

# TANNERY-SCALE EVALUATION OF HIDE PRESERVATION BY SULFITE ACETIC ACID APPLIED IN A DRUM AND A HIDE PROCESSOR

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## Abstract

A tannery-scale trial of the sulfite acetic acid method for short-term preservation of hides developed at our laboratory was carried out at the Seton Leather tannery. Fresh, washed, fleshed hides (4,500 lb) were treated in a wooden tannery drum and fresh, washed, unfleshed hides were treated in a lined hide processor in two runs (10,750 and 15,000 lb).

The hides were stored in containers that were lightly covered with plastic for three days at ambient temperatures of approximately 70°F. Microbial counts carried out on samples cut from the hides showed that microbial control was maintained. Hides from the first two tests were processed into shoe upper leather of good quality, but of slightly lower weight than normal production. Washing and addition of alkali before the hides were unhaired and limed corrected this condition in the third test. Control of the odor of sulfur dioxide is necessary for the adoption and practical use of this method of preservation.

## Introduction

Sulfite acetic acid preservation, developed at the Eastern Regional Research Center (1-4), was evaluated on fresh cattlehides at the Seton Leather tannery. Tannery-scale runs were carried out in both a wooden drum and a plastic-lined hide processor. The experimentally preserved hides were held in storage for three days at an ambient temperature of approximately 70°F. Without any preservation, fresh hides held for three days under similar conditions would have a putrid odor, hair slip, grain damage, and bacterial counts in the billions per

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gram of hide (1). The hides were processed into shoe upper leather and evaluated by comparison with leather from the tannery's normal production made from brined or fresh hides. This paper reports on the results of these experimental runs.

## Materials and Methods

*Drum Test.* A drum was charged with 4,500 lb of washed, fleshed fresh hides and a 20 percent float containing 1 percent acetic acid and 1 percent sodium sulfite based on the washed, fleshed weight. Since the drum turned at a high speed (16 rpm), it was necessary to prevent heat buildup in the pack. Therefore the drum was run intermittently on a schedule of 1 min on and 10 min off for a total agitation time of 7 min and a downtime of 70 min.

As the acetic acid was added to the float solution, the heat of reaction resulted in a temperature rise, and the temperature rose still further during the agitation. The temperature and pH of the solution at various points during this process were as follows:

Premix tank (float + 1 percent $\text{Na}_2\text{SO}_3$ )	50°F (10°C)
Premix tank (add 1 percent acetic acid)	54°F (12.2°C), pH 4.3
After first 1-min agitation	58°F (14.4°C)
After third 1-min agitation	58°F (14.4°C), pH 4.25
After seventh 1-min agitation	60°F (15.6°C), pH 4.7

Although this agitation cycle prevented excessive heat buildup, the agitation time was quite short. Considering that a short float was used, a much slower and constant agitation for at least one hr would have been preferable to ensure equilibration of the hides with the treatment solution.

*Hide Processor Test.* Two runs were made in the lined hide processor. In the first, 10,750 lb of fresh, unfleshed hides, which had been washed in the hide processor, were treated. The recirculation capacity of the hide processor required that a 60 percent float be used with this amount of hides. We assumed a 10 percent pickup of water from the washing and used this figure to adjust the float added. This float was kept at a 5 percent acetic acid strength, which amounts to 3 percent acetic acid added based on the weight of the unfleshed hides. One percent  $\text{Na}_2\text{SO}_3$  dissolved in the float was added and the hides were tumbled at 4 rpm for one hr.

The float solution containing the acetic acid and  $\text{Na}_2\text{SO}_3$  was added to the processor from the premix tank. Because of the size of this tank, three additions were necessary, with each containing  $\frac{1}{3}$  of the float water and  $\frac{1}{3}$  the treatment ingredients. The water was added first, then the  $\text{Na}_2\text{SO}_3$  was added and dissolved, and finally the acetic acid was added with constant mixing.

In the next run, 15,000 lb of fresh, unfleshed hides, which had been washed in the hide processor, were treated. A 40 percent float was used in this instance to

meet the recirculation capacity of the processor. The float was also corrected for a 10 percent water pickup in washing the hides. This float was maintained at a 5 percent acetic acid strength, which amounted to a 2 percent acetic acid addition based on the unfleshed hide weight. One percent  $\text{Na}_2\text{SO}_3$  was used and the hides were tumbled at 4 rpm for one hr.

*Hide Handling and Storage After Treatment.* After treatment in either the drum or hide processor, the hides and treatment liquor were dumped into wooden slotted boxes lined with a thin polyethylene bag. The float caused the plastic to stretch out between the slots and it burst or was punctured, allowing the float to run out. The boxes of hides were loosely covered with a layer of plastic and held in this condition for three days. The hides were then processed into upper leather.

The morning after the hides were treated, a number of samples were cut from various ones and transferred to plastic bags. These samples were returned to ERRC and held at room temperature. After three and six days they were observed for signs of microbial growth and assayed for microbial counts to monitor the effects of the preservation on the hides. The hair was checked manually for tightness to pulling.

*Analytical Methodology.* For determinations of microbial counts, 500 ml of sterile water was added to the sample and shaken for 15 min on a reciprocating shaker at approximately 200 rpm. The standard plate count was carried out with serial dilutions from the wash solutions. Samples from each dilution were plated in duplicate on standard plate count agar. The plates were counted after incubation for 72 hr at 30°C.

The 500-ml solution used for bacterial counts (referred to as the bacterial wash solution) was measured for pH.

## Results and Discussion

The hides, after treatment in either the drum or processor were held as described above. The next day these hides had a good appearance. They had a slight odor of vinegar, and, although damp, they were relatively dry and firm.

Test results on samples taken from the hides treated in the drum after three and six days' storage are shown in Table I. Control of microbial growth in the samples after three days' storage is indicated by the relatively low counts. The pH of the bacterial wash solutions are, from our experience, in an acceptable range to control microbial growth in the presence of sulfite. The hair was tight.

Two of the samples, after a six-day hold, had a small visible spot of mold on the flesh side. Before these two samples were tested for microbial count, the contaminated areas were removed. The counts indicated that the growth was confined to those areas where it was visible. The hair was tight and the pH's of the solutions used for bacterial counts were all 5.6, which was too high to maintain further control of microbial contamination on these hide samples under these conditions. In this instance, the higher pH after the six-day storage can be at-

TABLE I  
PRESERVATION DATA ON SAMPLES FROM WASHED, FLESHED  
HIDES<sup>a</sup> TREATED IN TANNING DRUMS

Sample	Bact. Wash pH	Hair Tightness <sup>b</sup>	Bact. / g Hide
Stored 3 days <sup>c</sup>			
1	4.3	+ +	28,000
2	4.9	+ + +	59,000
Stored 6 days <sup>c</sup>			
1	5.6	+ + +	35,000
2 <sup>d</sup>	5.6	+ + +	188,000
3 <sup>d</sup>	5.6	+ + +	82,000

<sup>a</sup> 4,500 pounds.

<sup>b</sup> + + +, tight; + +, intermediate; +, slight resistance.

<sup>c</sup> At ambient temperature.

<sup>d</sup> Growth starting on flesh surface.

tributed to insufficient agitation to allow equilibration between the hides and the treatment solution, the loss of float solution after the hides were dumped, the open condition of hide storage, and the volatility of acetic acid and SO<sub>2</sub>.

The hides treated in the drum were preserved satisfactorily for three days and then were processed into leather. For longer hold times with this system we would recommend a longer agitation time in the drum at a lower speed, or the use of higher concentrations of acetic acid in the treatment float.

Test results on samples treated in the hide processor (10,750 lb) are shown in Table II. These hides were processed into leather after a three-day hold. The samples we held at our laboratory showed no visible signs of growth after three or six days. The relatively low microbial counts on the three- and six-day samples indicated that microbial control was maintained. The hair could be pulled out with a slight resistance to the pull. This is probably not bacterial hair slip, but a reflection of the larger amount of acetic acid used in this run as compared to the drum run; note that after six days of storage the bacterial wash solutions of the samples treated in the hide processor had a lower pH than those treated in the drum. The higher pH (5.6) of one of the three-day samples, resulting in tighter hair, supports this conjecture of the effects of acidity. This sample had a large area of fatty tissue on the flesh side which is a probable explanation for a low pickup of treatment solution.

Shoe upper leather made from the preserved hides was evaluated as good quality, but slightly lower in weight than normal production. The pH's of the preserved hides were lower than those of either brined or fresh hides before

TABLE II

PRESERVATION DATA ON SAMPLES FROM WASHED, UNFLESHED  
HIDES<sup>a</sup> TREATED IN PLASTIC LINED HIDE PROCESSOR

Sample	Bact. Wash pH	Hair Tightness <sup>b</sup>	Bact. / g Hide
Stored 3 days <sup>c</sup>			
1	4.3	+	30,000
2	5.6	+++	148,000
Stored 6 days <sup>c</sup>			
1	4.4	+	26,000
2	4.5	+	22,000

<sup>a</sup> 10,750 pounds.

<sup>b</sup> See footnote b, Table I

<sup>c</sup> At ambient temperature

unhairing and liming, and this could have prevented proper penetration of the lime. Therefore, washing or addition of alkali before these steps might correct the slightly lower weight of the resulting leather. Whatever the cause, such action corrected this problem after the second processor run.

There is also a safety reason for raising the pH of hides treated with an acid sulfite preservation. If sulfhydrate is added to the unhairing solution before the pH is raised with lime, the evolution of toxic hydrogen sulfide gas could occur. Therefore it is essential that this precaution be observed.

We suggest that the hides be transferred to solid containers, rather than the slotted types lined with thin plastic that were used in these studies, to prevent the treatment solution present from draining off. Even with solid containers, the hides would displace much of any solution carried over. However, a small amount would be retained in the interstices of the piled hides and at the surface. The excess solution could be pumped off before the hides were dumped and possibly be recycled. Also, the hide containers should be well covered to prevent or minimize the loss of volatile preservation ingredients.

A major obstacle to adoption and use of the acid sulfite preservation is the problem with odor. We think that this can be overcome by properly designed equipment or modification of the present tanning equipment to treat, transfer, and store hides without releasing volatile constituents.

### Summary and Conclusions

Tests of the sulfite acetic acid short-term preservation were conducted at a tannery. A wooden drum was used to treat 4,500 lb of washed, fleshed hides. A

lined hide processor was used to treat 10,750 and 15,000 lb of washed, unfleshed hides.

The hides were held in storage for three days at room temperature during which time microbial control was maintained. The shoe upper leather resulting from these hides was evaluated as good quality, but slightly lower in weight than normal production. Washing and addition of alkali before the unhairing and liming steps corrected this condition. Control of the odor of SO<sub>2</sub>\* is necessary for the adoption and practical use of this method of preservation.

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