SOLE LEATHER FROM ENZYME-UNHAIRED HIDES

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ABSTRACT

Sole leather of saleable quality has been produced from hides unhaired with enzymes. Since the action of the enzymes leaves the hides flaccid and empty it was found necessary to plump or swell them before putting them into strong vegetable liquors. In these experiments a 24 hour liming process was used for plumping. In addition dialdehyde starch was used as a pretannage on the left bends and shoulders. The corresponding right bends and shoulders were put directly into strong vegetable liquors. The matched bends and shoulders were processed into sole leather at a commercial tannery and the finished leathers were evaluated by chemical and physical tests.

INTRODUCTION

Stringent effluent disposal regulations prompted continued investigations into the use of enzymes for unhairing (1, 2). An earlier commercial process for enzyme unhairing kidskins used an alkaline pretreatment (3, 4). An attempt to eliminate "liming" has led to special problems in the production of quality leathers (5, 6). It appeared to be desirable to evaluate the enzyme unhairing process for the production of sole leather.

The present work differs from the research of Pepper and Wyatt (2) and Roddy, Gilsdorf and Cordon (6) by the use of a (a) 24 hour liming with lime alone after unhairing with enzyme and (b) tannage with concentrated vegetable tanning liquors. Both Pepper and Roddy put the enzyme-unhaired bends into a conventional vegetable tannage. Roddy used an alkaline pretreatment before unhairing. Pepper experimented with and without alkaline pre-swelling before unhairing. He indicated the value of swelling will come after unhairing, preferring a chemical other than lime if possible.

The enzyme-unhaired hides were too flaccid to be in the right condition for vegetable tanning. Preliminary tests using an acidic buffer solution to swell the

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hides gave good results in some instances. However, acid swelling was too difficult to control to be practical. Thus it was decided to evaluate the effect of liming following enzyme unhairing using a small amount of lime in the absence of an inorganic sulfide.

Dialdehyde starch (7) was used primarily, because it hastens penetration and secondly, it was thought that it might contribute resilient firming action to the enzyme-unhaired limed stock. It was used as a pretannage on the left side of each hide. The right side was not pretanned.

PROCEDURE

Twelve heavy hides were obtained from a commercial packer. Six experiments were conducted using two hides each. The hides were soaked for 24 hours in a drum, washed, drained and weighed. The following unhairing liquor (8, 9) was made up. Percents are based on the drained weight of the hides.

2% "M-Zyme"†‡
200% Water warmed to 95°F.
0.1% Solution Dowicide G†
3.0% Borax
pH = 8.9

The hides were warmed with water separately to 90°F. and then put into the unhairing liquor. The drum was turned for 25 minutes at first then for four minutes each hour for seven hours. The drum remained stationary overnight but was turned briefly the following morning and again in the late afternoon. On the morning of the third day the hides were unhaired by the mechanical action of washing in the drum for 10 to 15 minutes (10).

After unhairing, the hides were cut into sides, numbered and then trimmed into bends and shoulders of approximately equal size, 22″ x 44″. The bellies were discarded.

One or two percent lime, in three experiments each, based on the white weight of the hides, was used to plump the bends and shoulders. Two bends and two shoulders were suspended on a frame and placed in a 100 liter vat containing lime for 24 hours with occasional rocking. The pH of the lime liquor was about 12.1. All of the bends and shoulders were partially delimed with two percent ammonium sulfate on the white hide weight for one hour. The hides were washed well after partial deliming.

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

‡"M-Zyme" is the registered trade-mark of Merck & Co., for a proteolytic enzyme preparation whose activity is expressed as 30,000 Keratinase units per milliter.

All of the left bends and shoulders were pretanned with the following dialdehyde starch solution (7) in a 100 liter vat for 48 hours.

Water — 48 l., to be diluted to 90–95 l.	
Sodium sulfate (solution basis)	8 %
Dialdehyde starch (white weight basis)	5 %
Sodium bicarbonate (white weight basis)	6.3%

The sodium sulfate and sodium bicarbonate were dissolved in the water. The dialdehyde starch was slurried with water and added to the solution. The solution was pumped into the vat and diluted to 90–95 l. The pH of the dialdehyde starch solution was 8.2–8.6. It was prepared fresh for each experiment. The pretanned sides were soaked in several changes of water for about one hour before going into the vegetable tan liquor. The washing was done in a vat. The matched right bends and shoulders were not pretanned with dialdehyde starch but were suspended directly after deliming and washing into a concentrated vegetable tan liquor blend (100°Bk.) prepared as follows: 28.1. of chestnut concentrate, 34°Tw., and 25 l. of bisulfited quebracho concentrate, 38°Tw., were diluted to make 90 l. of 100°Bk. solution. The pH was adjusted to 3.7 with lactic acid. Two vats of vegetable tan liquor were prepared, one for the hides pretanned with dialdehyde starch solution, and one for the hides with no pretannage. The vegetable tan liquors were reused throughout the experiment but were strengthened for each tannage to maintain the tannin content. Samples of the fresh and strengthened vegetable tan liquors were taken for analyses. Samples of the sapped vegetable tan liquors were taken after each tannage. The used liquor was strengthened by drawing off 10–12 percent of the volume and adding about 10–12 percent fresh concentrated liquor. The pH was adjusted to approximately 4.0 for each new tannage.

Penetration was completed in five to seven days but the hides were permitted to remain in the vegetable tan liquors for seven days. The tanned bends and shoulders were washed with running water for several hours and treated with 0.1 percent of a disinfectant (BSM 11).† They were sent to a tannery for extracting, tempering and conventional sole leather finishing.

Four composite samples of the finished bends were prepared for chemical analyses. Chemical and physical tests were made on the finished leather according to the official methods of the American Leather Chemists Association (11) and ASTM (12) where possible.

RESULTS AND DISCUSSION

All of the finished leathers were of saleable quality. The general appearance of the leather was good, the color was light tan, the flexibility was moderate and the grain was smooth. An exceptionally smooth grain is a characteristic of enzyme-unhaired hides.

It was thought that the use of dialdehyde starch might overcome some of the intrinsic shortcomings of enzyme unhairing. No definite trends toward a better product were indicated by its use either by chemical or physical tests. However, the DAS pretanned leathers were slightly more flexible and lighter in color than the leathers which were not pretanned. The properties of the finished leathers were characteristic of vegetable-tanned leather.

TABLE I

CHEMICAL ANALYSES OF FINISHED LEATHER*

Sides	2% Lime No Pretannage 1–6 Right	DAS Pretannage 1–6 Left	1% Lime No Pretannage 7–12 Right	DAS Pretannage 7–12 Left
Moisture, %	11.3	11.1	10.5	10.9
Petroleum Ether Extract, %	2.2	2.2	3.9	3.7
Insoluble Ash, %	0.1	0.1	0.1	0.1
Hide Substance, %	36.7	36.2	35.0	35.2
Soluble Matter, %	27.4	27.4	28.9	28.2
Combined Tannin, %	22.3	23.0	21.6	21.9
	100.0	100.0	100.0	100.0
Degree of Tannage	60.8	63.5	61.7	62.2
Soluble Non Tannins, %	17.7	17.2	18.4	18.1
Uncombined Tannins, %	9.7	10.2	10.5	10.1
Total Ash, %	6.5	6.7	7.1	7.0
pH	3.7	3.6	3.6	3.5
Yield, %	80.1	78.3	78.0	77.8

*Four Composite Bend Samples.

Chemical and physical tests showed no appreciable differences between the use of one and two percent lime. Apparently there was sufficient lime in solution to cause the necessary plumping without which the hides feel limp and empty, the penetration of the tanning liquor is hampered and drawn grain is prominent. Results of the chemical analyses are shown in Table I. There was little difference between the leathers which were pretanned with DAS and the leathers which were put directly into vegetable tanning. The chemical data for corresponding left and right sides are practically identical.

Results of physical tests are shown in Table II. The only definite trend is in the results of tensile strength and compressibility. The results for both tests were slightly higher for the sides put directly into the vegetable tan liquor than for the sides pretanned with DAS. The lower tensile strength for the DAS pretanned sides tends to indicate further (7) that DAS has tanning properties. The results

TABLE II

PHYSICAL TESTS OF FINISHED LEATHER

Sides	Tensile Strength[a] PSI	Compressibility[b] %	Grain Crack[c] Mandrel Diam. 16ths. of an in.	Water Absorption[d] Hours ½	2	24	Abrasion Loss[e] %	Gms.
1–6 R	2504	8.0	9	21.5	32.0	50.9	30.6	1.25
1–6 L	2338	7.5	10	23.0	32.4	51.8	32.5	1.32
7–12 R	2859	10.3	9	24.8	37.1	55.9	33.9	1.30
7–12 L	2683	8.7	8	23.9	35.4	53.2	32.8	1.28
Commercial Bends[f] (7)	3410	10.8	8	24.2	41.6	54.4		1.36

[a]ASTM, Book of ASTM Standards, 1963 Supplement, Part 6, D2209-63T, now Part 15, D2209-64. Average of 36 pieces.

[b]ALCA Method E-45. Average of 12 pieces.

[c]ALCA Method E-41 with modified mandrels. Samples ranged between 5.0 and 6.6 mm. Average of 12 pieces, 2 from each of 6 bends, adjacent to A sampling position.

[d]ALCA Method E-30. Reported as percentage of initial weight. Average of 12 pieces.

[e]Measured on a cylinder 8″ in diameter covered with standard abrasive cloth and rotating at 100 r.p.h. Leather pieces held against cloth by a weight of 250 g. Average of 60 pieces.

[f]Average of 4 experiments.

of grain crack, water absorption and abrasion tests are practically the same for both the leather with and without pretannage with only inconsequential differences. All of the results obtained compare favorably with the results of commercially-tanned hides (7).

The enzyme-unhaired hides have the appearance of over-bated stock. There is a tendency of the grain surface of the hide to become marked with small indentations when the grain surface is pressed against another surface. If these marks are not smoothed out before tanning, they are tanned into the leather. Eventually the defect is partially, but not completely, hidden by the finishing processes. The marks appear only on the grain surface. Their cause is unknown.

Another feature of the experiment was the use of concentrated liquors and their reuse (7). In this process concentrated tan liquors were used with success particularly on the hides that were not pretanned with DAS. When the hides were sufficiently plumped, concentrated vegetable tan liquor hastened the penetration and reduced the time required for complete penetration to five–seven days. A conventional rocker system requires 20–30 days in the rocker, followed by extracting and tempering.

Results of analyses for liquors used for hides with no pretannage are shown in Table III. Results of analyses for liquors used for pretanned hides are shown in Table IV. The purity of the liquors decreased with each reuse. The drop in purity varies from 3.4 to 7.7 percent for the liquor used with the DAS pretanned sides and from 3.5 to 5.7 percent for the liquor used for the sides not pretanned with DAS. This may indicate a preferential uptake of tannins as well

TABLE III

ANALYSES OF CONCENTRATED VEGETABLE TANNING LIQUORS

Tannage Right Sides	BK°		% Tannin		% Purity*		pH	
	Fresh	Sap	Fresh	Sap	Fresh	Sap	Fresh	Sap
2% Lime								
1 and 2	103	80	19.26	14.38	78.07	74.62	3.7	4.3
3 and 4	96	78	17.60	13.17	76.72	72.12	3.9	4.5
5 and 6	102	83	17.96	13.44	74.90	69.49	3.9	4.3
1% Lime								
7 and 8	102	82	17.63	12.72	73.18	67.34	3.9	4.2
9 and 10	102	84	17.21	12.78	71.38	66.29	3.9	4.2
11 and 12	103	83	17.14	12.58	70.68	65.01	3.9	4.25

*% Purity = Tannin/Soluble Solids × 100.

TABLE IV

ANALYSES OF CONCENTRATED VEGETABLE TANNING LIQUORS DAS PRETAN

Tannage Left Sides	BK°		% Tannin		% Purity*		pH	
	Fresh	Sap	Fresh	Sap	Fresh	Sap	Fresh	Sap
2% Lime								
1 and 2	103	85	19.00	14.48	76.80	73.43	3.7	4.5
3 and 4	100	88	18.16	13.97	74.37	69.64	3.9	4.6
5 and 6	100	83	16.86	12.93	72.61	66.75	3.9	4.5
1% Lime								
7 and 8	102	87	16.67	12.05	70.13	62.50	3.9	4.3
9 and 10	104	89	16.24	12.22	67.84	61.19	3.9	4.3
11 and 12	106	89	16.53	11.73	67.30	59.63	3.9	4.2

*% Purity = Tannin/Soluble Solids × 100.

as small amounts of salts being carried into the concentrated vegetable liquor from the DAS solution, but it is not excessive. The discarded spent liquor could be used in the preparation of fresh extract. In this way very little tanning liquor would be wasted.

As shown in Table V tannin uptake by the DAS pretanned sides was uniform, ranging from 26.1 grams tannin to 27.5 grams tannin per 100 grams of hide, except for tannage 5 and 6. In this tannage 21.5 grams tannin was taken up by 100 grams of hide.

TABLE V

UPTAKE OF TANNIN FROM VEGETABLE LIQUORS

After Tannage of Sides	Sappage of Tannin from Liquor %	Sappage of Tannin* g.	White Hide Weight g.	Uptake of Tannin/100 g. White Hide g.
		By Dialdehyde Starch Pretanned Sides		
1 and 2	4.52	4068	15404	26.4
3 and 4	4.19	3771	14757	25.6
5 and 6	3.93	3537	16481	21.5
7 and 8	4.62	4158	15559	26.7
9 and 10	4.02	3618	13853	26.1
11 and 12	4.80	4320	15687	27.5
		By Sides Not Pretanned		
1 and 2	4.88	4392	14559	30.2
3 and 4	4.43	3987	14361	27.8
5 and 6	4.52	4068	15692	25.9
7 and 8	4.91	4419	16349	27.0
9 and 10	4.43	3987	15307	26.0
11 and 12	4.56	4104	15459	26.5

*Each figure was obtained from the weight of the total volume of liquor which was 90,000 grams for each tannage and the percent sappage of each liquor.

The sides tanned with concentrated vegetable extract alone (no DAS pretannage) showed high uptake in the first tannage and remarkably uniform uptake in the other five tannages ranging from 25.9 to 27.8 grams tannin per 100 grams of hide. No striking differences in tannin content were noted in the finished leather because any differences between the sides were equalized during extracting and tempering in the tannery.

The yield of the leathers obtained, which is the ratio of the white weight of the hide to the finished weight of the leather, is shown in Table I. The yield is high for all the leathers.

SUMMARY

Hides unhaired with enzymes are capable of producing saleable sole leather. It is strong and serviceable and compares favorably with leather made from lime-unhaired hides. Liming after enzyme unhairing helps to eliminate the flaccid condition of the enzyme-unhaired hides.

The grain surface needs careful attention until it is in either the dialdehyde starch pretanning liquor or the vegetable tan liquor because any marks on the grain side of the delimed hide are tanned into it.

Concentrated liquors can be used for tanning hides with or without a pretannage. They can be reused many times by strengthening to maintain a high purity and tannin content, with very little waste. The dialdehyde starch solution can be reused (13, 14). It was not reused in this series of experiments.

ACKNOWLEDGMENTS

We acknowledge with thanks the assistance of Dr. T. C. Cordon, the Armour Leather Company, for finishing the leathers, W. E. Palm for physical tests and L. W. Adair for assistance with chemical analyses.

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