

# THE COMPATIBILITY OF GLUTARALDEHYDE AND WATTLE IN DRUM TANNING\*

MURIEL L. HAPPICH, W. E. PALM, W. WINDUS, AND J. NAGHSKI

*Eastern Regional Research Laboratory†  
Philadelphia, Pennsylvania 19118*

## ABSTRACT

Domestic sheepskins were tanned with wattle and glutaraldehyde simultaneously or successively to determine their compatibility during tanning and the properties of the leather after aging. Comparisons were made with wattle and wattle-formaldehyde tannages. Tanning studies indicated that wattle and glutaraldehyde and wattle and formaldehyde are compatible during tanning. Physical tests and a perspiration test indicated that these tanning agents in combination do not cause deterioration of the leather upon aging one year.



## INTRODUCTION

Following the demonstration of the versatile tanning power of glutaraldehyde (1-7) and its increased commercial use, a question arose concerning the compatibility of glutaraldehyde and vegetable tannins.

Formaldehyde, glyoxal and dialdehyde starch have been studied as pretanning agents for vegetable sole leather (8-11). Formaldehyde has been used to retan vegetable-tanned bellies to produce perspiration resistant leather for insoles (12). Other applications have been studied (13, 14). It is known that formaldehyde reacts with certain vegetable tannins to form polymers (15, 16). It is necessary to control the conditions carefully to avoid weakening the leather, and the industry is understandably cautious about the use of a combination vegetable-formaldehyde tannage. It appeared desirable to study the use of glutaraldehyde with vegetable tannins.

## EXPERIMENTAL

A preliminary screening test was made using 10 percent solutions of powdered chestnut, bisulfited-quebracho and wattle tannins separately in beakers. Varying

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

amounts of formaldehyde or glutaraldehyde were added. No precipitate formed from chestnut or bisulfited-quebracho with either aldehyde.

The solution of wattle and formaldehyde became cloudy almost at once, and a heavy precipitate formed overnight. The wattle and glutaraldehyde solution became cloudy in about 3 hours. A moderate amount of precipitate formed overnight, but this was considerably less than that produced by wattle and formaldehyde. Wattle was therefore selected as the tannin to evaluate with formaldehyde and glutaraldehyde in a drum tannage.

**Tanning tests.**—Domestic sheepskins were used for the tanning tests. They were cut down the backbone to permit comparison of opposite sides of the same skin. The left sides, depickled and tanned with 15 percent solid wattle extract at a pH of 4.2–4.5, were the control samples.

The right sides were treated in one of four ways. After depickling, they were tanned with wattle and either glutaraldehyde or formaldehyde, simultaneously or successively. Near the end of tanning, the pH was adjusted on all sides. After tanning, they were washed, fat-liquored, slicked out and tacked to dry. No other finishing was done.

**Simultaneous tanning.**—The following tanning procedure was used for the simultaneous tannages and the wattle controls. The percent of the chemicals is based on the drained pickled weight of the skins.

4 Pickled sheepskin sides	100%
Water	100%
Sodium acetate	1½%
Run 2 hr., pH 4.2–4.5	
Glutaraldehyde (25% soln.)	5%
or	
Formaldehyde (40% Formalin)	1.88%
Run ½ hr.	
3 Wattle feeds, 1 to 1½ hr. apart	
Wattle, each feed	5%
Water, each feed	20%
Run 1 to 1½ hr.	
Sulfuric acid	0.15–0.20%
Water	3%
Run and rest overnight, pH 3.9, T. 87–89°C.	
Final float 1.6:1	
Washed and drained.	

The aldehyde was omitted in the straight wattle tannage, and the first feed of wattle liquor was added at the end of the 2-hour depickling. Two subsequent

feeds of wattle were added at approximately 1½ hour intervals. In all tannages the wattle extract was essentially exhausted after each addition. No precipitate was formed in the liquor. Near the end of the tannage the pH was lowered to 3.9 by the addition of small amounts of sulfuric acid to help fix the tannin and adjust the pH for fat-liquoring. The shrinkage temperature was 87–98°C. (189–192°F.) for the simultaneously-tanned sides and 77–80°C. (171–176°F.) for the wattle-tanned sides.

Recently we tanned sheepskins simultaneously with 15 percent wattle and larger amounts of glutaraldehyde and formalin. Depickling time was ½ hour, and salt was used in the liquor. These leathers have been finished as hat sweat band leather and were considered satisfactory.

**Aldehyde retannages.**—Wattle-tanned sheepskins were retanned with either 5 percent glutaraldehyde or 1.88 percent formalin in a 100 percent float. The temperature of the tanning solution was 130°F., the sheepskin sides were warmed to about 110°F., and there was no adjustment of pH. The retannage was considered to be completed in 2 to 3 hours. The final pH was 3.8, and the final temperature of the solution was approximately 90°F. The shrinkage temperature was 86–91°C. (187–196°F.).

**Fat-liquoring.**—The sheepskins were fat-liquored soon after each tannage with 1 percent raw and 2 percent sulfated neatsfoot oil, based on the drained tanned weight of the skins. The fat liquor was completely exhausted in 1 hour at a liquor pH of 4.2–4.3. The skins were drained, slicked out and tacked to dry.

**Physical tests.**—Shrinkage temperature, tensile strength, slit tear, grain crack and ball burst determinations were made on the tanned sheepskin sides immediately after they were dried and on the same sides one year later. The methods of the ASTM (17, 18) were used for all physical tests except that of shrinkage temperature. Two skins from each tannage were sampled. Six pieces were cut for each test from matched sides as shown in Figure 1.

Three of them, marked with the lower case letters, were used for the original test. The other three, marked with the lower case prime letters, were stored 1 year in a drawer in a room which had a constant temperature around 75°F. for 5 days a week and an uncontrolled temperature over the weekend. The humidity was not controlled during storage. It was felt that these conditions were adequate to approximate those of normal civilian storage. The results for the shrinkage temperatures and all physical tests are given in Table I.

## RESULTS AND DISCUSSION

**Shrinkage temperature.**—The shrinkage temperatures on all samples decreased during storage. The wattle leather lost 3 to 7°C., the wattle-glutaraldehyde leather lost 5 to 7°C. and the wattle-formaldehyde leather lost 5°C.

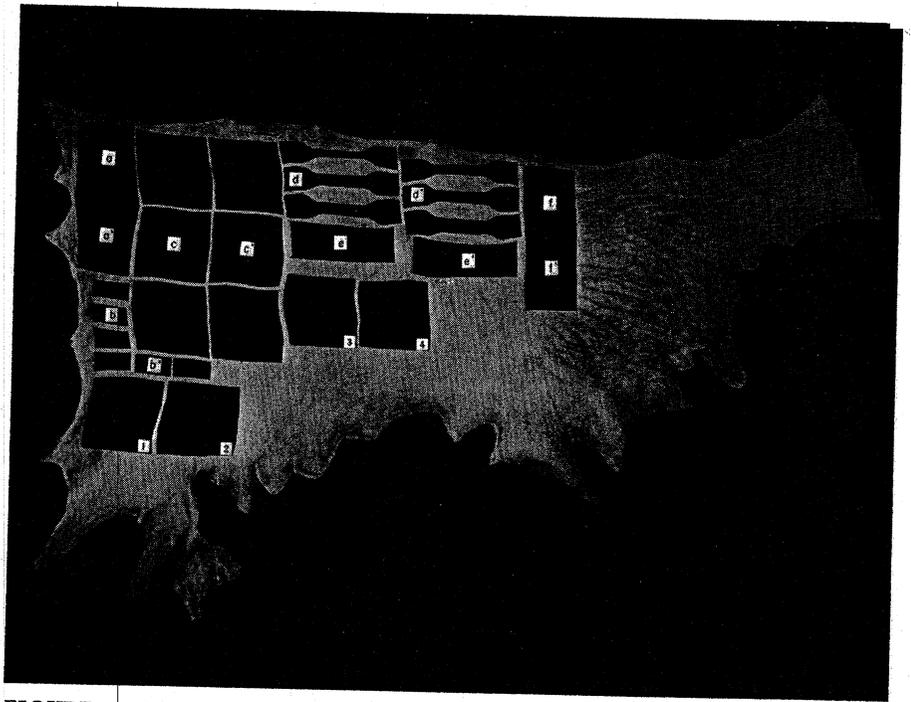


FIGURE 1.—Sheepskin side showing positions sampled for physical tests:  
 a and f—Two 2" x 3" pieces taken for artificial perspiration test on original leather.  
 b—Three specimens taken for slit tear determinations.  
 c—Three specimens taken for grain crack determinations.  
 d—Three specimens taken for tensile strength determinations.  
 e—Three ball burst determinations made on this specimen.  
 Corresponding samples marked a', f', b', c', d' and e' were aged for 1 year before testing.  
 1, 2, 3, 4. These specimens were not used in this study.

**Tensile properties.**—The tensile strength of the leathers was essentially unaffected by one year's aging. It will be noted that the wattle-glutaraldehyde and wattle-formaldehyde leathers had lower tensile strengths at all times than the control leathers tanned with wattle alone. This is not surprising since they are more fully tanned. It is also interesting to note that all the tensile strength measurements after aging, except for one wattle control, are substantially the same as they were on the initial leather. This control shows a loss in tensile strength of about 18 percent and is the only significant loss observed. All other changes were under 8 percent.

The percent elongation observed during the tensile measurements substantiates these results. The greatest loss in stretch was 15 percent of the original and was on the same wattle control; all other changes were under 12 percent. The



elongation data indicate a slight tendency toward stiffening of all leathers during the year.

**Slit tear.**—The slit tear determination has replaced the stitch tear test. This method is designed to measure the load required to tear leather at a slit cut perpendicular to its surface. It is of particular value in estimating the ability of leather to withstand tearing stresses encountered in the manufacture of shoes, garments and upholstered products (17). The slit on these samples was parallel to the backbone in all cases. After 1 year's aging, the load to tear is the same as or greater than it was on the leather when first made. Here again, there were no indications that the leathers were weakened by aging for 1 year.

**Grain crack (Mullen test).**—The data indicate that the grain crack did change on aging. These are average values and show a trend toward a higher load to crack, a 5 percent to 31 percent increase, on the aged wattle-tanned samples. There is, however, a 9 percent lower load to crack on the aged wattle-glutaraldehyde simultaneous tannage. The aged formaldehyde-retan and formaldehyde simultaneous tannages show this same tendency with a 12 percent and 8.5 percent loss, respectively. The percent extension observed during this test showed the greatest variation on the wattle tannages, ranging from 50 percent higher to 18 percent lower. The glutaraldehyde-retan leather showed a 12 percent higher percent extension. The other wattle-aldehyde tannages ranged from 6 percent to 13 percent lower.

The changes on grain crack and percent extension are greater on the leather tanned with wattle alone than on the leathers tanned with wattle and aldehyde. The data indicate that the combination-tanned leathers have aged as well as the wattle-tanned leathers.

**Bursting strength (ball burst method).**—The differences in bursting strength of the original and aged wattle leathers are not large. The greatest change is approximately a 7 percent increase. Differences are less on the wattle-glutaraldehyde and wattle-formaldehyde leathers, showing no more than a 5 percent change. The changes observed here are probably within the experimental error of the method.

**Perspiration test.**—Resistance to artificial perspiration solution was a chemical test used to help evaluate these leathers. This work was started in 1962, and a modified Roddy-Lollar method was used for comparative purposes (4, 19, 20). This method was originally designed for the evaluation of chrome-tanned leathers; however, it has been used successfully for the evaluation of glutaraldehyde and glutaraldehyde-chrome leather (4).

Table II shows the average percentage losses in area sustained by the various leathers when saturated with this artificial perspiration solution and held at 70°C. for 48 hours in a humid atmosphere. Of the fresh or unaged samples only two

TABLE II  
RESULTS OF ARTIFICIAL PERSPIRATION TESTS

Tannage	Before Aging		After Aging	
	Flexibility	Area Loss %	Flexibility	Area Loss %
Wattle control	good	15.0	failed	75.0
Glutaraldehyde-retan	good	5.0	good, except along two edges	18.0
Wattle control	good	6.0	failed	75.0
Glutaraldehyde simultaneous	good	5.0	good	8.0
Wattle control	good	4.0	failed	75.0
Formaldehyde-retan	good	3.5	good	3.5
Wattle control	good	13.0	failed	75.0
Formaldehyde simultaneous	good	8.0	good	8.0

of the four wattle-tanned controls showed any appreciable deterioration as a result of the treatment. The deterioration of these two wattle controls was manifested primarily as a loss in area, the flexibility being unaffected. Aging, on the other hand, had a pronounced effect on the resistance of these leathers to deterioration under the conditions of this test. All of the aged wattle controls became severely shrunken, hard and brittle and lost over 75 percent of their area, when subjected to the perspiration test. The wattle-aldehyde leathers showed good stability. Of the four different leathers only one showed some deterioration. This was the wattle leather retanned with 5 percent glutaraldehyde solution, which showed an 18 percent loss in area and slight hardening along two edges.

In the interpretation of the results on the aged wattle leather it should be borne in mind that the shrinkage temperature has dropped to within a few degrees of the temperature used in the test. Failure in this case may be due to the moist heat, and the result would not be indicative of the resistance of the leather to milder conditions of wear. The stability of the glutaraldehyde-combination-tanned leathers confirm previous results. The advantage of a higher shrinkage temperature than can be obtained with wattle alone is evident.

#### SUMMARY

Glutaraldehyde is compatible with wattle extract in a drum tannage. Since there was little or no precipitate formed between sulfited-quebracho or chestnut extract in beaker tests, it is assumed they would also be compatible with glutaraldehyde, singly or blended, in a drum tannage. Glutaraldehyde, as a retan or as

a simultaneous tannage with wattle, raised the shrinkage temperature of the sheepskin 8–11°C. above that obtained when tanning with wattle alone. The glutaraldehyde-wattle-combination-tanned leathers did not show any significant tendency toward weakness with aging, as measured by the physical tests. This leather aged as well as the wattle controls. Glutaraldehyde-wattle-tanned leather showed better resistance to the modified Roddy-Lollar artificial perspiration test as measured by area than the wattle-tanned leather. This was most evident in the aged leather. Formaldehyde was also compatible with wattle in drum tanning when used under the stated conditions. This leather did not show any significant tendency toward weakness upon aging.

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#### REFERENCES

1. Seligsberger, L., and Sadlier, C. *JALCA*, 52, 2 (1957).
2. Fein, M. L., and Filachione, E. M. *JALCA*, 52, 17 (1957).
3. Fein, M. L., Harris, E. H., Jr., Naghski, J. and Filachione, E. M. *JALCA*, 54, 488 (1959).
4. Filachione, E. M., Fein, M. L., Harris, E. H., 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. Fein, M. L., Filachione, E. M., Naghski, J. and Harris, E. H., Jr. *JALCA*, 58, 202 (1963).
7. Filachione, E. M., Fein, M. L. and Harris, E. H., Jr. *JALCA*, 59, 378 (1964).
8. Seligsberger, L. *Tanning Heavy Leather with Aldehydes*, Footwear and Leather Series Report No. 11, Textile, Clothing and Footwear Division, Quartermaster Research and Engineering Command, Natick, Mass., 1958.
9. Seligsberger, L., Mann, C. W. and Clayton, H. *JALCA*, 53, 627 (1958).
10. Beebe, C. W., Happich, M. L., Naghski, J. and Windus, W. *JALCA*, 54, 628 (1959).
11. Wagoner, J. F., Stemoski, J. C., Windus, W. and Witham, W. C. *JALCA*, 57, 203, 635 (1962).
12. Kremen, S. S. *JALCA*, 48, 333 (1953).
13. Mellon, E. F., in *Chemistry and Technology of Leather*, ed. O'Flaherty, F., Roddy, W. T. and Lollar, R. M., A.C.S. Monograph No. 134, Vol. 2, p. 66, Reinhold Publishing Corp., 1958.
14. Gustavson, K. H. *The Chemistry of Tanning Processes*, p. 339, Academic Press, Inc., 1956.
15. Theis, Edwin R. and Blum, W. A. *JALCA*, 37, 553 (1942).
16. Knowles, E. and White, T. *Adhesives and Resins*, 2, 226–230 and 255–258 (1954).

17. *ASTM, Book of ASTM Standards, 1963 Supplement, Part 6*, D 2207-63T, D 2209-63T, D 2210-63T, D 2211-63T and D 2212-63T.
18. *ASTM, Book of ASTM Standards, 1961, Part 6*, D 1610-60.
19. Roddy, W. T. and Lollar, R. M. *JALCA*, 50, 180 (1955).
20. Happich, W. F. and Windus, W. *JALCA*, 58, 646 (1963).

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#### DISCUSSION

HAROLD R. MILLER (Pfister & Vogel): I think that this paper by Mrs. Happich and her co-workers represents another step in the transition of our industry from an art to a science. The more we know about the products that go into our end product, the better off we are.

I have several questions that I would like to direct to Mrs. Happich. The first one is — what constituent of the wattle sets it apart from quebracho or chestnut in this precipitation test?

MRS. HAPPICH: Wattle tannin is a condensed tannin. It is a complex mixture of polyphenols, and these substances will react with formaldehyde to form resins. Quebracho is also a condensed tannin, and ordinary quebracho will act in this way. However, when it is sulfited, some of the reactive groups are blocked with sulfonic acid groups. This makes it less reactive with formaldehyde. It was not reactive under the conditions we were using.

Chestnut tannin, on the other hand, is a hydrolysable tannin and does not contain the same phenolic mixtures. It does not form resins with formaldehyde.

We have a resin here that we made in the laboratory recently, and brought along for you to see. It is formaldehyde and wattle.

This solid resin was formed in 50 percent wattle solution. It contained one part of formaldehyde to two of wattle, and it "set up" as a solid in about 48 hours.

Our tanning solutions were in the order of 10 percent solutions of wattle, and these did not "set up." On standing a precipitate was formed, but it did not become solid.

MR. MILLER: Thank you. There is one other question before I turn this over to questions from the floor. Is shrinkage the most valid criterion of resistance to deterioration by perspiration? In the method as it is being proposed, grain crack is the number or the figure which is normally used.

MRS. HAPPICH: I understand that grain crack is the criterion in a method for evaluating perspiration resistance recently made tentative by the ASTM-ALCA Joint Committee on Testing.

We did not do grain crack. This would have given us additional information.

WILLIAM T. RODDY (Tanners' Council Laboratory): Would you briefly explain about modification of the Roddy-Lollar test method?

MRS. HAPPICH: It is a low urea perspirant that also contained lactic acid, disodium phosphate and sodium chloride. Samples were soaked for two hours in this solution and then hung in a chamber which was placed in an oven at 70°C. for 48 hours.

This is the perspiration test we have been using and the one used in our laboratory for glutaraldehyde leather and glutaraldehyde and chrome combination leathers.

MR. MILLER: Is that a tightly sealed jar?

MRS. HAPPICH: Yes, tightly sealed. The humidity remains high during the test.

DR. LUDWIG SELIGSBERGER (United States Army Natick Laboratories): We at the Natick Laboratories have for years utilized climatic chambers to study the aging of leather. The chambers are described in Volume II, chapter 30, of the handbook by O'Flaherty, Roddy, and Lollar. With glutaraldehyde leather we found that the wet shrinkage resistance drops considerably even in a temperate summer climate and to a greater extent in a hot humid (tropical) climate whereas the decrease reported here was small because aging conditions were so mild. After three years, for instance, leather with an original shrinkage temperature of 80° had shrinkage temperatures of 62-65°C., without suffering in any way in appearance.

I believe aged leather, after years of use, in spite of this low shrinkage resistance, may still be perspiration resistant, but may not pass the test which is good for fresh leather; in short, this test would not show true resistance to perspiration even after mild aging.

RICHARD T. JONES (A. C. Lawrence Leather Company): Did I understand that the glutaraldehyde retan procedure was conducted at an elevated temperature and, secondly, was any attempt made to determine the glutaraldehyde exhaustion of this procedure?

MRS. HAPPICH: Glutaraldehyde retan was conducted at an elevated temperature, somewhere between 110 and 130°F. During the procedure it dropped to 90°F. This was not a controlled temperature. We did make an attempt to determine the glutaraldehyde in the exhaust liquors but the small amounts of wattle remaining interfered with the iodometric determination for glutaraldehyde.

WALTER MAY (Sandoz, Inc.): Mrs. Happich, going back to the subject of perspiration tests, we noticed in our work that if we dried the samples after the 2-hour immersion in the perspiration solution, we got a far greater destruction of the leather than if we hung it immediately in the humidity chamber. Do you have an explanation for that?

MRS. HAPPICH: We have not tried this test in this way. Did you hang them in your chamber without resoaking them and allow the chamber humidity to re-wet the samples?

MR. MAY: Yes, that is right. We had one test where we proceeded as you did. Samples were soaked in perspiration solution and then transferred to the jars. In the other case we dried the samples after soaking them in perspiration solution and then put them in the dry condition into the humidity chamber. The destruction of the leather was complete in the second instance.

MRS. HAPPICH: I don't know the explanation. Perhaps someone else may have it.

BORIS MONSAROFF (Consultant): May I try to give an explanation. I had a similar experience in testing. We were testing industrial cotton fabrics used for drying of paper during its manufacture. The fabric picks up acid from the pulp and when the concentration of acid reaches 0.5 percent, it starts to deteriorate very rapidly. I developed a process by which I tried to correct these conditions. During the tests on accelerated destruction of fabrics, I noticed that if I dried the samples the tensile strength deteriorated rapidly. If, after treating them with a solution of sulfuric acid, they are washed, the tensile strength is regained. The explanation is quite simple. When you dry the fabric, you increase the concentration of destructive agents which react with the substrate. Therefore it deteriorates more rapidly. If you don't dry it, and you wash it, although originally the reaction is taking place, you bring the sample to tolerable acid concentrations, and the tensile is restored.

DR. FRANK W. PANEPINTO (William Amer Company): May I suggest the possible reason for apparent further destruction of the leather in Mr. May's experiment. As you are evaporating it, you are concentrating the solution; and therefore have a highly concentrated solution of lactic acid and the other products. Under these conditions I would suppose if you had used a concentrated solution in the first place, you might have obtained the same results as Mr. Monsaroff explained.