1032

Tanning Studies With An Epoxy Resin. Preliminary Evaluation of the Leather*

I. D. CLARKE, E. H. HARRIS, JR., and E. M. FILACHIONE

Eastern Regional Research Laboratory†
Philadelphia 18, *Pennsylvania*

ABSTRACT

Steer hide blocks, split to 8 ounces, were tanned with an epoxy resin, Epon 562, and changes in the crust-dry leather relative to acetone-dehydrated stock were noted. The weight and thickness gain and the loss in area were comparable to those noted with chrome-tanned stock. Tanning with the epoxy resin resulted in lower stretch and greater stiffness in flexure than did chrome or vegetable tanning. The epoxy resin tannage also resulted in a greater loss of strength compared with chrome and vegetable tannage. The leather obtained upon tanning with Epon 562 showed reversible shrinkage (Ts 85°C.). The properties discussed above were not significantly altered upon boiling this leather in water for one minute or upon retannage with chrome or vegetable tannin.

INTRODUCTION

A previous paper from this laboratory (1) reported that an epoxy resin was found to react with cowhide and calfskin in an aqueous alkaline suspension to effect a tanning action. The tanning action was accompanied by an elevation of shrinkage temperature and by the unusual property of practically quantitative reversible shrinkage. In view of this unusual property of the leather it was of interest to gather data on the properties of the product obtained by this treatment.

This paper reports the effect on weight, area, thickness, stiffness, strength, and stretch of steer hide caused by tanning with an epoxy resin and also the effect of following this resin tannage with chrome or vegetable retannage. These properties were compared to those of the untanned, acetone-dehydrated hide as the basic reference substance. For purposes of comparison, straight chrome- and vegetable-tanned samples were also included. To simplify these systems it was considered desirable to evaluate the properties after tanning but before oiling and finishing. It should be kept in mind that incorporating oils into the leather would be expected to improve many of its properties.

EXPERIMENTAL

Acetone-dehydrated Hide Material.—The hide material was a steer hide split out of the lime to 9–11 ounces (0.14″–0.17″). It was obtained from a

*Presented in part at the Fifty-first Annual Meeting of the American Leather Chemists Association, Swampscott, Massachusetts, May 22-25, 1955.

†A laboratory of the Eastern Utilization Research Branch, Agricultural Research Service, United States Department of Agriculture.

local tannery in the limed condition and promptly delimed in the laboratory by drumming in two changes of a sodium acetate-acetic acid buffer to a final pH of 5.3. The side was then washed and cut into 12″ x 18″ pieces and dehydrated in three changes of acetone. The pieces, after blotting on towels, were tacked out, covered with towels, and the acetone permitted to evaporate slowly in a fume cupboard. The acetone-dehydrated side was then cut into 50 test blocks each 5 inches square.

Plan of Test.—As the blocks were cut they were numbered in order from tail to head, first in the row along the backbone, then in the 3 following rows toward the belly. A few blocks were discarded because of grub holes or other defects. Each block was numbered in India ink with the block number, the number *1* to *4* at proper locations for the tensile specimens, and the letters *a* to *d* for the burst locations, as shown in Figure 1.

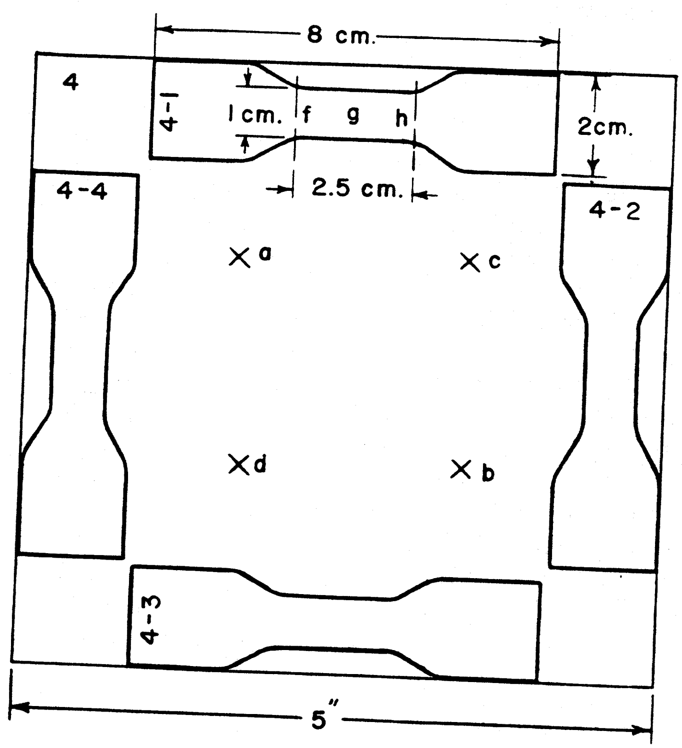

FIGURE 1.—Diagram of a block, numbered as for Block 4, showing location of burst tests and of die-cut tensile specimens.

After conditioning at 50% relative humidity and 73° F. to constant weight, the following measurements were made on each block of acetone-dehydrated stock: (*a*) weight to 0.01 g., (*b*) area with a planimeter, and (*c*) thickness at locations *a*, *b*, *c*, and *d*.

Specimens No. 1 and No. 2 (Figure 1) were then cut off leaving a 4.25″ x 4.25″ square. The thickness of specimens No. 1 and No. 2 was measured at *f* and *h* (Figure 1); also the average thickness was determined from measurements at *f*, *g*, and *h*. Stiffness in flexure at points *f* and *h* was measured on a Tinius Olsen 5-inch-pound tester with a 1-inch-pound load and a 1-inch span, after which tensile strength and stretch were measured on a 100-kg. Schopper tester. The burst strength, using a 0.25″ plunger, was measured at positions *a* and *b* (Figure 1) on the 4.25″ x 4.25″ block.

These tests were carried out in accordance with the official ALCA methods (2) with two exceptions. Stiffness readings were taken when the specimen had been bent through an angle of 10° rather than 50°, and tensile-strength measurements were made on small, 2 x 8-cm. specimens with 1 x 2.5-cm. test portions (Figure 1).

After collecting these data on the acetone-dehydrated stock, the blocks were divided into 10 lots of 5 blocks each (assigned at random), wet back in water, and tanned as described below.

Tanning with Epoxy Resin.—The epoxy resin used in this study was Epon 562*. This resin is stated to be an aliphatic modification of the usual epichlorohydrin and bisphenol-A condensation product (1, 3) with replacement of bisphenol by glycerol (4). Epon 562 is a moderately viscous liquid (viscosity C to F on the Gardner-Holdt scale) having an equivalent weight as an epoxide of 140–165. It apparently is of low molecular weight and slightly soluble in water. Analysis indicated that this resin contained approximately 11% chlorine.

Tanning was carried out at room temperature in bottles gently agitated by rolling on a low-speed jar mill. For the one-day epoxy tannage, one lot (E1) of 5 blocks of the acetone-dehydrated material, amounting to 87 g., was thoroughly wet back in water and then blotted on towels. These blocks were then placed in 870 ml. of an aqueous solution which was 0.2 *M* with respect to sodium carbonate and 10% with respect to sodium sulfate and agitated on the mill. After 2 hours, 43.5 g. of the epoxy resin were added to this sytem, and mixing by rolling on the jar mill was continued for 24 hours. During this time the pH of the solution remained in the range of 10.1 to 10.3. After the one-day treatment, the samples were removed and washed in running tap water for one day.

Other lots of the steer hide were tanned with the epoxy resin as described above for 3 days (E3) and for 5 days (E5), and another lot (E6) was tanned for 5 days, but with 15% sodium sulfate in the solution instead of 10%.

*The mention of specific brands or companies is not to be construed as an endorsement by the United States Department of Agriculture of these brands or companies over those not mentioned.

Still another lot (EB) was boiled in water after tanning as described above for E5.

Two lots were tanned 5 days with epoxy resin and then retanned, one (EV) with a vegetable tan liquor (two-thirds sulfited quebracho and one-third chestnut extract, on the tannin basis), and the other (EC) with a commercial one-bath chrome-tanning agent (Tanolin R).

For purposes of comparison other lots were vegetable-tanned (V), chrome-tanned (C), and chrome-tanned and vegetable-retanned (CV), with the above-mentioned liquors, by methods simulating conventional practice. An untanned lot of the acetone-dehydrated hide served as a control (R).

After tanning and washing, all the blocks were blotted on towels, dried in a current of air for a few hours, then dried to constant weight in a room maintained at 73° F. and 50% relative humidity. During drying the samples were placed occasionally, as necessary, between towels under brass plates to remove large wrinkles and correct curling. Constant weight was reached in 4 or 5 days. The various leathers prepared are shown in Table I.

TABLE I

PROPERTIES OF THE VARIOUS LEATHERS

			Analysis, %*				Weight Yield			
Lot	Tannage	T_s, °C.	Total N	Hide Substance†	Total Ash	pH of Leather	Nitrogen Basis†*	Weight Basis‡	Area Yield‡	Thickness Yield‡
E1	Epon 562, 1 day	85	16.17	90.9	0.51	8.4	1.08	1.12	0.84	1.06
E3	Epon 562, 3 days	84	15.60	87.7	0.55	7.9	1.12	1.14	0.87	1.03
E5	Epon 562, 5 days	85	15.49	87.1	0.67	7.9	1.13	1.15	0.84	1.06
E6**	Epon 562, 5 days**	84	15.41	86.6	0.66	8.2	1.13	1.15	0.87	1.03
EB	Epon 562 as in E5, then leather boiled in H_2O (1 min.)	83	15.31	86.0	0.53	8.2	1.14	1.15	0.83	1.04
EC	Epon 562 as in E5, then chrome-retanned	>100	13.71	77.1	5.21††	3.0	1.28	1.29	0.86	1.04
EV	Epon 562 as in E5, then vegetable-retanned	91	10.31	57.9	0.56	4.9	1.70	1.70	0.97	1.12
C	Chrome-tanned	>100	15.59	87.6	5.15‡‡	3.0	1.12	1.15	0.83	1.07
V	Vegetable-tanned	82	11.52	64.7	0.28	4.4	1.52	1.48	0.93	1.10
CV	Chrome-tanned, vegetable-retanned	>100	12.05	67.7	4.05†††	2.6	1.45	1.51	0.92	1.12
R	Untanned, acetone-dehydrated hide (control)***	60	17.54	98.6	0.31					

* On a moisture-free basis. The moisture content of the leathers ranged from 12 to 15 %.
† Total nitrogen x 5.62.
†* Calculated by dividing % N of raw hide by % N of leather.
‡ Expressed as ratio of the values for the air-dried tanned specimens to those of the raw acetone-dehydrated specimens.
** Tanned with Epon 562 in the presence of 15% instead of 10% aqueous sodium sulfate.
†† Cr_2O_3 content, 4.75% (MFB).
‡‡ Cr_2O_3 content, 5.05% (MFB).
††† Cr_2O_3 content, 3.42% (MFB).
*** Fat content, 0.2%.

Evaluation of the Experimental Leathers.—The epoxy-resin-tanned leathers had shrinkage temperatures of approximately 85° C., and the shrinkage was virtually quantitatively reversible, i. e., the shrunken specimen recovered its original length when cool. Recovery was rapid in cold water and somewhat slower in air. Tanning with this resin resulted in a white leather which was not detanned by treatment with strong acid or alkali, boiling water, or acetone.

Measurements as before were made of the weight and area of each tanned block and of thickness at locations *c* and *d* (Figure 1.) Specimens No. 3 and No. 4 (Figure 1) were cut out with a die and thickness, stiffness, strength, and stretch of the specimens measured in the same manner as for specimens No. 1 and No. 2. Burst strength was measured at positions *c* and *d*. After testing, the specimens were combined by lots and used for chemical analysis. The specimens were ground in a Wiley mill (10-mesh screen) for determination of the total nitrogen (5), total ash, chromium, and pH of the leather.

Tables I to IV summarize the data collected.

RESULTS AND DISCUSSION

Dimensional Changes.—The weight, area, and thickness changes are recorded in Table I as ratios of the values for the tanned specimens to those for the raw acetone-dehydrated specimens. The weight increase or "pickup" by the epoxy resin or chrome tannage was approximately 15%, and by vegetable tannage, 48%. Retanning of epoxy-resin-tanned hide with chrome doubled the pickup, whereas vegetable retannage resulted in a combined pickup of 70%. Vegetable retanning the chrome leather increased its weight by 51% (on the raw hide basis). The yield calculated from the gain in weight agreed remarkably well with that calculated from the nitrogen content.

The area of every block was decreased by tanning. For tannages with the epoxy resin and chrome the area decrease varied from 13 to 17% of the untanned acetone-dehydrated area. For vegetable tannage the decrease was only 7%. Vegetable retannage of either the resin- or chrome- tanned leather resulted in an area comparable to that of straight vegetable tannage.

Tanning increased the thickness of the blocks. The increase was from 3 to 6%, on the raw acetone-dehydrated hide basis, for the epoxy-resin tannage; 7% for chrome tannage; 10% for vegetable tannage; and 12% for vegetable retannage of either epoxy-resin or chrome-tanned skin.

Boiling the epoxy-resin-tanned specimens in water for 1 minute had no effect on weight, area, or thickness.

Stiffness in Flexure.—As shown in Table II, tanning increased stiffness in every case, as might be expected considering the soft nature of the acetone-dehydrated hide and the fact that the tanned pieces were dried without any mechanical working. Tanning with the epoxy resin increased stiffness in

TABLE II

STIFFNESS IN FLEXURE*

	Specimen Cut Parallel to Backbone Line			Specimen Cut Perpendicular to Backbone Line			Average		
Lot†	Raw (R)	Tanned (T)	Ratio T/R	Raw	Tanned	Ratio T/R	Raw	Tanned	Ratio T/R
E1	164.2	327.3	1.99	129.0	291.8	2.26	146.6	309.6	2.11
E3	132.6	411.6	3.10	128.2	376.4	2.93	130.4	394.0	3.02
E5	172.9	378.9	2.19	174.3	301.7	1.73	173.6	339.8	1.96
E6	200.7	292.6	1.46	139.9	286.9	2.05	170.3	289.8	1.70
EB	145.7	451.1	3.10	150.8	330.7	2.19	148.2	390.9	2.64
EC	99.0	123.8	1.25	88.6	148.0	1.67	93.8	135.9	1.53
EV	174.5	261.4	1.50	118.9	290.8	2.45	146.7	276.1	1.88
C	154.6	159.8	1.03	127.9	160.0	1.25	141.2	159.9	1.13
V	127.0	163.6	1.29	126.4	192.6	1.52	126.7	178.1	1.41
CV	95.5	141.9	1.49	104.0	156.6	1.51	99.8	149.2	1.50

*Measured in a Tinius Olsen Tester, 10° deflection, 1-inch span, 1-inch-pound load. Specimen 1 cm. wide.
All values in kilograms per square contimeter.
†For identification of the tannages of the various lots, see Table I.

flexure values 100% or more as compared to 41% for vegetable and 13% for chrome tanning.

Since the untanned specimens were uniformly distributed over the side, they provide information on the variation of stiffness at different locations on the acetone-dehydrated hide, as well as the difference in stiffness between specimens cut parallel and perpendicular to the backbone. Specimens cut parallel to the backbone, were, on the average, 1.14 times as stiff as those cut perpendicular, but since the significance level is 6%, this difference would usually not be considered significant. There was a highly significant difference (0.1 % level) between stiffness values for the various blocks. Those at the neck location were quite stiff as compared with those in the remaining area. Stiffness decreased towards the tail to an area above the rear break, then increased slightly near or at the tail. It also decreased from backbone to belly as a rule, although there were columns in which there was little change or even a partial reversal of this order.

An interesting point with regard to direction of test of the tanned specimens is that all the epoxy-resin-tanned lots were stiffer in the direction parallel to the backbone than in the opposite direction, whereas the chrome- and vegetable-tanned lots including the epoxy-resin-tanned lots retanned with vegetable or chrome, were stiffer in the perpendicular direction.

Tensile and Burst Strength.—Average tensile- and burst-strength values, as well as the strength ratios of tanned to raw skin, are given in Table III. Tannage with the epoxy resin caused the greatest loss of strength, approxi-

TABLE III

BURST AND TENSILE STRENGTH DATA

Lot*	Burst Strength†			Tensile Strength‡		
	Raw (R)	Tanned (T)	Ratio T/R	Raw	Tanned	Ratio T/R
E1	297.8	110.1	0.37	162.15	72.61	0.45
E3	278.8	128.2	0.46	153.91	95.82	0.62
E5	278.4	145.3	0.52	150.90	91.02	0.60
E6	311.6	136.5	0.44	174.97	93.19	0.53
EB	286.9	141.3	0.49	151.14	92.77	0.61
EC	277.7	141.0	0.51	137.66	91.64	0.67
EV	290.1	132.1	0.46	160.54	78.88	0.49
C	264.4	219.2	0.83	158.71	132.05	0.83
V	316.5	302.3	0.96	170.45	152.70	0.90
CV	251.4	221.7	0.88	132.83	103.60	0.78

*For identification of the various tannages, see Table I.
†In kilograms per centimeter of thickness.
‡In kilograms per square centimeter.

mately 40% in tensile and 50% in burst. Vegetable tanning resulted in a 10% loss of tensile and a 4% loss of burst strength and chrome tanning in a 20% loss of each. Increasing the proportion of sodium sulfate from 10 to 15% during the tanning with epoxy resin resulted in a further slight loss of strength. Boiling the epoxy-resin-tanned leather in water for one minute did not alter its strength.

Retanning the epoxy-resin-tanned leather with chrome resulted in a slight improvement in tensile strength but no essential change in burst strength. Vegetable retannage lowered the strength appreciably by either method of testing.

The correlation coefficient, r, for the relation between tensile and burst strength was 0.92, showing that the two test methods measured essentially the same property.

Stretch and Grain Crack.—The data in Table IV show that all the tannages except chrome resulted in lowering of stretch (elongation at break) in comparison with the acetone-dehydrated stock. Chrome leather had the greatest stretch, the epoxy-resin-tanned leather the least, and vegetable leather was intermediate. Retanning with chrome changed the stretch values of the resin-tanned specimens only slightly, whereas retanning with vegetable tannin appreciably lowered them.

A previous publication (6) on sumac-tanned sheepskin skivers showed a very high negative correlation ($r = -0.97$) between stiffness in flexure and stretch. In the present work the correlation coefficient for tensile stretch and stiffness, which were measured on the same specimens, was -0.58. Although

TABLE IV

TENSILE STRETCH AT BREAK AND GRAIN CRACK

Lot*	% Stretch at Break				Ratio‡ T/R	% Stretch at Grain Crack	Grain crack Ratio‡‡
	Raw (R)		Tanned (T)				
	Par.†	Perp†	Par.†	Perp.†			
E1	57.8	66.6	49.8	45.2	0.76	21.7	0.47
E3	59.6	69.4	51.6	47.8	0.77	28.3	0.58
E5	53.4	66.8	48.4	50.8	0.83	36.7	0.74
E6	60.8	71.4	52.0	51.6	0.78	30.3	0.58
EB	57.2	57.4	47.4	52.8	0.87	37.8	0.75
EC	65.4	76.6	54.6	48.6	0.73	32.0	0.62
EV	59.8	64.4	33.4	35.4	0.55	21.0	0.61
C	58.0	65.0	69.4	58.2	1.04	44.6	0.71
V	63.2	62.4	56.6	52.2	0.87	39.6	0.73
CV	62.8	62.2	53.4	48.0	0.81	31.3	0.62

*For identification of the various tannages, see Table I.
†*Par.* indicates specimens were cut parallel to backbone, *Perp.* that they were cut perpendicular.
‡The average of stretch values parallel and perpendicular to backbone were used.
‡‡Expressed as ratio of stretch at grain crack to average stretch at break for the tanned specimens.

this is a significant correlation, it indicates only one-third common elements, and stretch is therefore not a good measure of stiffness.

Table IV also shows the percentage stretch at grain crack and the ratio of this value to the stretch at failure for each lot. Crackiness of the grain decreased as the time of tanning with the epoxy resin was increased from one to five days. The material tanned for five days was almost equivalent to the chrome- or vegetable-tanned skin with respect to grain crackiness. All the retannages increased grain crackiness, as did tannage with the epoxy resin in the presence of 15% instead of 10% sodium sulfate. Boiling the epoxy-resin-tanned specimens in water did not alter the grain crackiness.

Light Fastness.—Stability of the epoxy-resin-tanned material to light was tested by exposing 2 specimens from each lot in a Weather-Ometer under dry conditions (7) and measuring reflectance for tristimulus green light after 0, 6, 24, and 48 hours of exposure. None of the epoxy-resin specimens darkened; rather after 48 hours of exposure the reflectance had increased on the average from 73% to 75%. During this exposure the vegetable-tanned leather first darkened, then bleached; the average reflectance values were 23.2, 12.5, 13.5, and 18.8% respectively for the 4 exposure times.

Effect of Neutralization.—Since tanning with this epoxy resin was carried out in alkaline solution (pH about 10) it was of interest to determine the effect of neutralization on the properties of this leather, particularly its strength. Specimens of the leather were compared with those which were neutralized in a sodium acetate-acetic acid buffer of pH about 5 prior to washing and drying. The results showed that there was no statistically significant difference between the ball-burst strengths of the neutralized and unneutralized specimens. Neutralization resulted in slightly thinner specimens (significant at the 5 or 6% level) and this caused slightly (but not significantly) higher burst values for the neutralized specimens when strength was calculated to unit thickness. The grain appeared to be somewhat less cracky after neutralization.

SUMMARY

Split steer hide was tanned with an epoxy resin, Epon 562, and the changes in the following properties evaluated: weight, area, thickness, stiffness, stretch, and strength. In addition to the absolute values for the various properties, the values after tanning were expressed relative to the corresponding values before tanning, the acetone-dehydrated hide serving as the basic reference material. For purposes of comparison chrome- and vegetable-tanned specimens were included.

The weight and thickness gain and the loss in area resulting upon tanning with the epoxy resin were comparable to those noted with chrome tanning. The increased stiffness in flexure was considerably greater in the case of the epoxy-resin tannage than in the chrome or vegetable tannage. The epoxy-resin tannage also resulted in the highest loss in strength, a 40 to 50% loss in tensile or burst strength as compared with 20 and 10% loss respectively for chrome and vegetable tanning. Neutralization of the epoxy-resin-tanned leather (to pH about 5) did not significantly alter the strength data. Tanning with the epoxy resin resulted in lowering of stretch to a greater extent than did chrome or vegetable tanning. Crackiness of the grain decreased as the time of tanning with the epoxy resin was increased from one to five days. The five-day tanned material was approximately equivalent to the chrome- or vegetable-tanned materials with respect to grain crackiness.

The leathers were all tested in the crust-dry condition. Oiling and finishing would be expected to improve considerably their physical properties, especially grain crackiness.

The leather obtained by tanning with the epoxy resin showed reversible shrinkage (Ts 85° C.). The properties discussed above were not significantly altered upon boiling this leather in water for one minute. The epoxy-resin-tanned material was capable of retannage with chrome or vegetable tannin, but no unusual change in these properties resulted upon such retannage.

ACKNOWLEDGMENT

The authors are grateful to the Shell Chemical Corporation for samples of Epon 562 and to the Diamond Alkali Company for samples of Tanolin R.

The authors are also deeply indebted to Dr. C. L. Ogg and members of the Analytical Chemistry Unit of the Analytical, Physical-Chemical and Physic Section of our Laboratory for the analytical determinations.

REFERENCES

1. Filachione, E. M., and E. H. Harris, Jr., *JALCA*, **51**, 160 (1956).
2. ALCA Provisional Methods, April, 1953.
3. Technical Publication SC:52–31, New York: Shell Chemical Corporation.
4. *Organic Analysis* (New York: Interscience Publishers, Inc., 1953) I, 140.
5. Association of Official Agricultural Chemists. *Official Methods of Analysis*, 8th ed., 1955, p. 805, par. 37.9–37.11.
6. Clarke, I. D., and E. T. Steiner. *JALCA*, **46**, 549 (1951).
7. American Society for Testing Materials, *Standards* 1955, Part 6, p. 1171, Method D–750–55T.