45-min.-cycle washing test. The Launder-Ometer test is severe compared to the usual laundering procedure.

When shearlings were tanned with glutaraldehyde alone, 5% was insufficient to provide stability to washing. The skin tanned with this amount of aldehyde showed considerable reduction in area and lowering of the Ts. The skins tanned with 10% to 25% glutaraldehyde showed increasing resistance to washing, as judged by the small reduction in Ts and area. Fifteen percent glutaraldehyde provided high stability to washing even in the more severe 45-min.-cycle test at 140°F.

The chrome-retanned skins gave wash test results similar to those of the skins tanned with the higher concentrations of glutaraldehyde alone. When skins

TABLE III

EFFECT OF WASHING SHEARLINGS TANNED WITH GLUTARALDEHYDE AND GLUTARALDEHYDE-CHROME ON THE SHRINK TEMPERATURE AND AREA

Glutar-* aldehyde %	Chrome† %	Sodium Formate %	Tanned Ts °C.	Processed‡ Ts °C.	Three 15-min. cycles at 120°F.** Ts °C.	Three 15-min. cycles at 120°F.** ΔTs†† °C.	Three 15-min. cycles at 120°F.** Area Loss %	Three 15-min. cycles at 140°F.** Ts °C.	Three 15-min. cycles at 140°F.** ΔTs†† °C.	Three 15-min. cycles at 140°F.** Area Loss %	Three 45-min. cycles at 140°F.** Ts °C.	Three 45-min. cycles at 140°F.** ΔTs†† °C.	Three 45-min. cycles at 140°F.** Area Loss %
5	—	—	71	68	72	+1	15	62	−9	17	62	−9	19
10	—	—	82	73	81	−1	16	80	−2	10	80	−2	13
15	—	—	84	79	80	−4	6	81	−3	5	79	−5	4
20	—	—	84	80	82	−2	12	81	−3	9	75	−9	8
25	—	—	85	81	82	−3	9	81	−4	6	74	−11	3
10	4	—	89	81	80	−9	6	81	−8	4	75	−14	5
10	4	1	92	82	86	−6	4	89	−3	0	87	−5	1
5	8	1	85	85	92	+7	8	89	+4	7	78	−7	7
5	8	3	99	87	92	−7	3	90	−9	4	88	−11	2
—	8	2	88	78	84	−4	3	81	−7	6	71	−17	11

*24 hr. tannage.
†24 hr. retannage.
‡Ts after processing into finished bed pads.
**0.5 percent Ivory soap solution.
††ΔTs refers to the change from the tanned Ts after three washes.

tanned with 10% glutaraldehyde were retanned with 4% chrome, the addition of 1% sodium formate to the chrome tanning liquor produced better chrome penetration. This resulted in a higher Ts and considerably greater resistance to washing with respect to both Ts and area losses. The skins tanned with 5% glutaraldehyde and retanned with 8% chrome showed less stability to washing than those tanned with 10% glutaraldehyde and 4% chrome even though their original tanned Ts's were higher before testing. Here again the addition of sodium formate in the ratio of at least one formate to four chrome was desirable to obtain a high Ts and high resistance to washing. When both Ts and area losses are considered, 10% glutaraldehyde–4% chrome produced the most stable tannage in this series. The skin tanned with 8% chrome alone showed a 17°C. loss in Ts at 140°F. but only a moderate loss in area.

In order to identify further the best tannages the samples were run through a series of three 15-min. Launder-Ometer washing cycles at 160°F. (71°C.). Since this temperature was near the Ts of the shearlings, all samples had considerable decreases in Ts and loss of area. The best glutaraldehyde tannage was the 20% concentration with 26% area loss and Ts 54°C. The best combination tannage was 10% glutaraldehyde–4% chrome with 31% area loss and Ts 52°C. The best 8% chrome control lost 50% area and had a Ts of 62°C.

Another series of Launder-Ometer tests was run to determine how the shearlings would stand up under long continued washing. Samples from four representative tannages were washed for six cycles and twelve cycles at 120°F. without drying between washes. The results are given in Table IV. The shearlings withstood the long washings very well. 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.* Ts °C.	Six 15-min. cycles at 120°F.* ΔTs† °C.	Six 15-min. cycles at 120°F.* Area Loss %	Twelve 15-min. cycles at 120°F.* Ts °C.	Twelve 15-min. cycles at 120°F.* ΔTs‡ °C.	Twelve 15-min. cycles at 120°F.* 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.

Glutaraldehyde conferred excellent perspiration resistance as judged by the results of the accelerated test shown in Table V. The best skins in regard to area stability were those tanned with 15% glutaraldehyde and 10% glutaraldehyde–4% chrome. The skins remained soft and flexible after testing.

The slit-tear resistance of the shearlings was determined after processing. Table V shows the averages of six slit-tear tests for each skin. The range varied from approximately 2 to 4 pounds, and all had commercially acceptable strength. There was little variation among any of the tannages. An interesting observation is that the 25% glutaraldehyde skin had the same strength as those tanned with smaller amounts, even though an excessive amount of tanning agent was used.

TABLE V

PERSPIRATION RESISTANCE AND STRENGTH OF SHEARLINGS TANNED WITH GLUTARALDEHYDE AND GLUTARALDEHYDE-CHROME

Glutaraldehyde %	Chrome %	Sodium Formate %	Cr_2O_3* %	Perspiration Resistance	Slit-Tear Strength Range		
				Area Loss %	Low lb.	High lb.	Avg. of 6 lb.
5	—	—	—	—	11.9	14.7	13
10	—	—	—	10	9.7	12.6	11
15	—	—	—	4	9.8	11.5	11
20	—	—	—	—	11.5	14.6	13
25	—	—	—	—	12.8	17.0	15
10	4	—	1.0†	—	15.6	17.5	17
10	4	1	0.5† 0.06‡	4	11.5	13.6	12
5	8	1	1.8†	—	12.6	15.0	14
5	8	2	1.4†	—	—	—	—
5	8	3	1.5†	25	17.2	21.0	18
—	8	2	1.5† 0.06‡	77	15.9	18.0	17

*Moisture-free basis.
†Leather.
‡Wool.

ACKNOWLEDGMENT

The authors wish to thank Howard W. Jones for deriving the equation for estimating area loss and Mrs. Marie F. Fisher for assistance in the washing tests and glutaraldehyde analyses. The A. C. Lawrence Leather Company kindly processed the shearlings into finished leather.

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DISCUSSION

DOMINIC MEO, JR. (Salem Oil & Grease Co.): This paper brings out one important fact, and that is, the importance of the Eastern Regional Laboratory to our Industry. Certainly the projection of a new idea in the processing of one of our articles in the Industry should bring forth wholehearted cooperation and encouragement from the Industry for this core of scientists at the Eastern Regional Laboratory. They are one of our better aids for diversifying not only the practical application but also the nature of our products.

I will ask Mr. Happich three questions, and I hope there will be many more from the audience. This whole subject brings up a host of questions, both theoretical and applied. The first question I would like to ask Mr. Happich is this: From the indication that he has shown us, there must be a substantial difference in quality between the conventional type of shearling and the one that they have been working on, with either glutaraldehyde or combined glutaraldehyde and chrome.

Secondly, due to the easy reaction of the glutaraldehyde with the wool, is there any toxicity problem between the wool and the patient's skin resting on it?

Lastly, some of you, I know, are more interested in production problems than in theoretical problems. Should this process be indicative of what we might expect, will Mr. Happich kindly give us some approximate costs and length of production schedule so that you may take with you some more substantial facts from this paper?

MR. HAPPICH: In answering the first question, on quality, we have not tested the commercial product extensively, but it would appear that there are certain advantages of the glutaraldehyde and the glutaraldehyde-chrome-tanned shearlings in the matter of shrink temperature, washing, and perspiration stability. Our product is also superior in these properties to shearlings tanned with chrome alone.

As to the second question, the matter of toxicity, the glutaraldehyde-tanned leather is only mildly irritating. Dr. Floyd DeEds, Chief of USDA's Pharmacology Laboratory (WURDD), reported on the toxicity of glutaraldehyde in June, 1960.

Scoring for inflammation and edema formation was done by the Draize Method for the appraisal of the safety of chemicals in foods, drugs, and cosmetics. In this test method, compounds producing combined averages of 2 or less for intact and abraded skin are considered only mildly irritating.

In toxicity patch tests on rabbit skins, 5% glutaraldehyde solution and glutaraldehyde-tanned sheepskin leathers were rated with averages of less than 2. Commercial hatband leather had approximately the same combined average as the glutaraldehyde-tanned leather. We plan to run toxicity tests on the shearlings.

Answering the third question, on cost, it seems to us that cost is not a primary factor in a product as important as hospital bed pads. Our process is feasible from a practical standpoint. The same tanning equipment and time as in the commercial process are used.

We have established the minimum quantity of glutaraldehyde required for optimum results. But in the glutaraldehyde-chrome combination tannage, we have not yet determined the most desirable proportion of glutaraldehyde and chrome.

OSCAR WEDERBRAND (Rohm & Haas Company, Philadelphia, Pa.): If I remember correctly your slides and your statements, you said that in the washing test you ran three cycles, and at the end of the three cycles (according to your slides) there was a certain loss in shrink temperature and a certain loss in area. What happens after three cycles? In other words, do the losses in shrink temperature and in area level out? Or do they still continue to decrease with further washing?

MR. HAPPICH: I should say we have done three washes at a lower temperature of 120°F. and three washes at 140°F., but we have not gone further than three washes on the small test. However, we have washed a whole shearling in the conventional-type washing machine, and after six complete 15-min. washing cycles we have found the shrink temperature to be exactly the same as it was in the beginning.

DR. EDWARD M. FILACHIONE (Eastern Utilization Research and Development Division, Philadelphia, Pa.): We carried out some wash tests using a nine-cycle test. The glutaraldehyde did not show much change after nine washes, whereas chrome showed a continued loss in shrink temperature. There was a great difference between the glutaraldehyde leather and the chrome leather in this nine-cycle test.

SIGMUND PANZER (John A. Lang & Sons, Ltd., Kitchener, Ontario, Canada): I notice that you are washing with sulfuric acid. What is the reason for it? And would washing with a weaker acid be sufficient?

MR. HAPPICH: Since the glutaraldehyde tannage is finished at a high pH of above 8, we must lower the pH to about 4 in order to fatliquor. We use sulfuric acid as a matter of convenience. A larger quantity of a weaker acid would have to be used to equal the same pH.

ANDREW SALAMATOV (Barrett & Company, Inc., Newark, N. J.): I am not quite clear why the 1 to 10 ratio is being used in the tannage. Then I am not quite clear, when you proceed to retan the glutaraldehyde with chrome, whether the chrome is added on top of your glutaraldehyde solution without draining it.

MR. HAPPICH: The 1 to 10 ratio is used to prevent matting and felting of the wool. If we use a shorter float, the wool will be completely matted and felted.

The second question was with regard to using chrome on top of glutaraldehyde. No, the chrome is not put on top in the same solution with the glutaraldehyde. We wash and acidify down to a pH of 3.6 and then chrome retan.

MR. SALAMATOV: What ratio? What is the volume when you use the chrome?

MR. HAPPICH: It is the same. In all tannages and acidifications we use the 1 to 10 ratio, as well as a minimum of agitation, to prevent matting of the wool. When we used five minutes of agitation every half hour we got complete matting of the wool, and it could not be combed out again.

MR. SALAMATOV: You did not get precipitation of the chrome with the 1 to 10 solution, at a pH of 3.6?

MR. HAPPICH: No, we did not.

DR. LUDWIG SELIGSBERGER (U. S. Army Natick Laboratories, Natick, Mass.): I am a little skeptical about the perspiration test, and I wonder if it would not be justified to run a test with water alone to see whether you actually measure any resistance to so-called perspiration solution or just resistance to

ater under the same conditions. I think that you also would need an accelerated ging test of some kind to see whether the tannage is stable over, let us say, ıe or two years, particularly since we know that formaldehyde and other aldeydes are not so stable in storage, as we found in our climatic chambers.*

MR. HAPPICH: Yes, we ran water controls on this at the same temperature ıd the area and shrink temperature were satisfactory. But it is true that a ɔnger storage test would be desirable.

N. CLIFFORD BENRUD (S. B. Foot Tanning Company, Red Wing, Minn.): What type of fatliquor did you use for the straight glutaraldehyde test?

MR. HAPPICH: All of these shearlings were fatliquored and processed commercially, so we don't have any direct information on that question.

*JALCA 58, 81 (1963).