

GASEOUS SULFUR DIOXIDE USED TO PRESERVE HIDES—AN EVALUATION*

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Abstract

Sulfur dioxide is the active preservative of the acid/sulfite method proposed and successfully evaluated by this Center. This report involves direct application of the active ingredient in the gaseous form. The sulfur dioxide was generated by adding various concentrations of NaHSO_3 to an acid solution. Treated hide samples that were stored for up to 28 days were preserved satisfactorily when judged by microbial counts and observation. Acidification of the hide samples before treatment significantly lowered the amount of sulfur dioxide needed for preservation.

Whole cowhides that were treated with 1.32 percent sulfur dioxide (generated from 2.0 percent NaHSO_3) based on hide weight were held in storage for 8 days and for 1 month. Cowhides that were acidified before treatment were treated with 0.33 percent sulfur dioxide (generated from 0.5 percent NaHSO_3) based on hide weight and were held in storage for 8 days. These hides were processed commercially into crust leather of acceptable quality.

Compared to drum salting or brine curing, the direct application of a gas has the advantages of (1) not needing water or agitation and (2) eliminating the high dissolved solids and sodium ion content of beamhouse effluents that would occur if salt-cured hides were used. Relatively small amounts of the preservative are needed and the estimated material costs are small.

Introduction

Extensive studies on the use of a low float acid sulfite treatment as a short term preservation system for animal hides have been reported (1-6). We have: (a) proposed and tested various methods of treatment application that could be used by both large and small operators and with other preservation systems (5),

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(b) defined an optimum preservation as one that results in a "fresh type" hide so as to maintain the many benefits that result from the use of fresh hides, and (c) reported on why dissolved solids and the sodium ion per se are considered serious pollutants and discussed their effects on health, agriculture, and industry (7).

This study presents the results of another approach to the use of an acid sulfite system to preserve hides, namely its application as gaseous sulfur dioxide*. Hydrated sulfur dioxide or sulfurous acid has been known to be a preservative since ancient times. Its use in the food industry depends on its well known properties as an antioxidant, an inhibitor of enzyme activity and microbes, and as a bleaching agent. It is readily available and relatively inexpensive (8). An additional advantage of its use to preserve hides might be to inhibit the oxidation of fat, thus maintaining the quality of byproducts.

Materials and Methods

For small-scale work, samples were cut from fresh, frozen hide pieces. Large-scale experiments were carried out on cowhides obtained and treated within 3 to 4 hr after slaughter. The source of sulfur dioxide used for treating the hides and samples was NaHSO₃.

NaHSO₃ (Baker Analyzed Reagent**) contains 66.3 percent sulfur dioxide by assay. Therefore the theoretical maximum amount of sulfur dioxide available from 1 percent NaHSO₃ is 0.66 percent. In the tables and initially in the text of this study, the concentration of NaHSO₃ used as a source of sulfur dioxide is followed by a figure in parenthesis which refers to this theoretical maximum amount of sulfur dioxide available, *e.g.* 1 percent NaHSO₃ (0.66 percent SO₂), 0.5 percent NaHSO₃ (0.33 percent SO₂), 0.1 percent NaHSO₃ (0.07 percent SO₂).

LABORATORY STUDIES

The sulfur dioxide was generated by adding sodium bisulfite to a solution of 1 ml concentrated sulfuric acid and 2 ml water in 50-ml Erlenmeyer flasks placed in the treatment vessel. In small-scale work, 2 ml of this solution was used for up to 1 g of NaHSO₃, 3 ml for 1.5 g, and 4 ml for 2 g, *i.e.*, 2 ml of acid solution per gram of hide. Hide samples were treated in either desiccators (250 mm ID) or wide-mouth quart Mason jars. In desiccators the samples were hung over plastic supporting rods. In Mason jars the samples were placed on end, usually self-supported or partially supported by the Erlenmeyer flask containing the acid solution. The NaHSO₃ was then added to the acid solution through a long-stem funnel and the container was sealed. When Mason jars were used, a piece of

* Sulfur dioxide is a toxic gas and must be handled carefully.

** Reference to brand or firm name does not constitute endorsement by the U.S. Department of Agriculture over others of a similar nature not mentioned.

doubled Saran wrap was placed between the lid liners and jars to prevent corrosion of the liner. All the samples were held in storage at 30°C.

LARGE-SCALE STUDIES

A 4 × 4 × 8 ft wooden box lined with urethane foam and fitted with wheels was used for large-scale work (Figure 1). Hides were suspended over notched wooden supports. The acid solution to be used for generating the sulfur dioxide was placed in a 4000-ml Pyrex cylindrical container.* Approximately 1350 ml of acid solution per pound of NaHSO₃ was used.

The container was placed in the wooden chamber. A length of 5/8-in. I. D. Tygon tubing led through a stoppered hole in the lid of the chamber to the mouth of the cylinder. A 4000-ml separatory funnel mounted on a support stand was attached to the tubing. The chamber was sealed by taping the lid edges. The NaHSO₃ was added through the separatory funnel in small amounts to allow the gas to be liberated gradually. After an overnight hold the lid was partially removed to allow excess sulfur dioxide to dissipate. The hides were transferred to plastic bags, taped shut, and stored in large fiberglass containers. The gas generation and removal of the lid and hides were done outdoors. Small samples were cut from the hides and placed in weighed Mason jars for microbial counts.

PREACIDIFICATION

To preacidify a hide sample before preservation, the hide sample was placed in a jar containing 2 percent NaHSO₄ and 20 percent water, based on the hide weight, and agitated on a reciprocating shaker at approximately 200 rpm for ½ hr. The sample was removed and drained for 15 min before being treated with sulfur dioxide. Full hides were acidified in a tannery drum, with the same concentrations of NaHSO₄ and water, tumbled at 10 rpm for ½ hr, and then the hides were horsed and drained for 30 min before being treated with sulfur dioxide.

Initially, samples were treated and held in the treatment vessels and were not removed until tested. Later, samples to be tested were held in the treatment vessels overnight and then transferred to a container for storage.

DETERMINATION OF EXCESS SULFUR DIOXIDE

Two desiccators, with volumes of approximately 9 l, were set up with each containing a plastic rack and four samples of hide each. The control desiccator contained 238 g of hide. The other desiccator, which was to have air passed through it, contained 273 g of hide samples. One percent NaHSO₃, based on the hide weight, was introduced to the acid solution in each of the desiccators. The lids were then put in place. The next morning the control samples were transferred to individual jars for storage. The center cork was removed from the lid of the other desiccator and quickly replaced with a cork with glass tubing and

* It is more practical to supply the gas from a cylinder, as has been done in later studies.

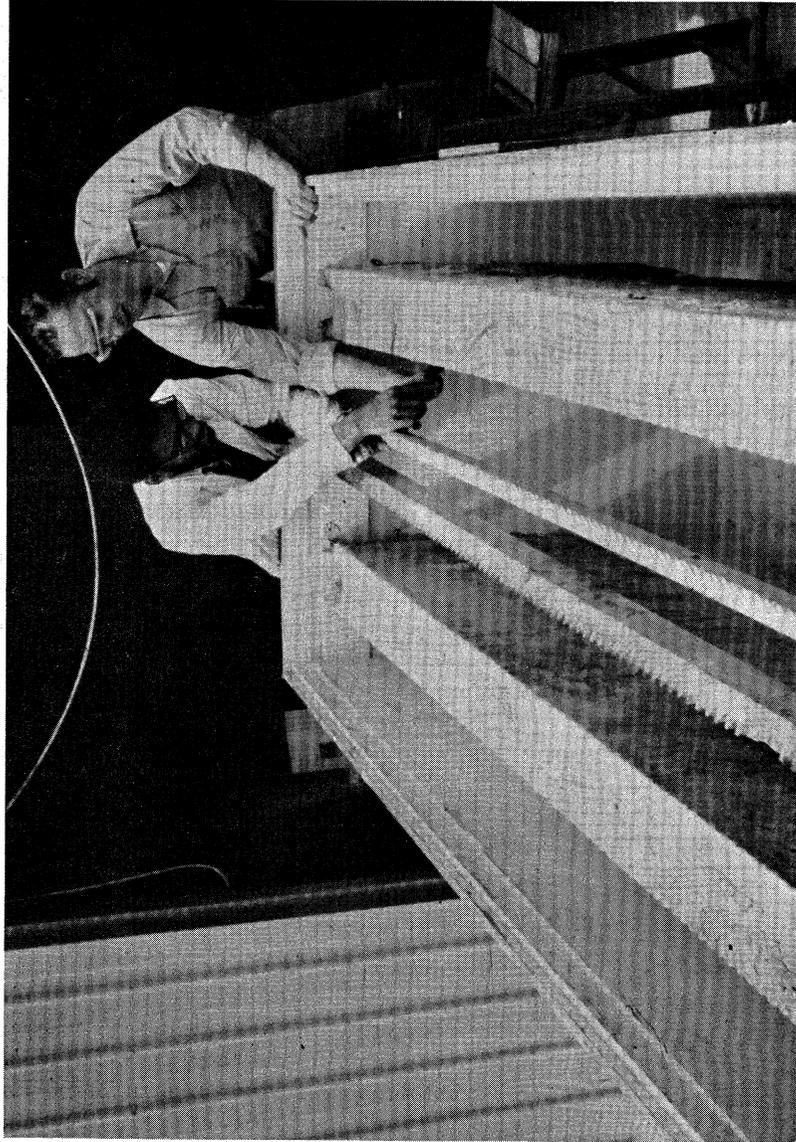


FIGURE 1.—Wooden container for exposing whole hides to sulfur dioxide gas. Container is lined with urethane foam. Two hides are shown draped hair-side down over notched wooden supports.

Tygon tubing attached. The apparatus used is shown in Figure 2. Air was introduced at the top of the desiccator and removed from the bottom. The air-stream was passed through three scrubbers, 125-ml filtering flasks connected in series with each containing 100 ml of an approximately 0.25 N NaOH solution. The rate of airflow was such that the bubbling through the alkaline solutions was as rapid as possible without creating excessive turbulence that would lead to loss of solution from one scrubber to the next. The air was allowed to flow through for 25 min. The alkaline scrubber solutions were acidified and assayed for free SO₂ (9).

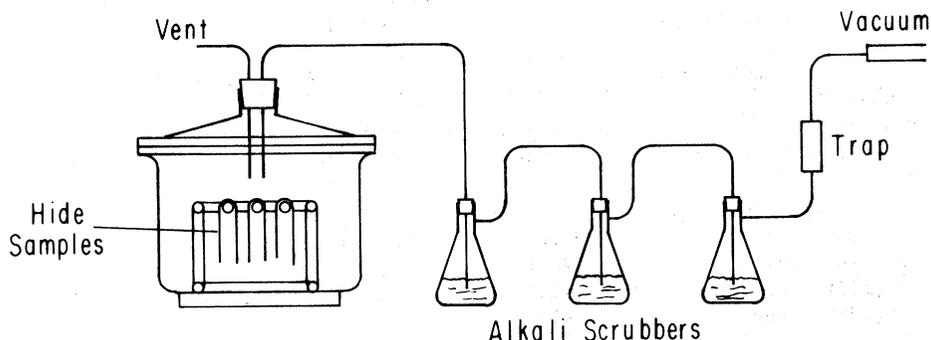


FIGURE 2.—Diagram of method used to remove excess sulfur dioxide from desiccator treatment chamber.

ANALYTICAL METHODOLOGY AND PHYSICAL TESTING

For microbial counts, 500 ml of sterile water was added to each of the sample jars, which were shaken for 15 min on a reciprocating shaker at approximately 200 rpm. Serial dilutions were made from these wash solutions. Samples from each dilution were plated in duplicate on standard plate count agar, and after 48 to 72 hr incubation at 30°C the bacterial colonies were counted.

The pH of the solutions used for bacterial counts (bacterial wash solution) was determined. During some of the small-scale studies, a test for the 1-hr gelatin film activity was run to look for delayed cure in hides, as shown by proteolytic enzyme activity in juice pressed from hide samples. The method was developed by Rolf R. Schmitt and Clara Deasy (10, 11).

The experimental leathers were tested for tensile strength (12) and SATRA grain crack (13, 14). This latter test followed the methods of the International Union of Leather Chemists' Societies, where it is called the "Ball Burst Test." A SATRA extension at grain crack of 7 mm or more should give a leather satisfactory for lasting in most cases. A result less than 6 mm indicates that the leather is unsuitable for lasting.

The leathers were also given a subjective evaluation by the commercial tanner who processed the experimental hides.

Results and Discussion

In the initial experiments, the effect of concentration of sulfur dioxide on the preservation of hide samples stored at 30°C for various time periods was examined. The samples treated were either fresh (unacidified) or fresh pretreated with an acidic solution (acidified) as described above. Table I summarizes the data obtained in these experiments. All these samples were treated

TABLE I
EFFECT OF SULFUR DIOXIDE CONCENTRATION ON PRESERVATION OF HIDE
SAMPLES TREATED AND STORED AT 30°C IN THE SAME VESSEL

Unacidified samples				Acidified samples ^c			
SO ₂ source ^a		Bact. wash ^b	Bact./g	SO ₂ source ^a		Bact. wash ^b	Bact. / g
% NaHSO ₃	SO ₂ odor	pH	hide	% NaHSO ₃	SO ₂ odor	pH	hide
(% SO ₂)				(% SO ₂)			
(6-day storage)				(6-day storage)			
0.5 (0.33)	none	4.6	1.25 × 10 ⁶	0.1 (0.07)	none	3.6	182 × 10 ³
1.0 (0.66)	slight	4.1	48 × 10 ³	0.25 (0.17)	v. slight	3.7	46 × 10 ³
1.5 (0.99)	strong	3.6	16 × 10 ³	0.5 (0.33)	strong	3.3	38 × 10 ³
2.0 (1.32)	strong	3.1	46 × 10 ³	—	—	—	—
(13-day storage)				(13-day storage)			
0.5	visible growth after 8 days			0.1	visible growth after 8 days		
1.0	slight	3.8	175 × 10 ³	0.25	none	3.7	11 × 10 ³
1.5	strong	3.6	45 × 10 ³	0.5	slight	3.6	11 × 10 ³
2.0	strong	3.2	15 × 10 ³	—	—	—	—
(23-day storage)				(27-day storage)			
1.0	none	4.0	182 × 10 ³	0.25	none	3.9	Heavy molds
1.5	v. slight	3.3	46 × 10 ³	0.5	slight	3.4	11 × 10 ³
2.0	strong	2.7	38 × 10 ³	—	—	—	—

^a Theoretical maximum SO₂ when NaHSO₃ (66.3% SO₂) is added to acid solution. Concentration based on sample weight.

^b Solution used for bacterial counts.

^c Sample added to 20% float containing 2% NaHSO₄, shaken ½ hr, and drained 15 min before treatment.

and stored in the same vessels. The treatment vessels were not opened until the samples were to be tested. This prevented loss of any excess gas or reinoculation or contamination of the sample. Low microbial counts were maintained for 23 days by the gas liberated from 1 to 2 percent NaHSO₃ (0.66 to 1.32 percent SO₂). The counts after 6 days of storage even at the 0.5 percent level of NaHSO₃ (0.33 percent SO₂) reflect some control, since untreated samples after 6 days would be putrid, with counts in the range of billions of bacteria per g of hide.

As expected, the pH of the bacterial wash decreased as the concentration of NaHSO₃ used to generate the gas increased, indicating an increased pickup of

sulfur dioxide by the hide samples. This also resulted in an increase in the sulfur dioxide odor, although as storage time increased, the odor decreased.

Table I also shows the effect of acidification before treatment. It was anticipated that with acidification less sulfur dioxide would be needed because acid conditions are necessary for the effectiveness of this system, and that additional sulfur dioxide would not be needed to lower the pH of the hide samples.

Results show that good microbial control was achieved at lower levels of treatment than in previous trials without acidification. The sulfur dioxide released from as little as 0.1 percent NaHSO_3 (0.07 percent SO_2) gave good microbial control for 6 days of storage at 30°C , with no odor of sulfur dioxide. However, after 8 days microbial growth was visible. As the sulfur dioxide level increased, the odor went from none to strong. Microbial control was still good for 13 days of storage at the 0.25 percent and 0.5 percent levels of NaHSO_3 . The sulfur dioxide odor at the 0.25 percent and 0.5 percent levels decreased from very slight and strong in 6 days to none and slight, respectively, in 13 days. After 27 days of storage, microbial control was still evident at the 0.5 percent level of NaHSO_3 . At the 0.25 percent level, the hide sample had no visible growth or off-odor, but the petri plates were overgrown with molds which would probably become visible on the hide sample in another day or so.

In practice, sides treated with gas might not be stored or shipped in the same containers in which they were treated. Therefore, in the next set of experiments, the unacidified and acidified samples were held overnight in the treatment vessel and then transferred to new containers and stored at 30°C . The unacidified hide samples were tested at concentrations of 0.6 to 0.9 percent NaHSO_3 (0.40 to 0.60 percent SO_2) to examine the effects of lower amounts of sulfur dioxide on preservation and odor of sulfur dioxide. The results from these experiments are recorded in Table II.

The unacidified samples showed good microbial control for 28 days at concentrations of 0.7 percent NaHSO_3 or greater. At the 0.6 percent level, microbial control was maintained for 14 days, but after 28 days there was visible growth in a fold of the sample. The odor of sulfur dioxide after storage at 30°C was not noticeable until the concentration of NaHSO_3 exceeded 0.8 percent. At the 0.9 percent level, the odor remained very slight even after 28 days of storage. The much higher pH levels of the bacterial wash explain the absence of a strong odor. They indicate a lower pickup of sulfur dioxide by the samples and also the presence of only very little sulfurous acid, since in this pH range the predominant ion is HSO_3^- .

Table II also shows the results for the preacidified samples that were held overnight in the treatment vessel and then transferred to new containers for storage at 30°C . Samples at the 0.25 percent level were examined after 22 days of storage because previous results had shown a loss of microbial control after 27 days. Preservation, as measured by microbial counts, was still evident after 22 days at 0.25 percent NaHSO_3 and 26 days at the 0.5 percent level. The odor of

TABLE II

EFFECT OF SULFUR DIOXIDE CONCENTRATION ON PRESERVATION OF HIDE SAMPLES TREATED, TRANSFERRED TO NEW VESSELS, AND STORED AT 30°C

Unacidified samples				Acidified samples ^c			
SO ₂ source ^a % NaHSO ₃ (% SO ₂)	SO ₂ odor	Bact. wash ^b pH	Bact. / g hide	SO ₂ source ^a % NaHSO ₃ (% SO ₂)	SO ₂ odor	Bact. wash ^b pH	Bact. / g hide
(7-day storage)				(7-day storage)			
0.6 (0.40)	none	5.2	36 × 10 ³	0.25 (0.17)	slight	3.6	4 × 10 ³
0.7 (0.47)	none	4.8	5 × 10 ³	0.5 (0.33)	strong	3.3	8 × 10 ³
0.8 (0.53)	none	4.6	11 × 10 ³	—	—	—	—
0.9 (0.60)	v. slight	4.3	11 × 10 ³	—	—	—	—
(14-day storage)				(14-day storage)			
0.6	none	4.9	10 × 10 ³	0.25	none	3.6	6 × 10 ³
0.7	none	4.6	6 × 10 ³	0.5	slight	3.6	6 × 10 ³
0.8	none	4.3	6 × 10 ³	—	—	—	—
0.9	v. slight	4.1	3 × 10 ³	—	—	—	—
(28-day storage)				(22-day storage)			
0.6	visible growth	—	—	0.25	none	3.6	8 × 10 ³
0.7	none	4.7	7 × 10 ³	(26-day storage)			
0.8	none	4.4	6 × 10 ³	0.5	none	3.6	4 × 10 ³
0.9	v. slight	4.6	6 × 10 ³	—	—	—	—

^a Theoretical maximum SO₂ when NaHSO₃ (66.3% SO₂) is added to acid solution. Concentration based on sample weight.

^b Solution used for bacterial counts.

^c Samples added to 20% float containing 2% NaHSO₃, shaken ½ hr, and drained 15 min before treatment.

sulfur dioxide after 7 days of storage at 30°C was slight at the 0.25 percent level and strong at the 0.5 percent level; as storage time increased, the odor became less noticeable.

Further tests were made on the unacidified sample at the 0.5 percent NaHSO₃ level and the acidified samples at the 0.1 percent NaHSO₃ level, and microbial counts were checked after 3, 5, 7, and 9 days. Although samples at these concentrations begin to show loss of microbial control after approximately 5 to 7 days, they do have potential for relatively short-term microbial control of up to 3 days under the conditions of the experiment. Eight hide samples were treated at each concentration level, with 4 samples in each desiccator. The samples were held overnight and then transferred to Mason jars and stored at 30°C. The results are shown in Table III.

The unacidified samples show that microbial control was maintained up to 5 days. After 7 days, one sample showed visible growth and the other began to show an increase in bacterial numbers. After 9 days both samples showed visible growth. The acidified samples showed low microbial counts for 7 days, but one

TABLE III

EFFECT OF LOW LEVELS OF SULFUR DIOXIDE ON PRESERVATION OF HIDE
 SAMPLES TREATED, THEN TRANSFERRED TO NEW VESSELS, AND STORED AT 30°C

SO ₂ source ^a — 0.5% NaHSO ₃ (0.33% SO ₂)			SO ₂ source ^a — 0.1% NaHSO ₃ (0.07% SO ₂)		
Unacidified Samples			Acidified Samples ^c		
Storage time (days)	Bact. Wash ^b pH	Bact./g hide	Storage time (days)	Bact. Wash ^b pH	Bact./g hide
3	5.0	15 × 10 ³	3	3.7	2 × 10 ³
3	4.6	14 × 10 ³	3	3.6	2 × 10 ³
5	5.1	70 × 10 ³	5	3.5	5 × 10 ²
5	4.9	12 × 10 ³	5	3.6	5 × 10 ²
7	Visible growth		7	3.8	4 × 10 ³
7	4.7	225 × 10 ³	7	3.7	52 × 10 ³
9	visible growth		9	visible growth	
9	visible growth		9	3.7	15 × 10 ³

^a Theoretical maximum SO₂ when NaHSO₃ (66.3% SO₂) is added to acid solution. Concentration based on sample weight.

^b Solution used for bacterial counts.

^c Sample added to 20% float containing 2% NaHSO₄, shaken ½ hr, and drained 15 min before treatment.

showed visible growth after 9 days. The gelatin film activity was zero for the unacidified and acidified samples tested, and no sulfur dioxide odor was noted after treatment and overnight hold or after storage in this experiment. The fact that in these tests acidification and treatment with this relatively low level of sulfur dioxide reduced the microbial numbers, and maintained these low counts for up to 5 days, suggests that such a process has a potential for preserving hides for 3-day storage.

The sulfur dioxide odor at many of the concentrations tested either disappeared or became weaker as storage time increased. Results from treating groups of four unacidified 100-g hide samples in desiccators and holding them in the treatment vessel overnight, indicated that the sulfur dioxide odor became very slightly noticeable at the 0.7 percent level of NaHSO₃. As the treatment concentrations increased, the odor of sulfur dioxide, as expected, became stronger.

It was also of interest to explore the possibility of reducing the odor by removing the excess sulfur dioxide and flushing it out of the treatment vessel with air. In addition, it was important to determine how the removal of excess sulfur dioxide, as defined by odor reduction, would affect the preservation. It was decided that the level of treatment for this test should be the sulfur dioxide evolved from 1 percent NaHSO₃, since under the conditions of the experiments, this is in excess of that needed for microbial control and gives a moderately

noticeable odor of sulfur dioxide after an overnight hold in the treatment vessel.

Four hide samples were placed in each of two desiccators for this treatment. One of these two sets of four constituted the control samples, and after being held overnight, they were transferred to jars for storage at 30°C. There was a noticeable odor of sulfur dioxide in the treatment vessel. The other set of samples were aerated for 25 min by passing air through the desiccator and then through three alkaline scrubbers. The apparatus used to sweep out and trap the excess sulfur dioxide and the method of measuring it have already been described. After the aeration, the desiccator lid was removed to allow transfer of the samples to storage jars; there was no noticeable sulfur dioxide odor at this point.

The alkaline scrubber solutions were assayed for free sulfur dioxide. The assay showed 21.8 mg of sulfur dioxide in the first scrubber and essentially none in the second and third scrubbers. The volume of the desiccator used for treatment was approximately 9 l. If we assume the sulfur dioxide recovered was contained in this volume, then the excess sulfur dioxide was 21.8 mg per 9 l or 2.4 ppm per 273 g of hide sample.

The results in Table IV show that the control and aerated samples from this experiment are comparable in terms of microbial count. This count remained low and the pH remained relatively constant over the 28-day storage period. None of the samples showed any gelatin film activity. The sulfur dioxide odor of the control samples was slightly noticeable after 8 and 14 days of storage but

TABLE IV

EFFECT OF FLUSHING OUT EXCESS SULFUR DIOXIDE WITH AIR

Sample ^a	Storage time ^b days	SO ₂ odor	Bact. wash ^c pH	Bacteria/g hide
Flushed	8	none	4.05	4 × 10 ³
Control	8	slight	3.9	3 × 10 ³
Flushed	14	none	4.1	3 × 10 ³
Control	14	slight	4.1	2 × 10 ³
Flushed	22	none	4.1	4 × 10 ³
Control	22	none	4.0	4 × 10 ³
Flushed	28	none	4.1	4 × 10 ³
Control	28	none	4.0	2 × 10 ³

^a Flushed with air after treatment with 1% NaHSO₃ (66.3%SO₂); control samples not flushed.

^b After treatment, samples transferred to new vessels for storage at 30°C.

^c Solution used for bacterial counts.

disappeared after 22 and 28 days of storage. The aerated samples had no noticeable odor of sulfur dioxide at any of the time intervals tested. These data show that, under the conditions used in this experiment: (1) excess sulfur dioxide as defined by odor can be swept out of the treatment chamber, and (2) this procedure does not affect the preservation of the hide as measured by microbial count and gelatin film activity. More experimentation will be needed to confirm these small-scale findings.

The next step was to test the gas treatment on whole hides. Cowhides obtained immediately after slaughter and used in the unfleshed "as received" condition were treated in the large wooden chamber described earlier (Figure 1). Two hides were treated in the fresh condition by the gas evolved from 2 percent NaHSO₃, and two hides were acidified first and then treated with the gas evolved from 0.5 percent NaHSO₃. After treatment, the samples were held overnight and then the lid was carefully removed from the treatment chamber to allow the excess sulfur dioxide gas to escape. At both concentrations, the sulfur dioxide

TABLE V
PHYSICAL TEST DATA ON GARMENT LIGHT SHOE UPPER LEATHER
MADE FROM COWHIDES PRESERVED WITH SULFUR DIOXIDE GAS

Condition of hide	Hide		Leather				
	SO ₂ source ^a	Days stored before tanning ^c	Side	Tensile Characteristics ^b		SATRA grain crack	
	% NaHSO ₃ (%SO ₂)			Elongation	Tensile strength	Extension	Breakload
				%	psi	mm	kg
Fresh	2.0 (1.32)	8	left	47.00	2340	8.66	26
			right	47.00	2575	8.79	26
			left	43.00	1720	8.56	25
			right	47.00	2440	9.08	32
Acidified	0.5 (0.33)	8	left	not recovered			
			right	50.00	2810	8.40	26
			left	47.00	2010	8.71	20
			right	46.00	1930	9.30	24
Fresh	2.0 (1.32)	30	left	32.00	1817	8.42	24
			right	35.00	2556	8.99	31
			left	41.00	1275	9.70	31
			right	51.00	1835	8.05	19

^a Theoretical maximum SO₂ when NaHSO₃ (66.3%) is added to acid solution. Concentration based on sample weight.

^b Average of 3 values, run parallel to backbone.

odor after the overnight holds was strong, but it appeared to be less at the 0.5 percent NaHSO_3 level. The hides were sealed in plastic bags, and the bags were sealed in fiberglass containers and stored for 8 days at ambient conditions. Two additional fresh cowhides were also treated with 2 percent NaHSO_3 and stored for 30 days to test extended preservation. Tests on all the hides after the indicated storage periods showed that the bacterial wash pH's ranged from 3.0 to 3.4 and that microbial control was good (bacterial counts ranged from 3,000 to 80,000 per gram of hide). A strong sulfur dioxide odor persisted throughout the storage periods.

The hides, which were in good condition and appeared much like fresh ones, were sided and taken to a tannery for processing to garment light shoe upper leather. The sides were tested for physical characteristics, with the results as shown in Table V. The tensile strength values for all the sides except one ranged from 1720 to 2810 psi. All the SATRA grain crack extension values were above 8 mm, so the leathers should have good lasting properties. Leathers prepared from the unacidified and acidified hides showed no obvious differences. The tanner judged all the leathers to be equal to or better than normal production.

Summary and Conclusions

Results have shown that cowhides can be preserved satisfactorily with sulfur dioxide for at least 30 days at ambient temperature. The preserved hides, much like fresh hides in appearance, were processed commercially into acceptable leather. Small-scale work suggests that the odor of sulfur dioxide can be controlled to some extent and that there is also a lessening or disappearance of noticeable odor during storage, particularly when lower levels of sulfur dioxide are used.

To this point, preservations of 2 to 3 days with the additional advantage of control of sulfur dioxide odor might be practical to some users. This potential has been shown by exposing hide samples overnight to relatively low levels of sulfur dioxide. The samples showed negligible sulfur dioxide odor when transferred from the treatment container to storage containers and microbial growth was controlled for 5 days. This latter point is important because fail-safe operation or reasonable reliability for 2- to 3-day preservation should provide an additional 48-hr leeway.

A small-scale experiment has also shown that when slight excesses of sulfur dioxide were used, as noted by odor after holding overnight, the excess could be removed by flushing the system with air. This procedure did not affect the preservation characteristics of the treatment as measured by microbial count, gelatin film activity, pH, and comparison with control samples. More work will be needed to confirm these small-scale studies.

Acidifying the hide to reduce the sulfur dioxide required can be accomplished in a wash that should lower the hide's pH to 5.0 or less. The optimum substrate for preservation by sulfur dioxide gas would be a hide that has been chilled, fleshed, demanured, and washed. Fleshing and trimming lower the weight of the hide to be preserved, and washing and demanuring lower the microbial load on the hide.

While the use of gaseous sulfur dioxide offers definite advantages as a hide preservative, it must be handled carefully. Sulfur dioxide is a toxic gas and, as with the acid sulfite system, the application of gaseous sulfur dioxide will depend on the development of a closed system to treat, transfer, and store the hides.

Since hides preserved with sulfur dioxide are on the acid side it is important to raise their pH before unhairing and liming. This is necessary because some tanners add sulfhydrate to unhairing solutions before they add lime, and an acid pH at this point would cause evolution of hydrogen sulfide. Therefore it is important to wash and add alkali to elevate the pH of the hides. This information was gained from a cooperative study on the acid sulfite preservation with S. B. Foote (4).

The material costs of treating hides with sulfur dioxide gas are relatively low. Assuming that a 60-pound hide could be preserved with the sulfur dioxide evolved from 0.5 to 2.0 percent NaHSO_3 (0.33 to 1.32 percent SO_2), that 100 percent of the theoretical sulfur dioxide is available and that the gas costs 10 cents per pound, the material cost would be from 2.0 to 7.9 cents per hide. Acidification of the hide before treatment lowers the material cost of the sulfur dioxide to 1 to 2 cents per hide, plus the cost of acidification. Although only estimates, these figures give some indication of the relatively low material cost of this preservative.

These preservations were carried out with no agitation or water, thus conserving energy and water and adding no weight to the hide. The treated hide is a "fresh type." It can be processed with or as a fresh hide; it should have the same byproduct uses as fresh hide; and it provides the same advantages as a fresh hide from the environmental standpoint, since the high dissolved solids and sodium ion pollution that result from the processing of hides preserved by NaCl are eliminated. These are additional economic advantages to be considered in the use of sulfur dioxide gas as a preservative.

The varied sizes and differing requirements of potential users of a preservation system make it seem likely that a variety of preservation methods and means of application will be needed. Our laboratory is working to meet these needs.

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