PRESERVING HIDES & SKINS WITH POTASSIUM CHLORIDE

The predominant commercial method of preserving fresh cattle hides is brine curing with sodium chloride. Curing is the temporary preservation of fresh, or "green" cattle hides from the time they are removed in the packing house until they can be permanently preserved, that is tanned, in a tannery. Preservation of food as well as hides and skins with common salt goes back well beyond recorded history. To understand the significance of preserving cattle hides with potassium chloride, it is first necessary to know a little about current hide curing practices using sodium chloride.

The hide is an ideal medium for growth of microorganisms. It is warm, wet and loaded with nutrients derived from blood and manure. It is well established that unless something is done within 12 to 18 hours to limit or eliminate the growth of microorganisms, grain damage will occur that will be visible on the finished leather. That something has traditionally been salt curing. Until the 1950s, hides were cured in salt packs. A salt pack consists of alternating layers of salt and hide piled together in a stack. About one pound of salt was used per pound of hide. After about 30 days, the hides stopped draining and reached an equilibrium between water removal from the hide and salt uptake by the hide. In this condition they were ready for shipping and storage for a year or more without any loss in quality.

Today, almost all cattle hides are cured in 20- to 30-thousand-gallon raceways filled with saturated sodium chloride brine. The hides reach equilibrium in about 18 hours. After being pulled form the raceway, they are wrung, stacked on pallets and are ready for shipment in about three days. In general, one green fleshed hide takes up about 10 to 12 pounds of salt and releases one gallon of water into the raceway.

This means that brine curing of cattle hides produces two waste streams. The first is at the packing plant where a 5,000-steer-a-day slaughter operation would require the disposal of more than a million gallons of saturated brine annually. The second waste stream occurs in the tannery where, in the first step of processing, the cured hides are soaked to remove the salt and to rehydrate the hide. A 1,000 hide-a-day tannery would generate eight to 10 thousand pounds of salt during the soaking process. Today, the disposal of any brine effluent is becoming more difficult and more expensive.

Table 1

EXPERIMENT 1
SAMPLE CONDITION
After Five Month Laboratory Scale Preservation Test

	KCl Concentration		
Temperature	3M	4M	5M
40°F	OK	OK	OK
RT	OK	OK	OK
106°F	FAIL	OK	OK

Two major changes have taken place within the last 10 years in the packing and tanning industries that I believe are an indication of just how much pressure there is to eliminate salt curing. The first is that the largest tanner in the world is a meat packer. I believe that one of the compelling considerations that went into the decision by IBP to begin tanning cattle hides was the difficulties they encountered in disposing of their excess brine.

The second major change occurred in the tanning industry. That change is the increasing use of fresh hides as the raw material for leather manufacture in place of salted hides. Several of the largest United States tanneries are going to great lengths to use fresh hides in as much as 60% of their production. To do this, hides are iced down at the packing plant, placed in refrigerated trucks and in some cases transported as much as several hundred miles to the tannery within 24 hours. While most tanners feel that the overall quality of leather produced from a fresh hide is better than from a cured hide, they are equally concerned about the concentration of dissolved solids in their effluents.

The effectiveness of refrigeration as a substitute for brine curing is limited to a period of several days at most. For the 18.2 million cattle hides that were exported in 1993, refrigeration was not a viable alternative. However, processing hides into blue stock at the packing plant for export is a viable alternative. In 1993, about two million cattle hides were exported in the blue.

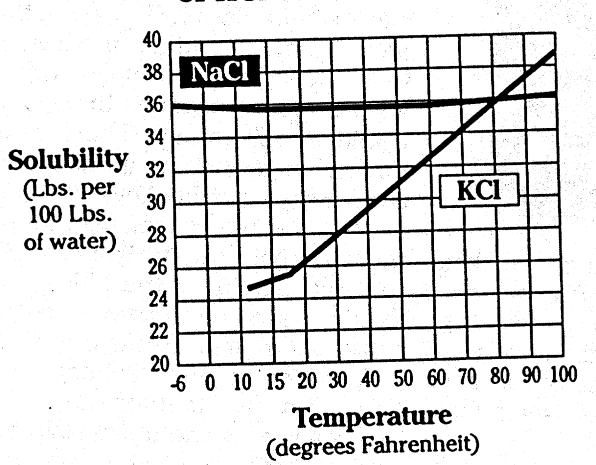
Which brings us to the subject of this report, a new alternative to sodium chloride for curing fresh hides for both the domestic and export markets. The substitution of potassium chloride for sodium chloride.

This research began with a call from Joe Gosselin, a senior research chemist from Kalium of Canada. Kalium is a major producer of potash fertilizer which they market all over the world as potassium chloride. He asked if we would be interested in setting up a research project to determine if it would be used in place of salt for curing hides and under what conditions? The main purpose for pursuing this idea is that if potassium chloride could preserve the hides as well as sodium chloride, then excess potassium chloride brine could be land applied in almost limitless quantities as a fertilizer. This would obviously be a tremendous advantage over the difficult and expensive disposal of excess sodium chloride brine. We were extremely interested in that concept.

I'm sure that many people have tested using potash as an alternate to sodium chloride to preserve hides and skins. A literature search revealed only one Russian patent and one Japanese paper. Both only mentioned potassium chloride as one of a number of salts investigated over sodium chloride.

Table 2

SOLUBILITY VS TEMPERATURE of KCl and NaCl



While it was Joe Gosselin of Kalium who called me to initiate this project, the idea's true origin is Pat Gummerson, the production manager of Lakeside Packers in Brooks, Alberta. Pat soaked a piece of cattle hide in potash (potassium chloride) solution overnight, allowed the excess solution to drain off for a few days and then sent the treated hide to a tanner to see if it could be made into leather. The tanner saw no difference between the piece sent by Pat and the brine rawstock he normally processed.

Pat then contacted Kalium of Canada, one of the world's largest potash producers, and Joe Gosselin was assigned the project to follow-up on the use of potassium chloride for hide preservation to expand the market for potassium chloride. Kalium wanted controlled research data to back-up Pat's observation. Eventually, Kalium and the Hides, Lipids and Wool Research Unit in Philadelphia worked out a Memorandum of Understanding to do the research, and this report is a summary of what we have learned so far and a discussion of the potential advantages and disadvantages of potassium chloride over sodium chloride.

The practical incentive for pursuing this work is that potassium chloride is a plant macro-nutrient. Kalium sells over two million tons of potassium chloride a year to the North American agricultural community for fertilizer. This means that the excess potassium chloride produced in a raceway could be disposed of by land application. Potentially, it could even be marketed locally as a fertilizer; certainly a distinct advantage over sodium chloride brine.

Why is potassium chloride a fertilizer and sodium chloride a pollutant? The answer is because when sodium ions in a salt solution are applied to the soil, they displace the minerals that are attached to clay particles in the soil. The more sodium that is added, the deeper these minerals are displaced. Since minerals are essential for plant growth, if they are driven deep into the ground, plants growth will be completely inhibited. Potassium ions are similar to sodium ions in many ways, but they do not displace the minerals in the soil to the same extent. In addition, large amounts of potassium are required for maximum plant growth, as we will see later.

Assuming that excess potassium brine can economically be used for fertilizer, there are two obvious questions: 1. What is the effect of potassium chloride on bacterial populations found on fresh hides? and, 2. What effect does potassium chloride curing have on leather quality?

Table 3

HIDE WEIGHTS (LBS.) AFTER CURING

KCl	
Pallet 1 Wt.	1692
Avg. Wt. (50)	33.8
Pallet 2 Wt.	1743
Avg. Wt. (52)	34.2
NaCl	
Pallet 3 Wt.	1651
Avg. Wt. (52)	31.8
Pallet 4 Wt.	1480
Avg. Wt. (47)	31.5

Table 4

GRADE SORT IN BLUE 86 MATCHED SIDES

	KCl	NaCl	TOTAL
M#1	0	0	0
M#2	8	4	12
M#3	4	1	5
H#1	12	9	21
H#2	59	57	116
H#3	20	26	46

Initial Small Scale Experiment

One hundred and eight, three-inch-diameter circles, were cut out of a fresh steer hide. One gallon of three different concentrations of potassium chloride were prepared: 3M, 4M and 5M. Thirty-six samples were placed into each solution. After soaking for several days, with occasional stirring, the pieces were removed, drained of excess moisture and further separated into three groups of 12. Each group was placed in a plastic bag and stored at either 4°F, 70°F or 106°F. After five months, the samples were removed from storage, examined for appearance, and odor and bacterial counts were performed. Plugs were removed from each sample, extracted with 4M potassium chloride in 0.01% peptone solution and various dilutions plated on PCA (plate count agar) and PCA containing 4M potassium chloride.

Observations

All samples that were refrigerated or held at room temperature were in excellent condition. The only samples that began to obviously deteriorate were the ones treated with 3M potassium chloride and held in the incubator at 106°F. The odor from these samples suggested that there was significant bacterial activity on them. All of the 4M and 5M potassium chloride treated samples were in good condition with no sign of bacterial growth (Table 1).

Bacterial Assays

Samples were extracted with 4M potassium chloride and then plated on both PCA and PCA containing the 3, 4 or 5M potassium chloride.

Results and Conclusions

The results of this first exploratory experiment clearly demonstrated that potassium chloride had preservative properties similar to sodium chloride.

Laboratory Scale Tanning Experiments

The first leather from potassium chloride cured hides was prepared in our pilot plant tannery two weeks after curing in 4M potassium chloride. Three hides were divided into eight sections, and all 24 sections were placed in an experimental drum. A 500% float of 4M potassium chloride was added and the drum rotated five minutes each hour for 18 hours. Four sections were to be tanned every two weeks out to a total of three months.

The first set of leather produced from these hide samples looked quite good. There was no reason to believe that anything unusual had happened to change the leather. However, after four weeks, it was clear that bacteria was growing on the hide samples. There was no odor indicating any putrefaction or any hair slip, but something was growing on the surface of the hides. Salt and moisture analysis showed that these samples contained only between 2.14 and 2.48M potassium chloride. It appears that a combination of insufficient mechanical action and the low concentration of potassium chloride were to blame for the poor preservation.

These same hide sections were then rerun continuously overnight in a 4.25M potassium chloride solution. The saturation in the hide

Table 5

AREA COMPARISON IN BLUE

KCl	NaCl
21.88 Sq. Ft.	21.74 Sq. Ft.
Std. Dev. 1.66	Std. Dev. 1.55

Table 6

BREAK COMPARISON IN BLUE

86 MATCHED SIDES

	KCl	NaCl
#1	59.2%	48.5%
#2	33.1%	37.1%
#3	7.7%	14.4%

Table 7

TENSILE STRENGTH COMPARISONS

40 Matched Pairs – Vacuum Dried

	KCl	NaCl
Tensile (psi)	3056	3065
Std. Dev.	743	868
Extension (in.)	.378	.372
Std. Dev.	.048	.043

increased to greater than three molar, and there was no further evidence of bacterial growth up to the time they were tanned.

Large Scale Test 100 Matched Sides

Standard Lakeside Packers, ***Hide processing (soaking)*** — Hides right off the kill floor are normally soaked in a paddle for two hours in 110°F water to loosen and remove manure. After soaking, the hides are fleshed and placed in the brine raceway.

In the matched side study, 100 hides were soaked as usual and fleshed. Then they were individually sided and marked using a system of punches for later identification. Alternating right and left sides were either sodium chloride brine cured or potassium chloride brine cured. Using matched sides eliminates any bias in the results in the event that there are some particularly poor quality hides. In our analysis, we are only comparing qualities of the left side of a particular hide to the right side of the same hide.

We ran into two interesting problems with the scale up. The first having to do with the temperature of the bath and the second with the mechanical action of the paddle during the potassium chloride curing.

One of the physical property differences between potassium chloride and sodium chloride is their temperature solubility. Table 2 shows that the solubility of sodium chloride is reasonably constant between 0° and 100°F, while potassium chloride solubility is much more temperature dependent.

Another physical property of potassium chloride is that it absorbs heat from the solution as it dissolves. It is the same phenomenon exhibited in the chemical

Table 8

TENSILE STRENGTH COMPARISONS

25 Matched Pairs – Paste Dried

	KCl	NaCl
Tensile (psi)	3078	1267
Std. Dev.	323	335
Extension (in.)	.328	.308
Std. Dev.	.050	.048

Table 9

KCl PRESERVATION EXPERIMENTS

IN PROGRESS

CATTLE HIDES, PADDLE CURED
Teh Chang Tannery, Taiwan

PIGSKINS, PROCESSOR CURED
Wolverine Tanning, Dyersburg, TN

CALFSKINS, SALT PACK CURED
North East Hides, Olyphant, PA

CATTLE HIDES, RACEWAY CURED
IBP, Joslyn, IL

Table 10

UPTAKE OF KCl BY VARIOUS CROPS

LBS./ACRE/CROP

Alfalfa		481
Clover		324
Grass		208
Corn Silage		324
Sugar Beets		229
Potatoes		
Tubers	346	Total 477
Vines	131	
Peas		219
Wheat		113
Oats		232
Rye		210
Corn		207
Sunflowers		59

cold packs found in first aid kits. In order to make up the 4.25 molar potassium chloride brine, we added 22.3 tons of potassium chloride to the 16,800 gallons of water in the paddle. As the potassium chloride dissolved, the temperature in the paddle dropped from 70°F to 55°F. A low-pressure steam line had to be used to bring the temperature back up to 70°F. This does not present a practical problem for routinely using potassium chloride in a hide processing plant. Once the raceway is filled the only potassium chloride that has to be added daily is an amount equal to the potassium chloride removed with the cured hides. This would be only a small fraction of the potassium chloride remaining in the raceway. This was confirmed in a raceway curing experiment that will be covered later.

The second problem had to do with the recirculation system for the soak paddles. Under normal conditions, the vigorous mechanical action of the soak paddle splashed substantial amounts of soak water from the paddle. This soak water would be collected in a sump and continuously recirculated back into the paddle to maintain a higher water level in the paddle. Since only one of the paddles was used in this test for potassium chloride curing, the recirculation system could not be used, and the liquid level in the paddle was reduced by almost 12" by the end of the potassium chloride brine cycle. As a result, the mechanical action in the paddle was greatly reduced. We were concerned that we would not get sufficient potassium chloride into the hide for good preservation. To compensate for the temperature drop and the lower mechanical action, the total soak time for the potassium chloride hides was extended to 28 hours.

The brine cured hides were removed from the brine raceway, pulled through a pair of vertical rollers that squeezed excess moisture out of the hides, and placed on a grading table. Safety salt was added, and the sides were then folded and placed on a pallet. The potassium chloride brined hides were treated in the same way. Fifty sides were placed on a pallet and hydraulically pressed to further remove moisture and then were weighed. There were a total of four pallets. As seen in Table 3, the sodium chloride cured hides were more dehydrated than the potassium chloride hides over the period of storage.

After five weeks all of the cured sides were shipped to Dominion Tanners in Winnipeg, Ontario. Exactly 40 days after curing, each side was examined before being placed in a drum to be soaked, unhaired and limed. The condition of both the potassium chloride and the sodium chloride cured hides were excellent. The potassium chloride cured hides appeared to contain more moisture. The weights of the four pallets and the average weight of the sides confirmed that sodium chloride had removed more water. There was no hair slip or odor problems in either cure. The edges of the sodium chloride cured hides were slightly more dried out, but this may be because the potassium chloride sides were wrapped in plastic during storage. After liming, the sides were fleshed and tanned together in the same drum with additional full hides to make up a full pack.

A normal blue sort was carried out after wringing. They were sorted into three grades of heavy- and medium-weight leather. The results are shown in Table 4.

Each of the sides were also graded for break and the area measured. The results of the analysis are in Tables 5 and 6. The slight difference in draw in favor of potassium chloride might correspond to the reduced dehydration seen in potassium chloride. In matched pairs, 59% were the same, 18% of the sodium chloride and 28% of the potassium chloride sides examined had less draw. The area difference was small and not statistically significant.

After grading into the normal selections for blue stock, the hides were separated again into two sets of matched pairs. Half were processed into a vacuum dried leather product, and the other half into a paste dried product.

In the crust sort for paste dried leather, eight potassium chloride and one sodium chloride brine sides were rejected. However, the rejections were based on scratches, rather than factors that might be related to the preservation salt. The other leather contained 11 sodium chloride and 10 potassium chloride rejections.

Tensile strength was done on the matched sides from both sets of crust. Again, the results were not different as presented in Tables 7 and 8.

The conclusion at this point is that leather produced from cattle hides preserved for five weeks with potassium chloride does not appear to differ significantly from cattle hides preserved with sodium chloride. Longer term preservation still needs to be confirmed as far as longer term resistance to microorganisms is concerned. The experimentally preserved three-inch samples were still in excellent condition after nine months.

The work described up until now suggests that the leather produced from potassium chloride cured hides cannot be distinguished from leather from sodium chloride preserved hides. However, the storage time in these experiments was limited to only about 40 days, not long enough in today's world hide markets. However, in addition to these experiments carried out at Lakeside Packers and Dominion Tanners, there are several other potassium chloride preservation experiments in progress. These are listed in Table 9.

Lakeside Packers, *Paddle cured cattle hides* — A second set of 150 hides was potassium chloride cured in a paddle at Lakeside Packers, Brooks, Alberta. These hides were shipped to Teh Chang Leather Products in Taiwan, along with 500 sodium chloride raceway cured hides. The total time that elapsed between the hide take off and tanning was approximately three and a half months. Upon examination of these hides, in the hide house the day before they were put into process there were two noticeable differences between the two cures. First, halophilic bacteria were quite noticeable on the brine cured hides and there was no sign of them on the potassium chloride hides. Second, the potassium chloride hides were considerably more dry on the edges of the hides exposed to the air than the corresponding areas on the sodium chloride cured hides. There was some concern at this point about rehydration of these hides. The interior of the hides was in good condition. Every hide was evaluated for break after liming. The average break for each set was not significantly different. The potassium chloride cured hides were firmer than the sodium chloride cured hides. The handle in the blue appeared to be the same. Shrinkage after a two-minute boil was 95% for the potassium chloride hides and 96% for the sodium chloride hides. Shrink temperature for both was greater than 96°C. The blue stock was graded into four categories: A, B1, B2 and C. Potassium chloride was 15.8, 28.4, 8.27 and 2.88%. Sodium chloride was 20.0, 23.0, 7.5 and 2.33%. Additional evaluations and physical testing will be done on the crust. The significance of this experiment compared to the initial one, produced at Dominion Tanners, is that these hides had been cured for a total of three and a half months before tanning.

Northeast Hides & Skins, Inc. *Salt pack cured calfskins* — We examined one pack of skins after standing for 30 days, just prior to shipment to Japan to be tanned. The potassium chloride hides were cleaner in some respects, but were also redder in color. It appears that the hemoglobin remains more oxidized in this treatment than in the sodium chloride salt pack. Uptake of potassium chloride and sodium chloride appears to be comparable in these skins. We have no further word from the tanner regarding this set of skins.

Wolverine Leathers, *Processor cured calfskins* — These hides were shipped from Dyersburg, TN, to the Wolverine plant to be processed into leather. There were no obvious signs of bacterial breakdown in these skins which were held for seven weeks between curing and tanning. These skins are being processed into leather at this time, and no further information is available.

IBP, *Brine raceway curing of cattle hides* — Three raceways containing approximately 300 hides each were cured using potassium chloride. An additional 900 hides were traditionally brine cured for controls, the following week. After a minimum of 18 hours, the hides were pulled, wrung, and placed on pallets for storage. These hides will be divided into groups to go to three different tanners at three months and at six months. These hides have been in storage approximately one month at this time.

Practical Considerations for Potassium Chloride Curing

At this point we can say the evidence is good that potassium chloride can replace sodium chloride for hide preservation. Now let's look at some of the practical considerations that affect potassium chloride curing.

1. ***Cost of potassium chloride*** — Potassium chloride costs more than sodium chloride per pound. But the significance of this difference will vary greatly with the location of the packing plant and the difficulty (and cost) of getting rid of the sodium chloride brine now produced in the hide processing area. For example, for Lakeside, the cost of potassium chloride, in the same quantities that they now purchase sodium chloride, would be about double. However, now they are building a new salt lagoon every to years for about $250,000 each, and they have not disposed of the salt — they are just storing it. The provincial environmental agency wants them to produce a plan of how they will get rid of the salt in the future. Elimination of the cost of additional lagoons would pay for a lot of potassium chloride, even if there was no financial return on it.

2. ***Use of potassium chloride brine as fertilizer*** — Potassium is a plant macro nutrient. All plants require large quantities of potassium for growth. In some cases, alfalfa for example, the uptake of potassium is quite high, and it is removed from the field entirely at harvest.

Table 10 contains a list of typical potassium-using plants, including the quantities consumed in a growing season. We calculated from this information that if the amount of potassium chloride brine produced from potassium is about the same as the amount of sodium chloride brine, a 5,000-hide-a-day packing plant would require about 15,511 acres of land, growing alfalfa to consume one year's production.

3. ***Other properties of potassium chloride*** — As mentioned earlier, the solubility of potassium chloride varies with temperature. This will be a disadvantage for hide processors, because it means that in cold weather the hide processing area or at least the raceways will have to be temperature controlled to a greater extent than they are now. If the temperature drops, then the solubility of potassium chloride decreases, and the level of potassium chloride needed in the hide for preservation will not be achieved. In terms of availability, potassium chloride can be obtained in about the same grades, from fine to course, that sodium chloride is available.

Benefits

Who does this work benefit? The primary beneficiary has to be the meat packer and the independent hide processor. They have the most severe effluent problems as a result of sodium chloride brine curing hides, and they have the most to gain from using potassium chloride as a hide preservative. While effluent dissolved solids may be a serious problem for a number of specific tanners, for most it is less important than some other environmental issues now before them. To take advantage of this type of cure, the soak would have to be isolated from the other beamhouse waste stream in order to be land applied. This may be an advantage for some, but probably not for most.

There may be, however, another significant advantage for the hide exporter and ultimately for domestic tanners as well. This has to do with hide quality, and to explain this concept I'm going to have to back-up a little and review some work done in our laboratory on the effect of halophilic bacteria on hide quality. This research was discussed at the 1993 USHLSA winter meeting and will appear shortly in the Journal of the American Leather Chemists Association.

Let me make three points:

1. Halophiles are everywhere, at least in the brine cured hide industry. In the past 18 months we have obtained more than 180 samples of brine cured hides from throughout the U.S. We isolated extreme halophilic bacteria from all but three of these samples. This suggests that halophiles are universally present on domestically cured cattle hides.

2. Halophiles grow rapidly under the right conditions. As demonstrated in work published in JALCA, at 106°F, extreme halophiles can grow as rapidly as bacteria that grow on fresh hides at room temperature.

3. Halophiles can damage hides. In recent unpublished experiments, we added cultures of isolated extreme halophiles to fresh hides being brine cured. The control hides did not have any halophiles added. We clearly demonstrated that the grain surface of hide samples, properly brine cured and stored at 106°F for seven weeks, was heavily grain damaged, while cured cattle hide samples stored at this temperature without added halophiles were not. The grain on all of the leather produced from the other samples was satisfactory.

The conclusion is that halophilic bacteria present on brine cured hides shipped to the Far East have the potential to cause serious damage, if the temperature of the hides reaches 106°F for several weeks. To date, in our experimentation with potassium chloride cured hides, we have not observed any halophilic organisms growing on the cured hides. In fact, we have preliminary evidence that when 10 to 15% potassium chloride is added to halophilic growth media in place of sodium chloride, halophilic growth is inhibited. In our export experiment described earlier, there appeared to be no halophiles present on the potassium chloride cured hides.

As far as the domestic tanner is concerned, it follows that if a great deal of grain damage can be done in seven weeks due to halophiles, then some smaller amount of damage could occur at lower temperatures in less time. It does not take much grain damage to reduce hide quality from aniline to corrected grain. This suggests that even if halophiles are responsible for only a small amount of damage to domestic brine cured hides, this damage could be eliminated by potassium chloride curing.

All of the test results to date support the concept that potassium chloride can replace sodium chloride as a preservative for fresh hides and skins with the obvious advantage in terms of disposal of the excess brine. There is still a great deal of work left to be done, but almost all of the necessary experiments are either complete or are in progress. A final report on all of the results should be available by late spring of 1995.

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