

III. COMBINATION TANNAGES WITH CHROME*

MARTIN L. FEIN, EDWARD M. FILACHIONE, JOSEPH NAGHSKI, AND
EDWARD H. HARRIS, JR.

*Eastern Regional Research Laboratory†
Philadelphia 18, Pennsylvania*

ABSTRACT

In this study the tanning properties of combination tannages of glutaraldehyde and chrome were evaluated under various conditions. Whole sheepskins (cabretta) were treated with three combinations: (a) retannage of chrome-tanned skin with glutaraldehyde, (b) simultaneous tannage with glutaraldehyde and chrome, and (c) retannage of glutaraldehyde-tanned skins with chrome. The rate of tanning by these agents was determined by measuring the disappearance of glutaraldehyde and chrome from the tanning bath. Tanning was effected over a wide range of conditions. The two tanning agents acted independently of each other, and the desirable characteristics imparted by each tanning agent were apparent in the leathers. The combination procedures listed produced leather with improved resistance to synthetic perspiration and to the effects of washing in hot, soapy water.



INTRODUCTION

Recent investigations have demonstrated the versatile tanning power of glutaraldehyde and the desirable properties it imparts to the leather (1-5). In view of the recent commercial availability of glutaraldehyde (6-9) and the importance of chrome in tanning, it was most desirable to obtain information on the combination tannage with these two tanning agents.

Aldehyde tannages have been known for some time; however, formaldehyde has been the aldehyde which has received the principal attention of investigators both from the theoretical and practical standpoint (10-14). The literature pertaining to combination tannages of aldehydes and chrome is not very extensive and is confined almost entirely to formaldehyde. Various investigators have studied the formaldehyde-chrome combination tannage

from the fundamental research standpoint (13, 15-20). On the practical side, Ushakoff (21) advocated a formaldehyde pretannage for producing a special side upper leather.

In this paper we report a study of the combination tannage involving glutaraldehyde and chrome. All three procedures for effecting the combination tannage were investigated. These were: (a) retannage of chromed stock with glutaraldehyde, (b) simultaneous tannage with chrome and glutaraldehyde, and (c) retannage of glutaraldehyde-tanned stock with chrome. In this study full sheepskins (cabretta) were used to evaluate analytically the rate of uptake of tanning agents and to examine the properties of the leather from this combination tannage.

EXPERIMENTAL

The raw stock was pickled, degreased cabretta skins obtained from a tannery. The glutaraldehyde was the commercially available 25% aqueous solution. The chrome tanning agent was Tanolin R, a commercial one-bath chrome tan containing about 23.5% Cr_2O_3 with an ALCA basicity of 34% to 37%. In experiments where rate of tanning was obtained, the stock was first brought to the pH desired before the addition of the tanning agent. This helped maintain a constant pH during the run.

Retannage of chrome stock with glutaraldehyde

Chrome stock preparation—The chrome stock was prepared in the conventional manner, in a laboratory mill, by treating a dozen pickled cabretta skins with 8% Tanolin R*, 4% salt, 1% sodium formate, and 100% water (all percentages based on the pickled weight), and neutralizing with bicarbonate to a final pH of 4.6. After completion of tanning, the skins were washed thoroughly. A Ts specimen showed very little shrinkage after five minutes in boiling water. Finished garment leather from this stock showed a Cr_2O_3 content of 3.44% (MFB) and Ts of 96°C. (205°F.). Individual skins from this lot were retanned with glutaraldehyde at various pH values in the range of 2.5 to 7.0.

Retannage with glutaraldehyde—The glutaraldehyde retannage of the chrome-tanned skins was carried out as described by the following typical example: The equipment and procedure were similar to those described in a recent paper on rate studies (3). When necessary, the chromed skin was brought to the desired pH by an overnight treatment with an appropriate acid or alkaline agent in a 100% float.

The next morning, the buffered skin, wrung three times, was treated in

a tanning solution comprising

Glutaraldehyde (commercial 25% solution)	10% blue weight (WW)
Sodium chloride	6% " " "
Water	100% " " "

The drumming was continuous during the day and intermittent overnight. Samples of the tanning liquor and skin were taken after 0.5, 1.5, 2.5, 4.5, 8.5, and 24.5 hours. The glutaraldehyde content of the tanning solution at these time intervals was determined by the iodometric procedure described in previous publications (3, 24). The initial concentration of glutaraldehyde in the tanning solution was calculated knowing the amount of commercial (25%) glutaraldehyde solution used, the water in the chromed stock, and the water added as float. The data obtained for retanning with glutaraldehyde are summarized in Table I. The data in Table I were recalculated to express fraction or percent of glutaraldehyde unused; and this, plotted against time, gave the rate curves shown in Fig. 1.

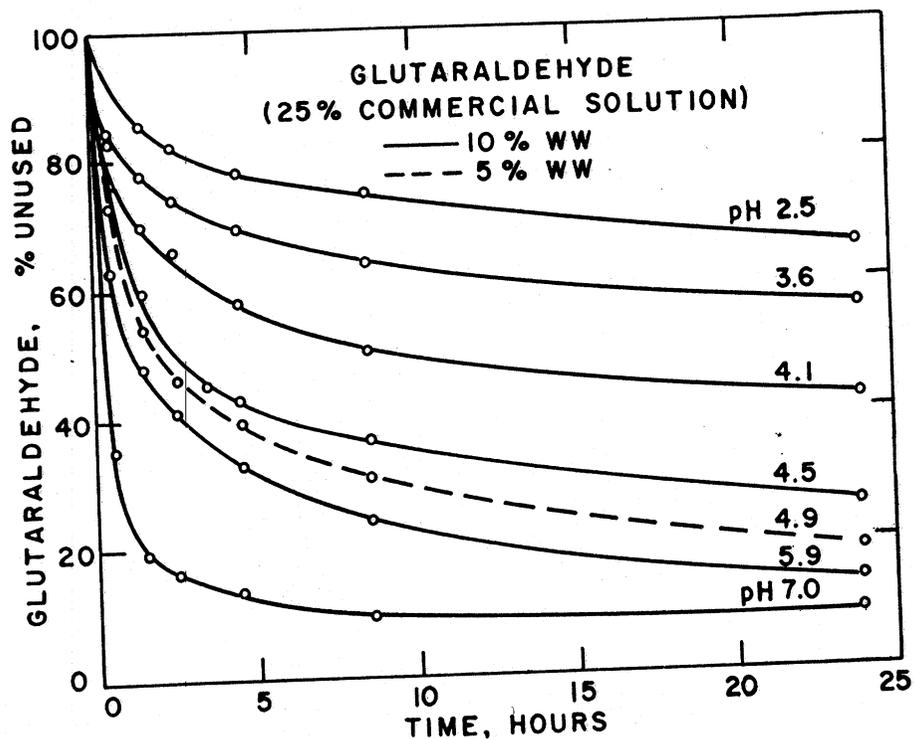


FIGURE 1—Tanning rate. Glutaraldehyde retan on chrome-pretanned skin.

TABLE I

UPTAKE OF GLUTARALDEHYDE BY CHROME-TANNED CABRETTA*

Exp. No.	pH†	Aldehyde Content of Tanning Solution, g/100 ml							Shrink Test**
		Initial‡	0.5 hr.	1.5 hr.	2.5 hr.	4.5 hr.	8.5 hr.	24.5 hr.	
1	2.4-2.7††	1.25	1.07	1.07	1.03	.98	.93	.82	99°C.
2	3.6††	1.28	1.08	1.00	.95	.89	.82	.72	3 min. boil
3	4.1††	1.29	1.07	.90	.85	.75	.65	.54	>3 min. boil
4	4.4-4.5	1.30	.94	.78	.59	.56	.47	.33	>3 min. boil
5	4.8-4.9	.65	.50	.35	.30	.26	.20	.12	>3 min. boil
6	5.8-6.0***	1.29	.81	.62	.53	.42	.31	.18	3 min. boil
7	7.0-7.1***	1.35	.48	.26	.22	.18	.13	.12	2 min. boil

*Tanning solution, based on wrung blue weight: 100% water, 6% NaCl, 10% aqueous commercial glutaraldehyde solution, except Exp. No. 5 in which 5% glutaraldehyde was used.

†Range during 24.5-hour tanning period.

‡Calculated from known amounts of glutaraldehyde and total water in each experiment.

**At the end of the 24.5-hour glutaraldehyde retannage.

††Chrome stock adjusted to proper pH with 3% concentrated HCl (on wrung blue weight).

‡‡Chrome stock adjusted with 0.6% concentrated HCl (on wrung blue weight) to appropriate pH value (about 3.5).

***Chrome stock adjusted to pH about 6.1 with 2% borax (on wrung blue weight).

Simultaneous chrome-glutaraldehyde tannage—The tannages were on a scale of two cabretta skins per test in the pH range of 1.5 to 4.5. The procedure (percentages based on drained pickled weight) was generally as follows:

The pickled degreased cabretta skins in salt (6%) and water (50%) were brought to the desired pH by an overnight pretreatment with a suitable buffer. The glutaraldehyde (6%) commercial solution and chrome (4% Tanolin R), dissolved in water (50%), were then added, and the drumming was continued. As before, the skin and tanning liquor were sampled at 0.5, 1.5, 2.5, 4.5, 8.5, and 24.5 hours to determine the Ts of the skin and the chrome and glutaraldehyde content of the liquor.

The analytical procedure was that described previously (3, 24). Since chrome interfered with the iodometric analysis for aldehyde, the aliquot for the latter determination was passed through a small column of a cation exchange resin to remove chromium (13, 24, 25). Details of the analysis are given elsewhere (24). For purposes of comparison, tanning runs were made under identical conditions with chrome or glutaraldehyde as the only tanning agent. As above, the initial concentration of tanning agents was calculated knowing the amount of each and the total volume of water in the system. A simultaneous formaldehyde-chrome tannage was also studied analytically for comparison. The amount used was 2.5% of formalin, which on an alde-

TABLE II

UPTAKE OF GLUTARALDEHYDE AND CHROME IN SIMULTANEOUS TANNAGE

Exp. No.	pH	Pretreatment and Buffering Agent % DFW	Aldehyde and Chrome Content of Tanning Solutions*, g/100 ml												Ts, °C.			
			Initial†		0.5 hr.		1.5 hr.		2.5 hr.		4.5 hr.		8.5 hr.			24.5 hr.		
			Aldehyde	Cr ₂ O ₃	Aldehyde	Cr ₂ O ₃ ††		Aldehyde	Cr ₂ O ₃	24-hr. Tan- nage								
<i>Glutaraldehyde and chrome</i>																		
8	1.3-1.5	H ₂ SO ₄ (conc.), 1	0.849	0.542	0.783	0.640	0.696	0.580	0.671	0.573	0.600	0.557	0.516	0.536	0.353	0.485	82	78
9	1.9-2.1	H ₂ SO ₄ (conc.), 0.5	.849	.542	.730	.556	.669	.539	.619	.528	.535	.486	.431	.404	.289	.333	88	85
10	2.4-2.5	none	.849	.542	.676	.565	.586	.517	.469	.464	.395	.397	.318	.326	.200	.226	88	86
11	3.0-3.3	Na Acetate (anh.), 1	.849	.542	.619	.436	.459	.324	.383	.270	.295	.212	.233	.181	.148	.124	95	90
12	3.6-3.8	Na Acetate (anh.), 2	.850	.544	.545	.328	.356	.196	.298	.156	.223	.118	.159	.086	.101	.057	97	93
13	4.3	Na Acetate (anh.), 4	.852	.544	.420	.217	.291	.150	.234	.130	.184	.115	.139	.101	.086	.081	98	96
14	4.6	NaHCO ₃ 2.5	.852	.544	.331	.043	.249	.020	.188	0	.098	0	.138	0	.058	0	97	90
<i>Glutaraldehyde (alone)</i>																		
15	2.7	none	.850	-	.659	-	.513	-	.448	-	.374	-	.280	-	.149	-	76	72
16	3.8	Na Acetate (anh.), 1	.852	-	.485	-	.335	-	.279	-	.224	-	.176	-	.105	-	80	78
17	4.3	Na Acetate (anh.), 2	.851	-	.404	-	.259	-	.213	-	.161	-	.111	-	.063	-	76	73
18	4.7	Na Acetate (anh.), 4	.853	-	.349	-	.226	-	.189	-	.144	-	.114	-	.074	-	82	72

TABLE II.- Continued
 UPTAKE OF GLUTARALDEHYDE AND CHROME IN SIMULTANEOUS TANNAGE

Exp. No.	pH†	Pretreatment and Buffering Agent % DPW	Aldehyde and Chrome Content of Tanning Solutions*, g/100 ml										Ts, °C.						
			Initial†		0.5 hr.		1.5 hr.		2.5 hr.		4.5 hr.			8.5 hr.		24.5 hr.			
			Aldehyde	Cr ₂ O ₃	Aldehyde	Cr ₂ O ₃ ††	Aldehyde	Cr ₂ O ₃	24-hr. Tannage	Processed Leather									
<i>Chrome (alone)</i>																			
19	2.5-2.7	none	-	.563	-	.580	-	.510	-	.453	-	.429	-	.305	-	.187	87	84	
20	3.7	Na Acetate (anh.), 2	-	.562	-	.294	-	.186	-	.151	-	.113	-	.089	-	.057	95	86	
21	3.8	Na formate, 4	-	.562	-	.430	-	.315	-	.268	-	.202	-	.130	-	.072	91	87	
22	4.3	Na Acetate (anh.), 4	-	.562	-	.258	-	.168	-	.143	-	.124	-	.109	-	.090	89	85	
23	4.4-4.7	NaHCO ₃ , 2.3	-	.565	-	.115	-	.019	-	.006	-	-	-	-	-	-	92	81	
24	4.9	Na Acetate (anh.), 8	-	.564	-	.350	-	.257	-	.242	-	.225	-	.216	-	.197	87	86	
<i>Formaldehyde** and chrome</i>																			
25	4.6	Na Acetate (anh.), 4	.592	.556	.550	.239	.441	.159	.434	.137	.416	.121	.395	.099	.347	.035	93	88	
<i>Formaldehyde** (alone)</i>																			
26	4.5	Na Acetate (anh.), 4	.593	-	.474	-	.440	-	.437	-	.425	-	.389	-	.343	-	75	70	

*Tanning Solution, based on drained, pickled weight (DPW):

Glutaraldehyde, 6%
 Tannin R, 4%
 NaCl, 6%
 Water, 100%.

†pH range during 24.5-hr. tanning period.

††Initial concentration of glutaraldehyde, chrome as Cr₂O₃, and formaldehyde were calculated from known amount of active substance and total water present.

**The amount of formaldehyde used was 2.5% on DPW of formalin, i.e., equivalent to the amount of glutaraldehyde used in the other experiments.

†††Values for Cr₂O₃ content higher than the "initial" are due to the slow rate of penetration of the chrome from the external tanning liquor to the aqueous phase in the skins.

hyde group basis was equivalent to 6% of the commercial 25% glutaraldehyde solution, i.e., 2 moles of formaldehyde in place of one mole of glutaraldehyde. Data for the simultaneous tannages are given in Table II. As before, the data were recalculated to express fraction of aldehyde and chrome unused. These were plotted against time to give the rate curves shown in Figs. 2 to 6. The upper portion of these figures shows the T_s data.

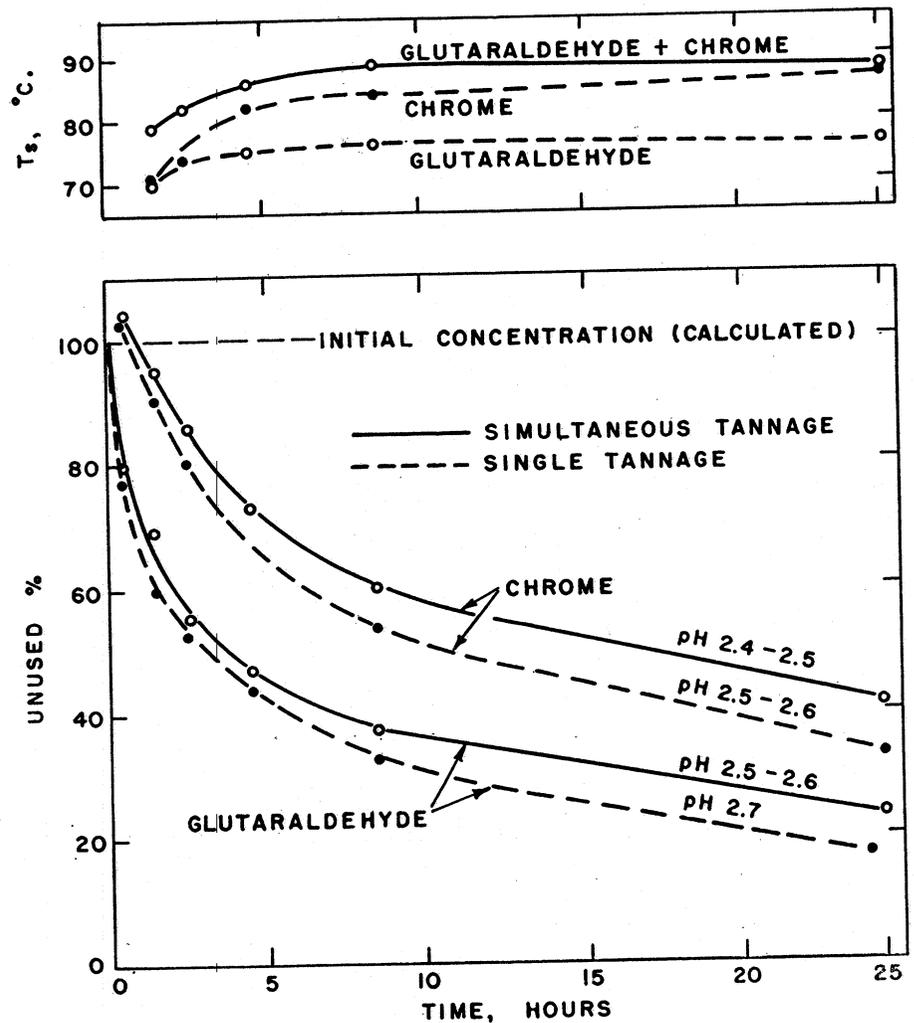


FIGURE 2—Tanning rates. Simultaneous tanning with glutaraldehyde (6% DPW) and chrome (4% DPW) at pH 2.4–2.7.

Retannage of glutaraldehyde-tanned leather with chrome

Glutaraldehyde-tanned stock.—Pickled, degreased cabretta skins were tanned with glutaraldehyde as follows:

Add: Water	100%
Salt	6%
Glutaraldehyde, 25% solution	6%
Drum: ½ hour, pH 2.9	
Add: sodium acetate	6%
Drum: 1 hour, pH 4.9	
Add: sodium bicarbonate	5%
Drum: 5 hours, pH 8.1, Ts 83°C.	
Add: dilute H ₂ SO ₄ to pH 4.0	
Wash: Ts now 79°C.	

A second lot of three pickled, degreased cabretta skins was tanned with 4% commercial glutaraldehyde solution in the same way. The Ts in this case was 78°C., which dropped to 72°C. after acidification at the end of tanning.

The tanned stock was wrung to about 73% moisture and retanned as described below (percentages listed are based on wrung-skin weight).

TABLE III

UPTAKE OF CHROME BY GLUTARALDEHYDE-TANNED CABRETTA SKINS

Exp. No.	pH†	Chrome Content (Cr ₂ O ₃) of Tanning Solution,* g/100 ml.							Ts °C**
		Initial‡	0.5 hr.	1.5 hr.	2.5 hr.	4.5 hr.	8.5 hr.	24.5 hr.	
<i>Skins tanned with 6% DPW glutaraldehyde (25% solution)</i>									
27	4.5	0.52	0.35	0.18	.014	0.11	0.08	0.06	99
(2% WW sodium acetate)									
28	4.3	0.52	.24	.13	.09	.05	.03		100
(0.75% WW NaHCO ₃)									
<i>Skins tanned with 4% DPW glutaraldehyde (25% solution)</i>									
29	4.4	0.52	.34	.19	.14	.11	.08	.05	99
(2% WW sodium acetate)									
30	4.3	0.52	.27	.13	.08	.06	.03		97
(0.75% WW NaHCO ₃)									
31	4.0	1.04	.69	.46	.36	.28	.20	.09	101
(1% WW NaHCO ₃)									

*Chrome tanning solution, based on wrung wt. (WW) of glutaraldehyde-tanned skins, contained the following: water (100% WW), Tanolin R (4% WW), and NaCl (6% WW). Tanolin R (8% WW) was used in Exp. 31. Buffers used are listed under pH.

†pH range during 24.5-hour tanning period, after pretreatment with buffer listed.

‡Initial chrome content as Cr₂O₃ calculated from known amounts of Cr₂O₃ and water present in each experiment.

**Shrink temperature at end of chrome tannage. Values above 100°C. determined in pressure equipment.

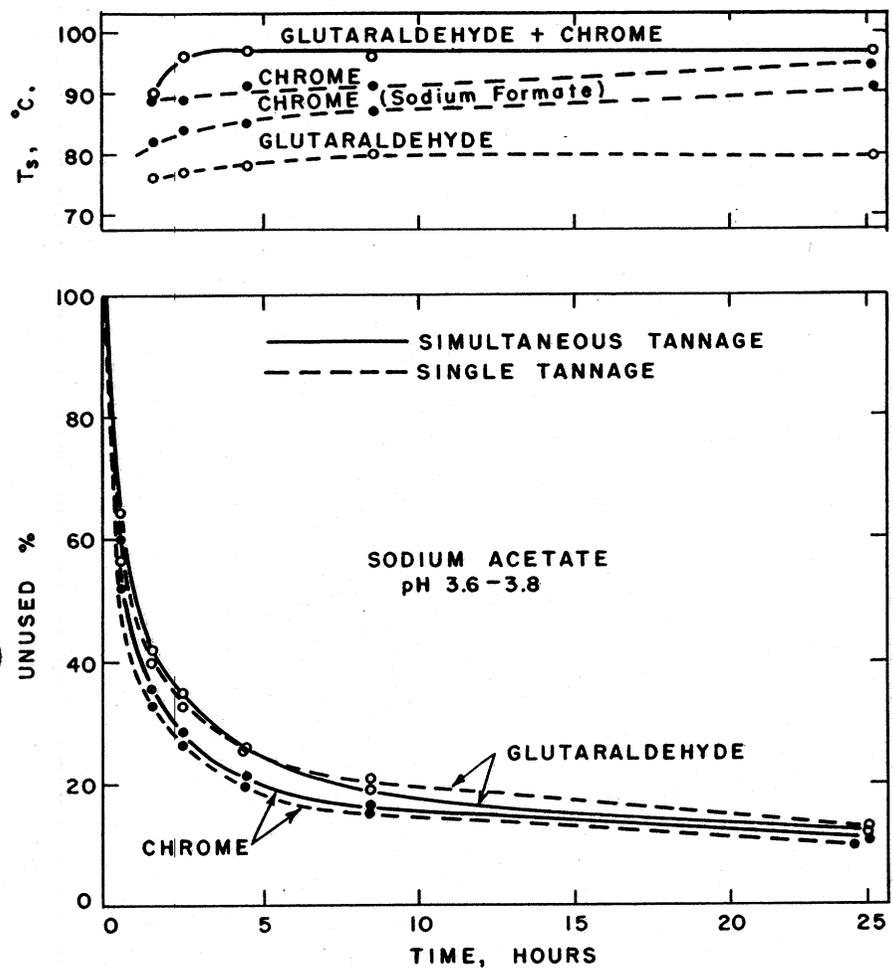


FIGURE 3—Tanning rates. Simultaneous tanning with glutaraldehyde (6% DPW) and chrome (4% DPW) at pH 3.6-3.8.

Retannage with chrome—Individual glutaraldehyde-tanned skins in 50% water and 6% salt were adjusted to the desired pH by overnight treatment with an appropriate buffer (Table III). The next morning 4% Tanolin R, dissolved in 50% water, was added, and the drumming was continued. Samples of stock and tanning solution were taken at various time intervals as above for the T_s measurement on the leather and Cr_2O_3 analysis of the liquor. The data are summarized in Table III. These data were recalculated to express fraction of chrome unused, which, plotted against time, gave the rate curves shown in Figs. 7 and 8.

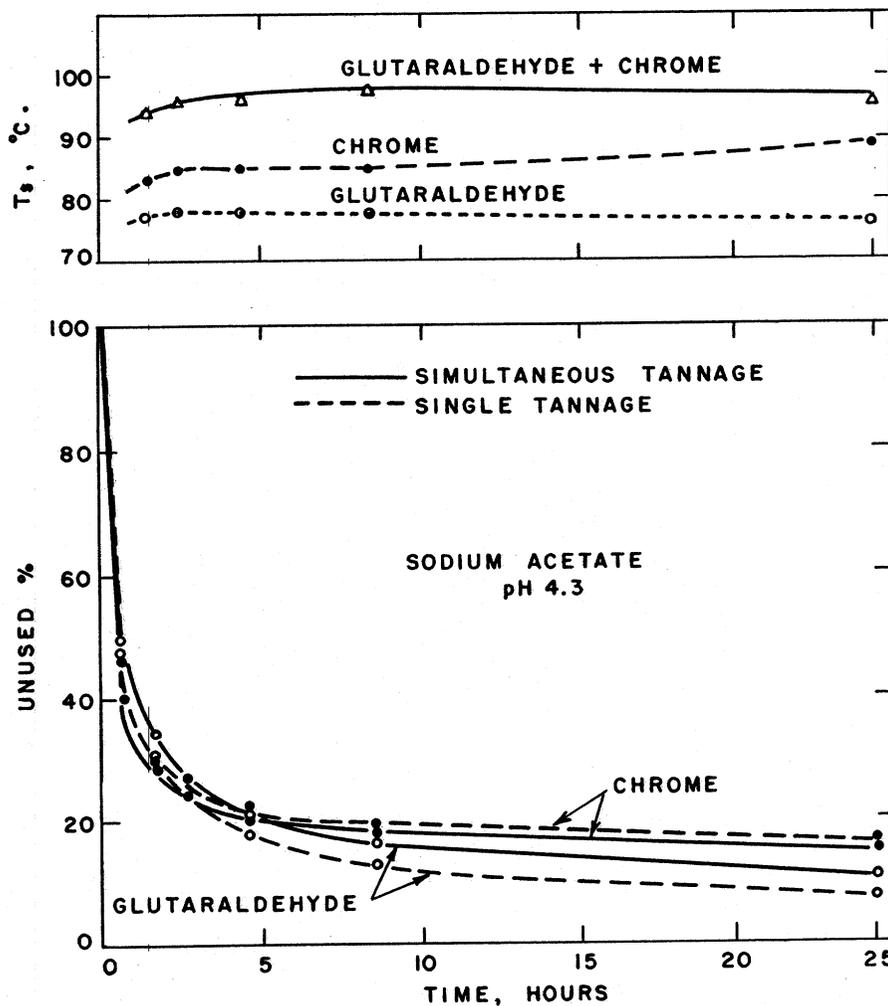


FIGURE 4—Tanning rates. Simultaneous tanning with glutaraldehyde (6% DPW) and chrome (4% DPW) at pH 4.3.

Evaluation of the leathers—At the end of the 24.5-hour tanning for the rate studies, the skins were processed with a regular pack into finished garment leather by a tanner. The resistance to a synthetic perspiration and to washing in hot soap solution was determined as described previously (4). The effect of the test on the dimensional stability of the test specimen was used as a criterion of resistance to perspiration.

The effect on Ts was relied upon as a criterion of resistance to washing in hot, soapy solution. The results of the wash tests are given in Table IV.

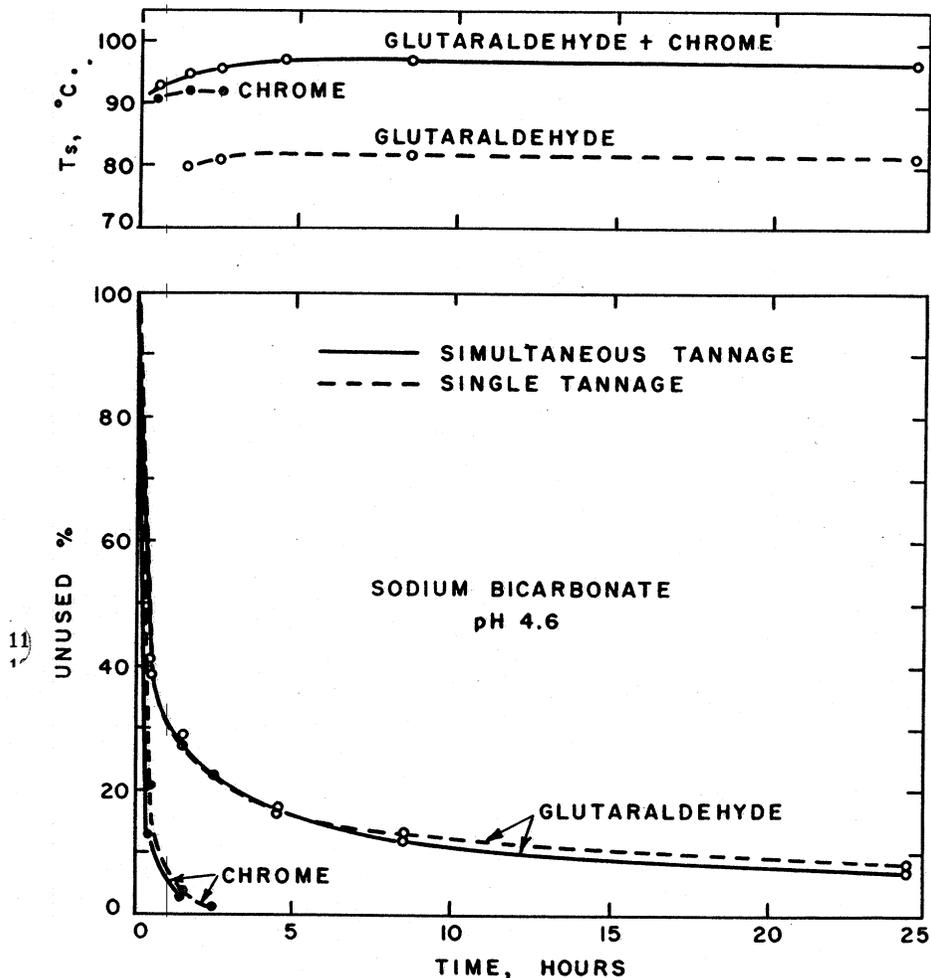


FIGURE 5—Tanning rates. Simultaneous tanning with glutaraldehyde (6% DPW) and chrome (4% DPW) at pH 4.6.

The finished leathers were analyzed for fat, ash chrome, and nitrogen by standard ALCA procedures. The results are summarized in Table V.

DISCUSSION

Glutaraldehyde is very reactive toward hide substance over a wide pH range. Suitable tanning ability was demonstrated by this aldehyde even at pH ranges most desirable for chrome. Thus it appeared that the glutaraldehyde-chrome combination tannage would lend itself quite readily to commercial practice. Data along this line of endeavor are presented in this study. For ease of interpretation, uptake of tanning agent was expressed as percent

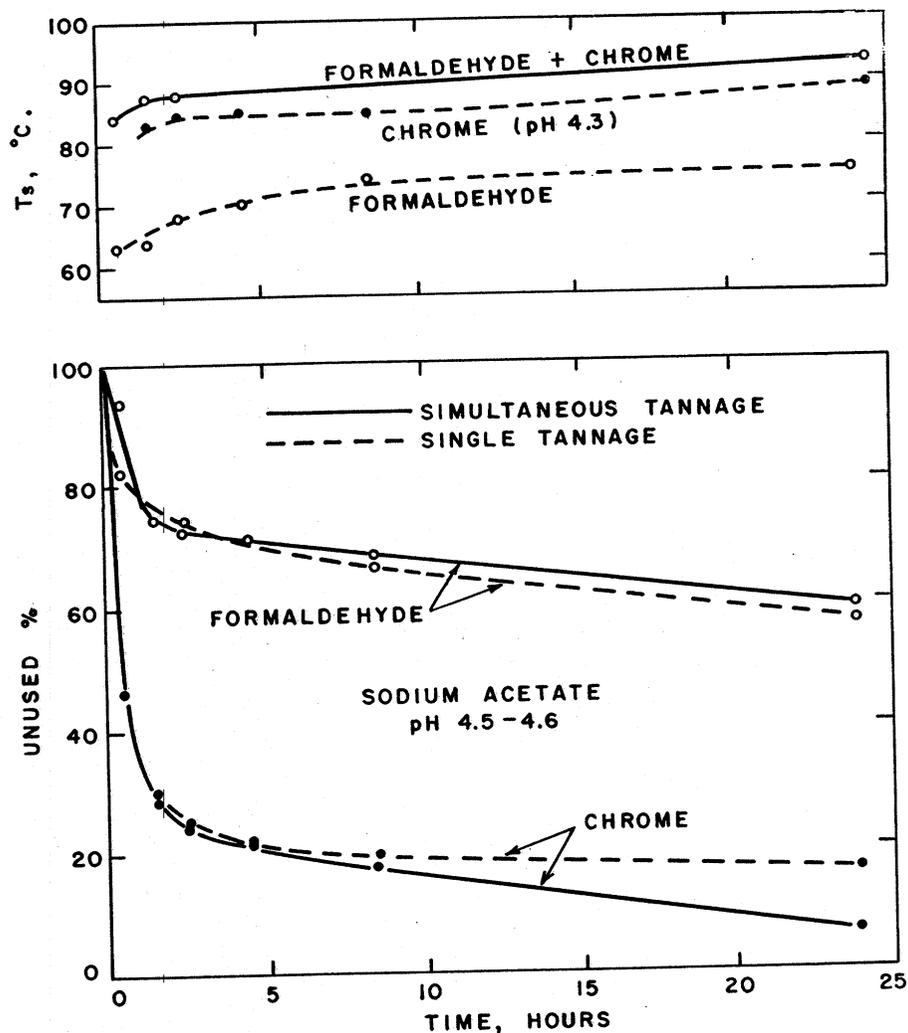


FIGURE 6—Tanning rates. Simultaneous tanning with formaldehyde (2.5% DPW) and Chrome (4% DPW) at pH 4.5-4.6.

of feed unused and plotted against time. These curves are a measure of the over-all rate of tanning and are valuable for comparison of the influence of various tanning factors on the tanning properties. These tests were on a scale of only one or two sheepskins per test, and factors, particularly time, could be considerably improved on a practical scale.

Retannage with glutaraldehyde.—This is perhaps the most attractive procedure for a chrome tanner to effect the glutaraldehyde-chrome combination tannage, since a greater degree of flexibility is provided to a tanner.

TABLE IV
EFFECT OF WASHING* ON GLUTARALDEHYDE-CHROME-
COMBINATION-TANNED LEATHER

Exp.† No.	pH of Retannage	Shrinkage Temperature, °C.				Δ Ts, °C.
		Before Washing	1st Wash	2nd Wash	3rd Wash	
<i>Chrome-tanned, glutaraldehyde-retanned</i>						
1	2.4-2.7	97	93	91	89	-8
2	3.6	100	96	92	90	-10
3	4.1	99	96	93	91	-8
4	4.4-4.5	98	95	92	91	-7
5	4.8-4.9	99	98	94	92	-7
6	5.8-6.0	99	96	95	93	-6
7	7.0-7.1	97	95	93	93	-4
Chrome‡ (Control)	—	96	90	87	74	-22
<i>Glutaraldehyde-chrome, simultaneous</i>						
8	1.3-1.5	68	70	69	68	0
9	1.9-2.1	76	76	74	76	0
10	2.4-2.5	83	81	83	80	-3
11	3.0-3.3	85	85	84	80	-5
12	3.6-3.8	80	83	83	82	+2
13	4.3	92	92	90	90	-2
14	4.6	91	91	90	89	-2
<i>Formaldehyde-chrome, simultaneous</i>						
25	4.6	86	85	84	75	-11
<i>Chrome alone</i>						
21	3.8	85	81	80	76	-9
23	4.4-4.7	85	82	76	75	-10
<i>Glutaraldehyde-tanned, chrome-retanned</i>						
27	4.5	90	87	86	86	-4
28	4.3	92	87	86	85	-7
29	4.4	89	80	75	75	-14
30	4.3	89	86	81	80	-9
31	4.0	95	87	83	82	-13

*Wash tests done in a Launder-Ometer. Each wash: ½ hour at 120°F. in 0.5% Ivory soap solution.
†Exp. Nos. correspond exactly to those listed in Tables I, II, and III.
‡Chrome-tanned stock used for Exp. 1-7.

The curves shown in Fig. 1 are a measure of the rate of retanning of chrome leather with glutaraldehyde and describe more precisely this tanning process. The rate of uptake of aldehyde and amount fixed increased with increase in pH. At pH of 4 about half of the glutaraldehyde in the feed was fixed in eight hours under our conditions. At pH of 7, relatively high for chrome

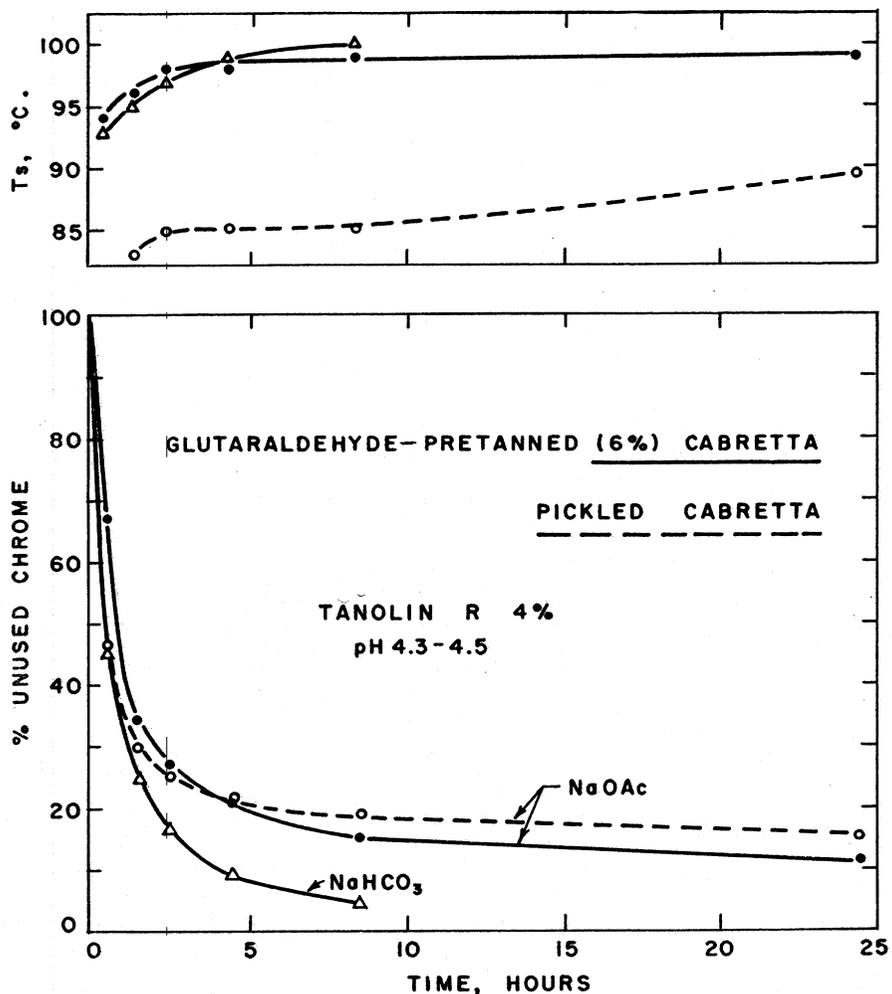


FIGURE 7—Tanning rates. Chrome retan on glutaraldehyde-pretanned skin.

leather, the efficiency of glutaraldehyde fixation was increased to about 90% and equilibrium established in eight hours. At pH values of 6 and below, equilibrium did not appear to be reached in 24 hours under these conditions. In comparison with our previous study (3), which dealt with glutaraldehyde tanning of Syrian sheepskin, the chromed cabretta seemed to fix this aldehyde at a somewhat slower rate. The shrinkage temperature, as measured by the boil test, was not markedly changed by retanning the chrome stock with glutaraldehyde.

TABLE V
ANALYSES OF LEATHERS FROM GLUTARALDEHYDE-CHROME
COMBINATION TANNAGES

Exp. No.	pH of Retannage	% Moisture	MFB				% N	% H. S., N × 5.62
			% Ash	% Fat*	% Cr ₂ O ₃ †	% N		
<i>Chrome-tanned, glutaraldehyde-retanned</i>								
1	2.4-2.7	9.38	3.38	14.4	2.53	13.1	73.62	
2	3.6	9.68	3.63	11.6	2.88	13.2	74.18	
3	4.1	10.58	3.75	11.3	2.92	13.6	76.43	
4	4.4-4.5	9.62	3.73	13.1	2.86	13.1	73.62	
5	4.8-4.9	9.36	4.69	13.6	3.45	12.9	72.50	
6	5.8-6.0	9.70	4.12	13.6	3.02	13.1	73.62	
7	7.0-7.1	10.17	4.36	13.3	3.16	13.2	74.18	
Chrome (Control)	—	9.64	4.45	13.3	3.44	12.9	72.50	
<i>Glutaraldehyde-chrome, simultaneous</i>								
8	1.3-1.5	5.36	1.44	24.7	0.50	11.8	66.32	
9	1.9-2.1	5.90	1.78	24.5	0.80	11.8	66.32	
10	2.4-2.5	6.14	2.23	23.4	1.16	11.8	66.32	
11	3.0-3.3	6.32	2.55	21.3	1.53	12.0	67.44	
12	3.6-3.8	5.86	2.53	22.7	1.62	11.5	64.63	
13	4.3	7.15	2.63	17.7	1.76	12.8	71.94	
14	4.6	5.84	3.21	21.2	1.26	11.5	64.63	
<i>Formaldehyde-chrome, simultaneous</i>								
25	4.6	7.37	2.14	22.4	1.64	11.7	65.75	
<i>Glutaraldehyde-tanned, chrome-retanned</i>								
27	4.5	10.72	3.16	17.2	2.21	12.6	70.81	
28	4.3	11.46	3.34	15.6	2.49	12.8	71.94	
29	4.4	11.01	3.15	15.8	2.16	13.2	74.18	
30	4.3	10.57	3.09	16.8	2.26	12.6	70.81	
31	4.0	10.49	4.91	16.6	4.00	11.8	66.32	

*CHCl₃ extractable.
†Official ALCA procedure.

Simultaneous chrome-glutaraldehyde tannage.—This combination tannage is the most convenient and time-saving, since no retannage is necessary. Because this procedure is limited to the narrow pH range required for chrome, the most efficient use of the glutaraldehyde cannot be attained. However, the pick-up of glutaraldehyde (when used at 6% DPW level) is quite good. In fact, as can be seen in Fig. 2, fixation of glutaraldehyde was more rapid and more complete than that of chrome at pH about 2.5.

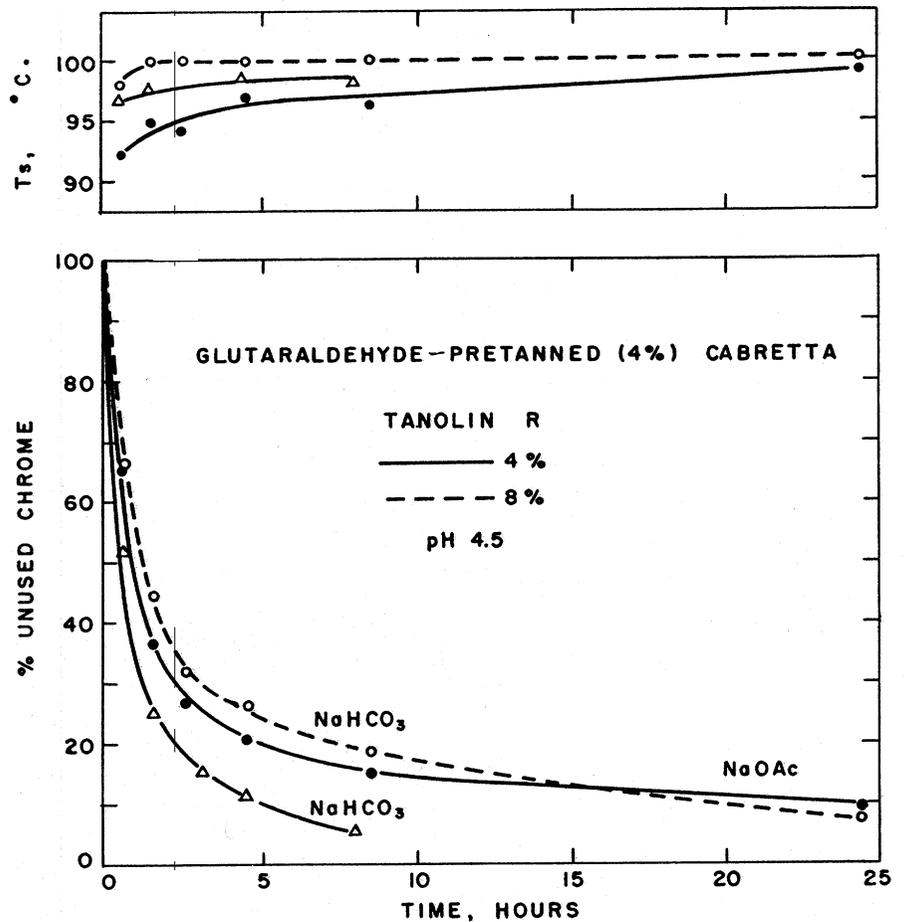


FIGURE 8—Tanning rates. Chrome retan on glutaraldehyde-pretanned skin.

There appeared to be some retardation in fixation of these two tanning agents when compared to the controls (dotted curves, Fig. 2) where each agent was used alone.

In the pH range of 3.5 to 4.5 in the presence of acetate the rates of fixation of both glutaraldehyde and chrome were very nearly the same (Figs. 3 and 4). Fixation of both agents, whether used simultaneously or individually, followed essentially the same curve under our conditions. After 24 hours efficiency of tannage was about 90% of the amount of agents introduced in the feed. At pH of about 4.5 in the absence of acetate (Fig. 5) chrome disappeared from the tanning solution more rapidly and completely than glutaraldehyde, illustrating the well-known masking effect of this organic anion.

Uptake of glutaraldehyde by pickled stock in the simultaneous tannages (Figs. 2-5) appeared to occur at a more rapid rate than uptake of glutaraldehyde by chrome stock (Fig. 1). At pH of about 3.6 glutaraldehyde was fixed more rapidly and completely by pickled stock than by chromed stock (Figs. 1 and 3), even though, in the latter instance, the glutaraldehyde concentration was higher. Calculations from the data (Table I and II) indicate that the pickled stock in the simultaneous tannage fixed 5.3% (out of the 6% available) of the commercial glutaraldehyde solution added, whereas the chromed stock fixed only 4.4% (out of the 10% available). The same trend was evident at higher pH values, but the difference in rate of uptake of glutaraldehyde in the two processes was not as pronounced.

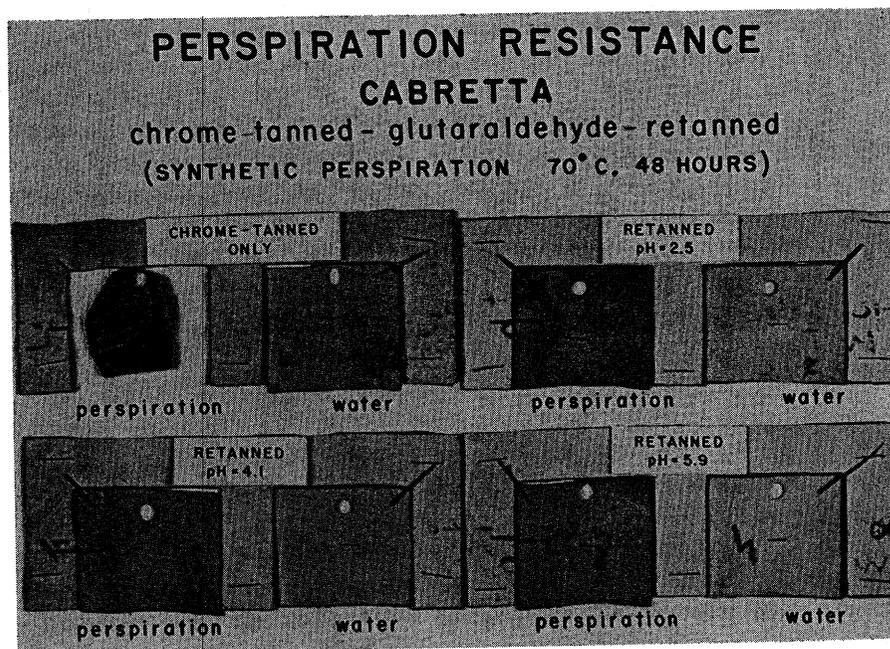
As can be seen from Figs. 3-5, the shrinkage temperature rapidly reached a maximum of about 97°C. in the simultaneous chrome-glutaraldehyde tannage. In the case of the tannage with chrome alone, there was a gradual rise in T_s (Figs. 3 and 4); however, the T_s almost reached that of the combination tannage in the 24-hour tanning time.

Figure 6 presents the data obtained from the comparable formaldehyde-chrome simultaneous tannage. This tannage was identical to that with glutaraldehyde and chrome (summarized in Fig. 4) except that formaldehyde was used on an aldehyde group equivalent basis, i.e., two moles of formaldehyde equivalent to one of glutaraldehyde. It is noted that uptake of formaldehyde is considerably less than the uptake of glutaraldehyde under similar conditions. Unlike the glutaraldehyde system, there is a gradual increase in shrinkage temperature which reached about 92°C. in 24 hours. As noted by earlier investigators, the aldehyde-chrome combination tannage does not appear to differ greatly in shrinkage temperature from the comparable chrome tannage alone. It is also evident from the curves in Figs. 2-6 that fixation of aldehyde and chrome under these conditions appeared to occur independently of each other.

Retannage of glutaraldehyde-tanned leather with chrome.— This procedure for the combination tannage was of interest because maximum benefits of each tannage can easily be attained inasmuch as the glutaraldehyde pretannage at a high pH, i.e., 8, was possible. Figures 7 and 8 show the uptake of chrome by glutaraldehyde-tanned skins. A comparison of chrome uptake by untanned skin is shown by the dotted curve in Fig. 7. In the acetate system, uptake of chrome by the two different stocks was quite similar, although there appeared to be a somewhat faster rate of chrome uptake by the pretanned skins in the later stages of tanning. However, in the bicarbonate system there appeared to be some retardation of chrome uptake by the glutaraldehyde pretannage (compare Fig. 7 with Fig. 5). There did not seem to be any difference in rate of chrome uptake between the two levels of pretannage with glutaraldehyde, i.e., 4% and 6%.

With regard to shrinkage temperature, however, the maximum was reached considerably more rapidly with the skins given the pretannage with 6% glutaraldehyde compared with those with 4% glutaraldehyde. Of course, the pretanned stock from the 6% glutaraldehyde pretannage showed a higher shrinkage temperature than that of the 4% pretannage. The final shrinkage temperature of the retanned leather was higher than the comparable chrome-tanned leather by about 7°C., as is evident from the Ts curves of Fig. 7. It should be pointed out that the retannage with chrome was studied only at pH of about 4.5, and comparisons should be limited to these conditions.

Evaluation of the leather.—The leathers were finished in a tannery with regular packs of garment leather. In general, all the leathers were judged to be of good quality. The glutaraldehyde imparted mellowness to the leathers without sacrifice of tightness of grain. The shrinkage temperatures of the finished leathers (Table IV) were as follows: (a) chrome stock retanned with glutaraldehyde, 97°–100°C. (207°–212°F.); (b) simultaneous chrome-glutaraldehyde, 80°–92°C. (176°–198°F.); and (c) glutaraldehyde stock retanned with chrome, 89°–95°C. (192°–203°F.). In general, these shrinkage temperatures are several degrees higher than the corresponding chrome leather. As expected, the lowest Cr₂O₃ content was noted in the



simultaneous tannage, where, of course, a low amount of chrome tanning agent was used. The fat content of this group of leathers was generally higher than those of the other tests.

The resistance of the finished leathers to an artificial perspiration was judged by visual inspection of the specimen after testing. The photograph (Fig. 9) of several of the actual test specimens after submission to the test is typical of the results obtained. As is evident, the leather tanned with chrome alone (Cr_2O_3 content 3.44%) was severely shrunken and embrittled. The other specimens in Fig. 9 are the same chrome leather retanned with glutaraldehyde and showed excellent resistance (practically no shrinkage) in this test. In our tests an adjacent specimen was taken and run as a blank to show that shrinkage was not due to moist heat (70°C ., 48 hours) alone. All of the leathers in this study showed excellent resistance to the artificial perspiration test. The formaldehyde-chrome-combination-tanned leather (Experiment 25) was severely shrunken and behaved essentially the same as the chrome leather in this test.

The resistance of the leathers to washing in hot soap solution at 120°F . (49°C .) is summarized in Table IV. Shrinkage temperature of the leather after washing was used as a criterion of resistance. The stock tanned with chrome alone showed the greatest loss in Ts, i.e., 22°C ., upon washing. Retannage of this stock with glutaraldehyde was effective in reducing the loss in Ts. After three washes the Ts of the latter was approximately 90°C ., compared with 74°C . for the chrome leather.

The glutaraldehyde-chrome-simultaneously-tanned leathers also appeared resistant to hot soapy water. Loss in Ts was about $2^\circ\text{--}5^\circ\text{C}$., compared with $8^\circ\text{--}10^\circ\text{C}$. for the comparable chrome-tanned leathers and 11°C . for the formaldehyde-chrome-simultaneously-tanned leather.

In the leathers pretanned with glutaraldehyde (Experiments 27-31, Table IV) it is evident that those pretanned with 4% of the aqueous commercial glutaraldehyde performed considerably less satisfactorily in this test than those given the 6% glutaraldehyde pretannage.

Thus, it appears that the desirable properties of the glutaraldehyde tannage are incorporated into chrome leather in combination tannages with these two agents. The maximum benefits of each agent are best attained by using the two consecutively. The two may also be used simultaneously to effect a saving of tanning time. Perhaps the most desirable procedure would involve retanning of neutralized fully-chrome-tanned leather with glutaraldehyde. Resistance to deterioration by perspiration and soap solution are markedly improved by incorporating glutaraldehyde into chrome leather; however, a minimum of about 6% of the commercial glutaraldehyde solution may be required to achieve this aim.

REFERENCES

1. Seligsberger, L., and Sadlier, C. *JALCA*, **52**, 2 (1957).
2. Fein, M. L., and Filachione, E. M. *JALCA*, **52**, 17 (1957).
3. ———, Harris, E. H., Jr., Naghski, J., and Filachione, E. M. *JALCA*, **54**, 488. (1959)
4. Filachione, E. M., Fein, M. L., Harris, E. H., Jr., Luvisi, F. P., Korn, A. H., Windus, W., and Naghski, J. *JALCA*, **54**, 668 (1959).
5. Fein, M. L., and Filachione, E. M. U. S. Patent 2,941,859, June 21, 1960.
6. Sanders, H. J., Walker, G. O., Edwards, H. S., Jr., and Hall, T. J. *Ind. Eng. Chem.*, **50**, 854 (1958).
7. "Cheap Acrolein Boosts Derivatives' Luster", *Chem. Week*, **85**, No. 22, 77 (1959).
8. Carbide and Carbon Chemicals Co., F-40005A, (Glutaraldehyde), New York, N. Y., 1957.
9. Shell Chemical Corporation, Industrial Chemicals Division, PD-121, (Glutaraldehyde), New York, N. Y., 1959.
10. Gustavson, K. H. *J. Intern. Soc. Leather Trades Chemists*, **24**, 377 (1940).
11. Bowes, J. H., in *Progress in Leather Science 1920-1945* (London: British Leather Manufacturers' Research Assoc., 1948), Chap. 25.
12. McLaughlin, G. D., and Theis, E. R. *The Chemistry of Leather Manufacture* (New York: Reinhold Publishing Corporation, 1945), 332.
13. Gustavson, K. H. *The Chemistry of Tanning Processes* (New York: Academic Press, Inc., 1956) 244-278, 336-344, 15-16.
14. Mellon, E. F., in *Chemistry and Technology of Leather*, ed. O'Flaherty, F. et al., A.C.S. Monograph No. 134 (New York: Reinhold Publishing Corporation, 1958) Vol. 2, Chap. 17.
15. Griliches, E. *Collegium*, (1922) 199.
16. Gerngross, O., and Roser, H. *Ibid.*, No. 621, 1.
17. Gustavson, K. H. *Ind. Eng. Chem.*, **19**, 243 (1927).
18. Theis, E. R., and Kleppinger, C. T. *JALCA*, **42**, 591 (1947).
19. Nayudamma, Y., and Krishnan, T. S. *Bull. Central Leather Research Inst., Madras*, **2**, 397-401 (1956).
20. Alexa, G., and Chiritza, G. *Rev. Tech. Ind. Cuir*, **49**, 113 (1957).
21. Nayudamma, Y., and Jayaraman, K. S. *Bull. Central Leather Research Inst., Madras*, **5**, 91 (1958).
22. Ushakoff, A. E. *JALCA*, **53**, 320 (1958).
23. Colin-Russ, A. *J. Intern. Soc. Leather Trades Chemists*, **31**, 329 (1947).
24. Fein, M. L., and Harris, E. H., Jr. *Quantitative Analytical Procedure for Determining Glutaraldehyde and Chrome in Tanning Solutions*, U. S. Agr. Res. Service, East. Util. Res. Dev. Div., ARS 73-37 (1962).
25. Adams, R. S. *JALCA*, **41**, 552 (1946).

Received October 29, 1962.