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Tanning With Glutaraldehyde

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Introduction

For several years our Laboratory and the Quartermaster Laboratory, have devoted considerable attention to studying the tanning properties of certain organic compounds known as aldehydes (1-9). A number of new aldehydes, especially dialdehydes, had become available, but no information existed about their tanning ability.

Our research clearly demonstrated the versatile tanning properties of one of these dialdehydes, glutaraldehyde, and the desirable properties it imparts to leather (1, 4, 5, 6, 8, 9). This, coupled with its commercial availability at reasonable cost, soon led to its commercial use in tanning by the leather industry in the U. S. (10). Tonight I want to discuss with you some of our research results with this interesting material.

Our tests were on a scale of one skin or side per test to more closely approach tannery practice.

Comparison of Aldehydes

Figure 1 compares the tanning ability of glutaraldehyde with glyoxal and the commercially important formaldehyde at pH of 5. Glyoxal showed no tanning power. Glutaraldehyde is fixed more rapidly than formaldehyde and in larger amount, roughly about twofold in comparison. At this pH, glutaraldehyde gave the highest shrinkage temperature, and this was attained very rapidly from the first hour of tanning. Formaldehyde showed a gradually increasing shrinkage temperature.

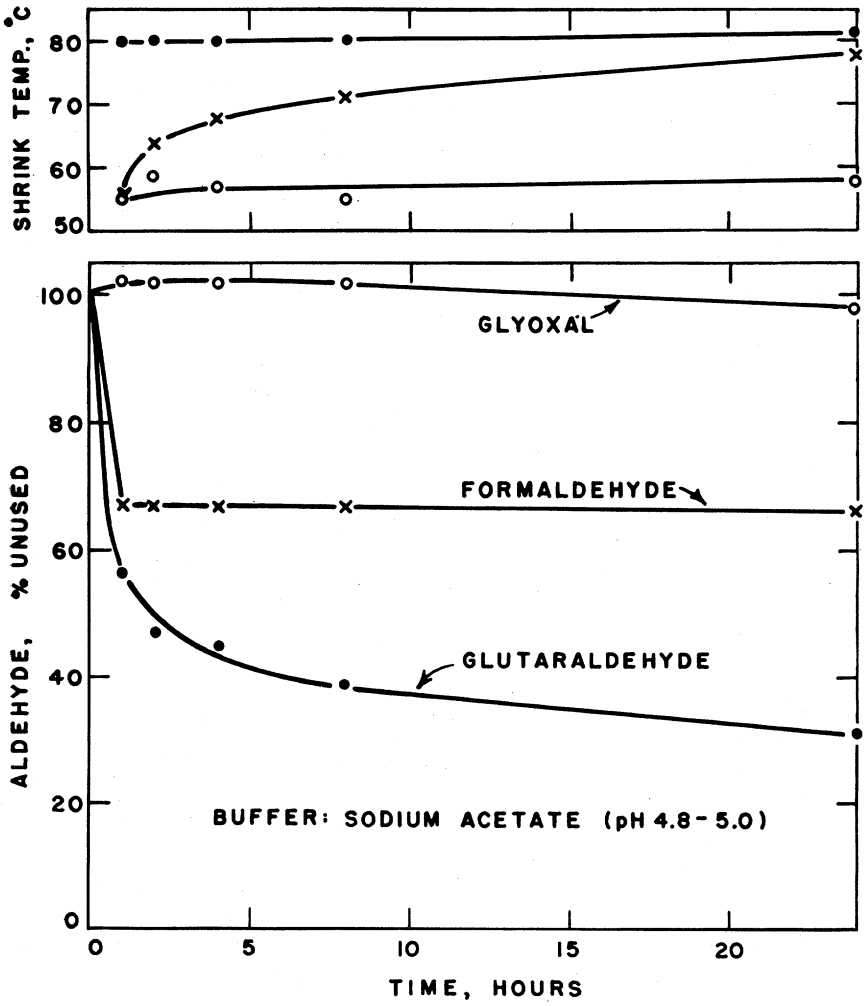

FIGURE 1

Figure 2 gives the comparison among these three aldehydes in alkaline solution; i.e., pH of about 8. As expected, the tanning rate of all three is greatly increased. Glyoxal is now a tanning agent. It is fixed gradually, and the shrinkage temperature rises slowly. Again formaldehyde was fixed less rapidly than glutaraldehyde, but the shrinkage temperatures of the two were more comparable than at the acid pH. I would like to point out the quantitative nature of tanning with glutaraldehyde. We note that it was almost completely exhausted from the alkaline solution. An important characteristic of glutaraldehyde is the very large proportion of the material that is fixed even in only 1 hour of tanning. Thus, during the first hour only 30% was unused, meaning that 70% of the glutaraldehyde input was consumed or fixed.

Clearly glutaraldehyde differs markedly from other aldehydes in its greater reactivity. Hence, it is not surprising that we find the leathers produced from it also differ from other aldehyde leathers. Figure 3 shows the effect of a synthetic perspiration on these three aldehyde leathers. Obviously, glutaraldehyde gave a decidedly superior result in this test. In fact, this new leather appears to be remarkably resistant in some other respects as well, for example, towards hot soap solutions. Our evidence indicates that the glutaraldehyde has become irreversibly bound to hide substance.

Tanning with Glutaraldehyde Alone

Figure 4 presents data on the rate of tanning with glutaraldehyde at various pH values. We note the higher fixation as well as rate of fixation of glutaraldehyde as pH is increased. When 12% of commercial glutaraldehyde solution, based on pickled weight, was used, the tanning liquor is about exhausted of aldehyde within 4 hours. At higher levels of aldehyde, in an experiment not shown in this figure, equilibrium was not reached, and fixation occurred slowly after an initially rapid rate. The range from 10 to 15% of glutaraldehyde, as the commercial 25% solution, is preferred for tanning. A maximum Ts of about 85°C. or 185°F. was attained very rapidly at alkaline pH. Bated stock would be a convenient raw material for tanning on the alkaline side. However, because of the high reactivity of glutaraldehyde in alkaline medium, care must be exercised to avoid drawn grain. This can be done by adding the aldehyde slowly in several feeds.

Table I outlines a procedure for tanning with glutaraldehyde alone on the acid side. Pickled stock is drummed briefly with glutaraldehyde in a salt solution. The pH is then raised to about 4.5-5.0 by adding sodium acetate. Drumming is continued for most of an 8-hour shift. The stock is then washed to remove unbound glutaraldehyde, and the tannage is finished. The leather has a Ts of about 81°C. (178°F.) and is a cream color.

"Setting" the tannage by letting the stock rest overnight in the glutaraldehyde tanning liquor is to be avoided since streaks may develop. The tannage can easily be completed in a working shift so that streaking is no problem.

The tannage can also be carried out on the alkaline side, and this procedure is outlined in Table II. Here pickled stock is drummed briefly with glutaraldehyde, and then formate is added to give a pH of about 4.0. One to two hours tanning at this pH is sufficient to stabilize the grain towards the astringency of glutaraldehyde at a higher pH. The pH is then raised

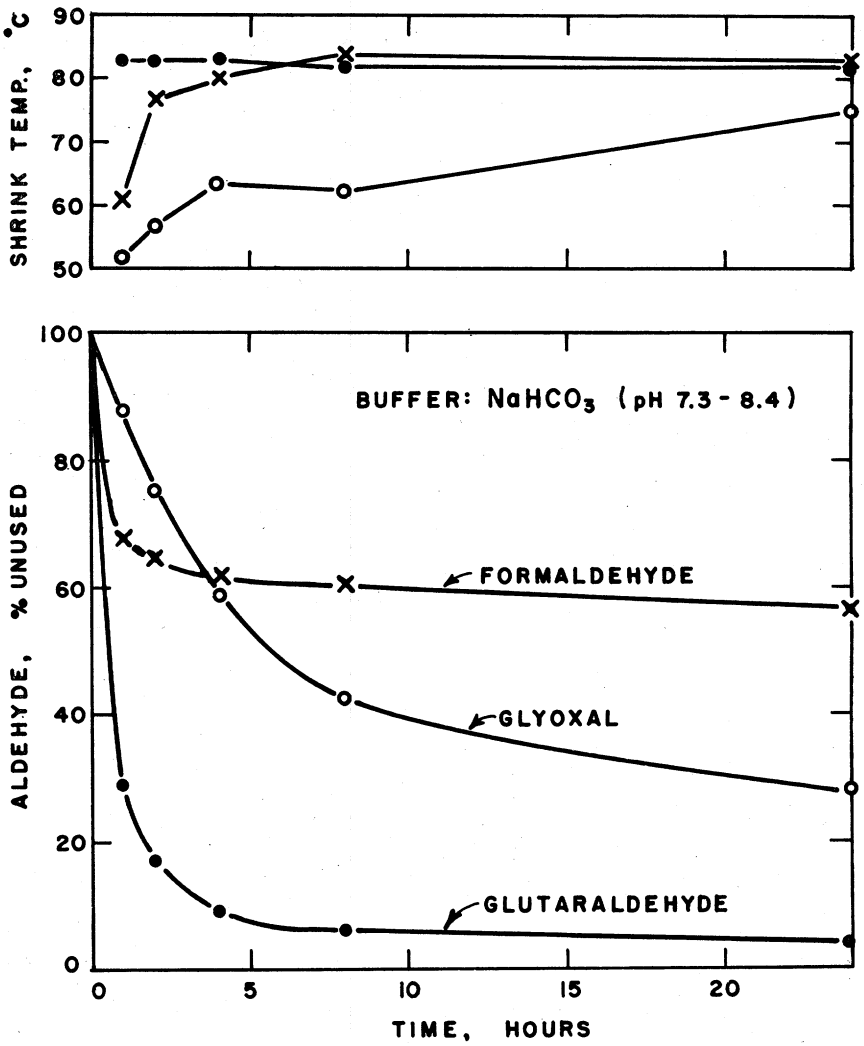

FIGURE 2

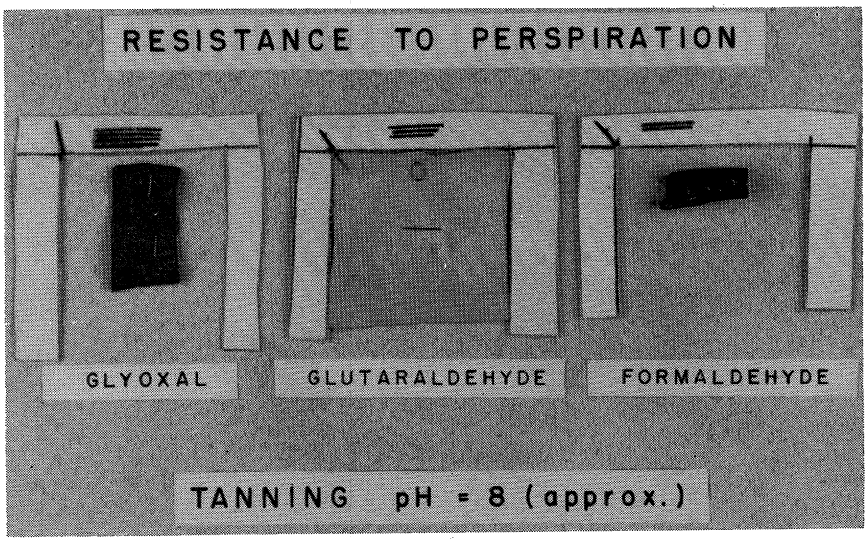

FIGURE 3

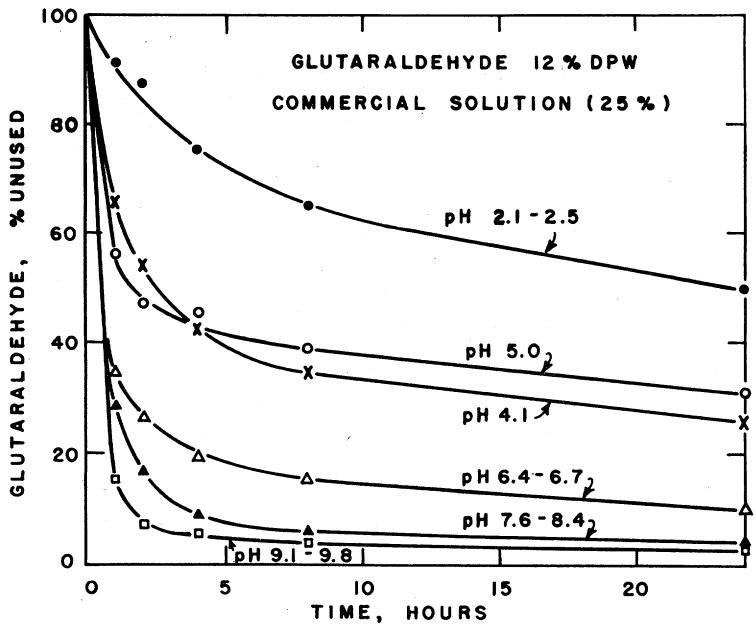

FIGURE 4

TABLE I

Tanning with Glutaraldehyde Alone (Acid Side)

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

TABLE II

Tanning with Glutaraldehyde Alone (Alkaline Side)

Pickled skin	100%
Water	100%
Sodium chloride	6%
Glutaraldehyde (25% solution)	12%
Drum ½ hour; pH 2.3	
Add:	
Sodium formate	4%
Drum 2 hours; pH 4.0; Ts 79°C	
Add:	
Sodium bicarbonate	3½%
Drum 3½ hours; pH 7-8; Ts 82°C	
Add:	
Formic acid	1¾%
Drum ½ hour; pH 4.4	
Wash ½ hour; Ts 83°C	

to 8 with bicarbonate and the tannage is completed in a short time. The leather is acidified and washed.

Because glutaraldehyde is an effective tanning agent and tans over a very wide pH range, there is considerable latitude for modification in these procedures. Equally good leather resulted whether the tannage was conducted on the acid or alkaline side. In the latter case, a more efficient use is made of the glutaraldehyde; however, the leather is somewhat darker in shade. The tannage is rapid and easily completed within a working day. For a full tannage with glutaraldehyde as the only tannage, 12% for sheepskin and 15% for cattlehide, based on the pickled weight, are suggested.

Simultaneous Tannage with Glutaraldehyde and Chrome

Because of the reactivity of glutaraldehyde in the acid pH range, it lends itself to a simultaneous tannage with conventional chrome tanning agents. Also, these two tanning agents are compatible.

Figure 5 presents data on the uptake of tanning agents by pickled grain split cattlehide when tanned with 6% one-third basic chrome and 6% glutaraldehyde in the same tanning solution at pH about 3.8. We can see that the glutaraldehyde disappeared more rapidly and hence was fixed at a greater rate than chrome. About 80% of the glutaraldehyde and 60% of the chrome present in the feed were fixed in 24 hours. A maximum Ts of 96°C. (205°F.) was reached in 8 hours. The shrinkage temperature of the glutaraldehyde-chrome combination tannage is essentially controlled by the chrome content of the leather. The glutaraldehyde, however, increases the rate of attainment of the maximum Ts.

A procedure for the simultaneous tannage with glutaraldehyde and chrome is suggested in Table III. The procedure is quite straightforward. Six to eight per cent of the commercial glutaraldehyde solution would be added to the normal amount of chrome, and the tanner would proceed with his normal chrome tanning

process. The stock should not be set overnight but should be washed thoroughly after completion of tanning. This procedure is desirable mainly from the standpoint of saving in processing time.

Retannage of Chrome Leather with Glutaraldehyde

Retannage of chrome leather is perhaps the most attractive way to carry out the glutaraldehyde-chrome combination tannage. Figure 6 presents data on such a retannage of side leather at pH of about 3.4 and at room temperature. Eighty per cent at the lower level and 65% at the higher level of glutaraldehyde in the feed were fixed by the blue stock. The Ts was increased by about 4°C. As expected, uptake of glutaraldehyde becomes more rapid and more efficient as the pH is increased.

Retannage of blue stock at elevated temperature is presented in Figure 7. In this test it was convenient to raise the temperature to 140° F. at the beginning. The temperature dropped to 120°F. in 3 hours running time. This was a conventional blue stock, and the retannage was carried out at its normal pH which ranged from 2.9-3.6. About 80% of the glutaraldehyde introduced was consumed.

Table IV outlines a procedure for retanning chrome leather with glutaraldehyde. This general procedure has been adapted for commercial use in tanning side leather. Ten per cent glutaraldehyde is suggested as an adequate amount with conventional blue stock. A 1 to 2 hour tannage at about 120°F. should be sufficient to introduce the desirable properties attributable to the glutaraldehyde. Retanning chrome leather at elevated temperature is a procedure we recommend and is being used commercially. If a tanner splits in the blue and chrome retans, an ideal way to use glutaraldehyde is to mix it with the chrome in this retanning step. The pH of retannage to be selected would be that which is optimum for the chrome leather.

Properties of Leathers Tanned with Glutaraldehyde

The shrinkage temperature of leather tanned with glutaraldehyde alone is in the range of 80-83°C. (176-181°F.). This is lower than desired, particularly for shoe upper leather. However, the Ts is easily increased to above the boiling point of water by tanning in combination with chrome. Other combination tannages also raise the Ts; i.e., vegetable retanning gives a Ts of about 94°C. (201°F.).

The leathers we tanned in our laboratory were processed into finished leather with regular packs in tanneries. No difficulty was encountered in the conventional post-tanning op-

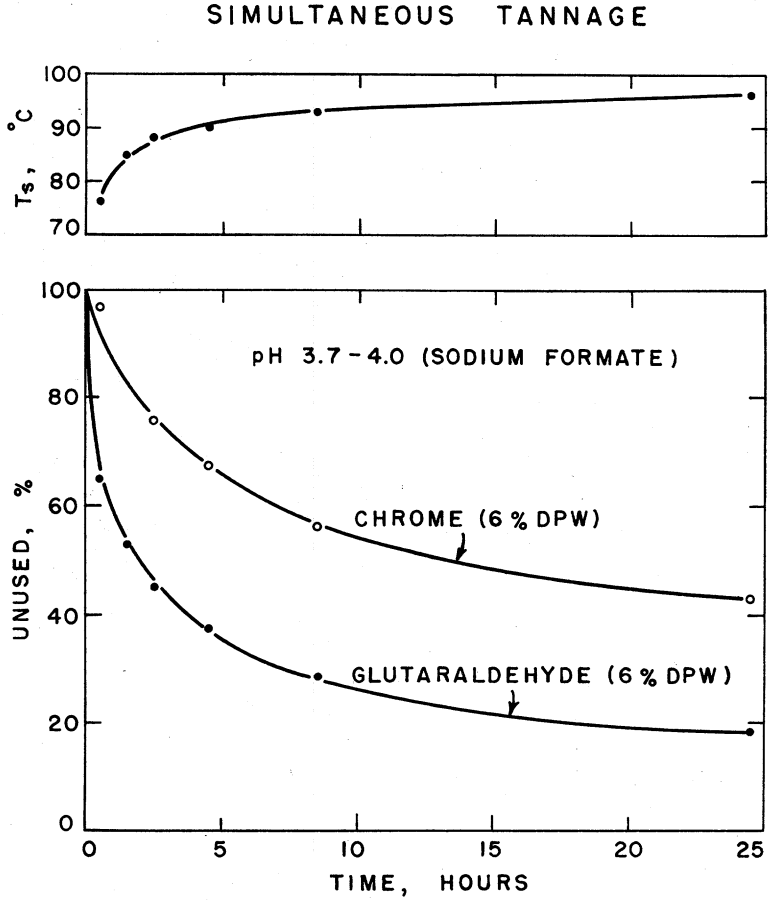

FIGURE 5

TABLE III

Simultaneous Tannage with Glutaraldehyde and Chrome

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

erations. Almost without exception the leathers were of good quality and were comparable to conventional chrome leather in strength. There was no indication of cracky grain in these experimental leathers.

It is claimed that glutaraldehyde actually assists many of the post-tanning processes (10). This leather is easy to fatliquor, and the oils appear to be more uniformly distributed. In coloring, glutaraldehyde leather yields a brighter, more level color. However, glutaraldehyde imparts a cream color to leather, and this base color changes the shade of some standard colors. For example, the cream color of straight glutaraldehyde-tanned leather changes a pastel blue in the direction of green. This can cause complications when certain pastel shades are desired. When chrome is present, there is less change since the base color is still bluish. Glutaraldehyde is undesirable for white garment leather because of the off-white result. However, white shoe upper leather can be made when adequate pigment finishes are used.

Glutaraldehyde-tanned leather resembles vegetable leather in that it absorbs water readily. This property is not a desirable one in the finished leather. However, combination tannages with glutaraldehyde and chrome give leathers with much lower water absorption. Thus, retannage of conventional chrome leather with glutaraldehyde produces leather that does not differ significantly in regard to water absorption from the normal chrome leather. The somewhat increased ease of wetting does assist in some of the post-tanning operations, such as sammying, impregnation, and finishing. The use of glutaraldehyde in the tannage does give a leather that retains much of its softness and mellowness upon repeated wet-dry cycles.

Glutaraldehyde, when used as the only tanning agent, produced a mellow leather. It also imparted mellowness to chrome leather as well as to other combination tannages. This property was imparted to leather without sacrificing tightness of grain. This characteristic of glutaraldehyde led to the first commercial application of glutaraldehyde. It is used in a combination tannage with chrome to soften the backbone and neck areas of some sheepskins for garment leather. The remainder of the skin did not become mushy and hence cutting value was improved.

Another property glutaraldehyde imparts to leather is improved resistance to hot soap solution. Table V shows the effect of washing on a conventional chrome garment leather and this same leather retanned with glutaraldehyde. The samples were washed three times in 0.5% soap solution at 120°F. for ½ hour. The Ts of the chrome leather was reduced 22°C., compared to a reduction of only 6 to 10°C. for the glutaraldehyde-retanned leather.

An outstanding property that glutaraldehyde imparts to leather is resistance to perspiration. This is true whether glutaraldehyde is used as the only tanning agent or whether it is used in combination with chrome or vegetable. Figure 8 shows the effect of the perspiration test on a chrome-tanned specimen of shoe upper leather before and after retannage with glutaraldehyde. The stabilizing effect of glutaraldehyde is clearly indicated. This greatly improved resistance to perspiration is desirable in footwear applications.

To obtain good perspiration resistance the following amounts of the commercial 25% glutaraldehyde solution are suggested when used as the only tanning agent: 12% for sheep-

TABLE IV

Retanning with Glutaraldehyde

Wrung blue stock (after neutralization)	100%
Water (preheated to given temp. of about 125°F)	100%
Glutaraldehyde (25% solution)	10%
Sodium chloride (optional)	6%

Drum 2 hour; pH > 3.0; float temp. > 120°F
Wash ½ hour

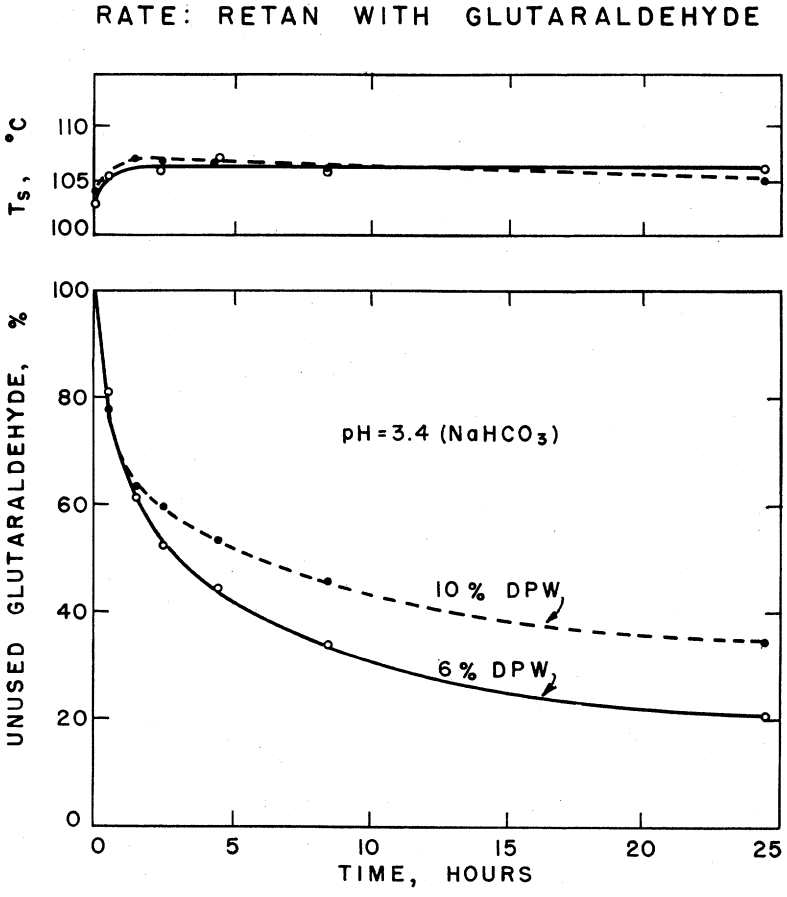

FIGURE 6

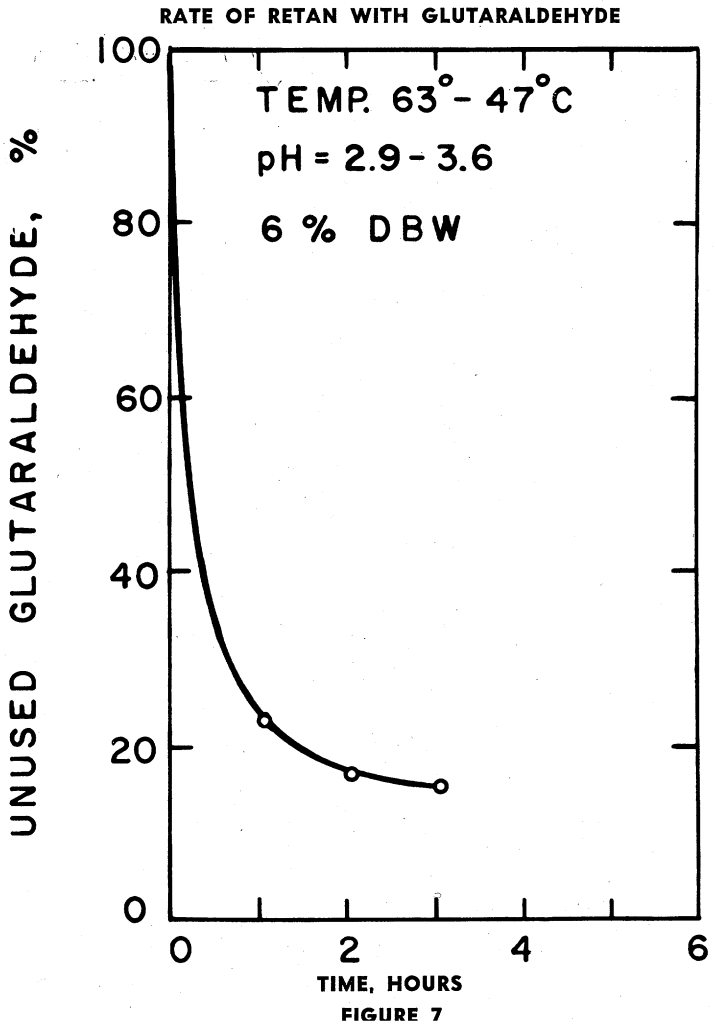

FIGURE 7

TABLE V

*Effect of Washing**

Chrome-Tanned - Glutaraldehyde-Retanned Cabretta

pH of Retannage	Shrink Temperature, °C Before Washing	1st Wash	2nd Wash	3rd Wash	ΔTs, °C
3.6	100	96	92	90	—10
4.1	99	96	93	91	— 8
4.4-4.5	98	95	92	91	— 7
5.8-6.0	99	96	95	93	— 6
Chrome only (Not retanned)	96	90	87	74	—22

*Samples washed in Launder-Ometer; each wash: ½ hour, 120°F., 0.5% solution.

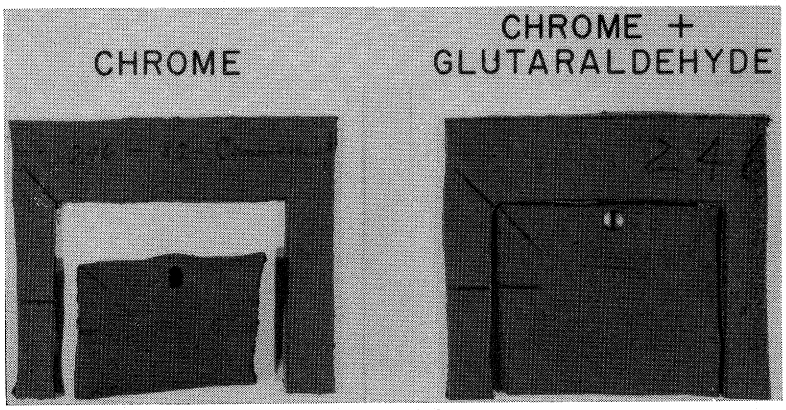

FIGURE 8

skin and 15% for side leather. As a retannage on chrome 10% should be adequate.

The notable resistance to perspiration of this leather has led to new applications. It has caught on in work shoe leather. Tests have been made with glutaraldehyde as the only tanning agent as well as in combination with chrome. Field tests have substantiated our laboratory tests for both these tannages. Work shoes made with leather tanned with glutaraldehyde alone or in combination with chrome have given excellent service to workers in dairy barns, paper mills, cement plants, and gasoline stations, where perspiration, alkali, and alkaline cleansing agents rapidly deteriorate leather. Glutaraldehyde and glutaraldehyde-chrome combination leathers are now available in work shoes at the retail level. It seems likely that glutaraldehyde will benefit other types of leather for footwear, particularly where resistance to perspiration is desirable.

We are presently doing some work on the use of glutaraldehyde in tanning of shearlings (11). In this case, the resistance of the leather both to perspiration and washing make this an attractive tannage for bed pads used by bedridden patients. Of course, in tanning pickled shearlings the procedure was modified.

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

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