5194

SOLVENT PRESERVATION OF PIGSKINS⊕

BY PETER R. BUECHLER*, JOHN S. FISHER, MATTHEW P. DAHMS
AND MARY V. HANNIGAN+
Eastern Regional Research Center[1]
PHILADELPHIA, PENNSYLVANIA 19118

Abstract

Some 90 million butcher hogskins per year are potentially available and can be utilized for leather manufacture. For optimum utilization with a minimum waste problem, a beamhouse and processing plant central to the currently concentrated pork packing plants is envisioned. Fresh pigskins brought to this facility would receive beamhouse treatment followed by a preservation process and could then be shipped to pigskin leather manufacturers wherever they are located. Studies of solvent dehydration preservation processes have shown that these processes can be used after bating. Dehydrated bated stock offers a number of advantages: (1) A light-weight product, one-sixth the shipping weight of fleshed raw pigskins is obtained. (2) The stock keeps indefinitely under most ambient conditions, unless contacted by liquid water. (3) The dehydrated stock can be graded and sold on the basis of its visible surface defects. (4) Water can be easily added to the stock with no adverse effect on subsequent tanning. (5) Leathers from the dehydrated pigskins subsequently re-wet and tanned have fewer oil spots and better chrome distribution than control leathers.

Introduction

In 1979, Feairheller, Bailey and Maire (1) showed that 98 million pigskins were available annually and that 90 million of these were from young butcher hogs and suitable for leather use. This represents a potential leather footage equivalent to 25% of that available from U.S. cattlehide. Yet only about 3 million pigskins per year were being used for leather at that time. If pigskins were employed for leather they would:

1) utilize an agricultural resource which is used primarily for gelatin;
2) reduce pollution from packing plant wastes;
3) increase availability of raw materials for the U.S. leather manufacture;
4) increase exports of leather and/or pigskins to aid the U.S. balance of trade.

To effectively use this large supply of pigskins, a central beamhouse-preserving plant could be built and located within a day's trucking of many pork packers. This centralized beamhouse would produce dehydrated bated pigskins that could be sold, already graded, on all leather markets.

Salt preservation of hides and skins is the accepted method, but solvent dehydration preservation has certain advantages. Primarily these are: no salt in tannery effluent, a gradeable product, and the reduction of fats and oils. Buechler (2) in 1975 showed that a sol-

⊕Presented at the 79th Annual Meeting of the American Leather Chemists Association at Hershey, Pennsylvania, June 22, 1983.
*Deceased.
+Emeritus status.
[1]Agricultural Research Service, U.S. Department of Agriculture.

vent process could be used to dehydrate and to preserve pickled cattlehide for an extended time. Solvent preservation processes were tried on pigskin and the effects of these processes on tanning pigskins to crust leather were studied. The results are reported in this paper.

EXPERIMENTAL

Small-scale Investigation

Pigskins obtained from a local packing house were prepared for tanning as outlined in the aqueous process shown in Table 1. One hundred gram samples were cut from the whole skins at the bated and pickled steps and prepared for dehydration studies to be done in one quart mason jars. Two procedures followed from this study. A) The samples were tumbled for 1½ hours in each of 3 one hundred percent floats of pure acetone. Some of the samples were treated with a 2.5% float of formalin (a 37% solution of formaldehyde) in the third and final 100% acetone bath. After processing, the samples were dried, either in ambient air or in a dry nitrogen atmosphere. B) A slower dehydration process starting with 30% acetone followed by 50%, 70%, 90%, and 100% acetone baths was tried. All baths were tumbled for 1½ hours. Formalin was added to the first 100% bath. The second 100% bath was used to remove the water added in the formalin solution.

Large-scale Investigations

The six-step dehydration schedule worked out in the mason jar runs was adopted for use in the drum. The typical drum run contained 9 or 10 well fleshed skins which weighed about 100 lbs. The skins were processed as matched sides through the bating (Bated Stock Run) or pickling (Pickled Stock Run) steps. Then one side of each skin was removed and stored. The remaining matching sides were dehydrated and treated with formalin, as outlined in the bottle tests. After the skins were dehydrated and dried, they were sampled for analyses and examined visually. The skins were then rewet, combined with their matched sides, and processed to crust leather as outlined in the aqueous process.

The rewetting procedure used for bated stock involved soaking the stock for 3 hours in a 200% float of water at a pH of 8. Sodium Bicarbonate was used to adjust the pH of the float. Pickled skins were rewet in a pickling solution (pH 2.4).

Another dehydration process studied involved the use of a stainless steel tank and toggle frame. Only about ⅔ of a side was used because the tank was small (30" x 48" x 2") and had a total capacity of 12.5 gallons. The selected side was toggled out using specially made spring loaded toggles which allowed for slight shrinkage without tearing the skin. After the toggled skin was inserted into the tank, acetone was pumped in and then circulated by a small pump for 24 hours. After the acetone bath was drained, dry nitrogen was used to completely remove the acetone from the skin without moisture damage.

The following chemical tests were made on bated stock before and after dehydration and on crust leather; moisture, ash, fat, and nitrogen. These tests were done according to the methods of the American Leather Chemists Association (3) when possible.

ASTM methods (4) were used for the following physical tests; stitch tear, torsion, and tensile strengths. Shrinkage temperatures were determined for crust leather using water at high pressure.

The acetone/water content of the baths was determined by gas chromatography using an internal standard. This method was used because it was accurate in the presence of fats in the exhausted baths.

TABLE I
AQUEOUS TANNING PROCESS

Scour:	100% H_2O @ 90°F
	2% Soda Ash Na_2CO_3
	0.3% Triton X 114
	Run 1 hr Drain
Unhair:	100% H_2O @ 85°F
	1 3/4% Sodium Sulfide
	1% Sodium Sulhydrate
	Run 20 minutes
	Add 2% Lime
	Run 5 hrs Drain
Relime:	200% H_2O @ 85°F
	4% Lime
	0.3% Triton X 114
	Run 5 min/hr overnight
	Wash continuously with 450% H_2O @ 90°F
Bate:	100% H_2O @ 90°F
	4% Ammonium Chloride
	1% 1500 EU Bate
	Run 1 hr
	Test for pH (8-9), Drain
	Wash 250% @ 78°F
Pickle:	50% H_2O @ 78°F
	5% Salt
	1% H_2SO_4
	Run 1 hr pH (~2.4)
Tan:	1% Sodium Formate
	8% Tanolin R (dissolved and heated in H_2O)
	Run 3 hrs
	Neutralize with 2 feeds of 0.5% Sodium Bicarbonate half-hour apart pH (~4.0)
	Rinse and horse overnight
	Find wrung weight
Blue Stock Retan and Fat Liquor:	Wash Stock @ 90°F
	Drain to 300% float
	Add
	1½% Amm Bicarb
	Run 30 min. pH (6.8)
	Wash 15 min @ 120°F
	Drain to 200% float @ 120°F
	Add 15% Quebracho liquid
	Run 30 min
	Add 1% Med Brown Dye dissolved in ⅔ qt. H_2O
	6% Solvent Fat X 76-31 (RRW)
	Run 45 min
	Add ⅜% Formic Acid in
	1 qt. H_2O @ 110°F
	Run 30 min pH 3.7
	Rinse 1 min. @ 90°F, Pull, Horse

Histological examinations were made to evaluate the effects of dehydration on the pigskin structure. Samples of the bated and dehydrated bated skin were fixed in a 3.7% formaldehyde solution. Cross-sections were cut at 50 microns on a freezing Spencer* sliding microtome. The sections were stained with Oil Red 0 (5) to determine presence of fats in the skin. Cross-sections of samples from crust leathers were prepared for microincineration (6). All sections were examined and photographed using a Zeiss Photomicroscope.*

Results and Discussion

Acetone was used to dehydrate pigskin because of its excellent fat removing ability and infinite miscibility in water. Acetone has a low boiling point, low latent heat of vaporization and high volatility. These properties facilitate economical recovery from liquid wastes. Acetone vapor is recoverable through carbon absorption/steam purging cycles.

There are six possible points in the tanning process where pigskin may be solvent dehydrated. They are before processing and after the unhairing, liming, bating, pickling and chrome tanning steps. Unhaired and limed stock were dismissed because of sulfide poisoning in the former and lime blast damage in the latter. Dehydration of bluestock eliminates tanners' options if they wish to tan without chrome.

TABLE II

DEHYDRATION POINTS STUDIED IN MASON JAR RUNS

TYPE OF STOCK	ADVANTAGE	DISADVANTAGE
RAWSTOCK	BEST FAT RECOVERY	CANNOT BE GRADED
BATED STOCK	OPEN STRUCTURE LIGHTEST WEIGHT OF THE THREE	ORIGINALLY FEARED TO BE DAMAGE PRONE
PICKLED STOCK	POSSIBLY LESS DAMAGE PRONE THAN BATED STOCK	NOT AS VERSATILE AS BATED STOCK BECAUSE pH IS PREDETERMINED

Table II shows the advantages and disadvantages of the 3 processing steps studied in the mason jar runs. Dehydrating rawstock offered the recovery of fats that were not sulfide contaminated, but pigskins often have surface defects and these defects cannot be seen in rawstock. Also, the value of the sulfide-free fat recovered from well fleshed, acetone dehydrated raw pigskin could not justify dehydrating rawstock. Dehydrated bated or pickled skins would be more valuable to the tanner than dehydrated raw skins. Tanners could grade the dehydrated bated or pickled stock and would pay premium prices for skins known to be free of surface defects. Only bated and pickled stock were investigated in this study.

Buechler (2) found it necessary to use formalin while removing acetone from dehydrated pickled cattlehide. This addition of 2.5% formalin prevented hard crusty spots that developed while the acetone evaporated from the skin in ambient air. He also found that drying in a dry nitrogen atmosphere without the use of formalin prevented hard crusty spots.

*Mention of brand or firm does not constitute an endorsement by the U.S.D.A. over others of a similar nature not mentioned.

Our own bottle tests confirmed these results. Another problem found in the early bottle tests was that the pieces of skin dehydrated in 100% acetone suffered from severe grain draw and area shrinkage. The grain draw and shrinkage can be attributed to the sudden removal of water from the skin and to high elastin levels in the skin. Elastin is scattered throughout pigskin and probably adds to the grain draw. To eliminate the grain draw problem the slower dehydration process was developed.

The six-step dehydration schedule worked out in the mason jar runs was adopted for large scale investigations and worked satisfactorily. A stainless steel lined wood drum with a capacity of 95 gallons was used for the large scale investigation.

Originally, it was felt that pickled stock would be better to dehydrate because it has a lower water content and is less prone to damage than bated skins. After several drum runs the bated stock was found to be undamaged during the dehydration process. Therefore, work on pickled stock was not pursued. The dehydrated bated stock (after rewetting) can be adjusted to any pH and thus any tannage can be employed. This versatility over dehydrated pickled stock makes dehydration in the bated condition the method of choice.

The use of formalin in the next to last dehydration bath was eliminated after a new method for drying the acetone from the dehydrated pigskin was developed. After removal of the final acetone bath, warmed air was delivered to the otherwise closed drum through the gudgeon. The drum was rotated at 3 rpm. The air was flashed from 70°F and 100 psi to 3 psi and warmed to 100°F which removed moisture thereby decreasing relative humidity to about 30%. This method, beside eliminating the use of formalin, also offered the advantage of recovery of the acetone from the skins by passing the exhaust air from the drum through a carbon absorption system.

The tank dehydration method also produced a good product. Pigskins were processed in the drum by the aqueous method (Table I) to the bated or pickled stage. They were removed, toggled on a frame and put into the tank. The six step dehydration method worked out in the bottle runs was used, but found to be unnecessary because the skins were not being tumbled and static molecular diffusion through a solid is a slow process. So one 100% acetone bath was used in the tank without causing grain draw from too rapid a dehydration. The tank process also allows recovery of acetone utilizing a carbon absorption system.

Histology

Photomicrographs of the bated skin before and after dehydration are shown in Figures 1 and 2. Note the quantity of fat in the cells around the hair follicles in Figure 1 compared to the empty fat cells shown in Figure 2. Pigskin has large quantities of fat on the flesh side. Most of the subcutaneous fat can be removed by fleshing, but the fat is also found deep into the hair shafts as seen in Figure 1. This fat is not removed by fleshing. The remaining subcutaneous fat with other fat often spues over the skins leading to grease spots on conventionally tanned pigskin (Figure 3), that detergent and other degreasing agents cannot remove. However, acetone dehydration offers the advantage of fat extraction and the removal of grease spots (Figure 4). Results obtained from chemical analyses shown in Table III indicate how low the extractibles or fats are in dehydrated versus conventional stock. The nitrogen analysis (on moisture free-ash free basis) for the dehydrated bated stock is high and indicates that the skin is mostly collagen.

Dehydrated pigskins also have an open fiber bundle weave as seen in Figure 2. This open weave is produced by the removal of extractibles and probably was aided by the drumming action used while drying the acetone from the skins. The open fiber weave in the acetone-

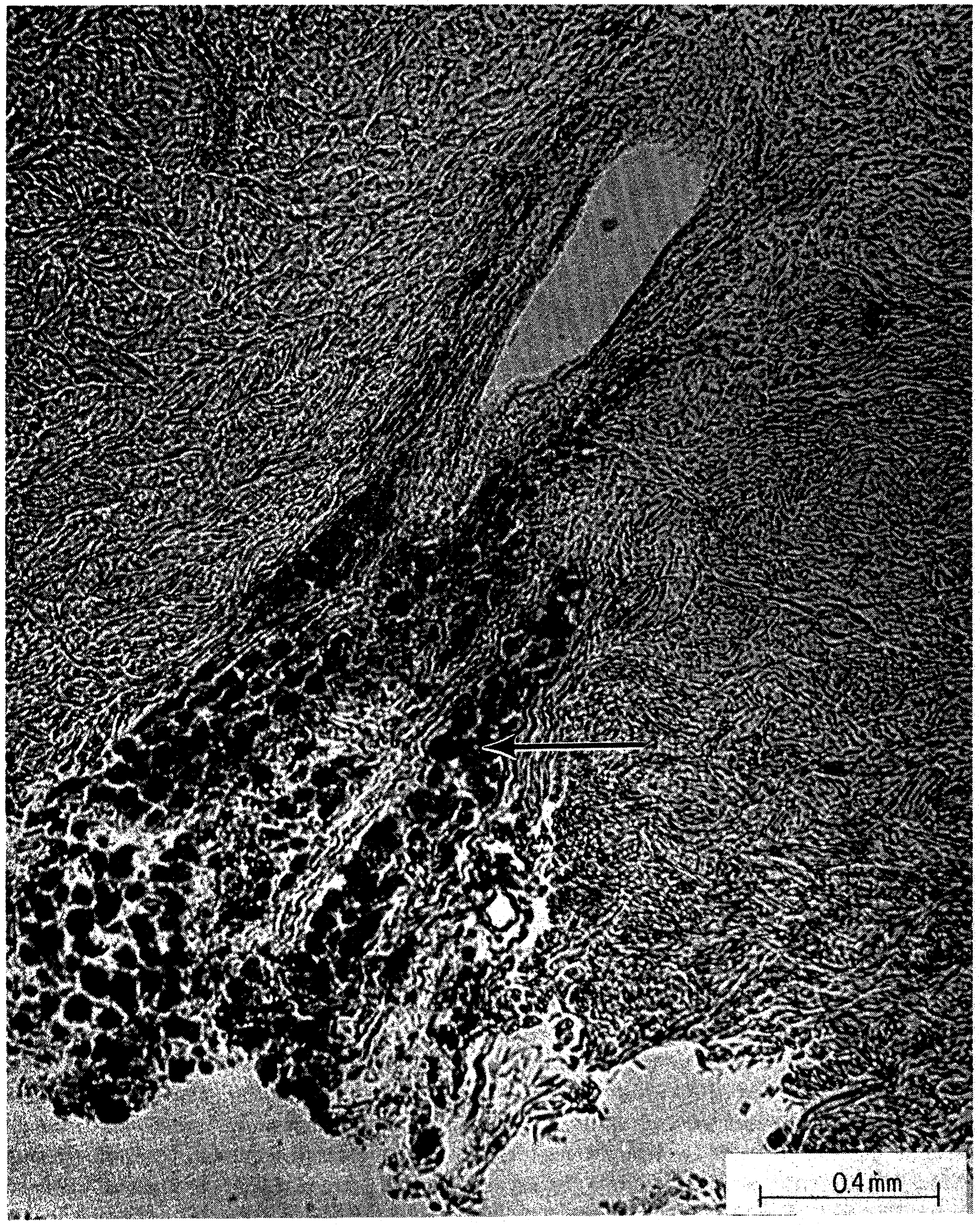

FIGURE 1. Bated Pigskin prior to dehydration (stained for fat - note arrow).

FIGURE 2. Bated Pigskin after dehydration (stained for fat - note arrow).

TABLE III

CHEMICAL ANALYSIS (AS IS BASIS)

	CONVENTIONAL BATED STOCK	DEHYDRATED BATED STOCK
MOISTURE	73.8%	16.08%
FAT	5.7%	0.65%
ASH	1.06%	1.42%
NITROGEN	4.54%	14.94%
ON MOISTURE FREE-ASH FREE BASIS		
TOTAL NITROGEN	18.60	18.07%

dehydrated, bated stock allowed it to be easily rewet and tanned. Microincineration results shown in Figure 5 show that chrome penetrated more uniformly in rewet dehydrated bated skin than in the conventionally processed control skin. Physical test data support the results shown by microincineration.

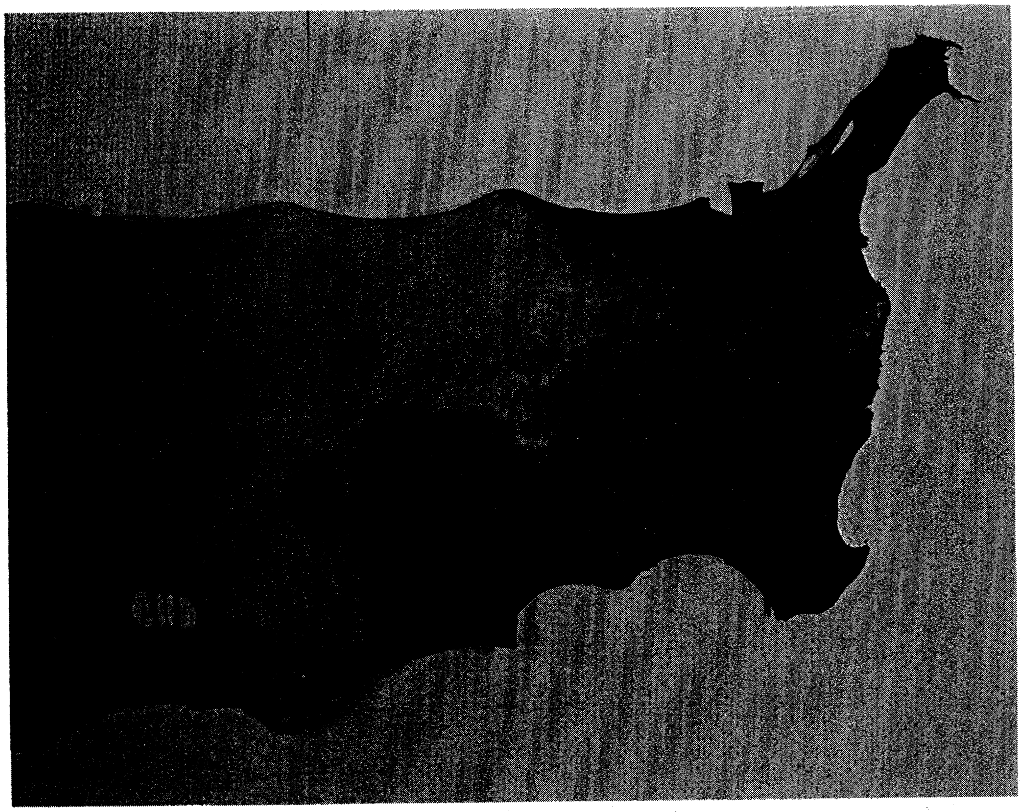

FIGURE 3. Oil spots present after conventional tanning process.

Physical Tests

Shrinkage temperatures were determined for twenty-four control crust leather samples. All values were 107°C. (The shrink test was conducted in pressurized water.) All of the shrinkage temperatures for crust leather made from dehydrated skin were evenly distributed in the 111°C to 113°C range. Twelve formalin treated samples and eighteen non-formalin treated samples gave the same even distribution of shrinkage temperatures.

Table IV summarizes the results of the physical tests performed on samples of crust leather made from control and dehydrated pigskins. The stitch tear and tensile strength for the controls and the dehydrated sides were not statistically different (using Runnett's test). The results of the torsion tests show that both formalin treated and non-formalin treated dehydrated pigskin produce crust leather that is significantly more supple than crust leather made from the controls. (Torsion and suppleness are inversly related.)

There are some differences in the intermediate product (dehydrated bated pigskin) produced by the tank and the drum methods. The tank method produced a very white, smooth, stiff, flat dehydrated skin. The drum product had a rumpled look from the drumming process. However, no skin defects were created by drumming and the wrinkles were eliminated when the skin was wet back. Both methods produced a very light weight, gradable, intermediate product that is one-sixth the weight of well-fleshed raw pigskins. For economic reasons, the drum method is recommended over the tank method. Some factors involved would be capital costs, manpower, and energy expenses.

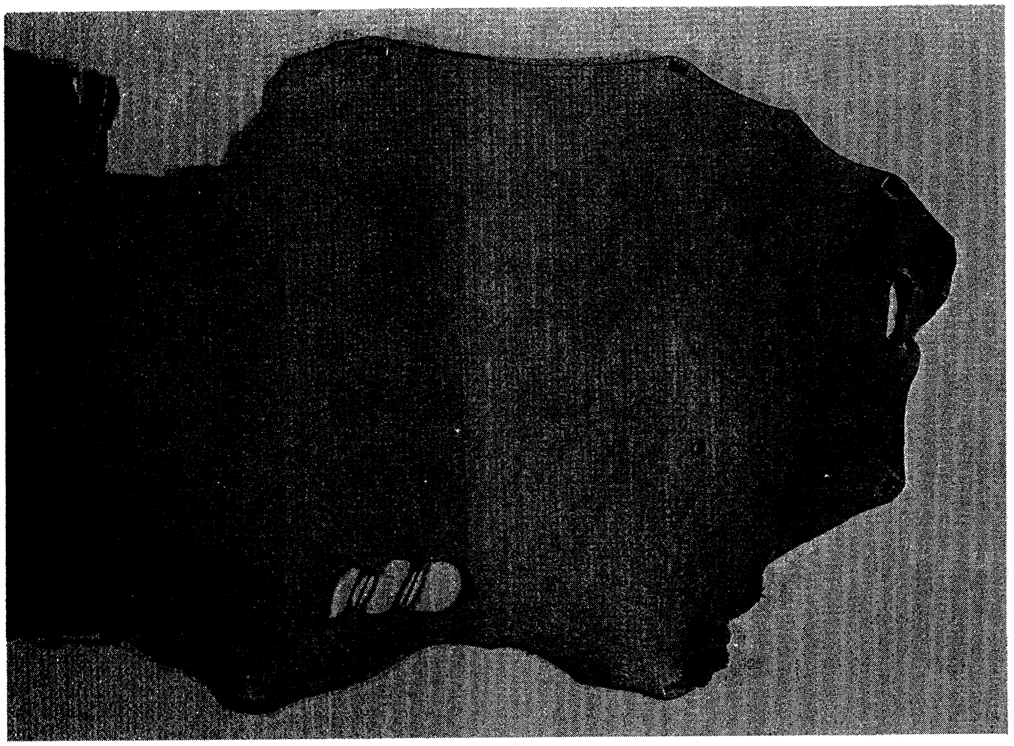

FIGURE 4. Note absence of oil spots after tanning and finishing dehydrated bated stock.

TABLE IV

STRENGTH OF CRUST LEATHER: DEHYDRATION PROCESS VS CONVENTIONAL PROCESS

	TORSION (PSI) (SUPPLENESS)	STITCH TEAR-2 HOLE (LB/IN)	TENSILE STRENGTH (PSI)
CONTROL	Average = 2257	Average = 627.4	Average = 2503
	Standard Deviation = 42	Standard Deviation = 78.3	Standard Deviation = 415
	No. = 2	No. = 4	No. = 18
DEHYDRATED WITH FORMALIN	Average = 2051	Average = 549.7	Average = 2251
	Standard Deviation = 20	Standard Deviation = 158	Standard Deviation = 460
	No. = 2	No. = 3	No. = 9
DEHYDRATED WITHOUT FORMALIN	Average = 2079	Average = 626	Average = 2523
	Standard Deviation = 31	Standard Deviation = 38.4	Standard Deviation = 430
	No. = 2	No. = 3	No. = 9

(Where No. is the number of sides tested.)

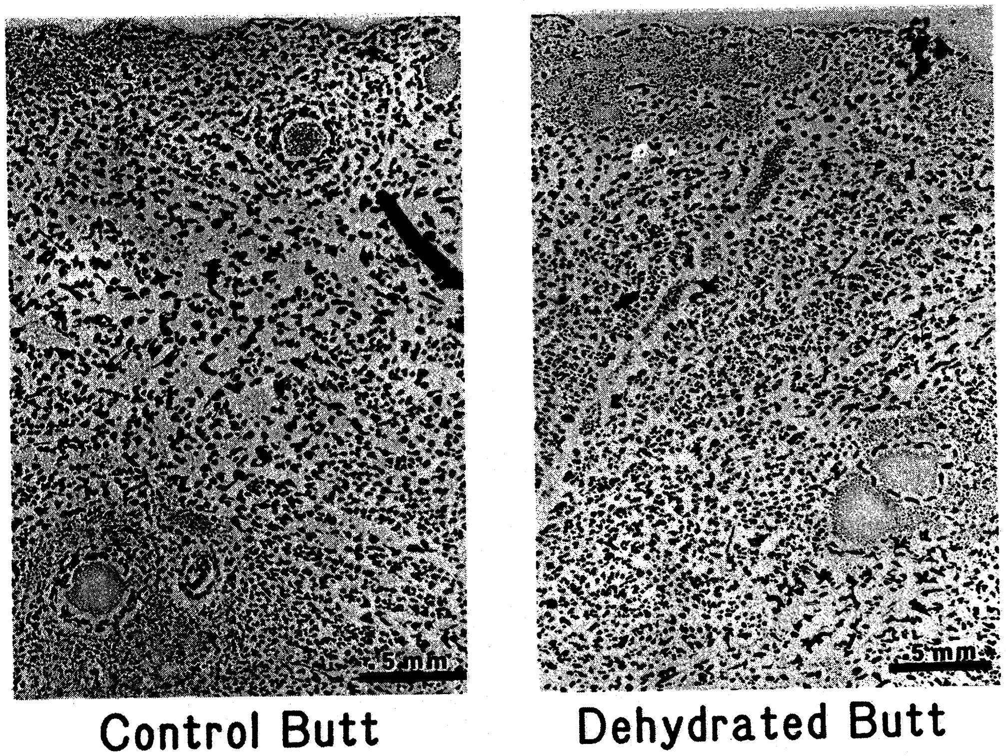

FIGURE 5. Microincineration of tanned pigskin.

If the drum method is adopted, a counter-current system for acetone recovery would maximize operating efficiency and is highly recommended. Figure 6 shows a simulated counter-current dehydration process used in some of the six-step mason jar runs. The average acetone/water content of each bath is listed. The material balance shown in Figure 6 shows a loss of acetone. There were evaporative losses of acetone to the atmosphere as the skin was transferred to different mason jars. In an industrial process, the skins would remain in the sealed drums, and acetone baths would be pumped from drum to drum eliminating these losses.

The experimental runs described in this paper were completed by February, 1982. In April, 1986, a dehydrated bated pigskin from one of these runs was tested in the laboratory. Pieces rewet quickly, absorbed chrome readily, and showed no visible or microscopic signs of bacterial damage. The dehydrated bated pigskin from these runs were stored in several locations. Some were air-conditioned environments and other locations were subject to temperature and humidity variations. There were no atmospheric monitors collecting data on ambient conditions. The stock did keep for more than 4 years in all of these locations. If a skin had water fall on it, the areas of the skin contacted by the water would putrify.

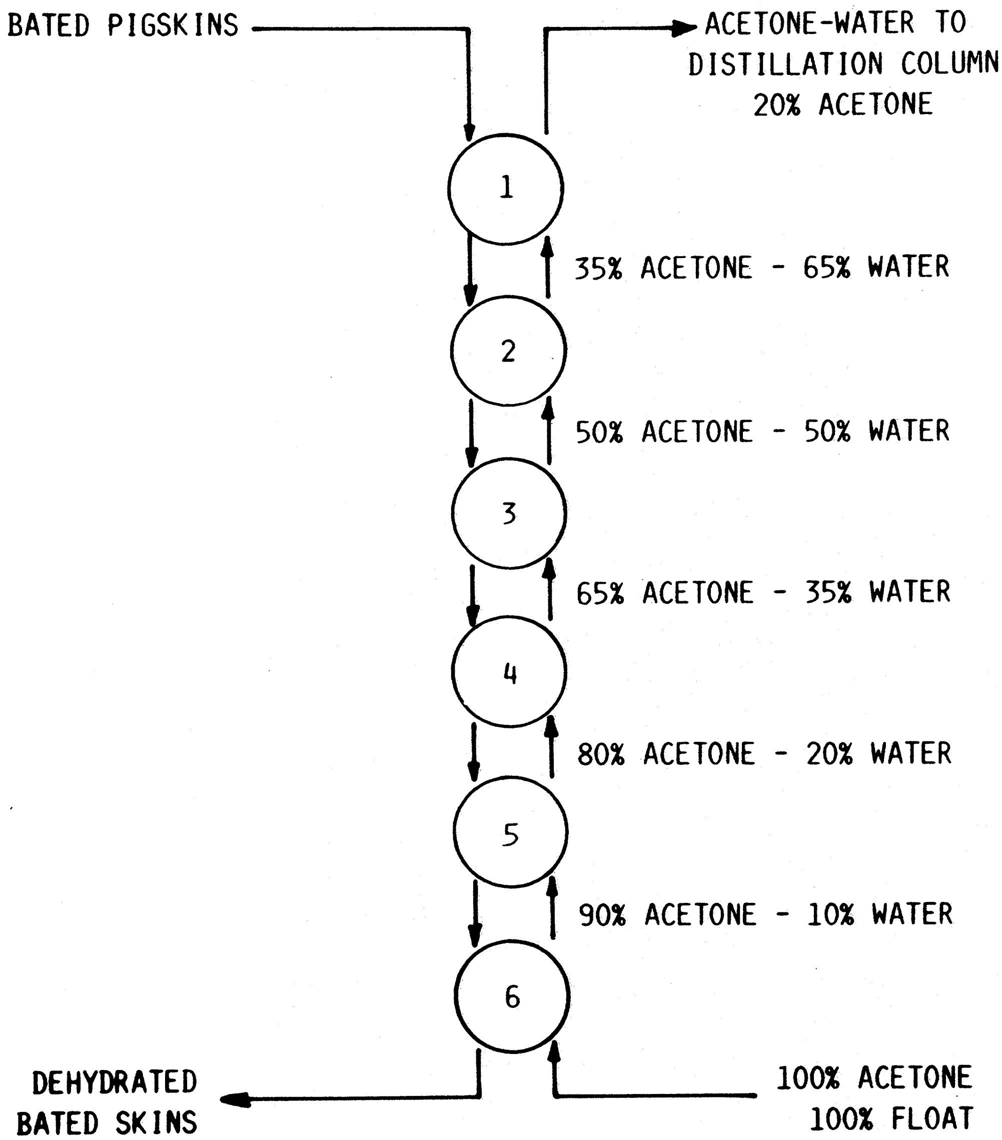

FIGURE 6. Simulated Counter-Current Dehydration Process

Summary

The research reported in this paper produced two processes both of which yielded dehydrated pigskins that could be made into desirable leather products. Dehydrating bated stock in a drum worked when acetone was removed with a current of warmed air while the drum was turning. Tank dehydration and subsequent acetone removal with nitrogen also worked on bated stock, however the drum process is more economical.

Dehydration of bated pigskins produces a preserved skin with an indefinite storage life. This product is one-sixth the weight of fresh, well-fleshed, pigskin thus minimizing freight costs when shipping. The dehydrated product can be graded, earning more money for the producer, while saving money for the leather manufacturer. It can be rapidly rewet and made into crust leather with a better appearance and better physical properties than conventionally processed pigskin.

An environmental advantage of acetone dehydration is that salt contamination of streams is minimal, another is with a centralized beamhouse system all beamhouse wastes would be confined to one location.

Acknowledgements

The authors wish to thank Dr. John G. Phillips for statistical analyses, Mr. Arthur I. Rivenburgh for photographic services, and Mr. Edward J. Diefendorf for assistance in the tännery.

References

1. Feairheller, S.H., Bailey, D.G., and Maire, M. "*Identification of Obstacles Delaying Production of Butcher-Hogskins as a Leather Manufacturing Raw Material and Recommended Approaches for Overcoming These Obstacles.*" Issued by U.S. Dept. of Agriculture, ERRC, (1979).
2. Buechler, P.R., *JALCA* **70**, 541-555 (1975).
3. Official Methods of Analysis, ALCA, 1957.
4. ASTM, Book of Standards, (1980), Part 21.
5. Lillie, R.D. "*Histophathologic Technic and Practical Histochemistry.*" 3rd ed., McGraw-Hill Book Co., New York, 1965.
6. Sleichter, G.M., *JALCA* **33**, 478-481 (1938).

Received February 27, 1987