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ABSTRACT

This paper is concerned with using glutaraldehyde, by itself and in combination with chrome, in the tanning of side upper leather. Using a full side per test, data were obtained on rate of tanning. Properties of the leather, particularly perspiration resistance, were evaluated.

Grain split pickled sides were tanned with glutaraldehyde alone at about pH 4.5 as well as 8.0. Amount and rate of glutaraldehyde fixation increased with increasing pH and concentration. Similar results were obtained in the simultaneous tannage with glutaraldehyde and chrome, the pH range being that most desirable for chrome fixation. Glutaraldehyde was fixed more rapidly than chrome. An attractive procedure for the chrome combination tannage is retannage of grain split chromed sides with glutaraldehyde. Fixation was rapid particularly at elevated temperatures, i.e., in the neighborhood of 130°F. (54°C.). The shrinkage temperature of the chrome-glutaraldehyde combination tannage is essentially determined by the chrome content of the leather.

Glutaraldehyde alone or in combination with chrome produced mellow leather. Tightness of grain of chrome leather was not sacrificed. The tannage lends itself admirably to the finishing operations, such as fatliquoring, coloring, finish coating, etc., given to conventional chrome leather. This leather showed excellent resistance to deterioration by perspiration.

INTRODUCTION

Previous studies have demonstrated the versatile tanning action of glutaraldehyde and the desirable properties it imparts to the leather (1–6). Our earlier work, limited to sheepskins, showed that this new leather was improved with respect to resistance to deterioration by various reagents, particularly perspiration. Hence, this tannage offers considerable promise for application to shoe upper

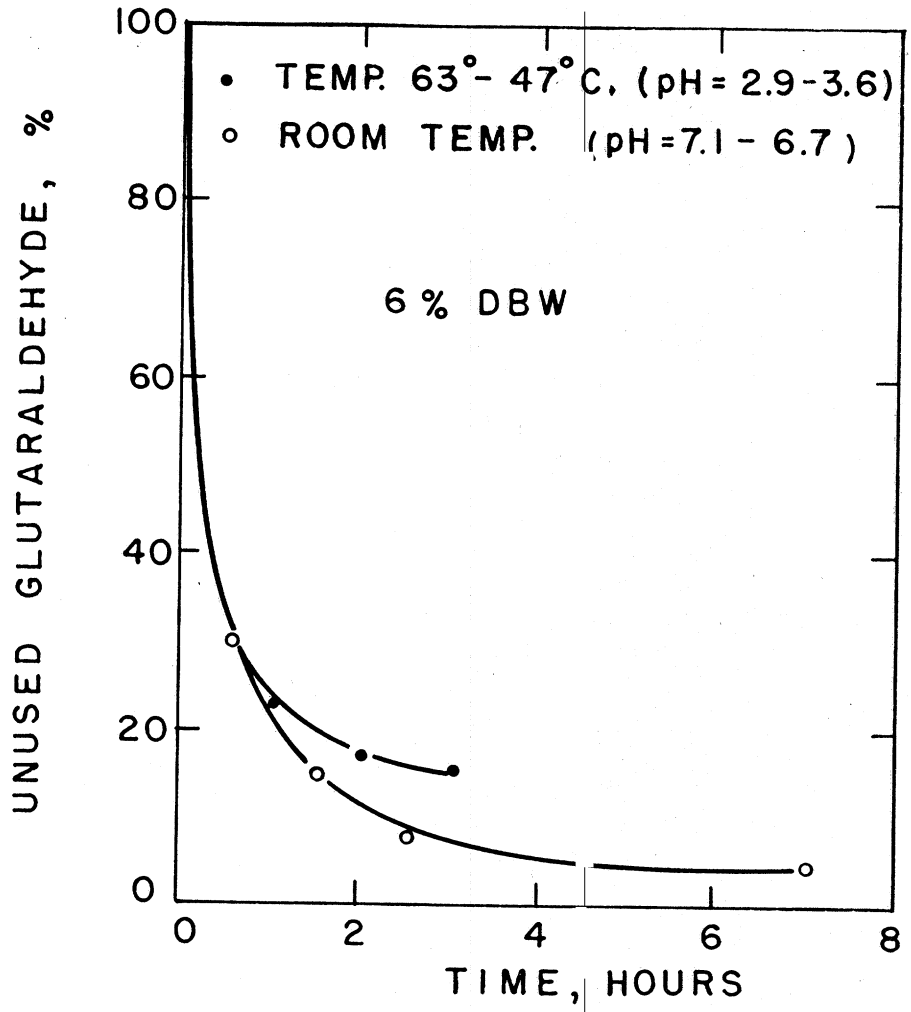


FIGURE 3.—Tanning rate. Retan of chrome stock with glutaraldehyde (Expt. 18 and 19, Table I). DBW = drained blue weight.

Figure 3 presents data from two additional tests: one at elevated temperature, the other at pH of about 7. In both tests glutaraldehyde was fixed very rapidly. Retannage of chrome stock at its normal pH (2.9–3.6) with glutaraldehyde at a temperature starting at about 140°F. (63°C.) and dropping to about 120°F. (47°C.) resulted in an uptake of over 80% of the 6% glutaraldehyde originally in the feed (solid points, Fig. 3). Retannage at room temperature but at pH values near neutrality also was efficient and rapid (open points, Fig. 3). In both tests fixation appeared to be complete within 3 hours with efficient use of glutaraldehyde. Of course, it is realized that retanning chrome leather at pH of

Previous results have indicated that uptake of glutaraldehyde by chromed stock was essentially the same as that by pickled stock.

Simultaneous tannage with glutaraldehyde and chrome.—In this series of tests pickled sides were tanned *simultaneously* with glutaraldehyde and chrome (Cr^{+++}) under various conditions. That is, the tanning liquor contained both glutaraldehyde and chrome. Apparently these two tanning agents are compatible. The tanning solution contained 6% (based on pickled weight) each of a 33% basic one-bath chrome tan and the commercial glutaraldehyde solution (Expt. 1, 2, 4, and 5, Table II) or 6% glutaraldehyde and 4% chrome (Expt. 3, 6, 7,

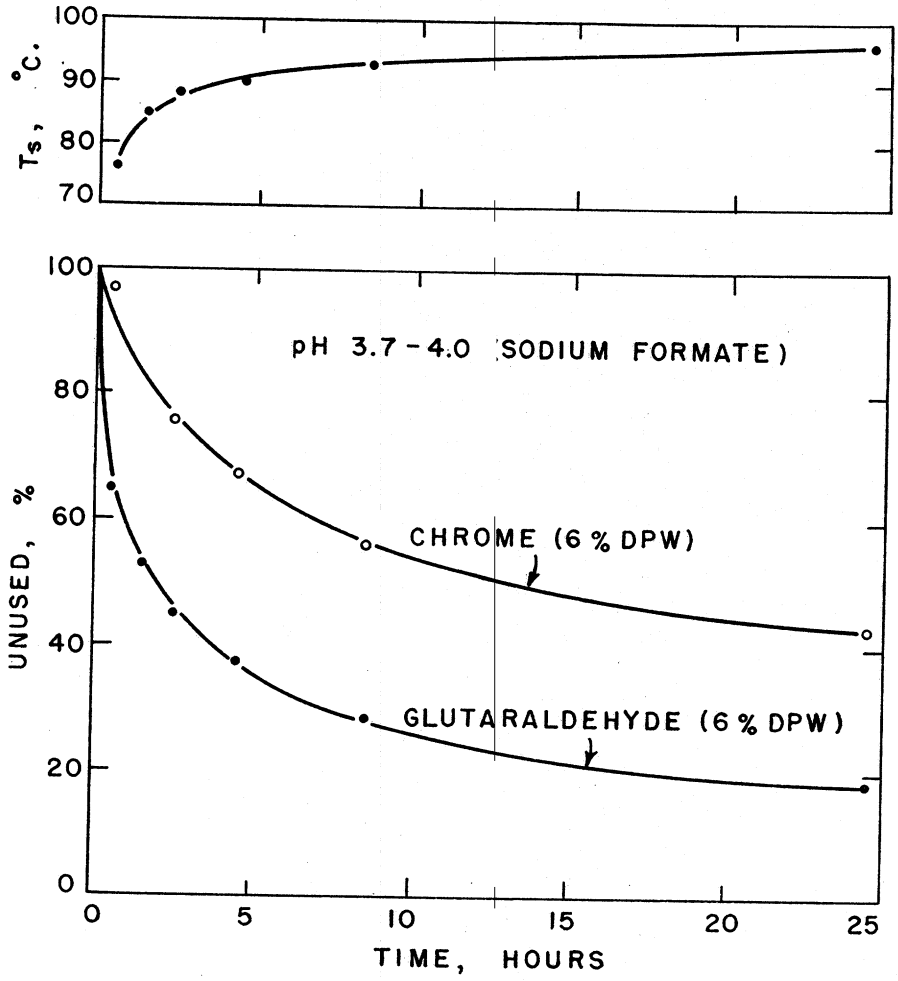


FIGURE 5.—Tanning rate. Simultaneous chrome-glutaraldehyde tannage (Expt. 5, Table II).

and 8, Table II). As before, the data in Table II were recalculated to give the percentage of tanning agent unused, and this was plotted against time to give the rate of tanning curves in Figs. 4, 5, and 6.

Figure 4 summarizes the data obtained at pH of about 3 using sodium bicarbonate. The glutaraldehyde disappeared more rapidly, hence was fixed at a greater rate, than chrome under our conditions. In a 24-hour run, approximately 70% of the glutaraldehyde and 45% of the chrome in the feed was fixed at this pH. A maximum shrinkage temperature of 92°C. (198°F.) was reached in about 8 hours.

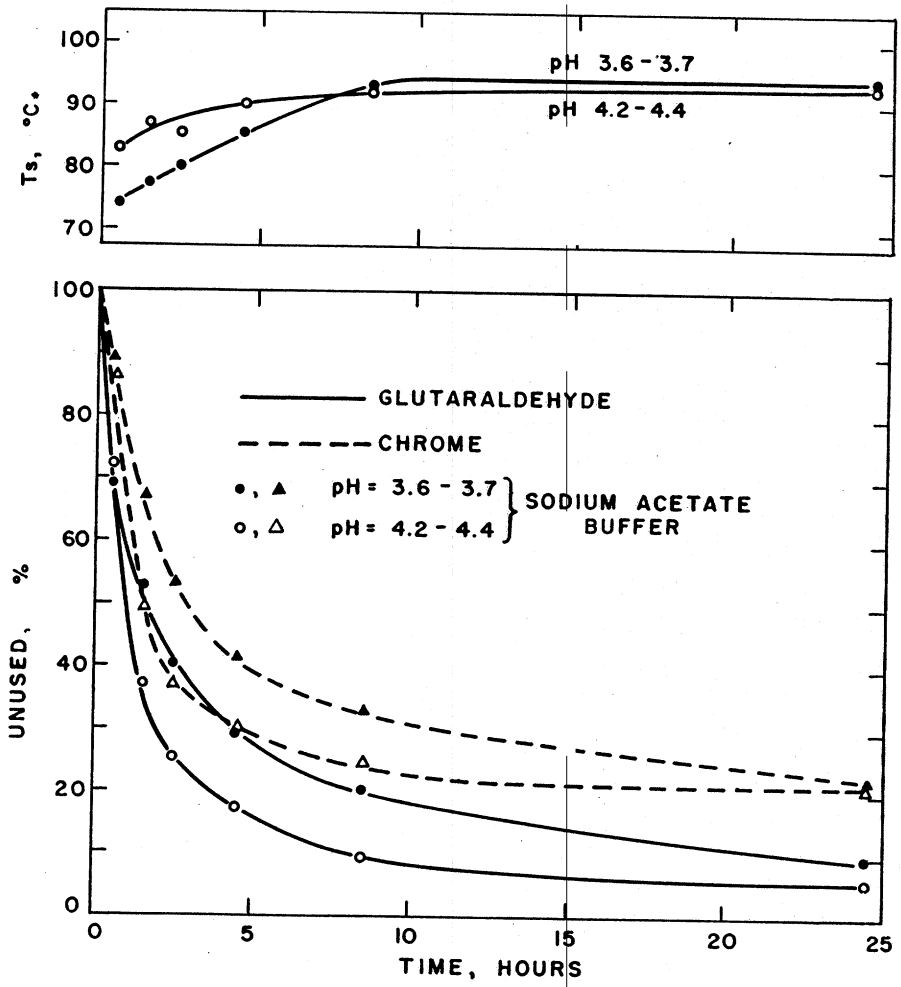


FIGURE 6.—Tanning rate. Simultaneous chrome-glutaraldehyde tannage (Expt. 7 and 8, Table II).

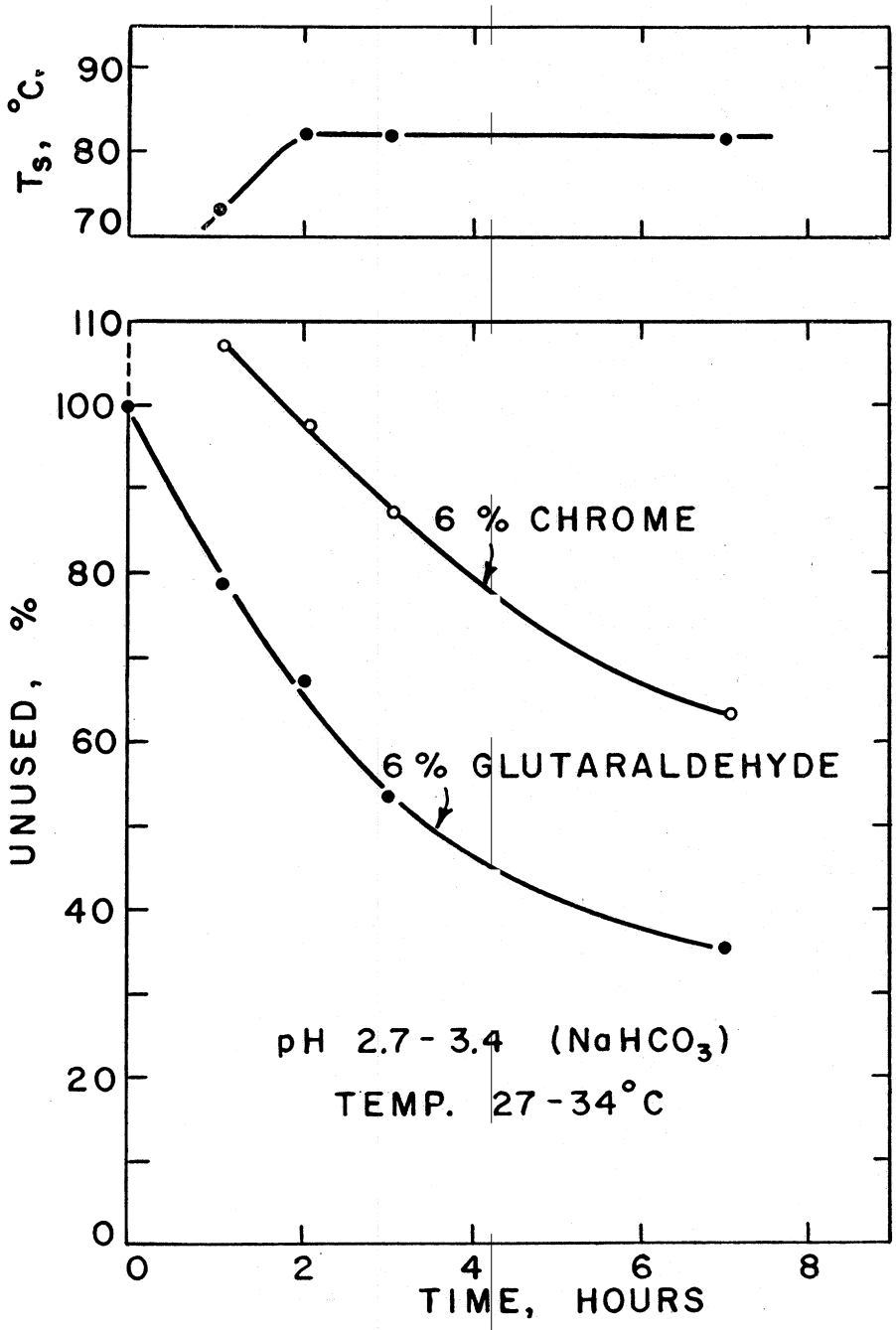


FIGURE 7.—Tanning rate. Simultaneous chrome-glutaraldehyde tannage, small pack.

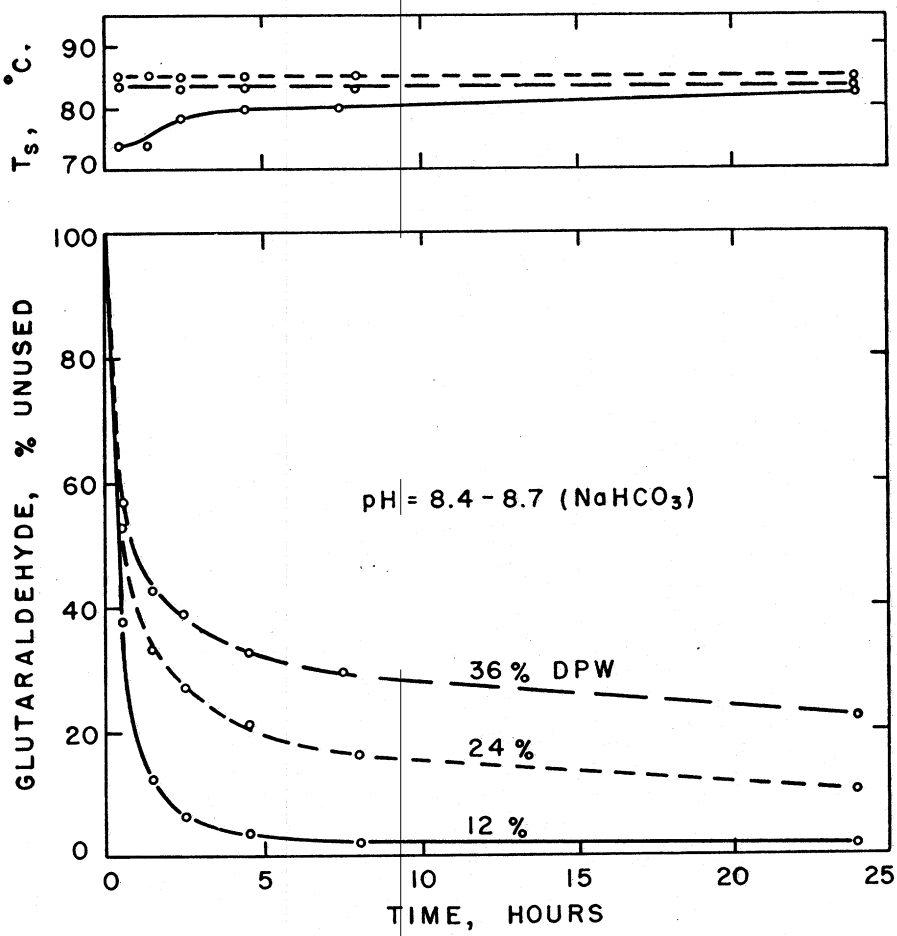


FIGURE 9.—Tanning rate. Glutaraldehyde alone (Expt. 13, 14, and 15, Table III).

Fig. 9. It is evident that the rate of fixation, as well as amount fixed, increased with increasing pH. It is noted that at pH about 8.5 the glutaraldehyde, when used at the 12% level, was virtually exhausted from the feed within 4 hours. At the higher levels of glutaraldehyde in the feed, equilibrium was not reached, and fixation appeared to occur slowly after an initially rapid rate.

The shrinkage temperature showed a gradual increase when 12% glutaraldehyde was used in the feed. In the case of 24% and 36%, however, a maximum Ts of about 84°C. (183°F.) was attained almost from the very beginning of the tannage (within 0.5 hour). It appears evident that 24% or more of glutaraldehyde solution is excessive for tanning. Bated stock would be a convenient raw material for tanning at this pH; however, because of the high reactivity of glutaraldehyde in alkaline medium, care must be exercised to avoid drawn grain.

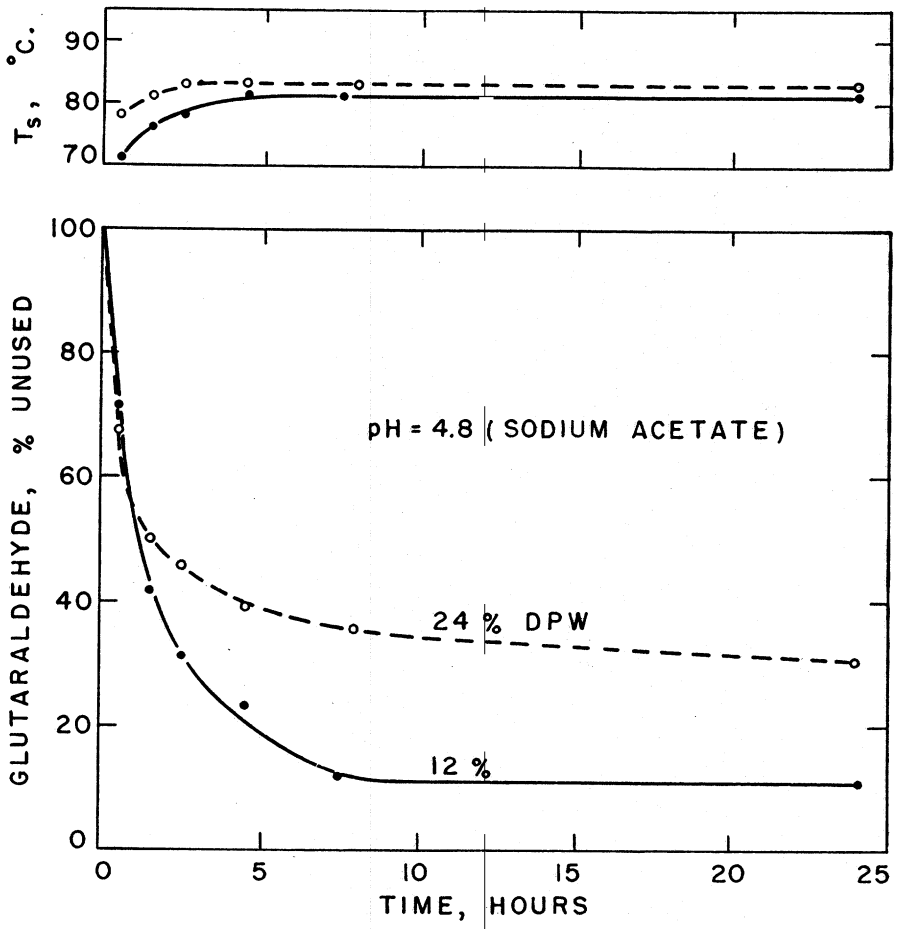


FIGURE 8.—Tanning rate. Glutaraldehyde alone (Expt. 16 and 17, Table III).

The results obtained at pH of 4.8 with two levels of glutaraldehyde, namely, 12% and 24% of the commercial solution based on the pickled weight, are summarized in Fig. 8. At the lower aldehyde level 10% of the glutaraldehyde added remained unused, whereas at the higher level 30% of it was unused. Thus, efficiency on the basis of glutaraldehyde was 90% and 70% respectively. Even without the benefit of the mechanical action of a pack, maximum fixation was achieved in 8 hours; however, it is noted that maximum Ts was attained sooner, i.e., in about 4–5 hours. The shrinkage temperature reached a maximum of about 83°C. (181°F.) at this pH. From a practical standpoint one may also conclude that 24% glutaraldehyde is an excessive amount.

The results at pH of about 8.5 with 12%, 24%, and 36% of the commercial glutaraldehyde solution(based on pickled weight of side) are summarized in

In Fig. 10 the data on uptake of glutaraldehyde at pH about 8.5 is presented in another way. In this case the amount of glutaraldehyde (25% solution) consumed, calculated as percent of the pickled weight, was plotted against time. It is noted that uptake increased with increasing concentration of glutaraldehyde; however, efficiency decreased. It appears that at the high concentrations equilibrium was not reached in 24 hours, and fixation continued slowly. The quantitative nature of the fixation was lost at the high concentrations, showing that 24% of the commercial solution is an excessive amount. Thus, at the 36% level fixation was slightly more than twice that at the 12% level even though three times as much aldehyde was present in the feed. The shrinkage temperature of the leather, however, was not materially increased by this higher fixation of aldehyde.

RECOMMENDED TANNING PROCEDURES

Listed below are procedures suggested for effecting the glutaraldehyde tannage either alone or in combination with chrome. These procedures are described for side upper leather; however, the principles can be applied to the tanning of other stock. One phase of the procedure deserves mention once again. "Setting" the tannage by letting the stock rest overnight in tanning liquors containing glutaraldehyde is to be avoided, since streaks develop in the leather. The tanned stock should be washed thoroughly to remove unbound glutaraldehyde. The tannage and subsequent wash can easily be completed within a period of about 2 to 8 hours, depending on the procedure, so that this complication need not be encountered.

Procedure for retanning with glutaraldehyde.—The following is a recommended procedure for retanning chrome leather with glutaraldehyde. This general procedure has been adapted for commercial use in tanning side leather.

Wrung blue stock (after neutralization)	100%
Water (preheated to 145°F. or 63°C.)	100%
Glutaraldehyde (25% solution)	10%
Salt (optional)	6%
Sodium bicarbonate (optional)	0.4%
Drum 2 hr.; pH 3.0; float temp. 125°F. (52°C.)	
Wash ½ hr.; Ts, 222°F. (106°C.)	

This procedure was run on a laboratory scale only (one side). The use of salt is probably of doubtful value when retanning chromed stock. The only function of the bicarbonate is to maintain the pH at a level suitable for a particular chrome tannage (after neutralization). In many cases, the bicarbonate probably can be omitted. In commercial practice where full drum loads would be involved, 1 hour of drumming may be sufficient.

Procedure B (acid side):

Pickled stock	100%
added to solution of:	
Water	100%
Sodium chloride	10%
Glutaraldehyde (25% solution)	15%
Drum 1 hr.	
Add:	
Sodium acetate	4%
Drum 7 hr.; pH 4.8; Ts 81°C. (178°F.)	
Wash ½ hr.	

In the procedures given above there is considerable latitude for modification, primarily because glutaraldehyde is an effective tanning agent and tans over a wide range of pH. Equally good leather resulted whether the tannage was conducted on the acid side (pH 4–5) or on the alkaline side. The advantage in bringing the tannage to the alkaline side is to obtain more efficient use of glutaraldehyde. Any alkaline type reagent, such as formate, acetate, borax, or bicarbonate, can be employed as long as the desired pH can be attained. Tannage on the alkaline side imparts a somewhat darker shade to the leather as compared to tannage on the acid side.

When glutaraldehyde is used as the only tanning agent, 15% of the 25% commercial solution is recommended to obtain a full tannage on sides. This amount corresponds to only 3.8% of glutaraldehyde on an anhydrous basis. With the chrome combination 6% to 10% of the commercial glutaraldehyde solution was effective in imparting the desirable properties of glutaraldehyde to the leather. Pretanning with glutaraldehyde probably is the most attractive procedure for carrying out certain combination tannages. This is particularly true for the combination tannage with vegetable tannins. The glutaraldehyde pretannage serves to greatly accelerate the penetration of the vegetable extracts.

PROPERTIES OF THE LEATHER

General.—At the end of the 24-hour tannage the sides from each test discussed above were processed into finished side leather with regular packs in a tannery. No difficulty was encountered in the conventional side leather post-tanning operations, such as coloring, fatliquoring, staking, and finishing, given to these experimental leathers. A tannery sorter rated the break and grain strength of these leathers mostly as good, and as judged by the sorter, the leathers were satisfactory. The leathers judged best were, in general, those from the tests in which conventional chrome-tanned stock was retanned with glutaraldehyde. This is fortunate from the practical standpoint since, in many respects, this procedure for tanning is preferable. The maximum benefits of both chrome and glutaraldehyde can thus be achieved.

Procedure for simultaneous tannage.—In general the glutaraldehyde is added to the conventional one-bath chrome solution, and the tanner would proceed as with his normal chrome-tanning procedure. The procedure below is recommended for tanning hides or skins simultaneously with glutaraldehyde and chrome.

Pickled stock (drained)	100%
Water	100%
Chrome tan	8%
Glutaraldehyde (25% solution)	6% to 8%
Sodium chloride	6%
Drum 1 hr.; pH 3.0; float temp. 81°F.	
Sodium bicarbonate	0.3%
Drum 1 hr.; pH 3.3; float temp. 83°F.	
Sodium bicarbonate	0.25%
Drum 5 hr.; pH 3.1; float temp. 93°F.	
Wash ½ hr.	

In following this procedure a tanner would employ his regular chrome-tanning procedure with the following exceptions: (*a*) 6–10% (on the skin weight) of commercial glutaraldehyde solution is added to the float along with the basic chrome sulfate; and (*b*) the stock should not remain at rest in the tanning liquor overnight, since this produces streaks in the leather. The shrink test will be essentially equivalent to that attained with chrome alone. It is usually desirable to reach a shrinkage temperature above the boil to insure adequate uptake of chrome.

Procedures for tanning with glutaraldehyde alone

Procedure A (alkaline side):

Pickled stock	100%
added to solution of:	
Water	100%
Glutaraldehyde (25% solution)	15%
Sodium sulfate (anhyd.)	10%
Sodium bicarbonate	0.8%
Drum 2 hr.	
1st hr.; pH 5.0; Ts 69°C. (156°F.)	
2nd hr.; pH 4.5; Ts 72°C. (162°F.)	
Add (after 2nd hr.)	
Sodium bicarbonate	5%
Drum 5 hr.; pH 8.3	
Wash ½ hr.; Ts 83°C. (181°F.)	

TABLE IV

CHEMICAL AND PHYSICAL DATA ON PROCESSED LEATHERS

Exp. No.*	Moisture† %	Fat‡ %	Ash‡ %	Cr_2O_3‡ %	Nitrogen** %	Tensile p.s.i.	Elongation % at Grain crack	Elongation % at Break	Ts, °C.†† Processed leather
Glutaraldehyde-chrome simultaneous tannage									
1	10.92	13.51	5.37	1.90	13.0	1460	—	30	88
2	10.72	11.83	5.34	1.82	13.3	1230	40	40	89
3	11.94	8.28	3.85	1.48	14.8	2700	40	70	90
4	10.65	11.91	5.46	1.94	13.4	2090	45	50	85
5	10.91	9.47	5.02	2.10	13.8	2030	50	55	89
7	12.07	9.83	2.58	1.58	14.0	2370	45	80	76
8	12.12	12.40	2.92	1.60	13.6	2210	45	90	78
Chrome-tanned (commercial), glutaraldehyde-retanned									
9	11.15	9.92	6.80	3.70	13.1	3120	—	50	102
10	10.52	10.17	6.92	3.57	13.0	2780	—	50	102
11	11.00	10.13	7.12	4.28	13.0	3230	—	50	102
12	10.00	11.59	7.49	4.16	12.3	1970	40	55	103
18	11.16	9.34	7.12	4.48	13.3	4160	50	55	103
19	10.25	12.34	8.16	4.82	12.2	2240	—	40	103
Glutaraldehyde-tanned									
13	14.92	6.99	1.82	0.20‡‡	15.9	—	—	—	82
14	14.54	7.64	1.90	0.20‡‡	15.4	—	—	—	83
16	14.23	7.02	1.76	—	15.8	—	—	—	80
Chrome-tanned (commercial)									
20	9.34	14.42	8.20	4.40	11.7	2200	—	50	93

*Experiment numbers coincide with those listed in Tables I, II, and III; No. 20 is the analysis of commercial chrome-tanned hide, from the same tannery, for comparison.
†Moisture determined in a vacuum oven at 50°C., at 5 mm., with a small stream of dry air flowing, for 48 hours
‡Official ALCA Methods ($CHCl_3$ used in fat extraction), data calculated on a moisture-free basis.
**Kjeldahl method, semimicro, total nitrogen (moisture-free basis).
††Shrinkage temperatures above 100°C. were determined in water with pressure apparatus.
‡‡Chrome picked up during processing with commercial pack.

Chemical and physical data.—Chemical analysis of the finished leathers is presented in Table IV. The leathers tanned with glutaraldehyde alone showed a higher moisture content after conditioning at 50% relative humidity and 73°F. than did those containing chrome. Moisture contents of leather from the glutaraldehyde-chrome combination were intermediate to those of the leathers from chrome or glutaraldehyde alone. Glutaraldehyde-tanned leather absorbs water readily. However, the incorporation of chrome will reduce this.

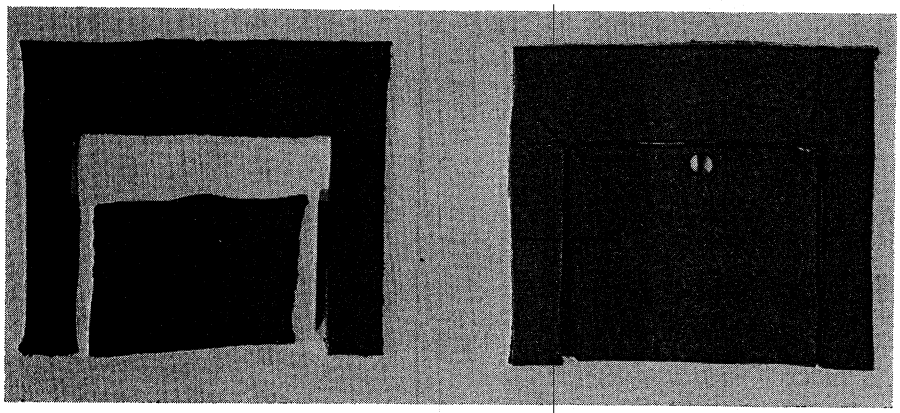
As can be seen in Table IV, the strength properties of glutaraldehyde-tanned leathers were comparable to conventional chrome leather. There is no indication of cracky grain in these leathers.

Shrinkage temperature.—The shrinkage temperature of the finished leathers tanned with glutaraldehyde alone were in the range of 80°–83°C. (176°–181°F.). If this is lower than desired, the Ts can easily be increased by a combination tannage. The Ts of the combination tannage with chrome is essentially governed by the amount of chrome that is fixed. The leathers given the *simultaneous* chrome-glutaraldehyde tannage showed a Ts ranging from 76°–90°C. (169°–194°F.). In these tests the amount of basic chrome sulfate was only 4–6% on the pickled weight. The low amount of chrome used in this simultaneous tannage resulted in a low Cr_2O_3 content of the leather (i.e., 1.48–2.10%), and this is the reason for the relatively low Ts of the leather. Leather withstanding a boil can be obtained easily when increased amounts of the basic chrome tan are used in the simultaneous tannage. Retannage of a full chrome leather with glutaraldehyde gave shrinkage temperatures above the boiling point of water, as expected. The chrome leather was commercial blue stock with a Cr_2O_3 content of 4.40%, and of course, this itself showed a Ts above the boil, i.e., 104°C. However, the finished leather from this stock was below the boil, whereas the finished leather from glutaraldehyde-retanned chrome stock remained above the boil. Generally, a full chrome tannage is desirable in the glutaraldehyde-chrome combination-tanned leather.

Mellowness.—Glutaraldehyde, when used as the only tanning agent, produced a mellow leather and also imparted mellowness to chrome leather as well. Mellowness, without loss of tightness of grain, seems to be a characteristic given to chrome leather when glutaraldehyde is incorporated in the tannage. The mellowness was not markedly changed by wetting and drying of the leather.

Perspiration resistance.—A notable property of glutaraldehyde-tanned leather is its outstanding resistance to deterioration by perspiration (3, 4), a property important in footwear application. All of the side leathers from our tests using glutaraldehyde in the tannage showed good resistance to a synthetic perspiration. The test method was essentially that described by Roddy and Lollar (10). As judged visually, the leathers tanned with glutaraldehyde were resistant to this test, and this property was carried over to the leathers given the glutaraldehyde-

chrome combination tannage (Fig. 11). The leather produced by retanning chromed stock with glutaraldehyde appeared to show the optimum resistance to deterioration by this test. Previous results from our laboratory have shown that glutaraldehyde in the tannage also produces leather with increased resistance to deterioration by alkaline agents such as soap (3, 4).



CHROME CHROME + GLUTARALDEHYDE

FIGURE 11.—Perspiration test on shoe upper leather.

Color.—Glutaraldehyde alone imparts a cream to light-tan color to the leather, while in combination with chrome a bluish-green color results. These color properties do not interfere with coloring except to modify the shade somewhat as compared to conventional chrome leather. This is true especially for pastel shades. With a proper pigment finish, a suitable perspiration-resistant white leather can be produced.

ACKNOWLEDGMENT

The authors are grateful to Mr. Samuel J. Viola for assistance in the chemical analyses, to Mr. William E. Palm for determining the tensile properties, and to Dr. Joseph Naghski and Dr. Wallace Windus for helpful discussions during this work.

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DR. FILACHIONE: That is right.

DR. LOLLAR: So that you were using basically 1½% chrome oxide on that basis and 6% commercial glutaraldehyde solution. Did you carry on any experiments in which the ratio was compared? If so, what influence did this have on the mellowness and break of the leather?

DR. FILACHIONE: No, we didn't carry out any experiments along that line. We arbitrarily selected 6% of each. We did change the concentration in the case of the tannage with glutaraldehyde alone and in the case of retannage chrome leather.

DR. LUDWIG SELIGSBERGER (Quartermaster Research & Engineering Center, Natick, Massachusetts): I would like to ask whether there is a lower limit to the amount of glutaraldehyde in leather where perspiration resistance is still effective and also whether the artificial perspiration solution contained urea and lactic acid.

DR. FILACHIONE: It contained lactate.

FRED LUVISI (Eastern Regional Research Laboratory): This was similar to a synthetic perspiration solution used by Roddy and Lollar in their deterioration studies on chrome leather.

DR. FILACHIONE: I have forgotten the composition of the synthetic perspiration.

DR. WALLACE WINDUS (Eastern Regional Research Laboratory, Philadelphia, Pennsylvania): It contains some urea; however, the urea content was fairly low, about 1 gram per 600 ml.

DR. FILACHIONE: The lactate content was quite high—about 50 grams of sodium lactate per liter of solution.

DR. SELIGSBERGER: How low can you go in glutaraldehyde?

DR. FILACHIONE: We can't put a figure on how low you can go. We have run tests using 6% or 12% of the commercial glutaraldehyde solution. At the 6% level, we sometimes failed to get a good perspiration resistance test. To be on the safe side we preferred to use 10% to 12% of the commercial solution which, of course, is three-fourths water. On a dry basis you are really using only 2½% to 3% glutaraldehyde.

DR. STUBBINGS: I would like to ask what the general economics of this type of retannage is in comparison to the retannage for leather of this character and I would like also to know if there is any effect from this retannage in terms of flank fill or improvement in the flank pocket or improvement of the character of the leather in that area as related to a pure chrome-type leather.

DR. FILACHIONE: Regarding the economics, the only information we have available is the cost of the glutaraldehyde, and I think we have a reliable source for that information right here in the audience. Would Mr. Aldrich of Union Carbide Corp., Chemicals Division, care to comment?

ROBERT HART ALDRICH (Union Carbide Corporation): The price of the 25% glutaraldehyde solution for the leather industry is 13 cents a pound in bulk quantities. We see no raising of this price now or in the long-term future. We actually anticipate that our costs and prices will drop as the volume of business rises. It has to be sold in a 25% solution because it is unstable at higher concentrations.

DR. FILACHIONE: Regarding your other question, we haven't noticed any particular filling effects in the flank areas from our tests.

DR. STUBBINGS: The reason I asked was that it is fairly simple for tanners to make a mellow leather which is primarily a straight chrome leather. This, apparently, is one of the attributes of the glutaraldehyde tannage. Do you feel there is any contribution to leather character other than mellowness with glutaraldehyde or would tanners have to use other materials from a practical viewpoint?

DR. FILACHIONE: Glutaraldehyde gives a good feel to leather. In combination with chrome there seems to be no sacrifice in tightness of grain with respect to additional mellowness. Then also I would expect improvement in perspiration resistance.

DR. LOLLAR: Were these leathers buffed in finishing?

DR. FILACHIONE: I am not certain, but I think they were full grain. Do you happen to recall, Wally?

DR. WINDUS: I think most of them were buffed. In connection with your question, Dr. Stubbings, we might cite an earlier example on sheepskins where glutaraldehyde found its first application. It was found that glutaraldehyde mellowed the backbone and shoulders and gave the skin a more uniform feel without making the skins stretch any more. Hence, the sorting value was actually higher.

DR. STUBBINGS: Do you think the same thing is true on sides?

DR. WINDUS: I doubt this would be as big a factor.

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DISCUSSION

DR. R. M. LOLLAR (Armour Leather Company, Chicago, Illinois): I certainly would like to extend the thanks of the association to Dr. Filachione and his associates of the Eastern Regional Research Laboratoy.

In these days of the need for new effects in leather to take advantage of our marketing opportunities, we certainly need the type of work that is represented by this continuing program at the Eastern Regional Research Laboratory.

I would like to ask a couple of questions with reference to the comparative properties of the simultaneous glutaraldehyde tannage and chrome tannage. Now, you mentioned that the glutaraldehyde used as a retannage tended to give mellowness. Do you get the equivalent mellowness in the simultaneous tanning?

DR. FILACHIONE: As far as I remember, the mellowness did not seem to be particularly influenced by whether we tanned the side with the two simultaneously or as a retannage with glutaraldehyde. Generally, the retannage of the chrome stock with glutaraldehyde rated better than the simultaneous tannage, and our perspiration test was significantly improved when we carried out the two tannages stepwise.

DR. LOLLAR: I would assume that the chrome leather on the basis of shrinkage characteristics contained more chrome oxide on the hide substance basis than you ever secured in your simultaneous tannage. Was this true?

DR. FILACHIONE: That's true, Dr. Lollar. The chrome content of the simultaneous tannages where we had 6% of one-third basic chrome sulfate was about half of the chrome content of the regular chrome retanned with glutaraldehyde. It was about 2% of Cr_2O_3 in the simultaneously tanned leather and about 4% in the other. Of course, the glutaraldehyde itself does give mellowness to leather, so this compensates for the lack of Cr_2O_3.

DR. LOLLAR: In your simultaneous tannage you used 6% of one-third basic chrome. I presume this was a 25% chrome oxide material?

TABLE III

UPTAKE OF GLUTARALDEHYDE BY PICKLED GRAIN SPLIT COWHIDE

Exp. No.**	Glutaraldehyde* % DPW	pH† (Buffer, % DPW)	Aldehyde Content of Tanning Solution during Tanning Process, g/100 ml.							Ts °C.	
			Initial‡	0.5 hr.	1.5 hr.	2.5 hr.	4.5 hr.	8.25 ± .25 hr.	24–24.5 hr.	24–24.5 hr. tannage	Processed leather
13	12	8.4–8.6 ($NaHCO_3$, 5)	1.792	.679	.225	.117	.067	.046	.036	82	82
14	24	8.4–8.7 ($NaHCO_3$, 5)	3.400	1.819	1.138	.925	.713	.553	.345	84	83
15	36	8.4–8.7 ($NaHCO_3$, 5)	4.857	2.763	2.075	1.900	1.600	1.438 (7.5 hr.)	1.088	84	††
16	12	4.8 (Na acetate, 4)	1.791	1.285	.750	.566	.423	.209 (7.5 hr.)	.194	81	80
17	24	4.8 (Na acetate, 4)	3.399	2.290	1.705	1.560	1.345	1.224	1.028	83	††

*25% commercial solution, used as supplied.

Tanning solution, based on drained pickled weight (DPW) of sides, also contained water (100%) and sodium sulfate (10%) in Exp. 13, 14, and 15, or sodium chloride (10%) in Exp. 16 and 17.

†pH range during 24.5-hour tanning period.

‡Calculated amount of active glutaraldehyde present at start of tanning period.

**Pickled hide equilibrated with buffer overnight; glutaraldehyde added next morning (at start of experiment).

††Processed leather lost in tannery.

The data obtained at pH of about 4 with formate buffer is shown in Fig. 5. As expected, the rate of fixation and the amount fixed were increased over those at the lower pH shown in Fig. 4. Here about 80% of the glutaraldehyde and 60% of the chrome was fixed, and the shrinkage temperature reached 96°C. (205°F.).

Data at two pH levels with sodium acetate as the buffering agent are shown in Fig. 6. In these cases about 90% of the glutaraldehyde and 80% of the chrome present in the feed was fixed. In these experiments only 4% chrome, on the weight of the side, was used instead of 6% as above, and the shrinkage temperature reached only 92°C. (198°F.) in these tests. As shown in our previous paper (4), the shrinkage temperature of the glutaraldehyde-chrome combination tannage is substantially the same as that of the corresponding chrome tannage alone. However, the rate of attainment of maximum shrinkage temperature is increased by glutaraldehyde.

The tanning rate data obtained in a small pack of six sides is presented in Fig. 7. This test simulated conventional practice more closely because the tanning agents (6% of each) were added to pickled stock, and the pH was then raised gradually with bicarbonate to about 3.1 (final value). Total tanning time was only 7 hours.

It is interesting to compare the rate curves with those shown for the one-side test (Fig. 4). The beneficial effects which may be attributed to mechanical action are evident. Fixation of each tanning agent was somewhat higher in 7 hours than the fixation in 24 hours in the single-side test. Thus, in the small-pack test, 35% of the chrome and 65% of the glutaraldehyde was fixed. This is to be compared to 25% of the chrome and 45% of the glutaraldehyde fixed in 7 hours in the single-side test (7 hour points in Fig. 4). Obviously, from a practical standpoint, running times can be considerably shorter and fixations higher than indicated in the single-side tests.

Tannage with glutaraldehyde alone.—In this series of tests the stock used was grain pickled sides obtained from a side leather tannery. Glutaraldehyde at two pH levels (4.8 and 8.5) and three concentration levels (12%, 24%, and 36% of commercial solution) was the only tannage given to this stock. In Table III is summarized the glutaraldehyde content of the tanning solutions at various time intervals. As before, the fraction of glutaraldehyde unused was calculated and plotted against time to give the tanning rate curves in Figs. 8 and 9. Also included are the curves showing the increase of shrinkage temperatures.

TABLE II

UPTAKE OF GLUTARALDEHYDE AND CHROME DURING SIMULTANEOUS COMBINATION TANNAGE

Exp. No.	Tanning Agents*: Glutaraldehyde** and Tanolin R†† % DPW	pH† (Buffer, % DPW)	Aldehyde and Chrome Content of Tanning Solution during the Tanning Process, g/100 ml.														Ts, °C.	
			Initial‡		0.5 hr.		1.5 hr.		2.5 hr.		4.5 hr.		8.25±.25 hr.		24–24.5 hr.			
			Aldehyde	Cr_2O_3	Aldehyde	Cr_2O_3	Aldehyde	Cr_2O_3	Aldehyde	Cr_2O_3	Aldehyde	Cr_2O_3	Aldehyde	Cr_2O_3	Aldehyde	Cr_2O_3	24–24.5 hr. tannage	Processed leather
1‡‡	6, 6	3.7–3.2 ($NaHCO_3$, 1)	.903	.813	.495	.759	.445	.700	.412	.652	.355 (5 hr.)	.593	.316	.536	.206	.400	93	88
2‡‡	6, 6	4.0 (Na formate, 6)	.899	.809	.440	.660	.429	.613	.392	.575	.308	.523	.245	.460	.164	.340	96	89
3‡‡	6, 4	4.1–3.9 (Na formate, 7)	.906	.550	.451	.470	.376	.420	.328	.389	.260	.339	.215	.291	.145	.214	95	90
4***	6, 6	3.4–3.1 ($NaHCO_3$, 1)	.838	.798	.614	.828†††	.530	.750	.490	.693	.430	.639	.355	.576	.250	.453	92	85
5***	6, 6	3.7–4.0 (Na formate, 6)	.893	.803	.580	.778	.476	.759	.403	.611	.334	.540	.255	.455	.164	.342	96	89
6***	6, 4	3.8–4.0 (Na formate, 6)	.898	.539	.555	.511	.439	.448	.388	.412	.305	.366	.230	.308	.133	.206	94	‡‡‡
7***	6, 4	3.6–3.7 (Na acetate, 1.4)	.911	.546	.631	.490	.480	.368	.369	.291	.274	.227	.188	.181	.089	.120	94	76
8***	6, 4	4.2–4.4 (Na acetate, 4)	.913	.545	.662	.474	.351	.270	.233	.205	.158	.164	.090	.136	.058	.115	93	78

*Tanning solution, based on drained, pickled weight (DPW) of sides, also contained water (100%) and NaCl (6%).
**25% commercial solution (used as supplied).
†pH range during 24.5-hr. tanning period.
‡Calculated amount of active glutaraldehyde and chrome (as Cr_2O_3) present at start of tanning period.
††Commercial chrome tanning agent (23.5% Cr_2O_3, ALCA basicity = 34%).
‡‡Pickled hide equilibrated with glutaraldehyde-chrome tanning solution overnight (pH range 1.6–2.0); dry buffer added next morning (at start of experiment).
***Pickled hide equilibrated with buffer overnight; both tanning agents added next morning (at start of experiment).
†††Values for Cr_2O_3 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.
‡‡‡Processed leather lost in tannery.

about 7 is not normal commercial procedure. However, conventional chrome-tanned stock after neutralization can easily be retanned in a short time with glutaraldehyde at an elevated temperature, and this is highly recommended as a practical procedure for carrying out the chrome-glutaraldehyde combination tannage. In this way, maximum benefits from both tanning agents are achieved readily.

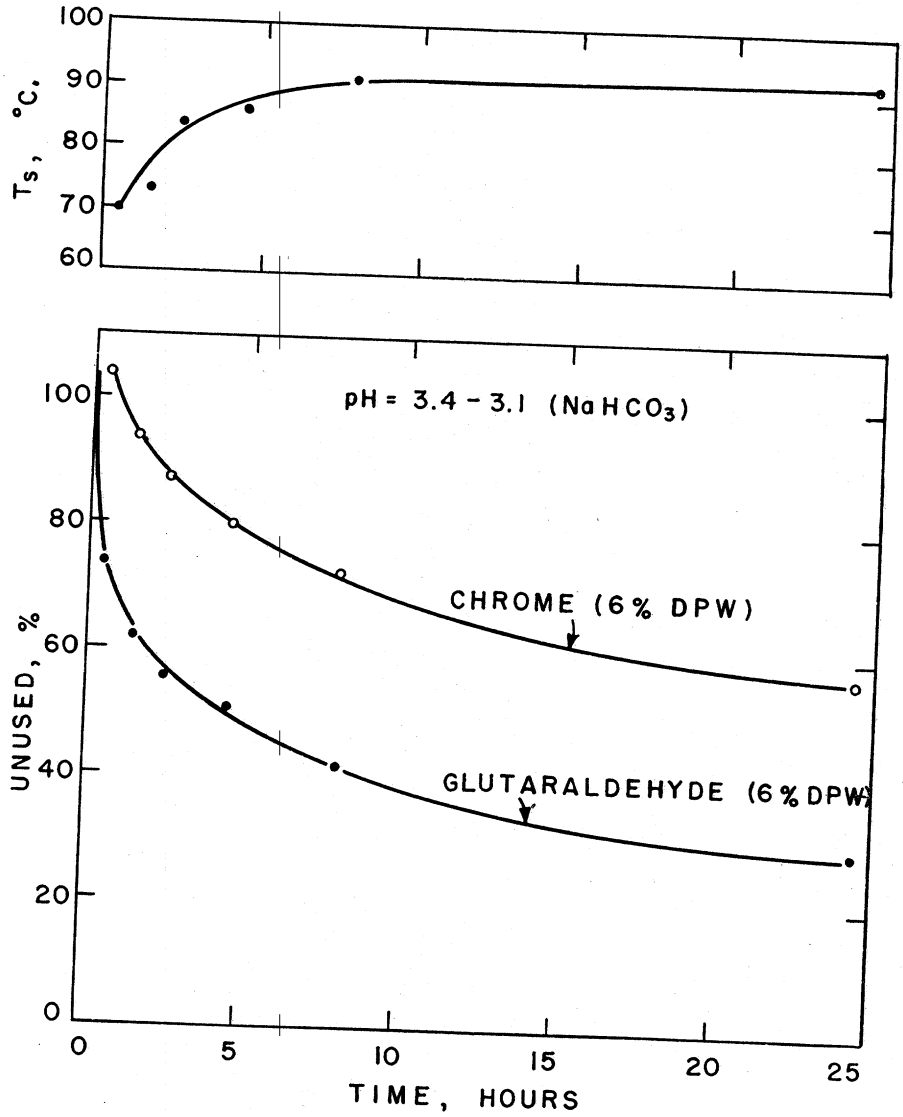

FIGURE 4.—Tanning rate. Simultaneous chrome-glutaraldehyde tannage (Expt. 4, Table II).

TABLE I

UPTAKE OF GLUTARALDEHYDE BY CHROME-TANNED GRAIN SPLIT COWHIDE

Exp. No.	Glutaraldehyde* % DBW	pH† (Buffer, % DBW)	Aldehyde Content of Tanning Solution during Tanning Process, g/100 ml.							Ts °C.**	
			Initial‡	0.5 hr.	1.5 hr.	2.5 hr.	4.5 hr.	8.25 ± .25 hr.	24–24.5 hr.	24–24.5 hr. tannage	Processed leather
9††	10	4.3 (Na formate, 5)	1.507	1.206	.800	.695	.595	.458	.301	104	102
10††	6	4.3 (Na formate, 5)	.922	.690	.484	.411	.316	.224	.126	104	102
11††	10	3.4 ($NaHCO_3$, 0.4)	1.503	1.169	.956	.899	.806	.693	.519	105	102
12††	6	3.4 ($NaHCO_3$, 0.4)	.926	.751	.569	.488	.412	.313	.193	106	103
18‡‡	6	2.9–3.6 ($NaHCO_3$, 0.8)	.947	—	.214 (1 hr.)	.166 (2 hr.)	.149 (3 hr.)	—	—	105	103
19‡‡	6	6.7–7.1 ($NaHCO_3$, 5)	.919	.276	.143	.076	.053	.045 (7 hr.)	—	105	103

*25% commercial solution, used as supplied.

Tanning solution, based on wrung or drained blue weight (DBW) of commercially chrome-tanned hides, also contained water (100%) and sodium chloride (6%).

†pH range during 24.5-hour tanning period.

‡Calculated amount of active glutaraldehyde at start of tanning period.

**Shrinkage temperatures (Ts) above 100°C. were determined in water with pressure apparatus.

††Chrome-tanned hide equilibrated with buffer overnigt; glutaraldehyde added next morning (at start of experiment).

‡‡Chrome-tanned hide retanned with glutaraldehyde—no equilibration; Exp. 18 run at elevated temperature (63°–47°C.).

chrome side. Calculated on the blue-weight basis, this corresponds to fixation of 4.8% when 6% of the commercial glutaraldehyde solution was used in the feed and 6.5% when 10% of the commercial solution was used.

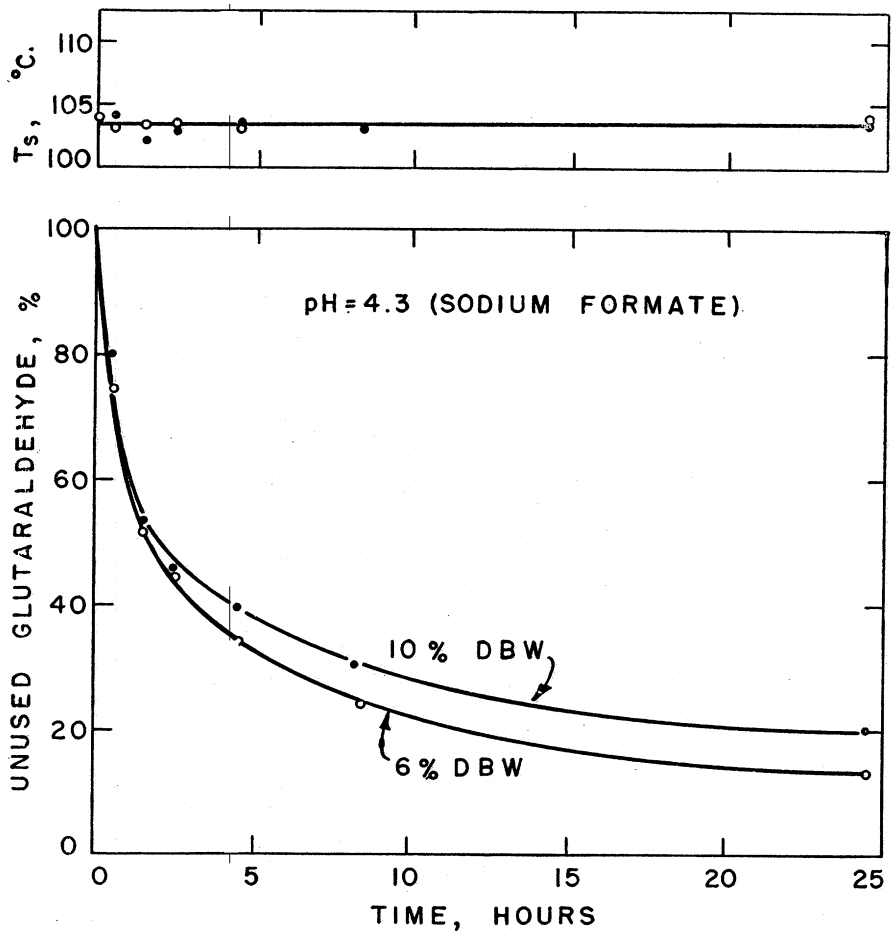

FIGURE 2.—Tanning rate. Retan of chrome stock with glutaraldehyde (Expt. 9 and 10, Table I). DBW = drained blue weight.

Figure 2 summarizes the data on aldehyde fixation by chromed stock at pH of 4.3 and shows the more efficient and more rapid uptake of glutaraldehyde at this higher pH value. Calculated as before, uptake on the blue-weight basis was 5.2% at the lower level and 8% at the higher level of glutaraldehyde. The shrinkage temperature of the chromed stock was virtually unchanged by retannage with glutaraldehyde.

leather. In the present paper the use of glutaraldehyde alone or in combination with chrome was extended to cow sides under various conditions, and the properties of the leathers were evaluated.

EXPERIMENTAL

Tannages.—The general procedure was similar to the full skin tests reported for sheepskins (2, 3, 4). The stock was the grain from lime-split cattlehides obtained in the pickle or in the blue from a side leather tannery. In most instances the stock in a 6% salt solution was buffered overnight to the desired pH before the tanning agents were added. The tanning agents of interest in this study were the commercially available 25% aqueous glutaraldehyde and a one-third basic, one-bath chrome tanning agent, Tanolin R*. This buffering procedure is not recommended as a practical tanning procedure, but it was selected because it permitted maintaining the pH reasonably constant throughout the run to determine the rate of tanning at a given pH. In order more nearly to approach tannery practice the tests were on a scale of one side per test. They were carried out in a drum, 16″ wide and 5′ in diameter, rotating at 8 rpm during the day and 4 rpm for the 16-hour overnight period. A word of caution is in order here. Hides and skins cannot be "set" overnight in a liquor containing a significant amount of glutaraldehyde without streaking the leather. However, as shown later, the tannage with glutaraldehyde can easily be completed in a few hours, eliminating the need for overnight treatment.

Uptake of tanning agents was determined by analysis of the tanning liquor at various time intervals as described previously (2, 7) to provide data on rate of tanning. Samples from the neck area of the side were taken at the same time intervals for determination of the shrinkage temperature.

Evaluation of leather.—At the end of the 24 hours of tanning, the sides were washed, brought to a pH of about 4, washed again, and processed into finished side upper leather with regular packs at a side leather tannery.

Chemical data were obtained on the finished leathers by Official Methods of Analysis of the ALCA (8). Physical properties were measured using Test Methods of the ASTM (9). Perspiration resistance was estimated in the same manner as described in previous publications (3, 4).

DISCUSSION OF RESULTS

Retannage of chromed stock with glutaraldehyde.—This procedure for effecting the glutaraldehyde-chrome combination tannage will be very attractive to many tanners. Retannage is fairly common practice in side leather tanning. It also provides the tanner with a degree of flexibility in lines of leather products.

In this series of tests grain sides in the blue, obtained from a tannery, were

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

retanned with glutaraldehyde under various conditions. As mentioned above, the blue stock was brought to the pH desired for the test before the addition of the glutaraldehyde for convenience in maintaining the preselected pH value.

The uptake of glutaraldehyde by the blue stock can be obtained from the data in Table I. This is more clearly seen in the curves shown in Figs. 1–3, which are simply the percentage of unused glutaraldehyde plotted against time. The uptake of glutaraldehyde by the chrome-tanned stock appears to follow essentially

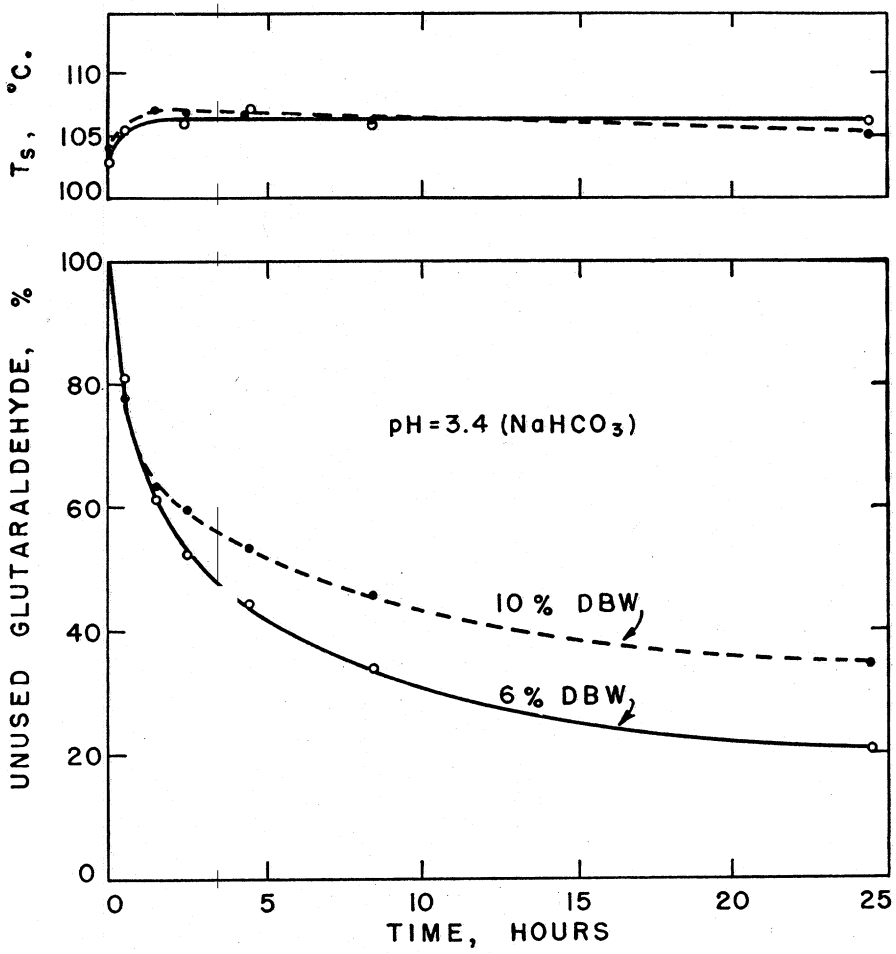

FIGURE 1.—Tanning rate. Retan of chrome stock with glutaraldehyde (Expt. 11 and 12, Table I). DBW = drained blue weight.

the same course as that by untanned stock. At pH of 3.4 (Fig. 1), from the amount unused at the 24-hour point, we can see that 80% at the lower level and 65% at the higher level of glutaraldehyde in the feed were fixed by the