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Paper B3

Preserving wool-on skins in pickle

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1. Introduction

Pickling has long been used as a means of preservation of lamb pelts and appropriate application of salt and acid together with a fungicide can preserve skin products for over 12 months. However, long-term pickling inevitably causes some changes to the structure of the skin because the proteins gradually hydrolyse as a result of the acid conditions [1, 2] so that there is some loss of strength over time and conditions such as looseness may be exacerbated. Mild hydrolysis may also be beneficial in that it can give a softer skin and break down adipocytes so resulting in improved degreasing[3].

Innes[4] concluded that immersion pickling was not a satisfactory method of preservation for wool-on skins because to obtain sufficient long-term preservation the initial acid concentration had to be so high as to be detrimental to the strength of the skin. He used a concentration of 1% (w/v) sulphuric acid in the initial pickle and found that after six months the leather made from these skins showed severe cracky grain due to degradation of the grain fibres particularly in the greasy areas of the skins.

This paper describes the development of a pickling system incorporating a suitable fungicide to provide preservation of wool-on skins for up to six months with no detrimental effects on leather quality and considerable savings in terms of salt use and ease of subsequent processing.

Table 1 outlines the relative advantages and disadvantages of pickling compared to salting as preservation methods for wool-on skins. Some of these claims are conjectural and it was the purpose of this research to determine whether they can be substantiated.

Table 1.Comparison of the qualities of pickling and salting preservation

Preservation method	Pickling	Salting
Advantages	Skins can go straight into processing without prolonged rehydration. Uses only ~ 50g salt/skin. Improved scourability of skin grease? Increased softness of leather as a result of mild hydrolysis?	Reliable long-term preservation if carried out correctly. No loss of strength of the skin during storage.
Disadvantages	Requirement for fungicide addition. Possible loss of skin strength during storage? Possible development of brittle (cracky) grain? Increased softness of leather?	Problems of salt disposal. Requires additives to protect against halophiles and to preserve during early stages of dehydration. Skins must be carefully rehydrated requiring additional processing time.

2. Materials and Methods

These trials were based on half-skin comparisons in which one half of each raw woolskin was processed and tanned immediately while the other half was pickled and held in storage for the

appropriate period. The chemical and physical properties of these half skins were then compared to determine any changes arising from the storage in pickle.

2.1 Pickling conditions

Raw skins with a wool length of about 50 mm and from the same line of New Zealand crossbred lambs were procured from a meat processing plant. The skins were washed, fleshed and pickled without scouring. The pickle solution was prepared as shown in Table 2.

Table 2: Composition of pickle solution

Salt	80 g/L
Sulphuric acid	3.0 g/L
Fungicides - one of these formulations added	
TCMTB 30%	0.1 g/L
Phenolic blend	0.3 g/L

The float ratio of woolskins to pickle was approximately 1:40 (w/v). The fungicide was added to the woolskins in the pickle by dispersing it in a portion of the float and adding it slowly to the goods as the paddle was working in order to maximise the distribution of the active agent. The pickling process proceeded for four hours to allow sufficient time for full pickling and distribution of the fungicide.

The pickled skins were then cut down the midline and each half skin was labelled for identification. Samples of the skins were taken for histological examination and chemical analyses and one half of each skin was returned to the pickle bath for scouring and tanning while the other half skins were drained overnight before being stacked for storage. One set of half skins was chrome tanned by a standard process while the other set was tanned with a white, THPS tannage (Albrite AD 75, Rhodia).

The pickled skin halves were stacked on palettes in a storeroom under a cover of plastic sheeting. One set of skin halves were sampled and put into tanning processes after three months and the other after six month's storage. The tanning processes were identical to those used for the processing the initial half skins. The temperature of the storeroom was monitored throughout.

2.2 Analyses

The pickled skin material was analysed for fat content and free fatty acids, free acid and salt and total and soluble protein using LASRA® standard methods as used for pickled pelts. The glycosaminoglycan (GAG) content of the skin was measured by digesting the tissue and analysing the GAGs by a dye binding method. Specific process liquors were analysed for protein concentrations. The concentrations of fungicide actives in the skin, wool and remaining pickle were analysed by HPLC.
In addition to subjective evaluation of the wool, samples were also taken for measurement of the alkali solubility to determine any damage to the fibre during storage.

2.3 Histology

Pieces of the skin were fixed in formalised brine, then sections were cut and stained with Sudan III and IV for examination of skin fat and with Azur A for the collagen and elastin fibres of the skin. Sections were examined at up to 50 x magnification.

2.4 Leather properties

Prior to evaluation of their physical properties the woolskin halves were conditioned to about 30% moisture content and staked (Molissa). Objective measurements of the softness of the leather were made by measuring the displacement of the leather by a standard load (BLC Softness Meter ST 300) and the force required to bend the leather sample in a standard bending rig (IWS test TM 226:1992). In the case of the softness meter readings the greater the displacement of the leather under the load the

greater the softness whereas in the bendability test the lower the load required to bend the test strip the softer the material.

Tear strength, tensile strength, grain strength and elongation at break of the leathers were determined following the relevant methods prescribed in BS 3144:1968 on samples cut from the OSP areas from the leathers made from each set of half skins.

The statistical significances of the results from the half skins were compared using the paired Student's t-test. Many of the text figures show the changes in the mean values and the standard deviations for the results from groups of paired skins but the statistical comparisons are all based on the paired results which exhibited much less variability.

3. Results

3.1 Changes in pickle composition with storage

There was a significant decrease in the moisture content of the skins as they dried during pickle storage (Figure 1) so all analytical values have been adjusted for the dry matter content of the skins.

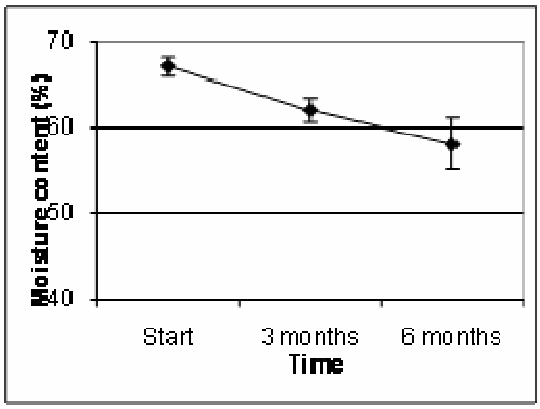

Figure 1: Change in moisture content of skins on storage

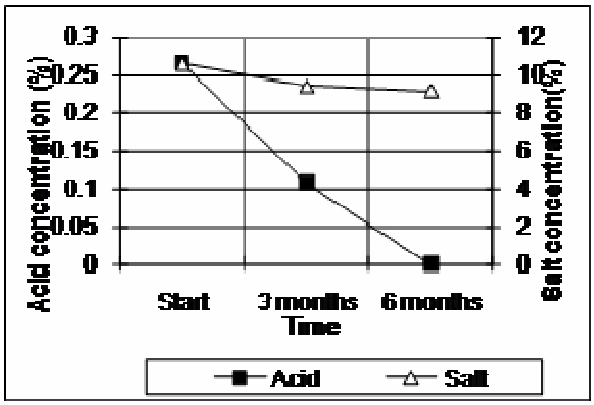

Figure 2: Change in acid and salt contents of skin

Acid and salt were extracted from the pickled material and analysed (Figure 2). The free acid content showed a sharp fall to zero after 6 months storage whereas the salt content remained relatively constant over the period. The surface pHs of the skins increased concomitantly from an initial pH 1.8 to 4.2.

The temperature of the storeroom ranged between 9.6°C and 31.5°C with an average temperature of 18.7°C during the course of the storage trial.

3.2 Effect of storage on pickle skin composition

Protein

Analysis of the total and soluble protein content of the skins provided a measure of breakdown of the material by acid hydrolysis (Figure 3). Total protein content remained relatively constant over time but there were increases in the soluble protein and consequently in the protein ratio (soluble protein/total protein x 100).

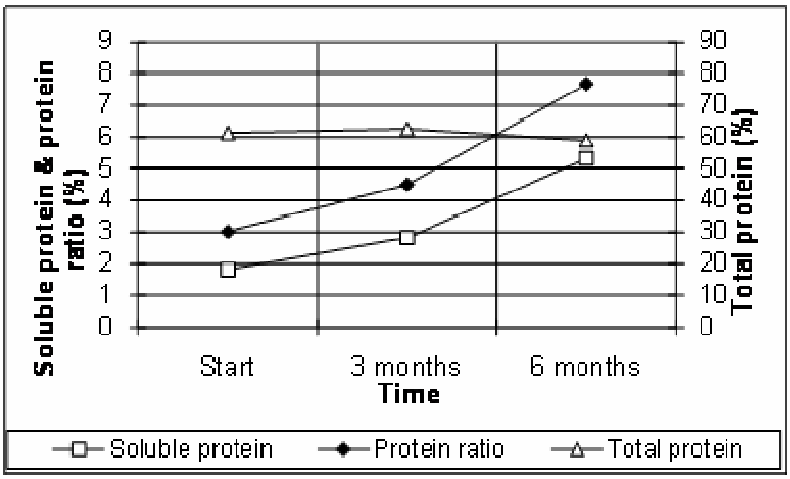

Figure 3: Change in total and soluble protein levels and the protein ratio during storage

The initial levels of soluble protein were higher than those encountered with pickled lamb pelts which are expected to have soluble protein values of 1% or less. This reflects the lesser processing of wool-on skins (no liming, no bating and minimal washing) so that more soluble protein remains in the skins. On storage the soluble protein content increased significantly, as did the protein ratio which indicated acid hydrolysis of the skin protein. For pickled pelts a protein ratio of greater than 7.5% is indicative of excessive acid hydrolysis of the skin but these benchmark values will not hold for woolskins. The protein ratio of skins held for six months had increased to 7.7%.

The loss of protein was also apparent on histological examination with the stored pickles showing greater evidence of 'opening up' than their fresh counterparts. Figure 4 illustrates cross sections of the same skin when freshly pickled and after six months of pickle storage. The sections were stained specifically for elastin which showed little change over time but there was evidence of increased disorganisation in the other fibrous proteins over time.

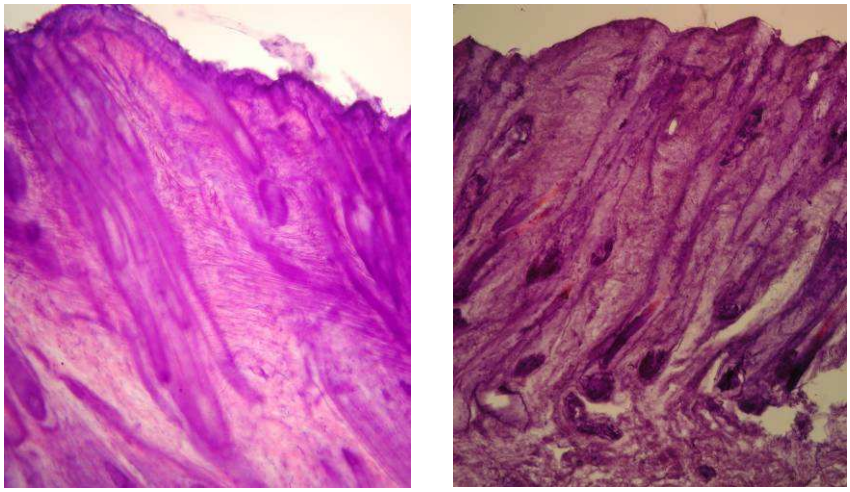

Figure 4: Sections of fresh (left) and six-month-old pickle (right) stained for elastin.

Grease

The total fat content of the skins did not change significantly over the period of pickle storage. The values reflect the large variations in grease content that were found within and between skins so that even using half skin comparisons it was difficult to establish significant changes in fat levels.

However the free fatty acid content of the grease increased significantly during the pickle storage (Figure 5).

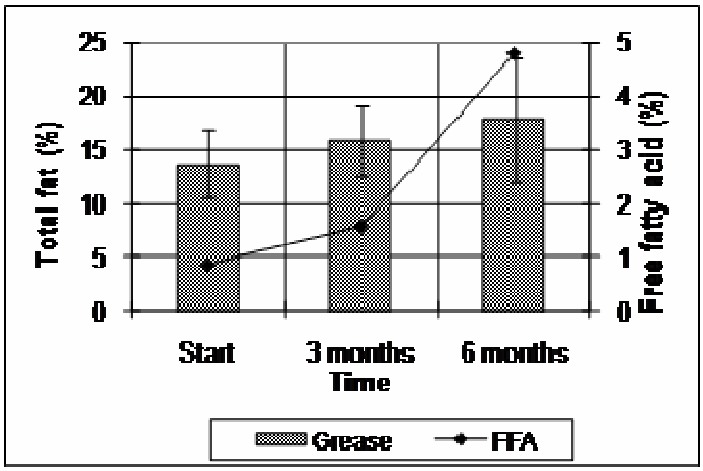

Figure 5: Changes in total grease and in free fatty acid during storage

Histological examination of skin sections showed that a breakdown of the adipocytes and distribution of the dermal fat through the corium occurred over time (Figures 6 and 7).

The sebaceous glands remained intact however and sebaceous wax was not dispersed in the same way. The scourability of the fat from the skins was determined by analysing for solvent-extractable grease and free fatty acid content after a standard scouring and bleaching process. Figure 8 shows the change in the post-scouring grease levels in relation to duration of pickle storage.

On a paired half skin basis there was no significant change in residual grease after scouring after three months of pickle storage but after six months the efficiency of skin scouring had improved significantly ($p<0.01$). However, while the overall effect of storage was to improve the ease of grease removal this did not ensure that all skins had acceptable levels of residual grease at the end of scouring. Most skins showed a slight decrease in remaining grease but those that had high fat content in the initial material continued to have higher levels after storage.

Glycosaminoglycans

Analysis of the pickled skins for GAGs showed a significant decrease in levels during the course of storage from an initial average level of 2450 ppm to 1675ppm after 3 months and 1510 ppm at six months. While the variability in values between skins was quite large when the data were compared on a paired basis there were significant ($p<0.05$) declines in values after both three and six months pickle storage. GAGs may be removed by dispersing in the draining pickle liquor or may be hydrolysed by the acidity of the pickle. Since GAGs are part of the interfibrillary matrix that binds the collagen fibres together their removal is consistent with greater opening up of the skin structure with improved softness and less substance in the skins.

3.3 Uptake and distribution of fungicides

Both fungicides were effectively exhausted from the pickle (>95% uptake) but around 70% of the actives were retained on the wool so that high application levels are required to ensure sufficient activity is applied to protect the skin from fungal attack.

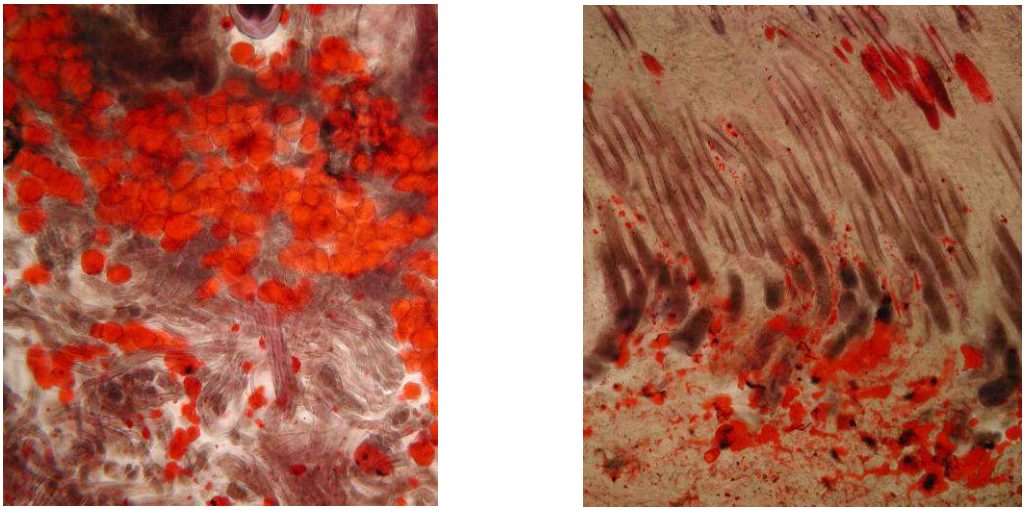

Figure 6: Fat in grain corium junction of fresh pickled woolskin showing discrete adipocytes (left) and showing some breakdown after three months storage (right)

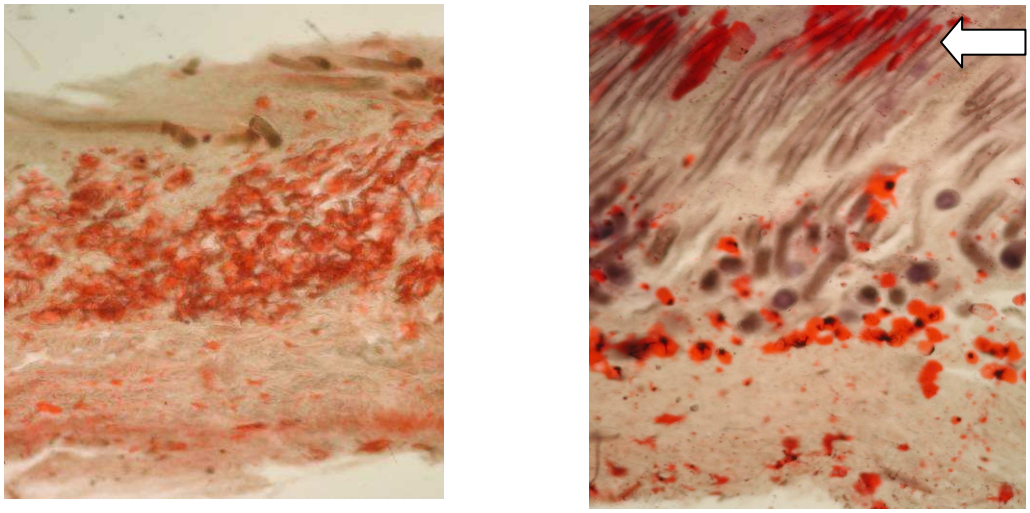

Figure 7: Fat cells in six-month-old pickled woolskin showing disintegration of fat cell walls (left) and sebaceous grease (arrowed, right)

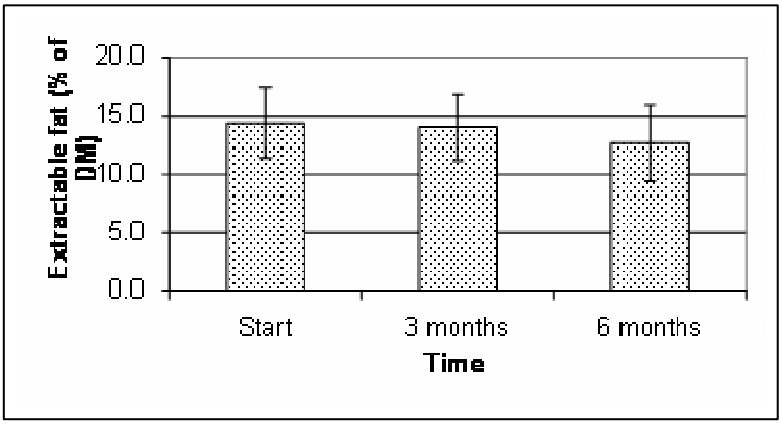

Figure 8: Extractable grease after scouring

3.4 Properties of leather from stored skins

Tannability

Table 3 shows the shrinkage temperatures achieved with the fresh and stored half woolskins with the chrome/syntan and THPS tannages.

Table 3: Mean shrinkage temperatures of woolskin halves after tanning

Tannage	Shrinkage temperatures (°C)		
	Initial	Stored 3 months	Stored 6 months
Chrome/syntan	83.0	81.5	81.5
THPS	85.5	85.0	88.0

The shrinkage temperature of the white-tanned leather after 6 months storage was significantly ($p>0.01$) higher than the initial and 3-months stored leathers. Possibly the hydrolysis of interfibrillary proteins had improved the opening up of the skin to the extent that the tanning agent could penetrate and crosslink more readily. This effect was not apparent with the chrome/syntan combination tannage however.

The physical properties of the leathers were affected by the tannage so the results for both the chrome tanned and the white tanned leathers are presented separately.

Skin thickness

There were significant decreases in skin substance during storage for both leathers (Figure 9). By the end of 6 months there was a 36% decrease in thickness for the chrome tanned leather and a 43% decrease in the phosphonium tanned leather.

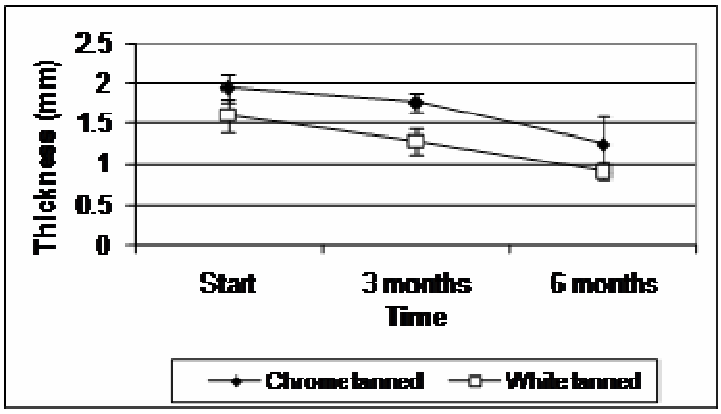

Figure 9: Effect of pickle storage on leather substance

All the white tanned leather had significantly less substance than the chrome/syntan leather as a consequence of the filling effect of the syntan.

Comparison of the paired leathers for looseness showed no discernable difference as a result of storage. These skins were not notably loose but possibly in skins with a propensity for looseness the effect may be exacerbated by pickle storage.

Grain strength

The grain strength and the extension of the leather at grain break were measured on the lastometer and the results for the grain break loads are shown in Figure 10. The chrome tanned leather showed significant increases in the load at grain break with the duration of storage in the pickle while the white tanned leather showed a similar trend but not a significant effect. The grain strength of the chrome/syntanned leather was consistently stronger than that of the phosphonium tanned leather.

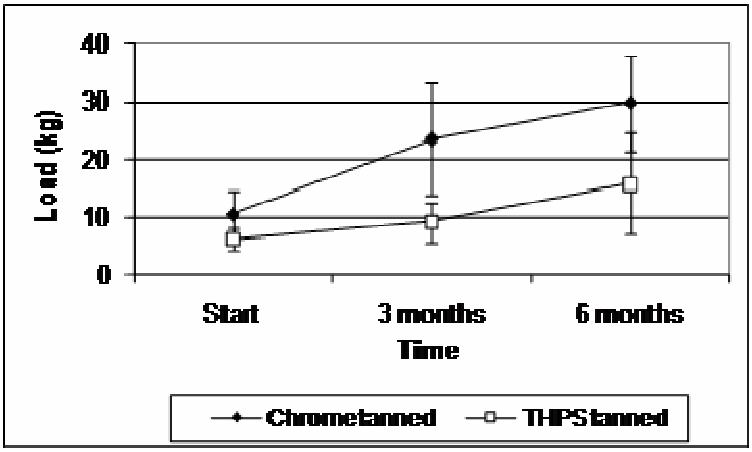

Figure 10: Change in grain break load for leathers from stored pickles

The extension of the leathers at grain break also increased significantly for the chrome-tanned leather from an average of 5.8 mm with the unstored skins to 8.1 mm after 3 months and 9.9 mm after 6 months storage. Again the THPS tanned leathers showed a similar trend without achieving significance.

These results show no indication of grain brittleness being induced by pickle storage rather that the strength and stretchiness of the grain has been increased.

Softness

There were significant increases in leather softness as measured by the Softness Gauge over the first three months of pickle storage but by 6 months the chrome-tanned leather had become firmer again (Figure 11). The softness of the white tanned leather did not change between three and six months.

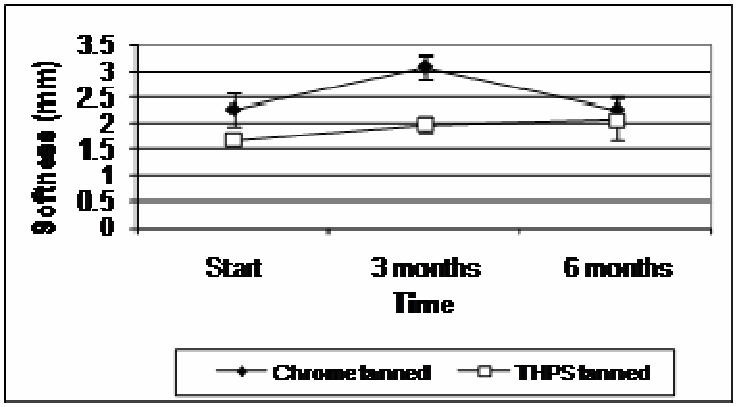

Figure 11: Change in leather softness from stored pickle

The other measure of leather softness, the bendability of the leather both parallel and perpendicular to the direction of the backbone, showed the same effect with a significant decrease in the load (ie increased softness) after 3 months but an increase in the chrome tanned leather after 6 months pickle storage. The phosphonium-tanned leather however did show consistently increasing softness with time in this test. The general trend for the softness of the leathers was for it to increase with time of storage in the pickle apart from the anomalous result with the chrome tanned material after 6 months.

Tensile strength
The absolute load at which the leathers broke under tensile testing did not change significantly between the fresh material and after 3 months pickle storage but were significantly lower by 6 months storage. However, when the tensile strengths of the leathers were calculated by dividing the breaking load by the cross sectional area of the test pieces there were no significant changes found in either leather as a result of storage. The extension of the leather at the point of breakage was also measured and found not to change significantly as a consequence of pickle storage.

Tear strength
The tear strength of the leathers showed no significant change over the first three months of pickle storage but after six months there was a significant increase in the tear strengths after both of the tannages (Figure 12). This increase was partly, but not completely, due to the loss of substance from the skin (tear strength is expressed as load per unit thickness).

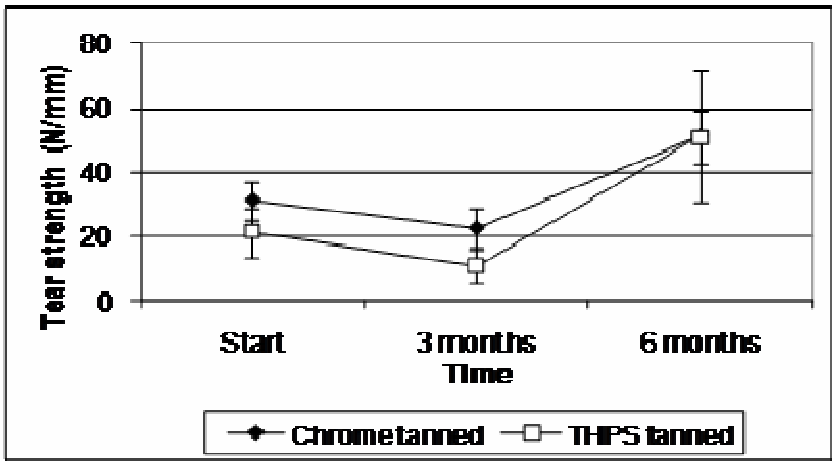

Figure 12: Change in tear strength with storage time

All of the reasons for this increase in tear strength are not clear but possibly the removal of non-structural material from the skin allows the collagen fibres to move in relation to one another and so accommodate the tearing load.

3.5 Effect of pickle storage on wool character
The wool tips of pickled skins exhibited some yellowing but this did not persist through tanning and scouring. Any effects of pickle storage on the wool were assessed subjectively on the tanned leathers and also by measurement of the alkali solubility of a representative sample of the wool. Alkali solubility is an indicator of acid damage to the wool. Neither evaluation showed any significant effect of storing in pickle on wool attributes.

Wool keratin is quite resistant to acid hydrolysis but some conversion of carboxylate anions to carboxylic acid groups occurs with exposure to strong (mineral) acids and high temperatures. Unscourable wool yellowing was not evident in this trial.

4. Discussion

Pickling green skins as a method of medium term preservation offers considerable advantages over salting in that the amount of salt used with its associated disposal problems is a fraction of that required for salt preservation. In addition skins can be put directly in to process as wool-on skins without the need for protracted rehydration. In the event that the skins are to be fellmongered it is

important that any residual acid be neutralised before the application of depilatory paint containing sulphide.

There were clearly some changes in the composition and physical properties of woolskins stored in pickle for a period of six months. Some of the changes may provide advantages to processors looking for soft, light wool-on skins. However, conditions of pickling and storage of the product need to be controlled to ensure a consistent outcome for the skin quality. Lower levels of sulphuric acid or partial replacement with formic acid resulted in reduced duration of preservation. The skins in this trial were stored at a temperature range between 10 and 32°C during the trial. Exposure to high temperatures will accelerate any effects of the pickle on the skin material.

During the storage period the acid of the pickle was neutralised as the protein of the skins was hydrolysed so that by the end of six months there was no remaining free acid and soluble protein had increased from about 1.8% to over 5%. The protein ratio (soluble/total protein concentrations) increased to 7.7% which indicated appreciable breakdown of skin proteins but, because there will be a high proportion of non-structural protein remaining in the skin, this value is less significant than it would be for pickled pelts. The decrease in free acid resulted in an increase in pH leading to increased vulnerability to microbial colonisation. Growth conditions for fungi are in the pH range 3.8 to 5.6 whereas bacteria grow better between pH 6.5 and 7.5[6] so fungi are the major threat. Consequently quite high levels of fungicide must be applied to provide adequate protection from fungal growth particularly as most of the active ingredients are taken up by the wool. Both of the fungicide formulations tested performed satisfactorily at these rates but lower application levels resulted in fungal colonisation before the end of the storage period. Because of the long floats used in the pickling process the fungicide used should have a high affinity for the substrate together with all the other requirements such as persistence during storage, low odour, no wool staining effect and environmental acceptability.

The histological evidence presented here indicates that some breakdown of fat cells occurred during pickle storage so that skin grease became spread through the skin. Also the free fatty acid fraction increased quite significantly. Both of these factors would be expected to increase the ease of scouring grease from the skins and this effect was evident from the residual grease left in scoured skins after six months storage. However, it was noted that skins with higher residual fat contents in the unstored material may still have high fat after storage so the need for additional degreasing of fatty skins may not be completely eliminated by pickle storage. Naturally, fewer skins should fall into this category.

The skin content of GAGs also decreased significantly with storage which is consistent with improved opening up of the structure. The loss of GAGs and the breakdown of protein during the course of storage lead to a decrease in substance of the tanned material. This hydrolysis was not sufficient to result in any loss of strength of the leather so probably much of the substance loss was non-structural protein. There was an increase in grain strength and elasticity after pickle storage rather than any indication of grain weakness and crackiness. The tensile and tear strengths of the leathers actually increased over the storage period when the decrease in substance was factored into the measurements. The response of leather softness tests to pickle storage was inconsistent but the general trend was for increasing softness by both of the measurements used.

There was no subjective effect found on wool quality and alkali solubility of the wool was not affected.

On the basis of these results holding woolskins in the pickled state offers a number of advantages in terms of increased process efficiency and in the quality of the final product. Notably these are: -

- Very much reduced requirement for salt.
- Suitability for putting directly into processing as woolskins.

- Removal of non-structural protein and GAGs so giving lighter and probably softer leather without any loss of normalised strength properties.
- Some improvement in ease of grease removal which means that more skins should be adequately scoured but grease removal may not be sufficient from all skins.

5. References

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6. Acknowledgements

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