# Development of an Alternative Low Salt Bovine Hide Preservation using PEG and Crude Glycerol, Part II: Mechanical Properties of Leather Products

*by*

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## Abstract

To obtain good quality leather products, the hides from which they are derived should be preserved properly while in storage and transit to prevent putrefaction. Current practice for hide preservation is salt curing via concentrated NaCl solutions. The objective of the current study is to develop alternative brining processes that require lesser amounts of salt and have no adverse effect on the resulting leather products. By incorporating a dehydrating agent such as polyethylene glycol polymers (PEG), only a fraction of the commonly used amount of salt is necessary (from about 50% to less than a 25% of the weight of raw hide) to generate an efficiently preserved hide. The scanning electron microscopic (SEM) images and mechanical properties of the resulting crust leather products were comparable to the control obtained from traditionally preserved hides. To compensate for the potential over drying and formation of very tight grain, a humectant such as glycerol (with sodium carbonate) was also included. The rehydration of the test preserved hides is completed in a shorter period of time because the amount of salt in the hides is already quite low. Considering the low cost in obtaining the crude glycerol and its positive effects on quality of leather, it is quite desirable as an ingredient in the new alternative less salt hide preservation.

## Introduction

Proper preservation of hides is very important in maintaining the quality of highly desired US hides while in storage and transit to the countries where they are processed to leather. Normally, the hides and leather industry uses high amounts of sodium chloride, about 40% to 50% of the weight of the raw hide, in order to effectively preserve the hide for months without fear of putrefaction.[1, 2] Due to the strong environmental impact of the excess salt being discharged into the waste water, an alternative low salt or salt-less preservation is needed.

As mentioned in Part I of this study,[3] previous researchers have tried several alternative preservation techniques. Each had its own advantages and disadvantages.[2, 4] The main goal of preservation is to stop putrefaction that can cause serious damage to the hides. By reducing the moisture content of the raw hide from ~70% to less than 50%, the microbial growth is inhibited and the major source of putrefaction is eliminated.[1-4] Adding a dehydrating agent such as PEG is one way to decrease the amount of salt needed to reduce water content during hide preservation.[5] In our recently concluded research project, the inclusion of crude glycerol and sodium carbonate in the presoaking solution proved to be beneficial in enhancing the efficiency of the adobe type manure removal from bovine hides and also generated good quality leather products.[6] The unique property of glycerol could be utilized in the effective bovine hide preservation to counteract the dehydrating effect of PEG and protect the hides from over drying. This is important because over dried hides may be very difficult to rehydrate. Humectants, such as glycerol, act as skin lubricants by absorbing water from the atmosphere and making the skin softer.[7] Humectants have a second advantage in that they reduce water activity and discourage growth of microorganisms. Likewise, sodium carbonate has been widely used as a salt additive for over 60 years. Thus the incorporation of sodium carbonate as well as crude glycerol is considered in our current studies in lowering salt concentration in the alternative brining solution that contains low molecular weight PEGs. The characteristics and usual means of production of PEG are detailed in Part I of this study.[3]

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In the previous study, where the standard formulation to which PEGs were added, consisted of 10% NaCl, 5% crude glycerol (CG) and 1% sodium carbonate (SC), the moisture content of the hide pieces at 24 h brining remained above 50%.[3] In this study, to further lower the moisture content at 24 h, the standard formulation to which PEG is added is 20% NaCl with 5% CG and 1% SC. PEG200, 400 and 600 at 2% were chosen because they are easy to work with and relatively inexpensive.

## EXPERIMENTAL

### Materials

All the chemicals used for the conventional processes are of commercial grade. The chemicals used for the preparation of the different alternative brining formulations are of analytical grade. The crude glycerol, from biofuel production, was obtained from Griffin Industries (Butler, KY) and was used as received. Fresh hides were obtained from a local beef cattle processing plant (JBS, Souderton, PA). The different PEGs and sodium carbonate were obtained from Sigma-Aldrich, (St. Louis, MO). The bulk sodium chloride, NaCl TX-10, was obtained from Superior Salt LLC, (Watkins Glen, NY).

### Laboratory Scale Protocol for the Alternative Hide Preservation

Freshly washed and defleshed hides were collected and split down the back into left and right segments. Samples to be toggled were cut into 600 g pieces as described previously,[3] samples to be stacked were cut into larger pieces of approximately 1000 g each, 12 inches by 14 inches in dimension. Curing formulations are detailed in Table I. A traditional amount of NaCl (40%) and half the amount (20%) were run as two separate salt preservation controls. The hide pieces were allowed to soak in their respective solutions in individual drums overnight at 6 rpm. The following day, the hide pieces were either hung (toggled), or stacked for drying and storage. The moisture content or rate of dehydration was monitored in each set. The control and alternatively cured bovine hide samples were stored for 2 weeks and then rehydrated as described previously.[3] Triplicate trials were performed for each curing condition.

### Chloride Content Determination

Chloride content was monitored as a function of time during both brining and rehydration of the hide pieces. For chloride determination, small samples (~ 2 g) were cut from the larger hide pieces. The sample piece was weighed, soaked in 25ml of deionized water, and the chloride was extracted by stirring constantly at about 150 rpm for 30min. Then 0.5 ml 0.5M potassium dichromate was added as indicator, and the solution was titrated with 0.1N silver nitrate to reddish end point (following the Mohr method).[8] When the color changed from yellow to orange the amount of silver nitrate used was recorded. The percent by weight of NaCl in each sample was calculated. Triplicate trials were run for each sample to improve accuracy.

**TABLE I**
**Curing conditions for hide pieces that were S=stacked or T=toggled for drying and storage.**

| Stacked | Toggled | Curing Formulation |
|---|---|---|
| 1-S | | 40% NaCl |
| 2-S | 1-T | 20% NaCl |
| 3-S | 2-T | 20% NaCl +5% CG +1% SC |
| 4-S | 3-T | 20% NaCl +5% CG +1% SC +2% PEG 200 |
| 5-S | 4-T | 20% NaCl +5% CG +1% SC +2% PEG 400 |
| 6-S | 5-T | 20% NaCl +5% CG +1% SC +2% PEG 600 |

### Tanning of Cured Hide Pieces

Rehydrated hide pieces were tanned following the standard USDA/ARS/ERRC tanning process[9] for production of crust leather from brined hides. Briefly, the cured hide pieces were sulfide dehaired, limed, delimed and bated, pickled, tanned, retanned, colored and fatliquored. The process was carried out in a Dosemat tanning drum (Dose Maschinenbau GmbH, Lichtenau, Germany).

### Mechanical Properties of the Crust Leather Product

From each crust leather sample, 5 dog bone samples were cut for mechanical property testing as described in ASTM D2813-03[10] with the long dimension parallel and the short dimension perpendicular to the backbone. Dog bone samples were conditioned at 50% RH and ambient temperature 25 ± 2°C at least 24 hours prior to testing. The mechanical property measurements included tensile strength, elongation-to-break ("strechability"), Young's modulus ("stiffness"), and fracture energy (the energy needed to fracture leather samples, its "toughness"). The leather samples were split to a thickness of 1.7 - 2.7 mm. An upgraded Instron mechanical property tester, model 1122 (Instron, Norwood, MA), and Testworks 4 data acquisition software (MTS Systems Corp., Minneapolis, MN) were used throughout this work. The strain rate was set to 25.4 cm/min with a grip distance of 5 cm. Each test was conducted on five samples to obtain an average value.

### Scanning Electron Microscopy

The crust leather samples were cut to ~1.5mm pieces and mounted on stubs and sputter-coated with thin layer of gold using a Scancoat Six Sputter Coater (Edwards Scancoat 6, West Sussex, UK) for 90 seconds in two orientations. The samples were then observed with FEI Quanta 200 FEG Environmental Scanning Electron Microscope (SEM) (Hillsboro, OR, USA) in high vacuum-secondary electron imaging mode with an accelerating voltage of 10KV. Digital images were collected at 100, 500, 1000, 5000 and 10000 x magnification.

## RESULTS AND DISCUSSION

### Dehydration Trends

With the exception of the sample that was brined in 20% NaCl alone, and toggled for drying, moisture content of all samples was below 50% after 24 h. The dehydration trend for toggled samples was quite similar in all curing conditions as seen in Figure 1. Moisture levels decreased significantly between 0 and 96 h and much more slowly after that. When samples were toggled, most of the sample area was exposed to the air, drying was very efficient, and the moisture contents after 1 week were ~15%.

Although samples used in the stacking trial (Figure 2) were relatively larger (1000g) than those used for toggling (Figure 1) (600g) the initial drying rates were similar. For stacked samples (Figure 2), the decrease in moisture level was slower, and in a more linear fashion. In both cases moisture levels were below 35% after one week, a sign of successful preservation.

### Chloride Content

The chloride content of a brined hide is a measure of the amount of salt that has penetrated the hide. After 24 h brining, The chloride content of the control hide piece cured with 40% NaCl was about 13-14% (Figure 3) based on a 30 min extraction of chloride from hide pieces of similar weights (~2g) with deionized (DI) water. The hide pieces cured with 20% NaCl, with or without CG, SC and PEG, contained about 6-7% chloride or half the amount of NaCl absorbed by the control.

Before tanning the previously preserved hides, the first step is to remove the excess salt. At the same time, the relatively dried and hardened hide has to be rehydrated and softened, returning to its original state prior to brining so that the tanning chemicals could take its effective course of action on as close to the raw hide state as possible. Rehydration of brine cured hides serves to remove excess salt from the hide and to soften the relatively dry and hardened hide prior to processing so that the beaming and tanning chemicals can be used effectively. Rehydration was in 150% float of water and biocide (0.15% Boron TS and 0.10% Proxel, based on recorded dry weight) in Dosemat mini drums for 18 hours at 6 rpm. The chloride content was monitored as a function of time as the hide pieces were rehydrated (Figure 4). Initially, the control hide cured with 40% NaCl, had 26% NaCl whereas the alternatively cured hides with 20% NaCl with and without PEG contained about 14% NaCl. The trend in the salt diffusion from the cured hides, was similar at every hour when aliquots were taken. The values were consistently half that of the control. The amount of chloride diffusing out of the cured hides hit a plateau after 3 h soaking where ~6% NaCl was found for the control and ~3% NaCl was found for the remainder of the tested hides.

The amounts of chloride remaining in the preserved hide pieces after rehydration to remove excess sodium chloride, and immediately before tanning the soaked hides are shown in Figure 5. The control hide piece preserved with 40% NaCl had about 6% NaCl, whereas the alternatively preserved hides with 20% NaCl, with and without PEG, each had about 3% NaCl remaining in the hide before tanning to leather. This suggests that a shorter rehydration time, and possibly a lesser amount of water might be adequate to remove excess NaCl from hides preserved with a 20% NaCl, 5% CG, 1% SC, PEG formulation.

### Mechanical Properties

The overall mechanical properties of the resulting leather products from the current low salt conditions were similar to those of the controls. For example the sample cured with 20% NaCl, 5% CG, 1% SC and PEG 200 compared to the control

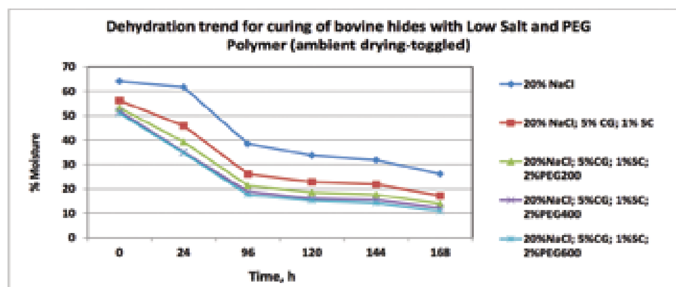


Figure 1. Dehydration trend for hide pieces that were toggled.

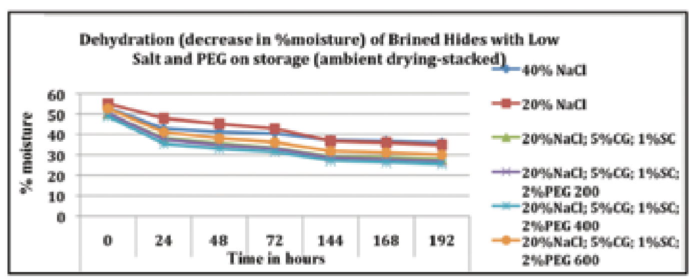


Figure 2. Dehydration trend for hide pieces that were stacked.

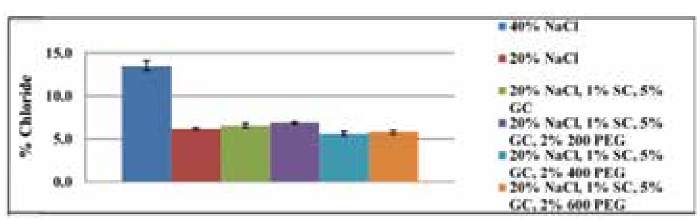


Figure 3. Chloride content of cured hide pieces after 24 h brining.

cured with 40% NaCl, the tensile strength (10.3 ± 1.7 compared to 9.8 ± 1.2 MPa), elongation-to-break (63.5 ± 1.7 compared to 59.7 ± 5.4%), Young's modulus (8.8 ± 1.2 compared to 10.6 ± 1.3 MPa), Fracture energy (2.09 ± 0.49 compared to 1.99 ± 0.34 J/cm$^3$), and the toughness index (1.29 ± 0.22 compared to 0.95 ± 0.18). The test leather sample is relatively tougher, more stretchable and softer than the control. Consistently, these are the properties of leather product that is considered to be of good quality.

**Scanning Electron Microscopy of Crust Leather**
Scanning Electron Microscopy images were taken to compare the microscopic grain and inter-fibrillar structure of the finished crust leather from alternatively preserved hide samples to the controls. At 100x, the grain layers at the top of the images in Figure 6 do show some visible differences. The control hide preserved with 40% NaCl (top left) showed somewhat rougher edges at the grain surface compared to the test preserved hides that appeared to have smoother surfaces both in the stacked and toggled samples (data not shown but similar behavior observed).

There were only minor visible differences (Figure 7) in the collagen fiber structure in alternatively preserved hides compared to the control SH-1, with 40% NaCl brining solution. The closest in terms of the collagen fiber structures are the control with 20% NaCl, 5% CG, and 1% SC (top right) and the test with those components plus 2% PEG 200 (bottom left) in Figure 7. The test sample that included PEG 600 also appeared similar, but with slightly tighter inter- fibrillar structure. The results are quite promising because the fibrillar structures did not undergo major changes during rehydration and behaved similarly to the traditionally preserved hides when tanned to leather.

## CONCLUSION

Rehydration of the alternatively cured hide pieces reduced the chloride content from the 6 – 7% range to ~ 3% within 3-4 h. Potentially, less water could be used during rehydration and soaking prior to tanning the hides to leather because the starting amount of salt included in the low salt brining solutions was already quite low. Therefore the amount of wastewater discharged into the environment could considerably be reduced. So far, the resulting crust leather

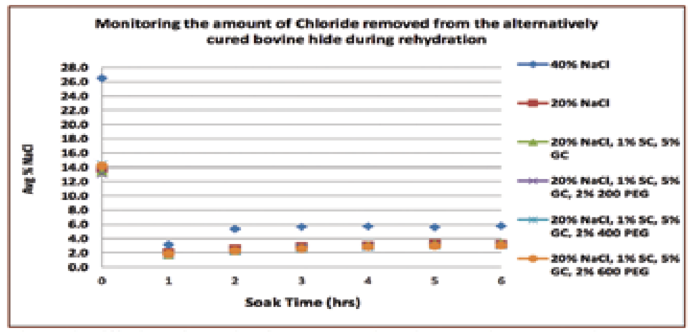


Figure 4. Diffusion of chloride from cured hide pieces during rehydration.

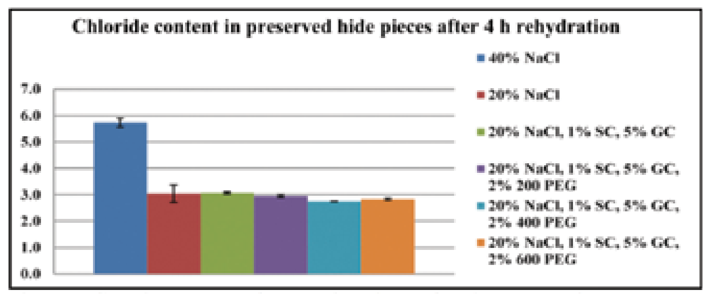


Figure 5. Chloride content of cured hide pieces after 4 h rehydration.

## TABLE II
**Mechanical properties of the finished crust leather from differently cured bovine hide pieces.**

| Curing treatments | Tensile Strenght, Mpa | Elongation, % | Young's Modulus, MPa | Fracture E, J/cm^3 | Toughness Index |
|---|---|---|---|---|---|
| 40% NaCl, std control | 9.8±1.2 | 59.7±5.4 | 10.6±1.3 | 1.99±0.34 | 0.95±0.18 |
| 20% NaCl, control | 9.2±1.6 | 62.2±3.7 | 9.6±1.5 | 1.89±0.29 | 1.15±0.17 |
| #3+20%NaCl+5%CG+1%SC | 15.5±1.1 | 66.7±4.9 | 20.1±3.6 | 4.33±0.44 | 0.68±0.24 |
| #3+2%PEG200 | 10.3±1.7 | 63.5±1.7 | 8.8±1.2 | 2.09±0.49 | 1.29±0.22 |
| #3+2%PEG400 | 13.7±1.2 | 60.1±4.9 | 20±2.8 | 3.43±0.03 | 0.63±0.12 |
| #3+2%PEG600 | 9.5±0.7 | 50.1±2.3 | 11.6±2.3 | 1.73±0.18 | 0.75±0.19 |

products did not show any signs of degradation of the collagen fibers. The presence of PEG and glycerol helped in the controlled drying process of the preserved hides and had positive effects on quality of the resulting leather being stronger, more stretchable and softer than the control. PEG, in the presence of crude glycerol and sodium carbonate are quite desirable as ingredients in the new alternative less salt and environmentally friendly hide preservation process.

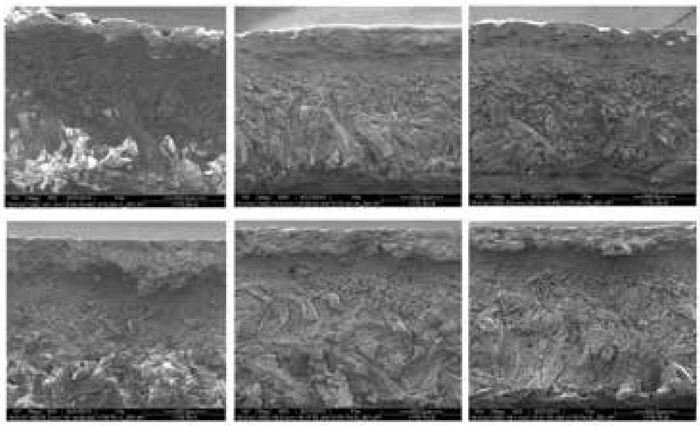

Figure 6. SEM images at 100 x of crust leather from hide pieces that were stacked for drying and storage.
Curing formulations: Top left to right: 40% NaCl; 20% NaCl; and 20% NaCl + 5% CG + 1% SC and Bottom left to right: 20% NaCl + 5% CG + 1% SC +2% PEG200; +2% PEG 400; and +2% PEG 600.

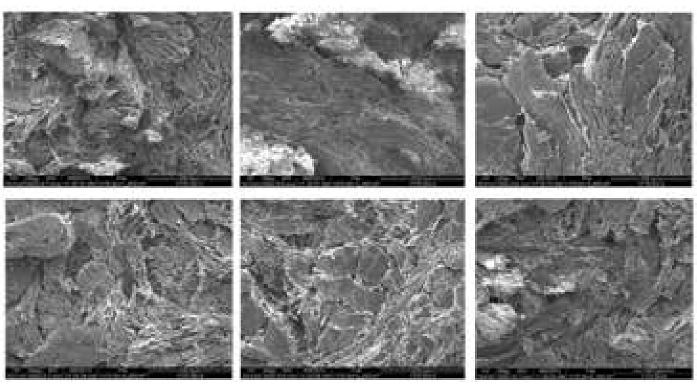

Figure 7. SEM images at 500 x of crust leather from hide pieces that were stacked for drying and storage.
Curing formulations: Top left to right: 40% NaCl; 20% NaCl; and 20% NaCl + 5% CG + 1% SC and Bottom left to right: 20% NaCl + 5% CG + 1% SC +2% PEG200; +2% PEG 400; and +2% PEG 600.

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