THE EFFECT OF GLUTARALDEHYDE ON VEGETABLE TANNING*

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ABSTRACT

Full thickness cattlehide was used as the substrate for investigation in the pickled condition as sides obtained from a tannery. These were tanned with 15 percent glutaraldehyde based on the drained pickled weight of commercial solution and were retanned with chestnut, wattle and sulfited quebracho extracts of varying concentrations over a 24-hour period. Data are presented on the rate of uptake of the vegetable tannins, as well as penetration of the vegetable tannins. Various properties of these vegetable leathers, such as shrinkage temperature, water solubles and perspiration resistance (insole test) were evaluated.

A tannage, in which glutaraldehyde, vegetable and glutaraldehyde were used alternately, was also investigated. The effect of this type tannage on hydrothermal shrinkage and water solubles of the vegetable leathers was determined.

INTRODUCTION

The tanning action of formaldehyde has been known for many years, and this aldehyde has been used on a very limited scale for tanning certain specialty leathers (1–5). In recent years our laboratory has conducted extensive research to evaluate new aldehydes, particularly dialdehydes, for tanning ability. This work demonstrated the versatile tanning power of glutaraldehyde and led to the commercial use of glutaraldehyde in tanning of leather (6, 7, 8, 9). This new aldehyde tanning agent is being used on a wide variety of leathers, but principally as a retannage of chrome leather (8, 10, 11).

There is little information in the literature on the use of glutaraldehyde in combination with vegetable tannins. However, other aldehydes, especially formaldehyde, have been studied in the vegetable combination tannage.

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Seligsberger et al. (12) developed a rapid sole leather tannage using formaldehyde and glyoxal as a pretannage. Later Beebe and coworkers at our laboratory (13) and Wagoner et al. in a pilot scale study (14) reported the use of dialdehyde starch as a pretannage for the rapid tanning of sole leather. Kremen (15) studied retannage of vegetable-tanned leather with formaldehyde and noted a significant increase in the chemical stability and insole serviceability of the leather. Recently at our laboratory sheepskins were tanned with wattle and glutaraldehyde with the latter used simultaneously or consecutively, to determine the compatibility of this particular tanning system (16).

A detailed study was made of the glutaraldehyde vegetable tannin system with the former as a pretannage and also as a retannage as applied to full thickness steerhide. Rates of tanning were determined as well as some of the properties of the rough leather, such as shrinkage temperature, water solubles and perspiration resistance.

EXPERIMENTAL

Full thickness cattle sides in the pickle were obtained from a tannery, and this stock was tanned in a drum with 10 or 15 percent based on the drained pickled weight of commercial glutaraldehyde solution (25 percent concentration) at a pH of 4.5 by recommended procedures (8, 10) over a twenty-four hour period. The glutaraldehyde content of the liquor was determined at various time intervals as described by Fein et al. (6).

After the full thickness sides had been pretanned for twenty-four hours with glutaraldehyde, they were washed in a drum with running water and horsed overnight prior to vegetable retannage. Strips 14″ wide running from backbone to belly were cut from the drained glutaraldehyde-tanned sides. The strips of glutaraldehyde leather (tanned with 15 percent glutaraldehyde) were then retanned with 5, 10, 20 and 40 percent (based on drained weight of leather) of the commercially available powdered extracts, i.e. wattle, sulfited quebracho and chestnut, in a churn over a twenty-four hour period. At regular time intervals the barkometer, temperature and pH of the vegetable tanning bath were measured and the shrinkage temperature (Ts) and the penetration of the extract determined. At the end of the twenty-four hour tanning period, the vegetable retanned strips were washed in running water and stored for future use. Tannin analyses were made on the spent liquors of the sulfited quebracho and chestnut retannage and residual tannin in the liquors was calculated.

RESULTS AND DISCUSSION

A plot of the glutaraldehyde concentration of the tanning liquor as a function of time is shown in Figure 1. In this plot the glutaraldehyde content of the liquor is expressed in terms of fraction of input that was unused. It is noted that

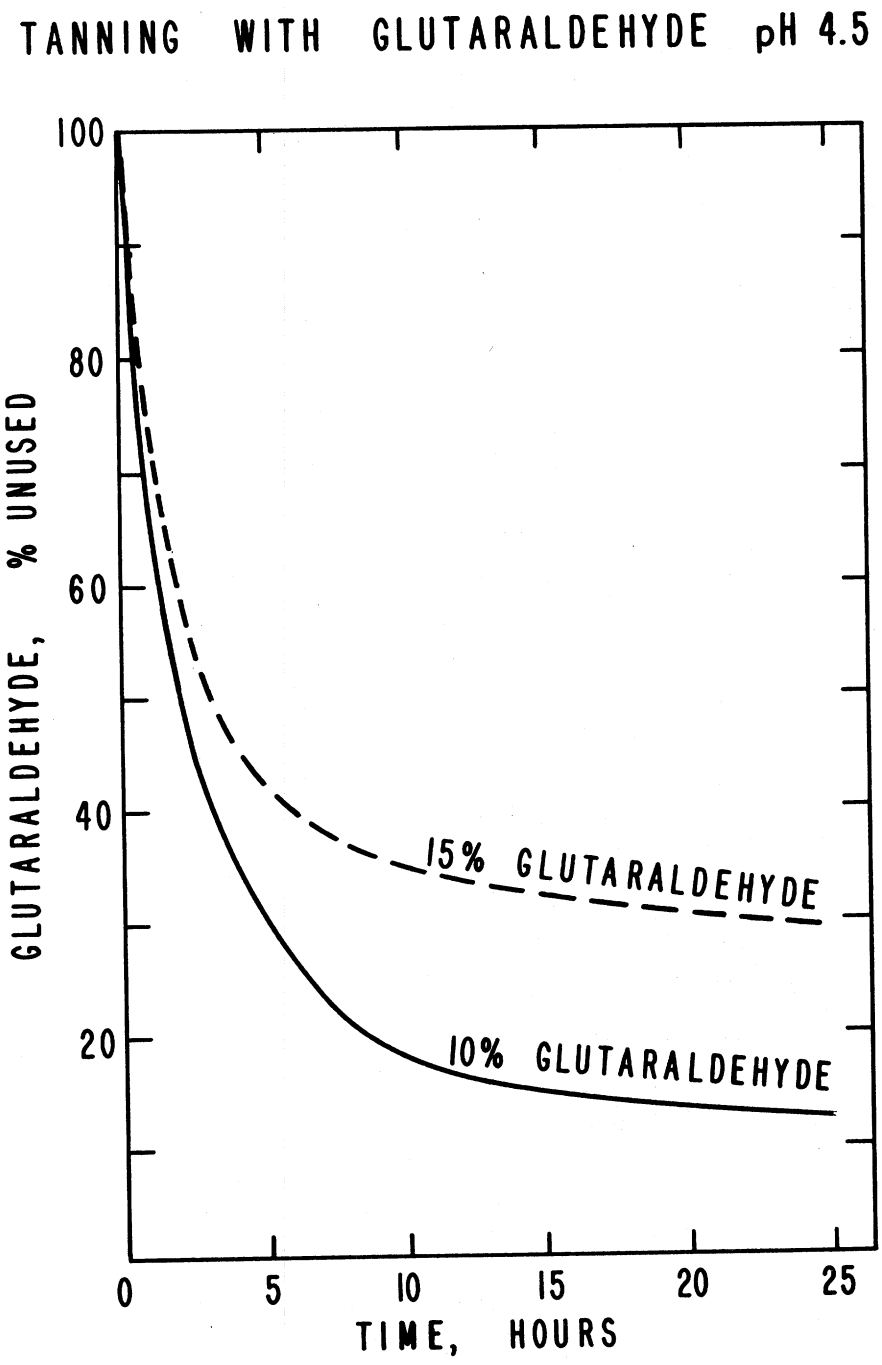

FIGURE 1.—Glutaraldehyde concentration of the tanning liquor as a function of time of tanning at pH 4.5.

after about 24 hours, 13 percent of the glutaraldehyde was not used in the case where 10 percent was offered to the hide as against 29 percent of glutaraldehyde unused when the larger amount was offered. By difference the amount consumed corresponded to 87 and 71 percent respectively in the two cases. These curves showing the rate of absorption of glutaraldehyde from the tanning solution are very similar to those reported earlier for tanning of sheepskins (6, 8). This indicates that full thickness cattlehide was tanned about as rapidly as sheepskins by glutaraldehyde despite the greater thickness of the former.

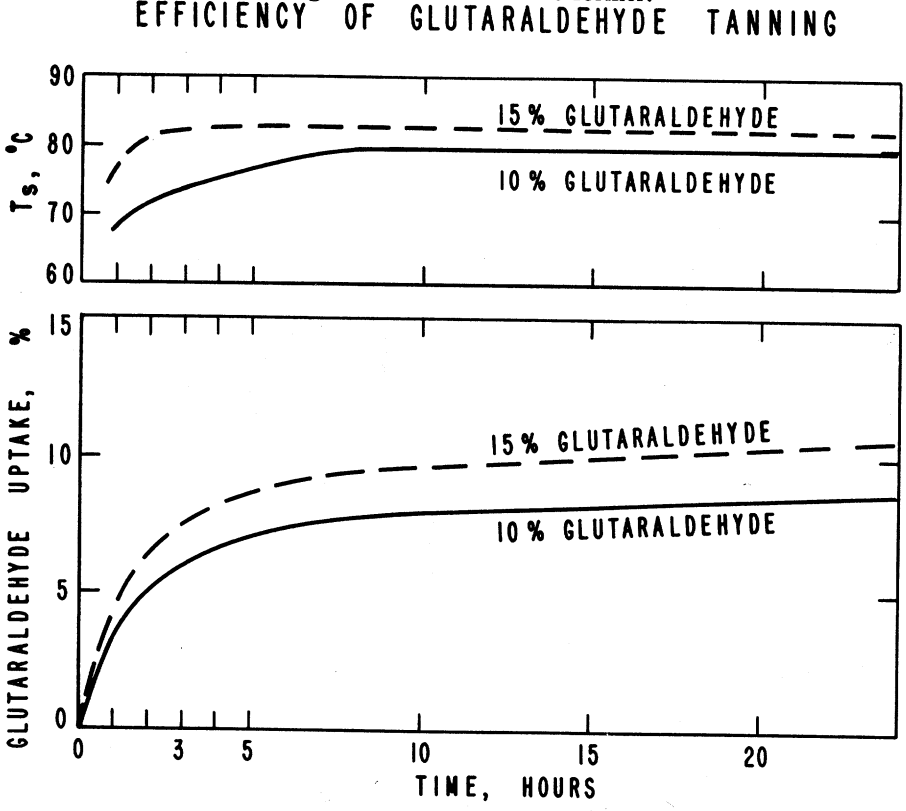

FIGURE 2.—The effect of time on uptake of glutaraldehyde and shrinkage temperature of the leather.

The same data are presented in Figure 2 in a way which is more familiar to the tanner. Here the glutaraldehyde consumed is plotted as percent of the aqueous 25 percent commercial solution (on the pickled hide weight) against time. This shows that uptake of glutaraldehyde at the end of 24 hours was about 8.5 percent when the hide was offered 10 percent, and about 11 percent in the case where 15 percent of the commercial glutaraldehyde solution was offered. Thus while a larger amount of offered glutaraldehyde showed lower

efficiency in consumption, the total uptake was higher. In other words the greater the input the greater is the uptake but at the expense of efficiency in consumption of glutaraldehyde. In both cases it can be seen that after the initial surge the uptake of glutaraldehyde continues, but very slowly and for practical purposes can be considered completed in about eight hours at pH 4.5. The shrinkage temperature data at the top of the graph indicate a similar conclusion. In the case of the higher concentration of glutaraldehyde the shrinkage temperature rapidly rose to its maximum, 83°C. (181°F.), within about two hours. Whereas with the lower amount of glutaraldehyde the Ts rose more gradually, attaining a value of about 80°C. (176°F.) in about eight hours.

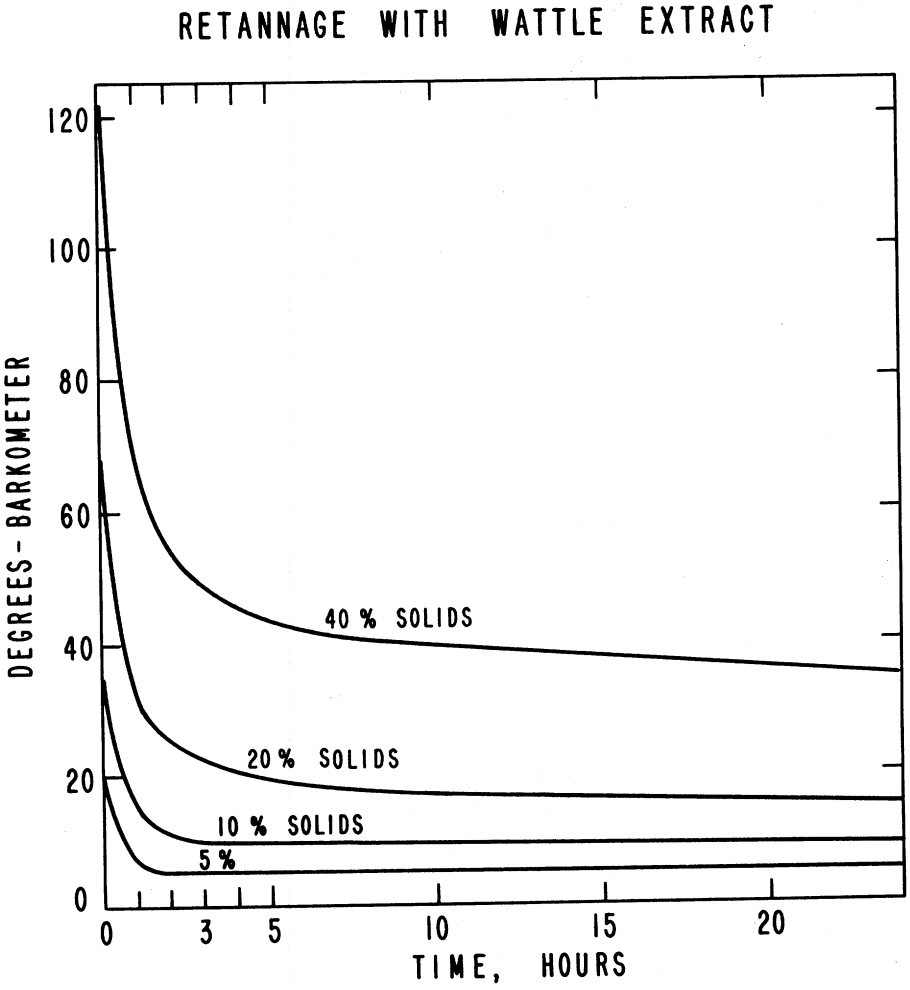

FIGURE 3.—Decrease in barkometer of the extract on retanning glutaraldehyde leather with wattle.

The fall in barkometer strength was measured for each vegetable retannage and the data are summarized in the curves that follow. The decrease in barkometer of the liquor for the retannage with the four different concentrations of powdered wattle extract is shown in Figure 3. In all cases the barkometer dropped rapidly in the early stages of tanning. The decrease in barkometer for the five and ten percent powdered extracts levelled off after two hours of retannage. For the higher concentrations, the barkometer decreased rapidly in the first four hours and levelled off for the remainder of the tanning period.

The data for retannage with sulfited quebracho are shown in Figure 4. The results are very much the same as those for wattle retannage. However, the 5,

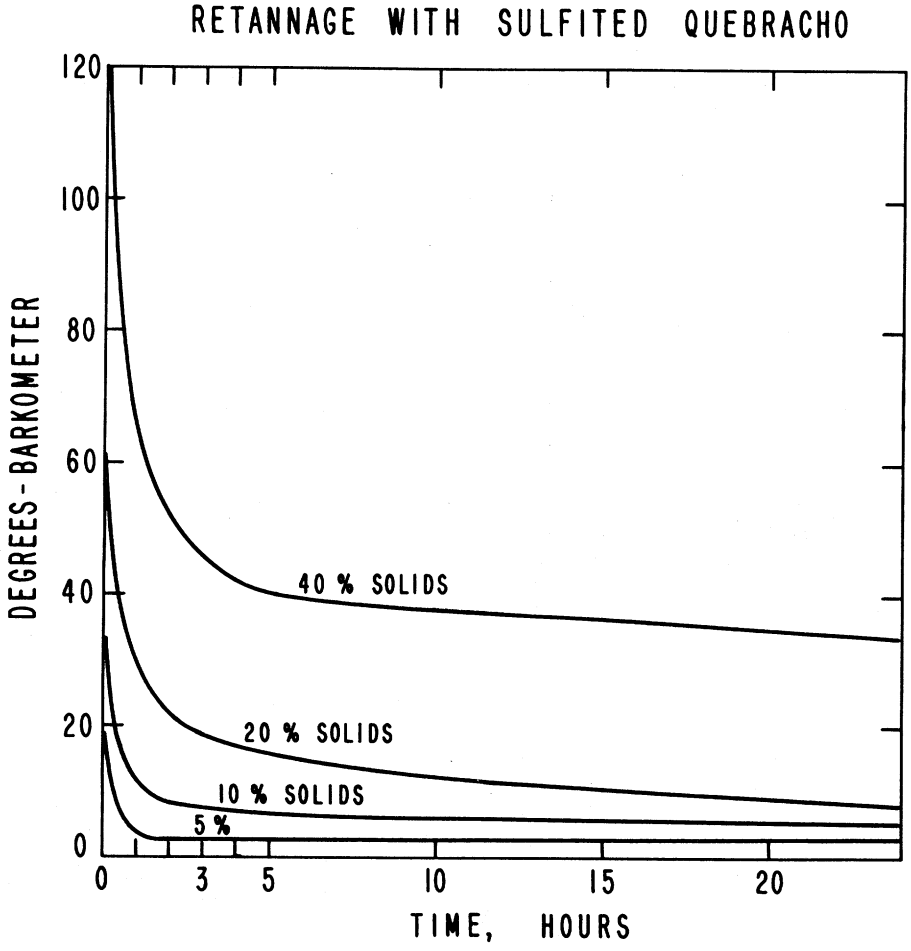

FIGURE 4.—Decrease in barkometer of the extract on retanning glutaraldehyde leather with sulfited quebracho.

10, and 20 percent solids curve for quebracho levelled off at somewhat lower values for barkometer.

Retannage with chestnut is indicated in Figure 5. Again the change in barkometer is rapid resembling that of wattle and sulfited quebracho with only minor differences shown in the 40 percent solids curve which decreased somewhat more slowly. An indication of the rate of uptake of vegetable tannin was also gained by visual examination of a freshly cut cross section. Spotting with ferric chloride aided in estimating penetration. Penetration both from the grain and flesh side was estimated and calculated as percent penetration.

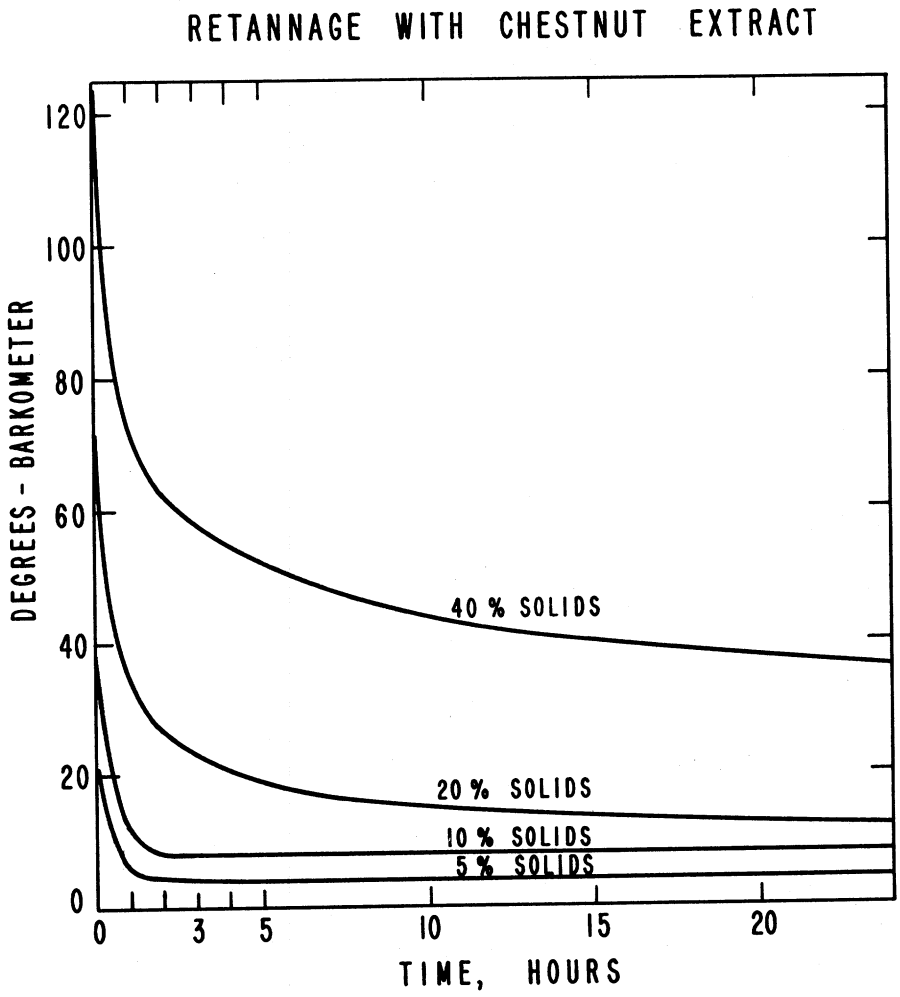

FIGURE 5.—Decrease in barkometer of the extract on retanning glutaraldehyde leather with chestnut.

The data from the retannage of the glutaraldehyde leather with wattle are summarized in Table I. Complete penetration was attained after eight hours at the 20 percent concentration and after two hours at the 40 percent concentration. Complete penetration was not obtained in the cases of the five and ten percent concentrations because insufficient tannin was present. It is noted that penetration occurred more rapidly from the grain side than from the flesh side.

TABLE I

RETANNAGE WITH WATTLE

Powdered Extract %	Time Hours	Barkometer Degrees	Shrinkage Temp., °C.	pH	Penetration, %	
					Grain	Flesh
5	0	20	82	—	0	0
	1	7	83	4.5	20	10
	2	6	84	4.5	25	15
	4	6	84	4.5	25	15
	8	6	83	4.5	30	30
	24	5	83	4.5	40	30
10	0	37	82	—	0	0
	1	14	84	4.6	20	10
	2	12	86	4.6	30	15
	4	10	85	4.6	30	20
	8	10	87	4.6	30	20
	24	9	88	4.6	50	20
20	0	68	82	—	0	0
	1	32	86	4.7	40	20
	2	25	86	4.7	60	20
	4	21	86	4.7	60	20
	8	18	87	4.7	60	30
	24	15	89	4.6	a	—
40	0	122	82	—	0	0
	1	66	87	4.7	40	20
	2	55	87	4.7	60	30
	4	47	88	4.7	a	—
	8	41	87	4.7	a	—
	24	34	91	4.7	a	—

a. Complete penetration had occurred at this point.

Table II summarizes the data on penetration upon retannage with sulfited quebracho. Complete penetration was noted after four hours at the 20 percent concentration level and after two hours at the 40 percent level. In comparison to the previous data on wattle retannage, sulfited quebracho appeared to show a slightly higher rate of penetration than did wattle. From analyses of the spent liquor the efficiency of tanning uptake was almost 100 percent for the 5, 10 and

20 percent concentration levels and about 70 percent at the 40 percent tannin level. Again penetration is more rapid from the grain side as compared to the flesh side.

The data obtained on retannage with chestnut extract are shown in Table III. Penetration of this tannin appeared to be much faster than with wattle and sulfited quebracho. Complete penetration was attained at all levels of tannin concentration, even the five and 10 percent levels which in the case of wattle and sulfited quebracho penetrated only to the extent of 65–70 percent. However

TABLE II

RETANNAGE WITH SULFITED QUEBRACHO

Powdered Extract %	Time Hours	Barkometer Degrees	Shrinkage Temp., °C.	Uptake %	pH	Penetration, %	
						Grain	Flesh
5	0	18	82	—	—	0	0
	1	3	83	—	4.7	20	10
	2	3	84	—	4.7	25	20
	4	2	84	—	4.7	25	25
	8	2	85	—	4.7	30	20
	24	2	86	98	4.7	35	20
10	0	33	82	—	—	0	0
	1	11	85	—	4.7	30	20
	2	9	85	—	4.7	35	20
	4	7	86	—	4.7	40	20
	8	7	86	—	4.7	40	25
	24	5	87	98	4.7	40	25
20	0	61	82	—	—	0	0
	1	28	86	—	5.0	35	20
	2	22	87	—	5.0	50	35
	4	17	90	—	5.0	60	35
	8	13	90	—	5.0	a	—
	24	8	91	94	5.0	a	—
40	0	119	82	—	—	0	0
	1	64	87	—	5.2	45	20
	2	57	89	—	5.2	55	35
	4	42	92	—	5.2	a	—
	8	39	92	—	5.2	a	—
	24	33	93	69	5.2	a	—

a. Complete penetration had occurred at this point.

at the highest tannin content level, chestnut penetrated slighly slower than wattle and sulfited quebracho. Efficiency of tannin uptake was almost 100 percent for the 5, 10, and 20 percent tannin concentration levels and about 80 percent for the 40 percent level. In this case, also, penetration occurred more rapidly from the grain side.

Wilson (17) showed that when untanned steerhide was treated with various tannins sulfited quebracho penetrated most rapidly, next was wattle, with chestnut the slowest penetrating tannin of the three. In our study, as a retannage of glutaraldehyde leather, chestnut appears to penetrate most rapidly of these three.

It is interesting to note the data on the shrinkage temperature (Ts) of the vegetable retanned leathers after twenty-four hours of tanning as shown in the preceding tables. The base stock (glutaraldehyde tanned side) showed an initial Ts of 82°C. The wattle retannage increased the Ts gradually with a maximum of 91°C. (196°F.) being reached at the 40 percent concentration level of tannin. The sulfited quebracho retannage also gradually increased the Ts of the leather with increasing concentration of tannin offered, with a maximum of 93°C. (199°F.) being reached. In the case of the chestnut retannage, however,

TABLE III

RETANNAGE WITH CHESTNUT

Powdered Extract %	Time Hours	Barkometer Degrees	Shrinkage Temp., °C.	Uptake %	pH	Penetration, %	
						Grain	Flesh
5	0	21	82	—	—	0	0
	1	5	82	—	4.0	40	10
	2	4	83	—	4.1	45	35
	4	4	83	—	4.5	45	35
	8	4	85	—	4.3	55	35
	24	4	85	98	4.5	a	—
10	0	38	82	—	—	0	0
	1	11	85	—	4.2	35	25
	2	8	85	—	4.2	45	35
	4	8	85	—	4.3	45	35
	8	8	85	—	4.3	a	—
	24	8	85	98	4.6	a	—
20	0	72	82	—	—	0	0
	1	33	85	—	3.4	35	20
	2	27	85	—	3.5	50	35
	4	21	85	—	3.7	55	30
	8	16	85	—	3.7	a	—
	24	12	85	95	4.0	a	—
40	0	124	82	—	—	0	0
	1	71	85	—	3.2	45	20
	2	62	85	—	3.3	55	25
	4	55	86	—	3.5	55	30
	8	46	86	—	3.6	a	—
	24	36	86	79	3.8	a	—

a. Complete penetration had occurred at this point.

the shrinkage temperature was essentially independent of the tannin concentration level and reached only 86°C. (187°F.) for all four levels of tannin offered.

The vegetable retanned leathers were analyzed for water solubles. This was obtained with the rough leather and the data are given in Table IV. The water solubles were, in general, of the same order of magnitude for all of the retanned leathers; however, the water solubles for the wattle retanned leather were somewhat lower than for sulfited quebracho and chestnut. As expected, the water solubles increased with increasing amount of tannin in the retannage.

TABLE IV

WATER SOLUBLES OF GLUTARALDEHYDE-VEGETABLE RETANNED LEATHERS

Powdered Extract %	Water Solubles, %[a]		
	Wattle	Sulfited Quebracho	Chestnut
5	0.9	1.8	1.8
10	1.5	1.9	3.4
20	3.7	5.6	5.9
40	8.6	11.9	11.5

[a]Twenty-four hour retannage.

To obtain a comparison with conventional vegetable leather, the following experiment was conducted. A pickled full thickness crop was tanned with ten percent glutaraldehyde (25 percent solution) for 24 hours at pH 4.5. The Ts of the glutaraldehyde tanned stock was about 80°C. (176°F.). This side was sent to a tanner for processing to the rough leather stage with his regular sole leather production. The rough glutaraldehyde-vegetable retanned leather gave a value of 11.8 percent water solubles (dry basis) in comparison to 21.3 percent water solubles for this tanner's rough commercial leather, a decrease of almost 50 percent. The Ts of the retanned leather was 86°C. compared to 80–82°C. for the commercial vegetable tanned rough leather.

Another property of interest was the perspiration resistance of the vegetable retanned leathers from the standpoint of insole leather. The method used was the insole leather tester devised by Clarke and Flaharty (18). This method uses a synthetic perspiration composed of sodium chloride (10g), ammonium carbonate (4g), disodium phosphate (1.9g), urea (240g) made up to one liter and pH 7.9, and differs markedly from the method used to evaluate the perspiration resistance of the glutaraldehyde-chrome combination leather, which is intended for upper leather. The results of the test were evaluated by measuring crackiness and grain extension and are summarized in Table V. All of the glutaraldehyde-

vegetable retanned leathers were quite flexible as shown by the data which were characterized by low mandrel size and high grain extension. Actually all of the leather specimens, except those from leathers given the highest level of extract, could be bent double without cracking before being subjected to the action of perspiration. The leather retanned with 40 percent sulfited quebracho was the poorest from crackiness standpoint. Since the leathers being tested were only at a rough leather stage and not bleached, excess tannin on the surface could contribute to the low grain extension in the cases where 40 percent tannin was used. The leathers retanned with ten percent vegetable appeared to be quite resistant to this test and showed only a slight increase in crackiness. The leathers retanned with the higher levels of vegetable tannins, although not as resistant to deterioration, also gave good results in this test. The leathers showed some damage from the test as indicated by the increase in crackiness (higher mandrel, lower grain extension).

TABLE V

PERSPIRATION RESISTANCE OF GLUTARALDEHYDE-VEGETABLE RETANNED LEATHERS

Powdered Extract %	Untreated			Perspiration Treated		
	Thickness Ounces	Mandrel Size	Grain Extension %	Thickness Ounces	Mandrel Size	Grain Extension %
Wattle						
5	11	0	100	12	0	100
10	12	0	100	12	0	100
20	11	0	100	11	3	48
40	12	2	60	12	5	37
Sulfited Quebracho						
5	10	0	100	10	0	100
10	12	0	100	11	0[a]	100
20	14	0[a]	100	14	2	64
40	13	10	25	13	3	51
Chestnut						
5	11	0	100	11	0[a]	100
10	10	0	100	10	2	55
20	14	0[a]	100	14	2	64
40	12	2	60	13	5	38

[a]Cracks at double-fold.

A commercial rough leather sample, thickness of 12 iron showed crackiness at the #7 mandrel, grain extension of 35 percent. The perspiration treated specimen was very stiff, cracked upon slight bending, and had almost zero grain extension.

Nayudamma and Rao (19) have found recently that a tannage of chrome, vegetable and chrome resulted in leathers with improved properties. We were interested in evaluating the effect of a glutaraldehyde, vegetable and glutaraldehyde tannage on the water solubles and shrinkage temperature. For this purpose, wrung pieces of the glutaraldehyde-vegetable retanned leather were tanned once again with 5, 10 and 20 percent of commercial glutaraldehyde solution for 24 hours. The leathers were washed in running water and dried. Water solubles were determined only on those leathers retanned with the 20 and 40 percent level of vegetable tannin. The results are summarized in Table 6. The water solubles prior to the second glutaraldehyde tannage are shown under the column headed 0. It is evident that the glutaraldehyde retannage reduces the water

TABLE VI

WATER SOLUBLES AND SHRINKAGE TEMPERATURE OF GLUTARALDEHYDE-VEGETABLE-GLUTARALDEHYDE TANNAGES

Powdered Extract %	Glutaraldehyde Retannage, %[a]							
	0		5		10		20	
	Water Solubles %	Shrinkage Temp. °C.	Water Solubles %	Shrinkage Temp. °C.	Water Solubles %	Shrinkage Temp. °C.	Water Solubles %	Shrinkage Temp. °C.
Wattle								
5	0.9	83	—	85	—	86	—	86
10	1.5	88	—	87	—	87	—	87
20	3.7	89	2.5	89	3.3	90	3.9	89
40	8.6	91	5.3	96	5.9	96	6.2	96
Sulfited Quebracho								
5	1.8	86	—	84	—	85	—	85
10	1.9	87	—	87	—	88	—	87
20	5.6	91	4.1	97	4.6	97	4.8	97
40	11.9	93	6.9	96	7.1	97	7.3	96
Chestnut								
5	1.8	86	—	86	—	86	—	86
10	3.4	85	—	86	—	87	—	87
20	5.9	85	3.8	89	4.0	88	4.7	88
40	11.5	86	8.0	92	8.0	91	8.1	91

[a]Twenty-four-hour retannage.

solubles by about 30 percent. However, five percent glutaraldehyde seems to be as effective as the 20 percent glutaraldehyde retannage. Water solubles were reduced to about six, seven, and eight percent for the wattle, sulfited quebracho and chestnut retannages, respectively. It is realized that the retannage in aqueous glutaraldehyde may be a factor in the lower water solubles in the retanned leathers. However, as judged from the color of the retanning solutions, removal

of vegetable extract during this treatment was quite low. The shrinkage temperature of the leather is again increased (by about 5°C.) over that of the glutaraldehyde-vegetable tannage.

SUMMARY

A study was made of the use of glutaraldehyde for tanning heavy leather. It was felt desirable to use glutaraldehyde as a pretannage in order to achieve a rapid tannage. Full thickness steerhide was readily pretanned with glutaraldehyde in less than 24 hours at pH of 4.5. Retannage with three vegetable extracts; namely, wattle, sulfited quebracho and chestnut, was studied. Concentrated extracts as high as 120° barkometer were found satisfactory for use. Penetration of the extract was very rapid and complete and was accomplished in about eight hours, or less, depending on concentration and type of extract.

Properties of the leather were improved. Retannage with vegetable extract raised the shrinkage temperature to 86–93°C. (187–193°F.) which is six to 11°C. above the shrinkage temperature of the glutaraldehyde leather, itself. The water solubles of the vegetable-retanned rough leathers were in the range of 8.6 to 11.9 percent. This value was about half that obtained from a conventional rough sole leather. Resistance of the retanned leathers to perspiration was enhanced as determined by an insole perspiration test.

A triple tannage using glutaraldehyde-vegetable-glutaraldehyde also was examined. This combination tannage further increased Ts by about 5°C. and reduced water solubles by about 30 percent, as compared to the glutaraldehyde-vegetable retanned leather.

The above properties imparted by glutaraldehyde to vegetable leather should be of interest in some applications; such as, insole, outsole, harness, and lining leathers.

BIBLIOGRAPHY

1. Gustavson, K. H. *JISLTC,* 24, 377 (1940).
2. McLaughlin, G. D. and Theis, E. R. *"The Chemistry of Leather Manufacture"* (New York: Reinhold Publishing Corp., 1945) 332.
3. Bowes, J. H. in *"Progress in Leather Science: 1920–1945"* (London: British Leather Manufacturer's Research Assoc., 1948) Chap. 25.
4. Gustavson, K. H. *"The Chemistry of Tanning Processes"* (New York: Academic Press, Inc., 1956) 244–78.
5. Mellon, E. F. in *"The Chemistry and Technology of Leather"* (New York: Reinhold Publishing Corp., 1958) Chap. 17.
6. Fein, M. L., Harris, E. H., Jr., Naghski, J., and Filachione, E. M. *JALCA,* **54**, 488 (1959).
7. 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).

8. Filachione, E. M., Fein, M. L., and Harris, E. H., Jr. *JALCA,* **59**, 281 (1964).
9. Fein, M. L., and Filachione, E. M., U. S. Patent 2,941,859, June 21, 1960.
10. Filachione, E. M., Fein, M. L., and Harris, E. H., Jr. *JALCA,* **59**, 378 (1964).
11. France, H. G. *Leather and Shoes,* **153**, 42 (1967).
12. Seligsberger, L., Mann, C. W., and Clayton, H. *JALCA,* **53**, 627 (1958).
13. Beebe, C. W., Happich, M. L., Naghski, J., and Windus, W. *JALCA,* **54**, 628 (1959).
14. Wagoner, J. F., Stemoroski, J. C., Windus, W., and Witham, C. W. *JALCA,* **57**, 302 (1962).
15. Kremen, S. S. *JALCA,* **48**, 333 (1953).
16. Happich, M. L., Palm, W. E., Windus, W., and Naghski, J. *JALCA,* **60**, 223 (1965).
17. Wilson, J. A. *"Modern Practice in Leather Manufacture,"* Reinhold Publishing Co., New York, N. Y., 1941.
18. Clarke, I. D., and Flaharty, R. M. *JALCA,* **49**, 624 (1954).
19. Nayudamma, Y., and Rao, C. K. *Leather Science,* **11**, 447 (1964); Abstracted in *JALCA,* **60**, 464 (1965).

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DISCUSSION

MR. MEO: The leader of the discussion will be John F. Wagoner of Nopco Chemical.

MR. WAGONER: Thank you very much, Mr. Luvisi. I am sure that all of us have grown to recognize and appreciate the high quality of research work and reporting from Dr. Naghski's group at Eastern Regional Laboratories. Certainly, this work of Mr. Luvisi and Dr. Filachione measures up in all respects to that established quality.

This is the kind of work that can conjure up a lot of possibilities. When we consider that they have taken two tanning agents, of quite similar shrink-provoking capabilities, superimposed one upon the other and come up with an increase of eight to ten degrees in the shrink temperature and then, by coming on again with the original tanning agent, are able to effect another five degrees increase, it is certainly very interesting. Also, that when the glutaraldehyde was used as a pretan, the rate of penetration of the chestnut exceeds that of either the wattle or the quebracho.

I think it is significant too, that they have worked with pickled hides. Now, this is not too unusual in laboratory scale work, but, as we all know, the increased availability of hides in the pickled condition, is more evident as more hide processors are working in that direction. Since the handling of pickled stock presents more of a problem to the vegetable tanner than it does to the chrome tanner, it might be of interest if Mr. Luvisi would briefly describe for us how he con-

ditioned the pickled hide, at pH of 4.5, give us any ideas he might have as to how it would be done on a practical scale, and how you would go about it if you were starting with bated hide.

MR. LUVISI: The pickled hide was drummed for 1 hour in a 1:1 float containing 15 percent glutaraldehyde (25 percent solution) and 6 percent salt based on the pickled weight. Anhydrous sodium acetate, 4 percent on the pickled weight, was added, raising the pH from 1.8 to 4.5–4.6.

However, it is not necessary to start with pickled stock. On tanning bated hide, it would be advisable to wash the hide thoroughly, add the salt and then the glutaraldehyde in 3 or 4 equal portions to the salt solution. At the pH of the bated skin, glutaraldehyde would tan rapidly and because of this the addition of glutaraldehyde in 3 or 4 equal feeds might prevent pebbling of the grain.

As far as tannery practice is concerned, our test was, of course, a drum tannage. For sole leather probably a vat system would be preferable.

MR. WAGONER: Do we have any questions from the floor?

DR. PRENTISS (Rohm and Haas Company): It is my understanding that glutaraldehyde's principal reaction in collagen is with the amino residues. If I understand your reaction correctly, you probably have very few of these available for further reaction after the first treatment with glutaraldehyde.

I do know that there is some discussion in the current British Literature as to the actual role of amino groups on the reaction of vegetable tannins with collagen. Would you theorize as to the type of binding mechanism which exists for vegetable tannins in these leathers.

MR. LUVISI: Conceivably the glutaraldehyde-tanned collagen could have aldehyde groups introduced. These could react with the vegetable tannins perhaps in the way formaldehyde does. Formaldehyde itself is quite reactive with wattle and quebracho but not quite as reactive with chestnut. When vegetable tannin is then offered to the glutaraldehyde tanned stock, you may get a reaction between free aldehyde groups and vegetable tan similar to the reaction when formaldehyde tanned leather is retanned with vegetable tannin.

Perhaps Dr. Filachione might want to make some comment.

DR. FILACHIONE: Well, there is one other point related to this. While we are sure the amino group is involved in the fixation of glutaraldehyde, we don't change the basicity of the amino group, therefore we still have a site for fixation of vegetable tannins which are acidic.

Then of course, you also have the peptide linkage involved in the fixation of vegetable tannins by hydrogen bonding. So I don't think that glutaraldehyde, because it reacts with the amino group, is necessarily going to prevent general fixation of vegetable tannin.

MR. BATTLES (A. C. Lawrence): I believe you mentioned that you had one crop finished by a sole leather tanner under commercial conditions. How did this compare for quality with the commercial leather?

MR. LUVISI: Most of the tests we made were carried to rough leather. In one test a glutaraldehyde tanned crop was retanned with vegetable and processed into finished sole leather but no physical tests were made on this. We were mostly interested in the rate of penetration of the vegetable tanning materials, and water solubles, therefore we stopped with rough leather.

MR. BATTLES: Thank you.

DR. TU (Union Carbide): The use of glutaraldehyde seemed to be advantageous; how does it compare with formaldehyde and glyoxal tannages?

MR. LUVISI: Glutaraldehyde tannage gives a more perspiration-resistant leather.

Formaldehyde might do this also, but I doubt whether it would give the same properties as a glutaraldehyde pretannage. At the tanning pH of 4.5, a glutaraldehyde tanned leather has a shrinkage temperature of 82°C. Formaldehyde tanned leather at this pH would have a lower shrinkage temperature and be less stable.

DR. TU: I understand that glutaraldehyde tannage is more stable than formaldehyde tannage because of the difference in reaction reversibility of these aldehydes with collagen. How does glutaraldehyde pretannage compare with formaldehyde pretannage in the vegetable retannage?

MR. LUVISI: Well, glutaraldehyde tanned leather by itself is fairly stable. We have not investigated the formaldehyde pretannage ourselves, perhaps you may have some comment on this.

DR. TU: I believe that glutaraldehyde is more versatile to apply and the resulting vegetable retanned leather should be more stable for the same reason.

MR. WAGONER: Would the pH conditions for optimum tanning with formaldehyde and glutaraldehyde enter into it?

DR. FILACHIONE: Well, with formaldehyde you get a better tannage at high pH. The same thing applies to glutaraldehyde. At lower pH, say 3.5 to 5, we believe that glutaraldehyde is a more effective tanning agent than formaldehyde. Therefore we believe the glutaraldehyde pretannage would be preferable.

MR. WAGONER: We certainly hope that this use of glutaraldehyde as a pretanning and post-tanning is investigated further, on a larger scale, including other vegetable as well as synthetic tanning materials and combinations thereof. Thank you very much, Fred.