

**PROGRESS ON THE USE OF GASEOUS SULFUR DIOXIDE
TO PRESERVE HIDES.
THE EFFECT OF CONCENTRATION
AND EXPOSURE TIME***

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Abstract

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Previous studies showing that gaseous sulfur dioxide can be used to preserve freshly flayed hides for at least 28 days have been continued. The advantages of this preservation procedure are that it reduces dissolved salt pollution in tannery effluents and requires no water or agitation. In this study, the effect of time of exposure to various concentrations of sulfur dioxide based on the hide weight was examined. Hide samples exposed to approximately 0.33, 0.5, and 0.66 percent sulfur dioxide from 0.5 hr to 20 hr and stored at 86°F were adequately preserved for 3 to 28 days and in some cases up to 17 + weeks. Preservation was judged by microbial counts, 1-hr gelatin film test, and observation. Unfleshed cowhides that were exposed to 0.66 percent sulfur dioxide for 3 and 6 hr were preserved for 14 and 21 days, respectively, and produced acceptable leather when tanned in a commercial tannery.

Factors that are important to the preservation of fresh hides with this gas are discussed.

Introduction

Sulfur dioxide has been shown to be an effective hide preservative. Hides exposed for approximately 20 hr to the SO₂ evolved from 2.0 percent NaHSO₃ (1.32 percent SO₂) were preserved for 28 days and produced acceptable leather when processed in a commercial tannery. Relatively small amounts of the gas are needed and the estimated material costs are low (1). The advantages of preserving hides by exposure to gaseous sulfur dioxide are: 1) not needing water or agitation, and 2) elimination of the high dissolved solids and sodium ion content from beamhouse and curing plant effluents that would occur if salt-cured hides were used. The disadvantage of using sulfur dioxide is that it is a toxic gas and therefore must be handled carefully.

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Sulfur dioxide is reported to serve a greater variety of purposes than any other single food additive. It is used as a preservative for fruits, vegetables, meats, fish, and alcoholic beverages. It reduces or prevents microbiological spoilage, and also acts as a reducing agent and antioxidant (2, 3). Recently scientists at the USDA's Northern Regional Research Center, reported on the use of sulfur dioxide in the ambient air drying of corn and received EPA approval for corn so treated to be used for animal feed. (4, 5).

This paper presents the results of a study on the effect of time of exposure to various concentrations of sulfur dioxide on hide preservation.

Materials and Methods

For small-scale work, samples were cut from fresh, frozen hide pieces. Large-scale experiments were carried out on cowhides obtained immediately after slaughter and treated within 3 to 4 hr. The source of sulfur dioxide used for treating the hide samples was NaHSO_3 (Baker Analyzed Reagent*). When hides were treated, the gaseous sulfur dioxide was added from a lecture bottle.

NaHSO_3 contains 66.3 percent sulfur dioxide by assay. In the tables, and initially in the text, the concentrations of NaHSO_3 used as a source of sulfur dioxide are followed by a figure in parenthesis which refers to the theoretical maximum amount of sulfur dioxide available, e.g., 1 percent NaHSO_3 (0.66 percent SO_2), 0.5 percent NaHSO_3 (0.33 percent SO_2), etc. The amount of NaHSO_3 was based on the weight of the hide to be treated.

Laboratory Studies. The sulfur dioxide was generated by adding NaHSO_3 to a solution of 1 volume of concentrated sulfuric acid (96.3%) plus 2 volumes of water contained in a 50 ml Erlenmeyer flask placed in a treatment vessel. Two ml of this solution was used for up to 1g of NaHSO_3 and for more than 1g, 2 ml of solution was used per gram. Hide samples were treated in desiccators (250 mm I.D.). Plastic racks were constructed to fit into the desiccators and the hide samples were draped over supporting rods on these racks. The NaHSO_3 was then added to the acid solution through a long-stemmed funnel and the container was sealed. After the samples had been exposed to the sulfur dioxide for the prescribed time, they were transferred to mason jars, sealed, and held in storage at 30°C. A double thickness of Saran wrap was placed between the lid liners and jars to prevent corrosion of the liner.

Large-Scale Study. The hides were treated with gaseous dioxide in a large 4' x 4' x 8' plywood box fitted with wheels and lined with urethane foam panels. The hides were hung hair side down over notched, wooden 2" x 4" supports. A lid was placed on the box and the edges were taped. The SO_2 was added from a lecture bottle through Tygon tubing which led to a trap and then into the box. The

*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.

percent SO_2 used was based on the weight of the hides to be treated. The amount of gas added was determined by weighing the lecture bottle before and during gas addition. An exit tube led from the box to a bubbler containing water to detect the buildup of pressure and to relieve any excess pressure. It took about 30 min to add the gas. The lecture bottle must be warmed by immersing in warm water (not to exceed 125°F) to overcome the cooling effect of the effluent gas. There was no evidence of pressure buildup in the container as indicated by gas bubbling through the water in the exit trap in any of our large-scale tests.

After the designated exposure time, the lid was partially removed and then totally removed to allow the excess gas to dissipate. (This latter procedure should be done out-doors and with adequate ventilation because sulfur dioxide is a toxic and irritating gas.) The hides were transferred manually to fiberglass boxes using one box per hide. The lid was put on and the edges were taped. In later studies, the treated hides were first put into large polyethylene bags which were sealed and then transferred to the fiberglass boxes for storage. The storage temperature was approximately 70°F . Before the hides were taken to the tannery for processing, samples were cut from the edges, and transferred to weighed mason jars. These samples were used for the 1-hr gelatin film test and microbial counts.

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's of the solutions used for bacterial counts (bacterial wash solution) were determined. During some of the small-scale studies, the 1-hr gelatin film activity test of Schmitt and Deasy (6, 7) was run to look for delayed cure in the hides. The test determines proteolytic enzyme activity in juice pressed from hide samples.

The experimental leathers (garment light shoe upper leather) were tested for tensile strength (8) and SATRA grain crack (9, 10). 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 quality evaluation by the commercial tanner who processed the experimental hides.

It is important to note that the pH of the SO_2 treated hides will need to be raised before processing. If sulfides are added to the unhairing solution before the pH is raised with lime, the evolution of toxic hydrogen sulfide could occur. Therefore, it is essential that this precaution be observed.

Results

Hide samples which were exposed overnight (≈ 20 hr) to the levels of SO_2 evolved from 1.0 and 0.75 percent NaHSO_3 (0.66 percent and 0.50 percent SO_2) were preserved for at least 28 days on the basis of microbial counts (1). Table I lists the effects of shorter times of exposure to these levels of SO_2 in terms of

TABLE I
EFFECT OF SULFUR DIOXIDE CONCENTRATION AND EXPOSURE TIME ON
PRESERVATION OF HIDE SAMPLES STORED IN GLASS JARS AT 30°C

Time of exposure (hr)	Storage time (days)	1.0% NaHSO_3 (0.66% SO_2) ³		0.75% NaHSO_3 (0.5% SO_2) ³		Time of exposure (hr)	Storage time (days)	0.50% NaHSO_3 (0.33% SO_2) ³	
		Bact. wash pH	Bact./g hide x 10 ³	Bact. wash pH	Bact./g hide x 10 ³			Bact. wash pH	Bact./g hide x 10 ³
6	8	4.9/4.5 ^a	17/15			20	3	5.0/4.6	15/14
	14	4.1/3.8	8/14	4.1	35		5	5.1/4.9	70/12
	21	3.8/4.1	17/15	4.1/4.4	15/4		7	Visible Growth	
	28	4.1/4.1	4/19	4.2/4.1	61/3	8	3	4.7	19
3	8	4.9/4.1	26/20	4.3/4.4	5/9		5	5.0	35
	14	3.9/4.0	20/18	4.6/4.5	18/10		7	Visible Growth	
	21	4.0/3.8	2/11	4.4/4.4	14/9	6	3	4.8	54
	28	3.7/3.9	2/8	4.4/4.4	5/7		5	4.9	41
1	7	5.0/4.7	19/28	4.5/5.1	16/6		7	Visible Growth	
	14	4.6/4.5	20/20	4.3/4.5	4/11	4	3	5.3	34,000
	21	4.4/4.7	19/25	4.4/4.8	6/34		5	Visible Growth	
	28	4.3/4.3	19/20	Visible Growth		2	3	5.3	87,000
0.5	7	5.1/5.0	15/6				5	Visible Growth	
	14	4.5/4.7	12/28						
	21	Visible Growth							

^aResults from two samples

microbial counts, pH, and the 1-hr gelatin film activity (GFA) tests. This experiment was set up to cover a 28-day preservation period and the results show that a number of samples were still under effective microbial control when the experiment was terminated. Hide samples that were exposed for only 1 hr to the SO_2 evolved from 1.0 percent NaHSO_3 were preserved for at least 28 days (28+). The data in Table I demonstrate the excellent control of microbes and proteolytic enzyme activity that were obtained. At the 0.5 percent NaHSO_3 (0.33 percent SO_2) level of treatment however, the maximum preservation time that could be attained was 5 days even after a 20-hr exposure time.

Table II summarizes the data from Table I as well as the results from a following experiment which examined the long-term preservation potentials of these conditions of treatment. Based on the results from the first experiment, hide samples were exposed for 1 and 3 hr or for 3 hr to the SO₂ evolved from 1 percent NaHSO₃ or 0.75 percent NaHSO₃, respectively. The samples were tested periodically for microbial numbers and GFA and showed that a 3-hr exposure at either concentration of SO₂ resulted in control of microbial numbers and proteolytic enzymes for 120 days.

TABLE II
EFFECT OF SULFUR DIOXIDE CONCENTRATION
AND TIME OF EXPOSURE ON THE DURATION OF
MICROBIAL AND PROTEASE CONTROL ^a

SO ₂ source % NaHSO ₃ (% SO ₂) ³	1.0 (0.66)	0.75 (0.50)	0.50 (0.33)	1.0 (0.66)	0.75 (0.50)
Time of exposure (hrs)	Length of preservation (days)				
	Table I (summary) ^b			Long term exp. (summary)	
0.5	14	*	*	*	*
1	28 +	21	*	56	*
2	*	*	3	*	*
3	28 +	28 +	*	122 +	120
4	*	28 +	5		
6	28 +	28 +	5		
8	*	*	5		
20	*	*	5		

^a 1 hr gelatin film activity on all samples = 0.

^b Test terminated after 28 days.

*Not tested.

These experimental results on hide samples indicate that it is possible to achieve extended or long-term preservation by a relatively short exposure to an excess of gaseous SO₂. The SO₂ is defined subjectively as in excess when it can be detected readily by odor after hide samples are held in the gas overnight (20 hr). In addition, experimental evidence has shown that this is sufficient SO₂ to control microbial numbers for 28 days. By this definition the SO₂ evolved from 0.75 percent NaHSO₃ might be considered a lower limit (1).

When hide samples were exposed for varying periods of time to the SO_2 evolved from 0.5 percent NaHSO_3 , the maximum time that microbial control could be maintained was 5 days. This point was reached after a 6-hr exposure and increasing the exposure to 20 hr did not increase the preservation time beyond 5 days under the conditions of this experiment. Even when hide samples were treated and stored in the same container, this pattern of microbial control was maintained (1).

The odor of SO_2 after an overnight exposure of hide samples to this concentration of SO_2 was fleeting or unnoticeable. This was interpreted as an indication that the SO_2 was not in excess. Therefore, as might be expected, a limiting factor for extended preservation was insufficient SO_2 . This experiment and other experimental evidence support the qualitative detection of SO_2 that we have proposed as a method of estimating whether sufficient SO_2 is available for an extended preservation of 28 days.

The next series of experiments were carried out on fresh cowhides that were treated with 0.66 percent SO_2 supplied from a lecture bottle as described in the Materials and Methods section. After these hides were exposed for 1, 3, or 6 hr to this concentration of SO_2 , they were transferred directly to fiberglass boxes which were then covered, sealed, and stored at ambient temperatures.

The data collected from this experiment on hides numbered 1 through 8 is listed in Table III. A minimum of 3 hr exposure was needed under the conditions described to give a satisfactory 7-day preservation based on odor, observation, microbial counts, a 1-hr GFA, and the commercial acceptability of the leather. Hides exposed for 6 hr were preserved satisfactorily on this basis for at least 21 days.

Hides numbered 1 and 2 that had been exposed for 1 hr and held for 7 days had a slightly sour odor and several small spots of visible growth. Hides numbered 4 and 6 that had been exposed for 3 hr and held in storage for 14 days also had a number of small spots of visible growth on the upper exposed hair surfaces and hide number 4 had a slightly off-odor. Although the microbial control had deteriorated, the leather from these latter hides was judged as acceptable as were their physical test values. This indicates that the microbial control probably did not begin to breakdown in various portions of the hides until about 11 or 12 days of storage time had elapsed.

While running this series of experiments, it was observed that the underside of the lid of the fiberglass storage containers were showing signs of attack by the hydrated SO_2 . It was covered with a white film of powder and the surface got lighter in color and appeared to be etched. Therefore, a series of experiments were conducted to determine the effect of storing the treated hides in polyethylene bags before they were put into the fiberglass storage containers. The treatment used was a 3-hr exposure to 0.66 percent SO_2 .

TABLE III

EFFECT OF TIME OF EXPOSURE TO 0.66% SULFUR DIOXIDE ON
MICROBIAL COUNTS AND LEATHER PROPERTIES.
HIDES STORED IN FIBERGLAS BOXES AT ROOM TEMPERATURE

Hide no.	Time of exposure/ storage hr/days	Microbial count		Side	Physical test data			
		Bact. wash pH	Bact./g hide (x 10 ³)		Elongation %	Tensile strength ^b psi	SATRA grain crack	
						Extension	Breakload	
						mm	kg	
1 ^a	1/7	4.9	200,000	left	30.63	872	6.95	9.3
2	1/7	4.1	510	left	29.00	1448	8.31	18.3
				right	27.25	1603	8.94	23.3
3	3/7	4.2 ^d	92	left	37.63	2314	8.70	28.3
		3.2 ^e	40	right	41.00	2094	8.79	25.0
4	3/14	4.9	5,000	left	37.13	1801	8.58	19.3
		3.8	150	right	49.63	1731	8.20	19.3
5	3/7	3.9	110	left	46.25	1735	8.59	20.5
		3.3	11	right	38.13	1640	8.11	20.2
6	3/14	4.5	1,300	left	42.58	2077	7.96	15.7
		3.6	40	right	34.08	1973	8.84	20.3
7	6/14	4.5	830	left	39.83	973	8.10	7.0
		3.8	10	right	48.75	1315	7.95	10.0
8	6/21	3.5	29	left	39.17	2042	8.46	19.7
		3.7	10	right	39.08	2356	8.11	19.3
9	3/14	3.9	<1	left	41.25	1643	8.37	22.3
		3.9	8					
	3/14	3.9	<1	right	46.33	2094	8.72	22.7
		3.8	3					
10	3/21 ^c	3.9	15	left	40.00	1751	8.23	16.0
		4.0	15	right	40.58	1487	8.24	14.3
11	3/13 ^c	4.1	2	left	32.50	2574	9.06	23.7
		4.1	3	right	37.42	2113	8.96	25.0
12	3/20 ^c	3.6	400	left		Not Recovered		
		4.1	130	right	45.75	2105	8.38	20.3

^aLeather from hides 1 to 6 in crust, the rest finished.

^bAverage of three samples ran parallel to backbone.

^cPut in polyethylene bag before storing in Fiberglas box.

^{d,e}Sample (d) from location near top part and (e) near bottom of stored hide.

In the first experiment, washed, sided, and fleshed cowhides were treated (hides 9 and 10) and in the second experiment, unfleshed cowhides (11 and 12) were treated. After treatment, one side of hide 9 was stored directly in a fiberglass box. The remaining matching side as well as all the other sides or hides were first put in polyethylene bags and sealed before storage in the fiberglass containers. The treated side stored directly in the fiberglass box showed visible spots of growth after 14 days storage which further corroborates the results obtained in the previous experiments. However, the hides or sides that were first sealed in polyethylene bags before storing in the fiberglass containers were satisfactorily preserved for 14 days based on previously described criteria. After 21 days storage however, both the fleshed and unfleshed hides, numbers 10 and 12 respectively, showed spots of visible growth in the folds.

The results obtained in these experiments are also listed in Table III. The microbial counts that were obtained on the edge samples taken from those hides that showed visible growth indicated satisfactory microbial control, but the microbial growth that was observed showed that control was failing in certain areas of these hides. The leather produced from these hides was judged to be commercially acceptable and the physical test data all fell in the range normally observed with this leather. The loss of microbial control in certain areas of the hides probably began about 2 days before the hides were sampled and the protease levels had not reached a point where serious damage to the hide could be observed in the leather-making process.

A general comment about the leather produced from the preserved hides throughout this study, whether in the crust or finished stage, was that it had a tendency to be slightly more loose than leather from normal production. The finished leather had a higher grain than normal, but it was acceptable. The sides let out well, took up the finish well, and no adjustments were needed in the finishing process.

When the treated hides in Table III were sampled, some extra samples were taken and stored in glass jars at ambient temperatures. These samples were observed occasionally for visible signs of microbial growth and periodically a few samples would be assayed for bacterial counts and a 1-hr GFA. The data collected are listed in Table IV and they show that microbial growth and GFA was controlled after 39, 54, and 365 days. The hair could be wiped easily off the grain surfaces of these samples which had been held for 1 year but there was no obvious damage to the grain. The samples held for 365 days were tanned with 8 percent Tanolin® and gave a Ts range of 105 to 109°C.

The treated hides from which these samples were cut, except for samples 7 and 8, did show spots of visible growth after 2 or 3 weeks. This indicated that certain areas of the hides had taken up insufficient SO₂ to maintain the microbial control in these spots. The data in Table IV also indicated that storage of the treated hide samples in glass jars which are inert to SO₂ and which prevent any loss of SO₂ was probably an important contributing factor to the long-term preservation obtained with these samples. This suggests that in the use of this preservative, the container is an important consideration.

TABLE IV

EFFECT OF STORAGE IN GLASS JARS ON LONG TERM PRESERVATION. SAMPLES CUT FROM HIDES EXPOSED TO 0.66 PERCENT SO₂ FOR 3-6 HR^a

Sample from hide no.	Time of storage (days)	Gel. film test	Bact. wash pH (range)	Bact/g hide x 10 ³ (range)	Ts °C
10,11,12	39	0	4.1-4.3	4-40	—
7,8	54	0	3.3-3.4	3-17	—
5,6,9	>365	0	3.3-3.7	<1000	105-109

^aSamples 7,8 exposed 6 hr, rest 3 hr, stored at room temperature.

Discussion

Hide samples that were exposed to 0.66 percent SO₂ for 3 hr were preserved for 17 + weeks while full hides treated similarly were preserved for only 1 to 2 weeks. Hides that were exposed to 0.66 percent SO₂ for 6 hr were preserved for at least 3 weeks. Therefore, under the conditions of our experiments, hides needed longer exposure times at this concentration of SO₂ (0.66 percent) than hide samples in order to approach the extended and long-term preservations that were obtained with hide samples. The difference was important because it pointed to factors that will need to be considered to maximize storage time and reduce the chances of damage to leather-making properties during storage using this method of preservation.

For example, it took 10 to 15 min to transfer the treated hides to storage containers. Undoubtedly some SO₂ was lost and the hides were exposed to contamination from the air and from manual handling. Treated hide samples were transferred to storage in seconds and it was done aseptically. This is one factor that would favor a more effective preservation for the hide samples. However, to be practical, the use of SO₂ would need equipment designed to treat, transfer, and store the hides which would not allow the escape of SO₂. Such equipment would increase the effectiveness of this preservation system for hides by preventing the loss of SO₂ from the hides and by preventing the contamination that resulted from our having to manually transfer the hides to storage.

A hide is more heterogeneous than a small hide sample. The hide has fatty deposits, manure, blood, and filth creating differing SO₂ demands over the larger surface of the hide. We also observed that during the time a hide was hanging in the treatment container, the flanks became quite moist while the backbone area became relatively drier. In Table III, the pH's of samples taken from hide locations that were lower in the storage container were, in some cases, one unit lower than samples taken from top locations. These are additional factors that can cause or do show differences in SO₂ distribution over the hide surface.

The importance of the containers for storing the treated hides in order to obtain an effective preservation has been demonstrated in this study. The design and testing of appropriate containers for the storage and transport of preserved "fresh type" hides and the role such containers play as an integral part of a preservation system for such hides is an area that needs further study.

Past work has shown that if the pH of the hide was lowered by a pre-treatment with an acid salt (NaHSO_4), the amount of SO_2 needed for preservation was lowered significantly (1). We have also reported that if hide samples were treated with the low concentration of SO_2 that was evolved from 0.5 percent NaHSO_3 (0.33 percent SO_2) and then were stored at 4°C , the preservation could be extended from 5 days to 8 weeks (11). Hides treated similarly and stored at 4°C were preserved for 5 weeks. These techniques could be used to increase the effectiveness of this preservation system when short exposure time to SO_2 are desirable.

Sulfur dioxide can be applied to the hide in other ways than those we have described. For example, it should be possible to agitate the hides in an atmosphere of SO_2 or in a sulfurous acid solution and this might be one way to effect adequate pickup and distribution of SO_2 in relatively short time periods.

Summary and Conclusions

Studies carried out on hide samples show that the higher the SO_2 concentration the shorter was the exposure time needed to give a 28-day preservation. Hides that were exposed to 0.66 percent SO_2 for 3 hr and placed in polyethylene bags before storage in fiberglass boxes were preserved for 2 weeks at ambient temperatures of approximately 70°F . When the exposure time was extended to 6 hr, hides were preserved satisfactorily for at least 3 weeks. The hides should be stored in containers that do not lose SO_2 and that are inert to hydrated SO_2 .

Sulfur dioxide is a toxic gas and it must be handled appropriately. The practical use of this gas as a hide preservative will depend on the design and development of a system that will prevent the loss of SO_2 during the treatment, transfer, and storage of the hides. The problem of SO_2 odor that could occur when a container of SO_2 treated hides was opened for processing or grading can be eliminated if the pH of the system is raised to 6.0 or above before the container is opened.

The studies conducted on SO_2 gas show that it has the potential to effectively preserve hides for 28 days. Small-scale studies have indicated that longer term preservations of 4 months or more are possible. The preservation of hides with SO_2 gas offer certain advantages since it does not require water or agitation and it does not increase the weight of the hide significantly. It will also eliminate the high dissolved solids and sodium ion pollution of beamhouse and curing plant effluents that result from the use of brine cured hides.

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