**RURAL INDUSTRIES RESEARCH
& DEVELOPMENT CORPORATION**

Enhancing the Unique Properties of Kangaroo Leather

**A report for the
Rural Industries Research
and Development Corporation**

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In submitting this report, the researcher has agreed to RIRDC publishing this material in its edited form.

Foreword

The commercial kangaroo industry has grown over the last thirty years to be worth $200M and accounts for over 4000 jobs mainly in rural regions. The use of the meat, skins and leather in products for the domestic and export market has made it the largest native animal industry in Australia. One key factor in the growth of the industry has been the move away from the exporting of raw skins and a greater emphasis on further processing of the skins in Australia.

Kangaroo leather is unique, compared to other types of leathers, in that it offers high strength whilst remaining lightweight and flexible. This combination of properties makes it in demand for high quality leather goods particularly high performance sporting products. Despite these inherent characteristics, there exists the opportunity for further improvements in leather quality to address the increasing customer demand for performance and the future competition from synthetic materials.

This collaborative project funded by CSIRO Textile and Fibre Technology, Packer Tanning and RIRDC aimed to determine the factors during the various stages of the processing of raw skins through to the final leather which have a significant effect on the strength. This report identifies components related to preservation and the chemical and mechanical operations that influence the strength of the finished leather.

This project was funded from RIRDC Core Funds which are provided by the Federal Government.

This report, a new addition to RIRDC's diverse range of over 800 research publications, forms part of our Prospective New Industries: New Animal Products R&D program, which aims to accelerate the development of viable new animal industries.

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Simon Hearn
Managing Director
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Executive Summary

The commercial use of kangaroo meat and skins has developed into the largest native animal industry in Australia, estimated to be worth $200M and providing over 4000 jobs mainly in rural areas. One of the factors associated with the significant growth of the industry has been the decline in exporting raw skins and an increase in processing in Australia. Due to the unique skin morphology of kangaroo, leather produced is high in strength but remains lightweight and flexible which has resulted in increasing demand from the manufacturers of high-quality leather goods including footwear. Despite this uniqueness there is a strong push for continual improvement especially to protect the existing leather markets from potential competition from improving synthetic products.

The aim of this project was to determine the factors that affect leather strength during the various stages of processing kangaroo skins including the effects of preservation methods of the skins prior to processing at the tannery, pickle storage, chemical processing and mechanical operations carried out during the tanning and retanning processes. In addition to these factors the effects on strength of species (Red and Grey) and harvest season (winter, summer) were also investigated. Although the effect on the tensile and tear strength was examined during the course of the work, the majority of the report focused on the tear strength due to its significance in regards to leather quality. The results in this report were determined using commercial processes. The complexity of leather processes and the broad range of reagents that are available may mean that the findings may not apply to other processes.

The findings are summarised as follows:

- Leather from grey skins generally has increased tear strength compared to red skins. The tensile strength of grey kangaroo leather is only marginally stronger than red kangaroo.

- The tear strength of the Western Australia red and grey skins appears to be intermediate between the Queensland red and grey skins.

- The different preservation methods appear to only have marginal effects on strength.

- Summer harvested skins show more variability in skin properties than winter harvested skins, especially within certain preservation groups.

- Commercial pickled skins were able to be stored for periods of 6 months without losses in strength. Longer storage time, particularly at ambient Queensland temperatures resulted in losses in strength of greater than 10% and as high as 40% after 18 months in some cases.

- Increased levels of chromium III salts added during the tanning stage or in the retanning, dyeing and fatliquoring step cause a decrease in tear strength. The potential loss of strength needs to be balanced against adequate long-term preservation, acceptable hydrothermal shrinkage temperature and the changes in handle of the final leather.

- Tear strength is affected significantly during the retanning of the wet blue, with the resulting leather doubling in strength using the commercial process. Only marginal improvement in the tensile strength was evident going from wet blue to crust leather.

- Tanning and retanning with organic based resins and syntans gave mixed results with most systems lowering strength, although, there were some exceptions. A modified polyaminecarboxylic acid provided an increase of 20% in tear strength and low levels of a dicyanamide resin increased tear strength when added either in the main tannage or in the retanning, dyeing and fatlquoring step. Glutaraldehyde in the main tannage was found to have

a significant detrimental effect on the tear strength but in contrast, a modified glutaraldehyde reagent can offer a moderate improvement in the tear properties of the leather.

- Fatliquors in the tanning and RDF process produced variable results. Modified fish oils, when compared to other types of fatliquors, were found to produce the leather with the best tear results. Some fatliquors such as sulfochlorinated paraffins were found to have a significant detrimental effect on tear strength. In the standard process used in the project, addition of fatliquors during the tanning process did not improve the tear strength of the final crust leather.

- Significant improvements in tear strength ranging upto 63% could be obtained by incorporating certain types of waterproofing systems into the process as lubricating agents. Addition of some of the waterproofing agents in the retan stage increases tear strength >20%, while addition late in the process, during the fatliquor stage, can increase tear strength by >50%. The required addition of chromium salts late in the process to fix the reagents and introduce waterproofing properties were found to significantly reduce the gains in tear strength from these systems.

- In the neutralisation step, modifying the pH and time, to allow sufficient time for neutralising salts and fatliquors to penetrate, results in improved tear strength.

- Colourants, dyes and pigments, added to the RDF were found to decrease tear strength in certain cases by >20%.

- Preliminary work on the effect of drying on tear strength, suggests longer times or higher drying temperatures may improve tear strength. The observed behaviour of kangaroo appears to be different from that reported for bovine.

- Overall the mechanical staking and shaving conditions examined generally cause a decrease in thickness but do not cause any significant change in strength of the leather.

- The potential exists to gain improvements in strength by changing several factors during the course of the process. For example a dicyanamide resin increased strength by 18% and separately a waterproof agent increased strength by 43%. A combination of the resin and waterproof agent produced a 60% increase in tear strength compared to the standard process. This value is comparable to the combined total of the two individuals trials and demonstrates the potential gains that may be achieved by small modifications to several parts of the process rather then one major change that may have a bigger impact on the properties of the leather.

1. Introduction

Over the last thirty years, the commercial use of kangaroo has developed into the largest native animal industry in Australia. Through a tightly controlled, Government run kangaroo management scheme, 2-3 million kangaroos are harvested every year and processed into meat, furs, skins and leather for domestic and export markets. In the early 80's, the majority of the skins were exported in the intermediate pickled state with the total export market for all kangaroo products worth approximately $10 million. However, in the last 15 years there has been an increasing number of skins being exported as leather. The expansion in the industry in processing and manufacture of skins has seen the export value of finished leather grow from less than $500,000 per year in the early 80's to nearly $12 million in 1991-1992.[1] Although accurate data is not available for recent years, the industry suggests that the figure for the export market for finished leather is now close to $20 million. The current view is that total kangaroo industry for meat, skins and leather has grown to be worth $200 million and accounts for 4000 jobs, mainly in rural Australia.[2]

The increasing market demand for kangaroo leather in the manufacture of high-quality leather goods, including footwear, is due to the fact that it has unique properties. On the basis of thickness it is one of the strongest leathers, which gives it a competitive advantage over most other leathers for use in products where strength, light weight and flexibility are premium requirements. Despite these inherent characteristics, there is a strong push for continual improvement in the overall performance and reliability of the leather, especially strength. This is driven in part by the increasing consumer demand and the need to keep ahead of competition from rapidly improving synthetic products. In addition, the there is increasing pressure on the Australian leather manufacturers as the international market supplying high quality kangaroo leather becomes more competitive.

The small volume of kangaroo skins processed annually compared to others species such as bovine and ovine has meant that only limited research has been carried out aimed specifically at kangaroo. The relatively recent growth in the market demand presents an opportunity for the Australian industry to improve the quality of finished kangaroo leather through R&D to ensure that it remains internationally competitive.

Although Wilson and Daub[3] first identified the high strength of kangaroo leather, in 1926, there has been little work aimed at improving our understanding of the factors affecting the properties of kangaroo compared to hides and skins from other animals. The majority of the kangaroo literature is from the mid 80's in which the CSIRO Leather Research Centre, in a series of papers, examined the performance of kangaroo skins using various early stage tanning processes.[3-11] This work established the effect of gender on skin characteristics and confirmed the difference in strength between red and grey kangaroo. The effect of variations in properties of leather over the skin area and due to different tannages and processes were also examined. Several papers[12-18] associated with the development of processes for kangaroo leather to be used in the manufacture of garments, have appeared in recent years, by Chinese and Japanese research organisations.

CSIRO has recently renewed its interest in kangaroo leather, initially through the development of leather suitable for incorporation into the new design of combat army boot.[19] A second project, in conjunction with the RIRDC and AUS-MEAT, aimed at improving handling and preservation of kangaroo skins has also been completed and the results are currently being circulated through the industry.

The aim of this project was to determine factors during the various stages of processing of kangaroo skins that have a significant effect on strength of the resulting leather. The processing of skins from the raw state through to finished leather is a complex, expensive and time consuming process made up of a number of distinct stages (Figure 1.1). Potentially, all of the chemical processes and mechanical operations involved can influence the physical properties of the final product, particularly its strength. The influence on the tensile and tear strength was determined, the greater emphasis on the later, which

is considered more relevant to the quality of finished leather. In order to address the concerns expressed by the industry and, to remain within the budget and time constraints of the project, the main objectives of this study were:

- To determine what effect differences in the species of kangaroo, type of preservation, geographic origin has on the properties of wet blue and crust leather

- To determine how prolonged storage of pickled skins at different temperatures affects the strength of the leather

- To identify key factors associated with the chemical processing that affect the strength of the leather. This included determining the effect of chemical reagents added during the conversion of pickled skins to wet blue (Tanning) and wet blue to leather (Retanning)

- To determine if the strength of the kangaroo leather is affected by the mechanical operations performed at various points in production.
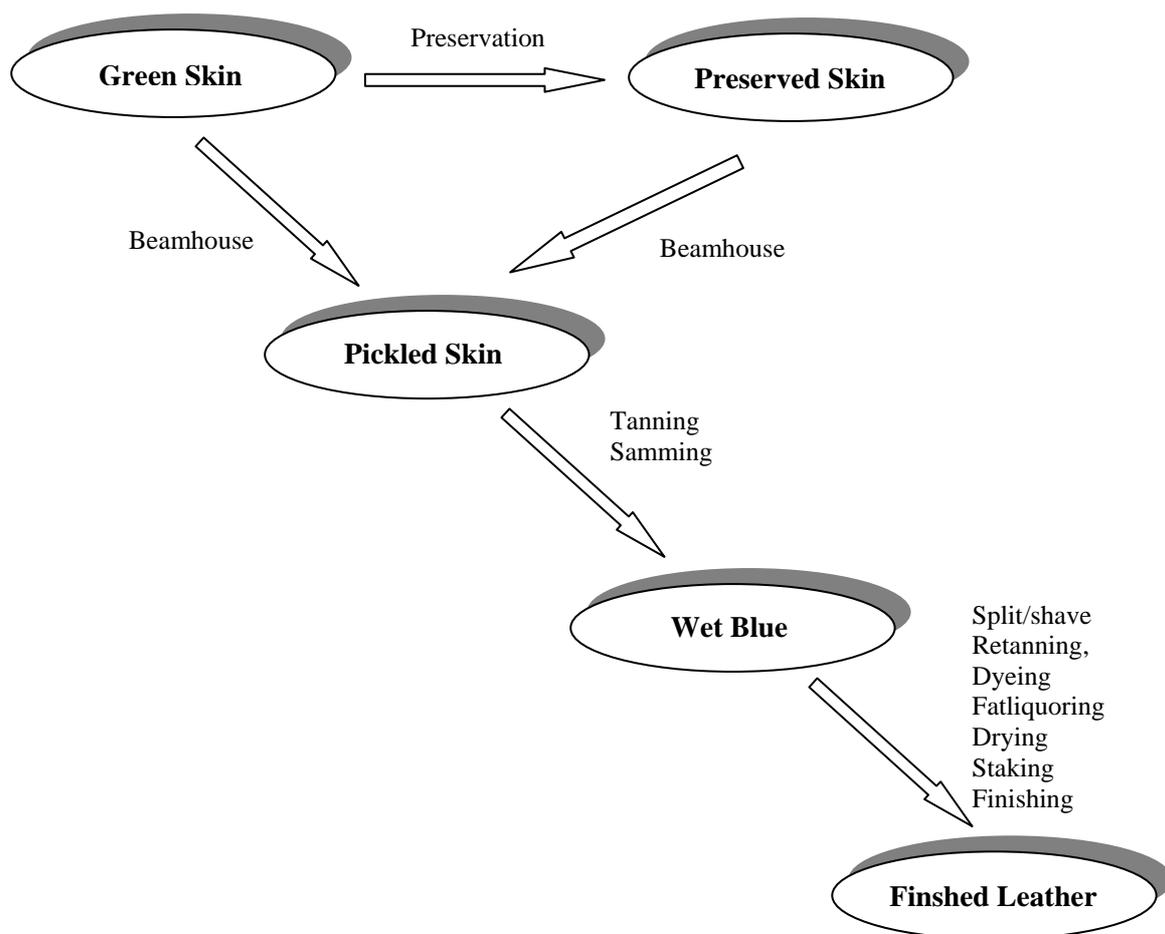
Figure 1.1. *Schematic of the major steps involved in the conversion of an animal skin/hide to finished leather*

2. Methodology

2.1 Supply of skins, hides and chemicals

Kangaroo skins from various stages of the processing chain were supplied by the industrial collaborator, Packer Tanning Australia, Narangba, Queensland. The species of kangaroo skins were Red kangaroos (*Macropus rufus*) from Western Australia and Queensland as well as Eastern Grey (*M. giganteus*) and Western Grey (*M. fuliginosus*).

Bovine wet blue used in Chapter 5 was commercially sourced from Michell Leather, Australia.

The chemicals used in the standard processes were obtained from Packer Tanning. Other specialist chemicals such as waterproofing agents, amino resins etc were provided by various chemical suppliers.

It should be noted that reference to a particular brand name or chemical does not constitute an endorsement by CSIRO of products or brands over others of a similar nature not mentioned here. In addition, reagents were not necessarily used as recommended by chemical suppliers and processes were not optimised for particular reagents, materials or circumstances. It is strongly advised that tanneries carry out their own trials, to ascertain the suitability of products and processes for their own purposes.

2.2 General Processes

Skins tanned or retanned at the CSIRO Leather Research Centre were processed in either 40L or 100L DOSE Maschinenbau (GmbH) stainless steel experimental drums as appropriate.

2.2.1 Pickle to wet blue

Chrome tanning of commercial pickled skins to wet blue was based on a commercial process. The pickled skins were added to a 12% NaCl solution (200% float), with a slip reagent, at ambient temperature (<30ºC) and the pH of the mixture was increased using sodium bicarbonate to pH4.5-5.0. After an intermediate wash, fatliquor was added to the skins at ambient temperature and the pH of the float lowered to 3.0-3.5 using formic acid, to fix the reagents and to reach a point suitable for tanning. In some cases, the skins were treated with an organic tanning agent prior to the addition of chromium (III) salts (9% based on weight of skins). The skins were basified, at 40ºC, to a pH of 3.8-4.2 to complete the chrome tanning step. After processing, the skins were drained and left for 24 h prior to pressing under minimum pressure (samming), to remove excess water, to finish with a moisture content approximately 55-60%.

In the area of work examining the effect of prolonged storage of pickled skins on strength, skins from Packer Tanning that had dried to low moisture contents (<30%) were soaked back overnight, in 12% NaCl solution (200% float) with the slip reagent, prior to addition of the remaining skins.

2.2.2 Wet blue to crust leather

Wet blue prepared according to the procedure in Section 2.2.1 or commercially supplied material was processed to crust leather based on a standard retan/dye/fatliquor (RDF) procedure carried out in three separate stages. Firstly, the wet blue was soaked in water (200%) containing a wetting agent at 40°C and the pH standardised with formic acid. The skins were then neutralized using sodium formate and ammonium bicarbonate followed by addition of the required fatliquors and syntans. During the retanning stage, the skins are treated with dyes, pigments, vegetable tanning agents, fatliquors, and

syntans in a concentrated float (30% water), then acidified to a pH of 3.5-4.0 with formic acid, at 60ºC to fix the reagents. The final step of the process involved addition of a range of fatliquours, at 60ºC, followed by lowering of the pH, by addition of formic acid to a final pH value of 3.5-3.8. The wet crust leather was left to stand for 24 hours and then vacuum dried for 2 minutes at 50°C unless otherwise stated. After the initial vacuum drying the skins were hung at ambient temperatures for 4 days prior to conditioning (20°C ± 2°C and 65 ± 2 %) and physical testing.

2.2.3 Methodology for pre-tanning and preservation factors.

2.2.3.1 Effect of Species and Preservation Method on Strength
Medium sized skins were selected by Packer Tanning in September 1999 (Winter harvested skins) according to preservation method (chilled, frozen or salted), species (Red, Grey) and origin (Queensland, Western Australia). The skins (Table 1) were processed to pickle then wet blue and shaved prior to transporting to CSIRO. The 8 packs of shaved wet blue were halved at CSIRO and left hand side (LHS) of the skins were tested at wet blue stage using the physical strength tests described in Section 2.3.1. The moisture content of the wet blue was determined on the day of testing. The right hand sides (RHS) of the skins were processed to crust leather using the standard RDF process. The skins were conditioned for 24 h prior to staking, if required, and reconditioned (24h) before physical testing. The halving of the skins allows the direct correlation of the wet blue physical properties to be related to the properties of the crust leather. The technique of matched side trials is used to reduce the difference in testing associated with the natural variation that occurs between skins.

The effect on harvesting season was investigated by using a second set of skins collected six months after this first set. The second set of skins was selected during the 1999-2000 summer harvest period according to the same criteria (Table 2.1). A third set of skins was collected in the 2000-2001 summer harvest period to confirm the differences observed between the winter and summer harvested skins.

Table 2.1   Skin Selection used in preservation work

Preservation Method/State of Origin	Species	
	Red	Grey
Chilled/Queensland	10 skins	10 skins
Salted/Queensland	10 skins	10 skins
Frozen/Queensland	10 skins	10 skins
Salted/Western Australia	10 skins	10 skins

2.2.3.2 Effect of Pickle Storage on Strength.
Additional skins, from the first two harvest periods described above, were removed at the end of pickle processing for storage trials. These skins were halved and the LHS stored at Packer tanning under their usual conditions. The temperature experienced by the Packer Tanning stored pickle skins were monitored using temperature loggers (StowAway TidbiT) with a working range of -20°C to 70°C and Onset software. The RHS of the skin was placed in storage at the CSIRO in a cold room at 4ºC. After set storage periods (6, 12 or 18 months), the LRC and Packer Tanning stored sides were combined and processed to wet blue and then to crust using the standard process and drying conditions. The moisture content and pH of aqueous extract of selected matched skins were determined prior to processing. The crust halves were all staked prior to physical testing.

2.2.3.3 Effect of Commercial Shaving of wet blue on Strength
The effect on strength due to shaving the kangaroo wet blue was determined on the 1999-2000 summer harvested skins. Skins were processed to wet blue but 5 additional skins per pack were left unshaved to compare with the remaining 10 skins that were shaved to the desired thickness.

2.2.4 Matched Side trials for tanning and retanning experiments

In each trial three kangaroo skins were halved down the backbone (Figure 2.1). Both tanning and re-tanning processes were carried out in 40 L drums with left hand side used for standard conditions (control) and the right hand side used for a modified process (variable). For the tear strength of matched side experiments, the average for the 3 skins (3 samples per skin) is reported as the percentage difference in the average strength value for the three skins of the modified process (RHS) compared to the control side (LHS) as determined by the following equation:

$$\% Difference = 100 * \frac{(Variable - Control)}{(Control)}$$

A negative and a positive value imply a decrease or an increase, respectively, in strength of the variable or experimental process relative to the standard or control process.
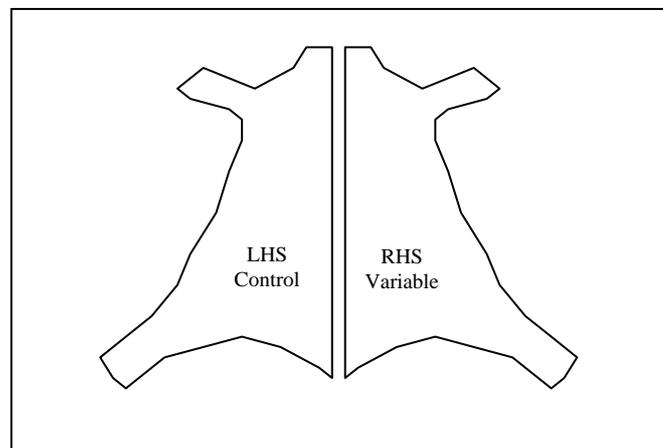
Figure 2.1. *Halving of Kangaroo skin used for matched side trials.*

2.3 Testing of Skins

2.3.1 Physical Testing

Strength testing of samples was carried out in a standard controlled environment, 20°C ± 2°C and 65 ± 2 % R.H according to ISO 2419 (IUP 3, SLP 3).[20] Samples were conditioned for 24 hours prior to testing unless otherwise stated. Physical testing was performed on an Instron (Model 5500R 1122) tester using Merlin software version 4.03. The sampling positions for all tests are shown in Figure 2.2. In matched trials, samples for physical and chemical testing were taken from identical areas in the skins from the two sides. Samples were taken parallel or perpendicular to the backbone of the side as shown in Figure 2.2 for Slit Tear and Tensile Test. Testing was performed according to standard methods with results quoted as either Newton (N) or Newton per millimetre (N/mm) with three samples taken for each test.

Tear strengths were determined according to tear test DIN 53329,[21] unless otherwise stated.

Tensile Testing was performed according to ISO 3376 (IUP 6, SLP6),[22] the leather test for measurement of tensile strength for load at maximum extension.

The average tearing load was determined according to slit tear test ISO 3377 (IUP 8, SLP7).[23]

The accuracy in the physical testing results for matched side trials was determined by making a direct comparison of the RHS and LHS samples for six skins, which had been processed in the same drum. The results showed that for the series of 6 skins, the RHS and LHS samples had SD of 2.3 and 3.8 for Red and Grey skins respectively, which corresponds to an RSD of 9% for strength measurement. Therefore differences in strength are significant when the difference between treatments is 9% or more.

The shrinkage temperature (T_s) of samples was determined in fresh water using a pressurised shrinkage temperature apparatus designed and constructed by CSIRO.[24] Wet blue samples from skins processed at CSIRO were tested 7 days after chrome tanning. Samples from pickled skins were soaked overnight and the shrinkage temperature determined using a 6% salt solution.
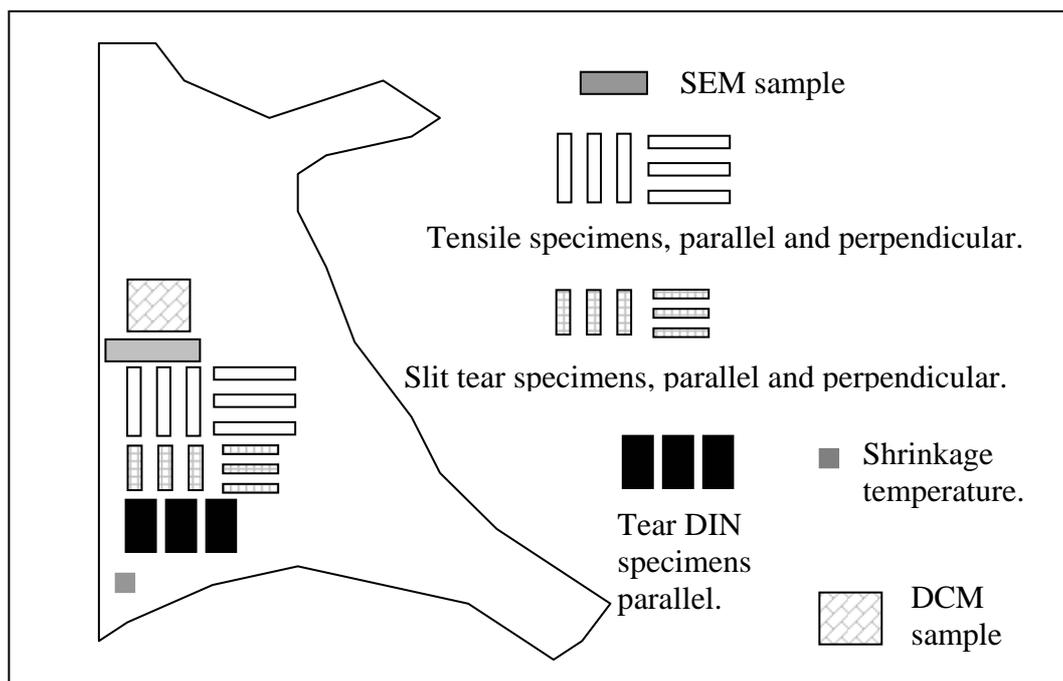
Figure 2.2. *Diagram of location of sampling for testing.*

2.3.2 Chemical Testing

2.3.2.1 Moisture Content of Skins.
The moisture content of kangaroo skins was determined according to SLC 3 (IUC 5; BS 1309:3).[25]

2.3.2.2 Measurement of specific gravity of Liquors.
The specific gravity or barko of tanning liquors were measured using a Specific Gravity hydrometer (Carlton Glass Company Pty Ltd, Australia) which complied with B. S. 718.

2.3.3.3 Measurement of pH
The pH and temperature of all liquors were measured using a WTW PH 330 meter and calibration was performed daily with pH 4 and pH 7 buffers.

2.3.3.4 pH of pickle skins
The pH of an aqueous extract of pickled skins was determined by shaking at room temperature pickled skin (10g chopped, approximately 60% moisture content) in an aqueous salt solution (1000ml, 6% W/V) and measuring the pH of the liquor after 24 hours.

The mass of sample required for aqueous extraction for skins with reduced moisture contents (<60%), due to prolonged storage, were determined by the following calculation:

$$x \; g \; of \; Dry \; Sample = \frac{(100 - \% \, Moisture \; of \; Wet \; Sample) * 10.0 g}{(100 - \% \, Moisture \; of \; Dry \; Sample)}$$

2.3.3.5 Chromium Analysis
The analysis of chromium content was carried out according to the ISO DP 5398 (IUP8)[26] and was reported as % of chromium oxide (Cr_2O_3) in the oven dried leather sample.

2.3.3.6 DCM Extraction
The solvent extractable content of kangaroo wet blue and crust were determined according to ISO 4048 (IUP 4)[27] using dichloromethane.

2.4 Microscopy

2.4.1 Scanning Electron Microscopy (SEM)

Samples of wet blue and crust leather for SEM examination was taken from the location shown in Figure 2.2. A thin (2-3 mm) cross section of this sample was then cut with a straight edge and a sharp blade, and mounted on a stub using silver conducting colloidal paste. The samples were vacuum coated with approximately 300nm of carbon. Analysis of the samples was carried out on a Hitachi S-4100 Field Scanning Electron Microscope (FESEM). All images were taken at an accelerating voltage of 1KeV, with a specimen tilt of 12.5°, a working distance (WD) of 5mm, condenser lens setting of 9. Digital images were collected with a Digital Image Processing System (DIPS) version 2.3.2.5, with a resolution of 1250 pixels X 1250 pixels.

2.4.2 Light Microscopy

Samples of crust leather 15x3 mm were wet back in deionised water under vacuum for a minimum of 1 h and embedded in a water –soluble tissue freezing medium. Longitudinal (vertical) sections were obtained using a Bright freezing microtome (cryostat). A toluene based mounting medium (RI 1.495) was used to coverslip the sections and maintain their quality for long-term storage.

Sample investigations were performed using an Olympus BHS transmitted light microscope at x1000 magnification with oil immersion. True colour 1300 x 1000 digital images were captured and analysed using a SPOT digital coloured camera and associated software. Image manipulation involved brightness adjustments, smoothing or sharpening and conversion to greyscale. All measurements were performed after calibration with a graduated micrometer slide with a scale of 0-0.2 mm.

3. Species, Season, Preservation and Pickle Storage

3.1 Introduction

Currently there are five species of kangaroo and wallaby belonging to the Macropous family that are harvested commercially under the Commonwealth approved management plan. Products from these species can be used domestically and traded in export markets. The two species of grey kangaroos, the Eastern Grey (*Macropus giganteus*) and the Western Grey (*Macropus fuliginosus*) mainly inhabit the forests and woodlands of Australia. The Western Grey kangaroo is found in a broad band across Southern Australia and the Eastern Grey generally inhabits areas of higher rainfall and is found along the east coast of Australia.[28,29] Despite its wide distribution throughout the arid zone of Australia, there is only one species of red kangaroo (*Macropus rufus*). The Eastern and Western grey and the red kangaroo are the most abundant species and make up over 90% of the commercial harvest. The remaining commercial species are the Euro (*Macropus Rubustus*) and the whiptail wallaby (*Macropus parryi*). Closely related to kangaroos, the Euro or common wallaroo is similar to a chunky medium sized kangaroo and ranges in colour from dark grey to deep rusty red. They prefer drier areas of the continent and rocky hillside habitats. The whiptail wallaby is a small light grey to brownish grey member of the marcopous family. These last two species make up only a small percent of the overall commercial quota for macropods and are not generally harvested for human meat consumption. There are two additional species that are harvested but are of little commercial value as products from the Bennett's wallaby (*Macropus rufogriseus*) and Tasmanian pademelon or Rufus wallaby (*Thylogale billardierii*), cannot be exported.

Although kangaroo leather has become a valuable commercial product over the last thirty years, there is still limited knowledge of the behaviour of the skins compared to the amount of information available for other leathers. Although the high tensile strength of kangaroo was first reported in 1926,[3] there is limited information on how the different types of skins affect the final properties of the kangaroo leather. The only related study, carried out by CSIRO, reported the difference in tear and tensile strength between red and the significantly stronger grey kangaroo skins for chrome tanned leather.[7] It was found that grey kangaroos produced thicker leather than the skins of red kangaroos. When the effect of thickness was removed, the strength properties of male and females of the same species were approximately equal, and the grey kangaroo was still stronger than the red kangaroo. This work was based on chrome-tanned leathers produced from frozen NSW skins. The concern of kangaroo processors that kangaroo skins preserved by freezing gave weaker flatter leather than similar salt preserved skins was also investigated and no deleterious effects on the leather properties were observed.[5] The current project aimed to extend this early study by investigating the effects of species, location and time of harvest and the type of preservation on the properties of the crust leather prepared using commercial tanning/retanning processes.

Table 3.1. *Kangaroo showing species, location and preservation methods used in this study.*

Preservation /Source	Red	Grey
Chilled Queensland	10 skins, shaved	10 skins, shaved
Salted Queensland	10 skins, shaved	10 skins, shaved
Frozen Queensland	10 skins, shaved	10 skins, shaved
Salted Western Australia	10 skins, shaved	10 skins, shaved

3.2 Effect of Species/Preservation/Place of Origin on Strength

3.2.1 Characterization of Wet blue Strength for Winter Harvested Skins.

Table 3.1 lists the kangaroo skins according to species, location and method of preservation used in the study for the winter and summer seasons.

3.2.1.1 Tear DIN
The tear DIN (N/mm) for the wet blue and crust sides for skins harvested during the 1999 winter period are given in Figure 3.1. The crust results are discussed in section 3.2.2. The three columns on the left show the effect of the different preservation methods on the strength of red kangaroo from Queensland. The results indicate that at the wet blue stage, there appears to be good correlation in the tear strength (16.3, 15.9, 16.2N/mm) between the three preservation methods, chilled, salted and frozen respectively. The fourth column from the left refers to the salted red kangaroo skins from Western Australia, which appears to have comparable strength (15.7N/mm), at the wet blue stage, as the red kangaroo skins from Queensland.

The four columns on the right depict the effect of the preservation methods on the tear DIN (N/mm) strength of grey kangaroo from Queensland and Western Australia. The wet-blue Western Australian grey kangaroo skins (19.6N/mm) are stronger by 24% than all the average value for the red skins (16.1N/mm), but are also weaker in tear strength compared the average value for the grey skins from Queensland (23.4N/mm). The three sets of grey skins from Queensland do not appear to differ greatly in their respective tear strengths (23.6, 24.0, 22.6N/mm). The average tear strength for the Queensland grey skins is 45% stronger than for the Queensland red kangaroo skins and these results are in good agreement with the previous study.[7]
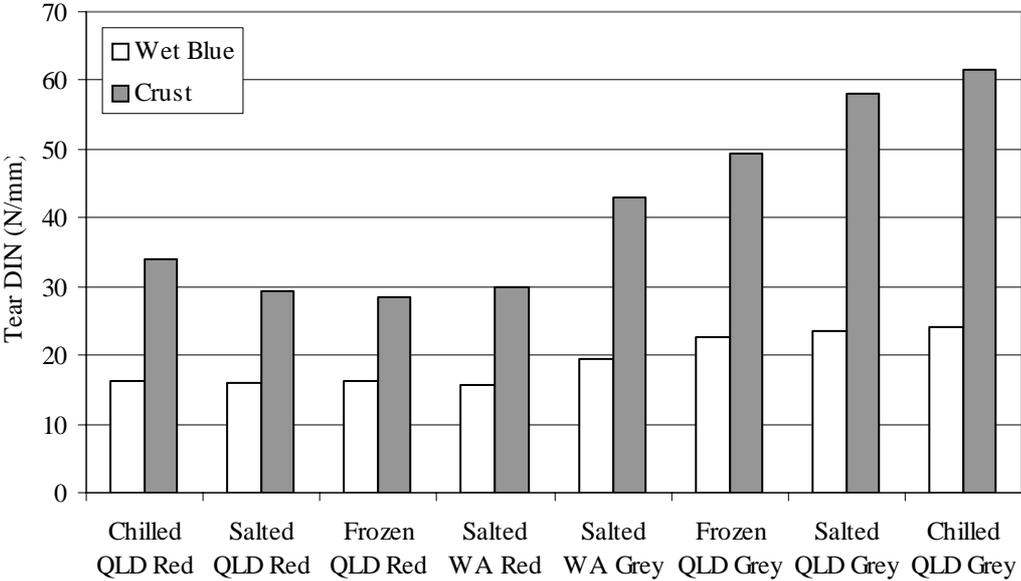
Figure 3.1. *Comparison of Wet Blue and Crust Tear DIN (N/mm) results for Winter Harvested skins.*

3.2.1.2 Directional Effects in Slit Tear Testing
An alternative tear test, which uses smaller test samples, enabled the direction effect (parallel and perpendicular to the backbone) on strength to be determined. It has been shown that in bovine leather there can be substantial differences in the physical testing results due to different areas of the hide and the direction of samples relative to the backbone. As part of this study, the degree of variation in kangaroo leather strength due to the different sampling orientations was determined.

Figure 3.2 *Comparison of Wet Blue and Crust Slit Tear (N/mm) results, parallel to the backbone, for Winter Harvested skins.*

The overall trends observed in the slit tear results, sampled parallel to the backbone, (Figure 3.2) were the same as the tear DIN method. There was little variation in the results for the red skins due to the various preservation types with the Western Australia salted skins being marginally stronger than the Queensland skins (6%). The grey skins from Queensland were also very similar for the different preservation methods. The Western Australia salted grey skins were weaker (12%) than the Queensland grey skins but were stronger than all of the red skins. Overall the Queensland grey skins were found to be considerably stronger (35%) than the Queensland red skins.

Figure 3.3 *Comparison of Wet Blue and Crust Slit Tear (N/mm) results, perpendicular to the backbone, for Winter Harvested skins.*

Samples taken perpendicular to the backbone (Figure 3.3) were significantly stronger than the parallel samples. Queensland grey skins were 9% stronger when sampled perpendicular to the backbone while the red kangaroo skins showed an 11% increase in the strength values. The data showed no significant differences in strength due to preservation type.

3.2.1.3 Directional effects in Tensile testing

The results from the tensile testing of the wet blue, sampled parallel to the backbone (Figure 3.4) indicates that there is only small difference (6%) between the red and the stronger grey kangaroo skins. Overall, the results indicate that there is no significant difference in the tensile test results between the types of preservation or the place of origin with variations between all the different groups, within 6% of the average.
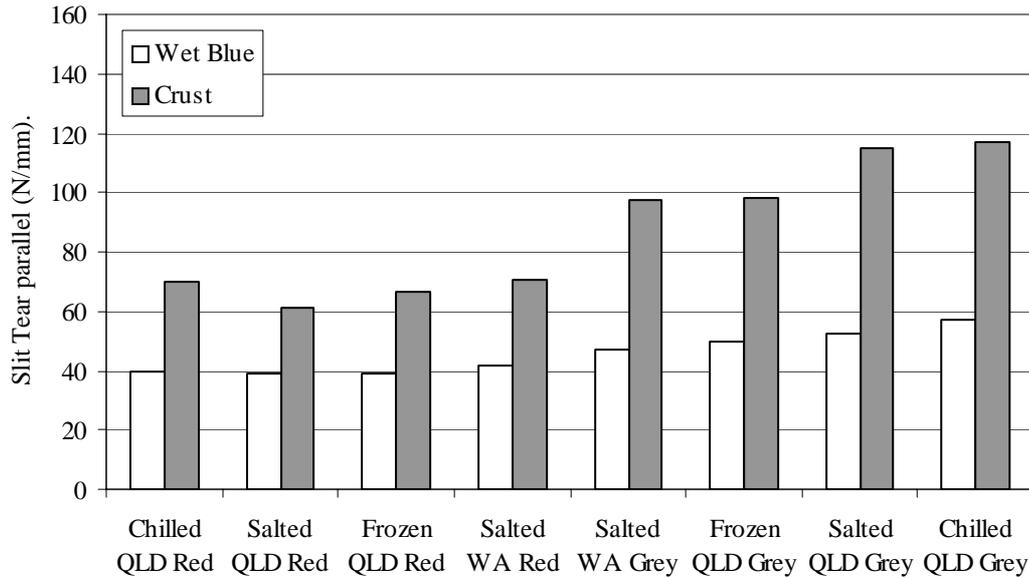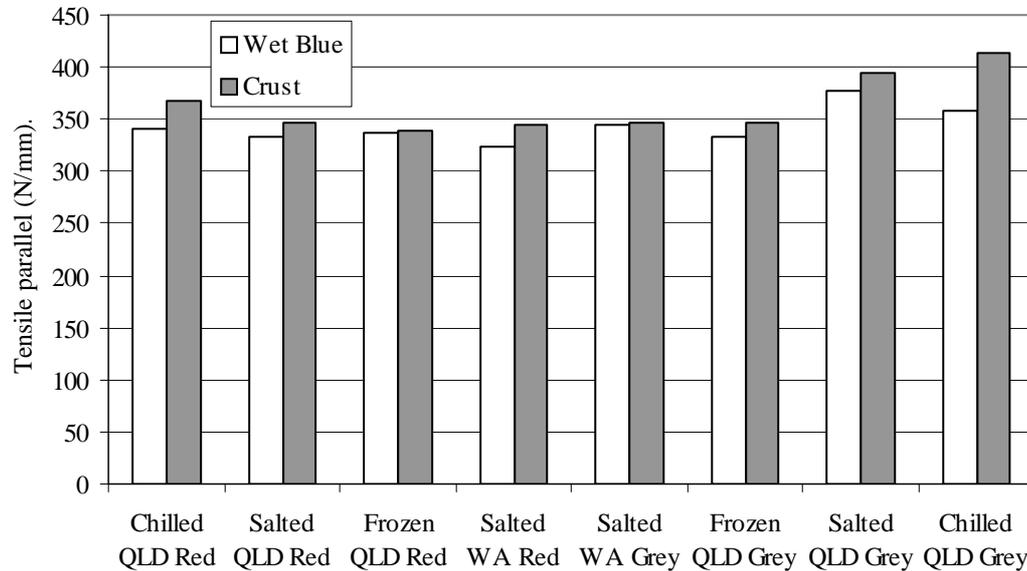

Figure 3.4. *Comparison of Wet Blue and Crust Tensile (N/mm) results parallel to the backbone for Winter Harvested skins.*

Tensile test results perpendicular to the backbone are summarised in Figure 3.5. The results are not as consistent as the tensile testing taken in the parallel direction. In the perpendicular direction, the Queensland grey skins are 19% stronger than the corresponding red skins compared to 6% in the parallel position. The type of preservation still does not appear to be a factor in determining the strength of the samples. The overall strength values from the perpendicular samples are lower than the parallel samples. The perpendicular Queensland grey skin samples are 10% weaker than the parallel samples. In contrast, the perpendicular Queensland red skin samples are 23% weaker than the corresponding parallel samples.

Fibre orientation parallel and perpendicular to the back bone is expected to influence tensile strength. As reported by Mitton and Hall[30] "close correlations between tensile pieces cut at right-angles cannot be expected unless the fibres run uniformly in all directions".
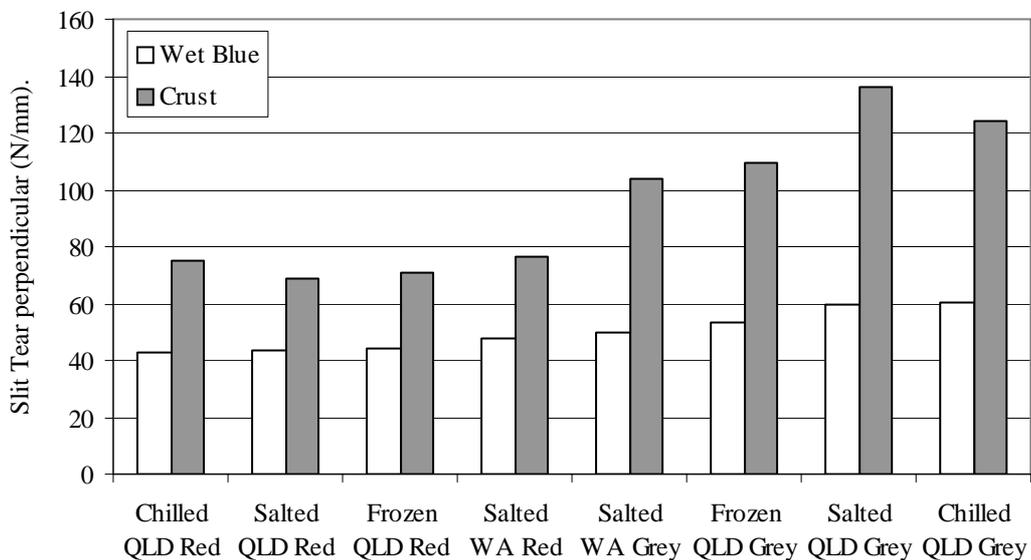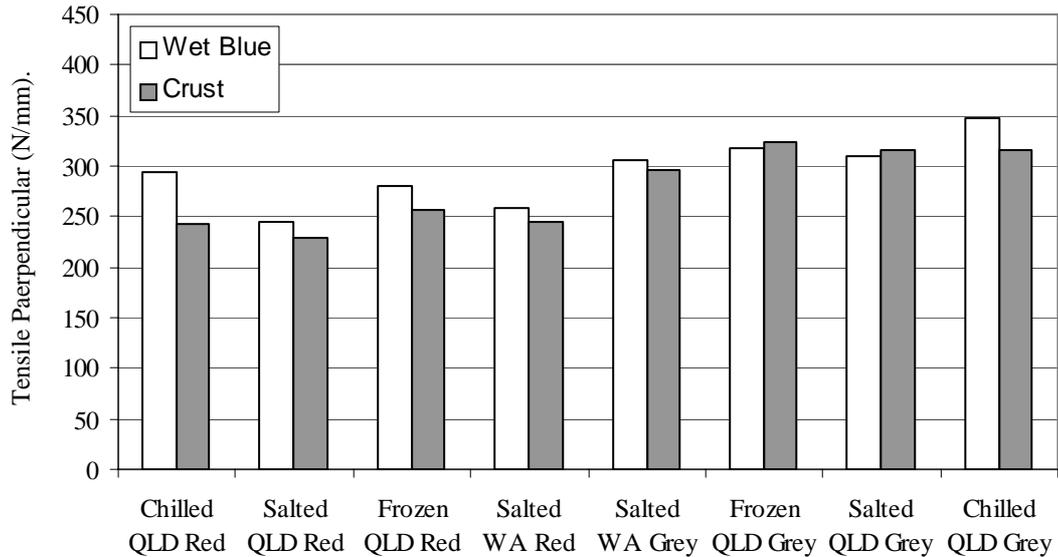
Figure 3.5. *Comparison of Wet Blue and Crust Tensile (N/mm) results perpendicular to the backbone for Winter Harvested skins.*

Out of the three different types of physical test methods used, tear DIN gave the highest percentage difference in strength between the grey and the red groups.

3.2.2 Crust Strength of Winter Harvest.

3.2.2.1 Relationship between wet blue and crust
The relationship between the wet blue results and the crust leather are very different for the tear and tensile strength properties. The parallel and perpendicular tensile results in Figures 3.4 and 3.5 show that overall there is no significant difference between the tensile strength of the wet blue and the crust leather.

The tear DIN and the parallel and perpendicular slit tear results all show that there is a very significant increase in the tear strength of the leather compared to the values for the corresponding wet blue. In the case of tear DIN, the Queensland grey skins have increased in tear strength by 140% compared to the wet blue. The Western Australian grey skins have increased in strength by 120%. The leather form the Queensland red skins has tear strengths approximately 89% greater than the wet blue and a similar increase in strength is observed for the WA red skins (90%). The greater improvement in tear strength for grey skins compared to the red kangaroo further suggests that there is an important difference in the fibre structure of the two species and the way chemicals interact with the fibre structure, resulting in different behaviour upon retanning.

3.2.2.2 Effect of preservation/origin on tear DIN strength.
The tear DIN results in Figure 3.1. show that the leathers from Queensland grey kangaroo have tear strengths approximately 90% stronger than Queensland red kangaroo. This has increased from 44% difference at the wet blue stage. There is an indication from these results that the leather from the frozen skins is not as strong as the other preservation methods. For Queensland red skin, leather from chilled skins is 19% stronger than that from frozen skins. This is further supported by leather from Queensland grey chilled skins which is 25% stronger in tear strength than leather from Queensland grey frozen skins. Figure 3.6 shows SEM cross-section of chilled versus frozen red skins. The frozen skin seems to have a fracture plane across several clumped fibril bundles (Figure 3.6 B)whereas the chilled skin has more open and relaxed fibril structure. The more open chilled structure may be more capable of distributing load and therefore have a higher tear strength.
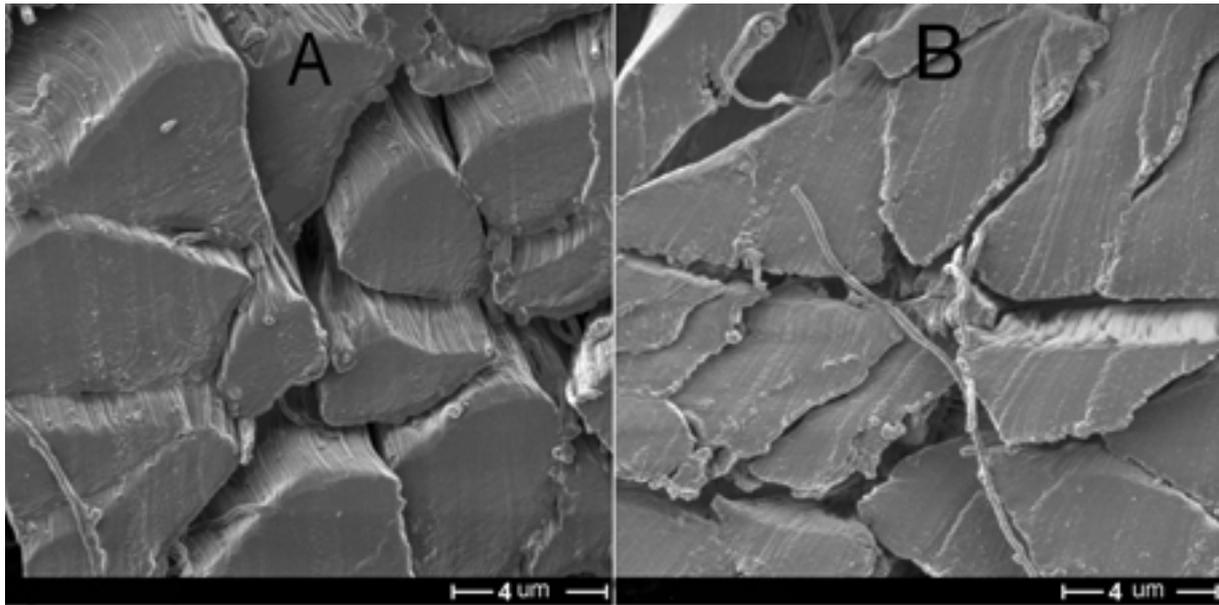
Figure 3.6. *SEM cross-sections of leather from A. Chilled Queensland Red and B. frozen Queensland red. The two sections look different. In frozen Queensland red several fibril bundles appear as a clump with a single fracture across the plane on these group of fibril bundles. In the chilled Queensland red the fibrils appear well separated and the fractures more random.*

The place of origin does not have an effect for the red skins, with the strength of the WA red skins comparable to the average for the average tear strength for Queensland skins. However, the WA grey skins are significantly weaker (31%) than the average for the Queensland grey skins, but still stronger than the red kangaroo skins by approximately 40%.

3.2.2.3 Directional effects in slit tear testing
The increases in tear strength for the slit tear results (parallel and perpendicular) are similar to those observed in the tear DIN method with a greater improvement in strength for grey skins compared to the red shown in Figures 3.2 and 3.3. The increases in strength in going from wet blue to leather for the Queensland skins was 67% and 64% for parallel and perpendicular directions respectively. For Queensland grey skins, the increase due to the retanning of the wet blue was 108% and 113% for parallel and perpendicular sampling respectively. The directional effect is the same as previously. The leather samples taken perpendicular to the backbone have tear strengths 8% greater for red and 11% for grey kangaroo compared to samples taken in the parallel direction.

3.2.2.3 Directional effect for tensile testing
Overall the retanning of wet blue does not appear to have a significant effect on the tensile strength of leather with the differences due to processing <10% for averaged values for the Queensland and Western Australian skins. The results do show that the direction of sampling has an effect on the tensile values. For the samples taken parallel to the backbone, the retanning of the wet blue causes a marginal increase in tensile strength for both Queensland red (4%) and grey (8%) and Western Australian red (6%) and grey (1%) kangaroo. On the other hand, for samples taken perpendicular to the backbone, retanning results in a marginal decrease in tensile strength with leather from Queensland red and grey kangaroo weaker by 11 and 2% respectively. The Western Australian kangaroo skins showed a similar trend, with perpendicular tensile being weaker in strength by 5% and 3% for red and grey leather.

The parallel tensile test data indicate that the frozen skins afford weaker leather than the chilled skins. The leather from chilled skins is 9% stronger than the leather from frozen skins for red skins and 20% for grey skins.

The Western Australia red had similar strength to the Queensland red groups (2 and 1% for parallel and perpendicular samples respectively). The trend observed in the wet blue that Western Australia grey had weaker strength compared to the Queensland grey, regardless of preservation type, was now more pronounced in the crust (11% and 7% for parallel and perpendicular direction respectively).

In both Queensland red and greys skins, a trend was observed for the strength order amongst the different preservation methods. In general the chilled skins were higher than the salted, which were slightly higher than the frozen.

Unlike reported work[7], where tensile strength of grey kangaroo was found to be significantly stronger than red kangaroo for chrome tanned leather, there was very little difference in the tensile strength observed in this study. The tensile strength differences between red and grey species, for parallel position were approximately 6% and 7% compared to tear strength of approximately 29% and 60% for wet blue and crust respectively. For samples taken from the perpendicular positions, there were significant differences in tensile strength between grey and red species, which were 19% and 28% for wet blue and crust respectively. This was still much less than for the both types of tear strength, 25 and 63% for slit tear for wet blue and crust respectively, and 40 and 74% for tear DIN wet blue and crust respectively.

3.2.3 Effect of Harvest Seasons.

A second series of skins were processed six months after the first set, in the summer of 1999-2000. The aim was to determine if the time of harvest influenced the strength. The results will be discussed mainly in context of the leather although the wet blue results are presented in the figures for comparison. There was increased variability in the strength values for the 10 skins from each type of preservation method and place of origin. The skins from the summer harvest were of lower quality, with a majority of the skins being damaged to some degree. The most common faults were related to tick and pock damage. This occurred in several areas the skins and in many cases was found in the butt area, where most of the physical test samples were taken. The skins affected with tick and pock also tended to have other more serious damage such as scratches and marks consistent with the kangaroo clawing the infected areas or rubbing against hard objects. The scarring of the skins can affect the physical strength of the skins.

3.2.3.1 Tear DIN
The initial comment that has to be made from the results in Figure 3.7 is that we see a much more complex pattern than in Figure 3.1 for the winter harvest. Taking this into consideration, the chilled and salted Queensland reds and Western Australian red have tear strength values of 30.6, 30.4 and 32.6N/mm that are very similar to values expected, based on the winter harvest results. Overall, these are in good agreement with the average values for the leather tear DIN strengths values from the winter harvest for Queensland and WA red skins of 30.6N/mm and 30.1N/mm respectively. However, leather from summer harvest frozen red skins has an average value of 51.7N/mm, which is far greater than expected. A closer examination of this pack of 10 skins revealed that the skins appeared to fall into two distinct categories. One group of skins averaged 36.0N/mm whilst the remaining skins averaged 62.0/mm. Even taking the lower value of 36.0 N/mm, the frozen skins are still 15% stronger than the other red kangaroo skins.
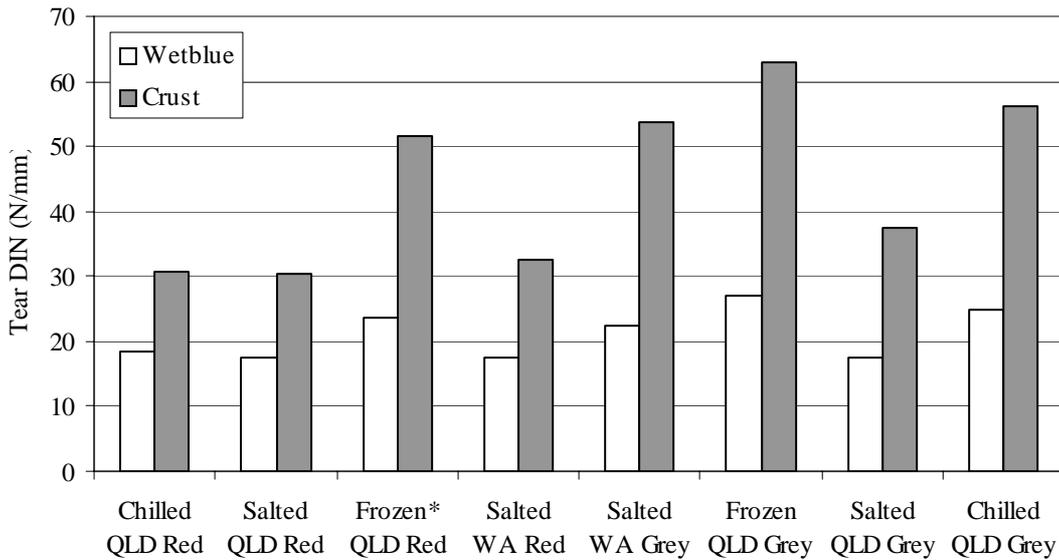
Figure 3.7. *Comparison of Wet Blue and Crust Tear DIN (N/mm) results for Summer Harvested skins.*
* This pack contains a combination of Queensland red plus a "third" species. Refer to section 3.2.3.4. for more detail.

Examination of the results in Figure 3.7 for the grey skins found that the leather from Queensland salted grey skins was significantly weaker than either the chilled or frozen skins. All of the Queensland salted grey skins had lower values than the winter skins indicating that salting gives weaker skins in summer. The chilled and frozen Queensland grey and salted Western Australian skins have tear DIN strength of 56.2, 62.9 and 53.8N/mm compared to their winter counterparts of 61.7, 58.2 and 42.9N/mm respectively. The chilled Queensland grey were stronger in winter by 10% compared to the summer skins, while the frozen Queensland greys and salted Western Australian greys were stronger in the summer by 25 and 28% respectively.

The comparison of the wet-blue and crust results for the Queensland chilled and salted reds and the WA salted reds indicates that the strength of the leather has increased by approximately 75, 70 and 86% respectively compared to the wet blue values. The tear results for the leather samples from Queensland chilled and frozen grey and WA salted grey leather showed improvements in the leather strength of 130% and 140% respectively. The red and grey kangaroo in the summer series were also found to have different improvements in strength although they were processed together. These values are similar to those determined in the winter harvested skins and confirming that the tear strength of the wet blue can be greatly improved by retanning.

3.2.3.2 *Effect of direction on slit tear strength.*
The slit tear parallel and perpendicular results are shown in Figures 3.8 and 3.9. They follow the same trend as the tear DIN results in Figure 3.7. In the summer skins, the samples taken in the perpendicular direction on average are stronger compared to the samples from the parallel direction by approximately 10% for both red and grey skins.

Figure 3.8. *Comparison of Wet Blue and Crust Slit Tear (N/mm) results, parallel to the backbone, for Summer Harvested skins.*

Figure 3.9. *Comparison of Wet Blue and Crust Slit Tear (N/mm) results, perpendicular to the backbone, for Summer Harvested skins.*

3.2.3.3 Effect on tensile strength

Parallel and perpendicular tensile results for the summer series of skins are shown in Figures 3.10 and 3.11. The tensile strength measured in the parallel direction shows good correlation between the wet blue and leather samples with differences on average of <11%. This trend is in agreement with the initial set of tensile results from the winter harvested skins, which indicated that retanning did not significantly influence the tensile strength of the wet blue. The results from samples taken in the perpendicular direction are less consistent, with large differences between the wet blue and leather tensile strength for Western Australia salted grey (44%) and Queensland chilled grey skins (20%). Surprisingly the two effects for these systems are opposite, with leather from Western Australia salted grey being stronger by 44% and for Queensland chilled grey skins the wet blue is stronger by 20%.

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The tensile strength of leather sampled parallel is 45% and 35% stronger than the perpendicular samples for Queensland red and grey skins respectively. For Western Australian red and grey skins the parallel samples are 36% and 19% stronger respectively than the perpendicular.
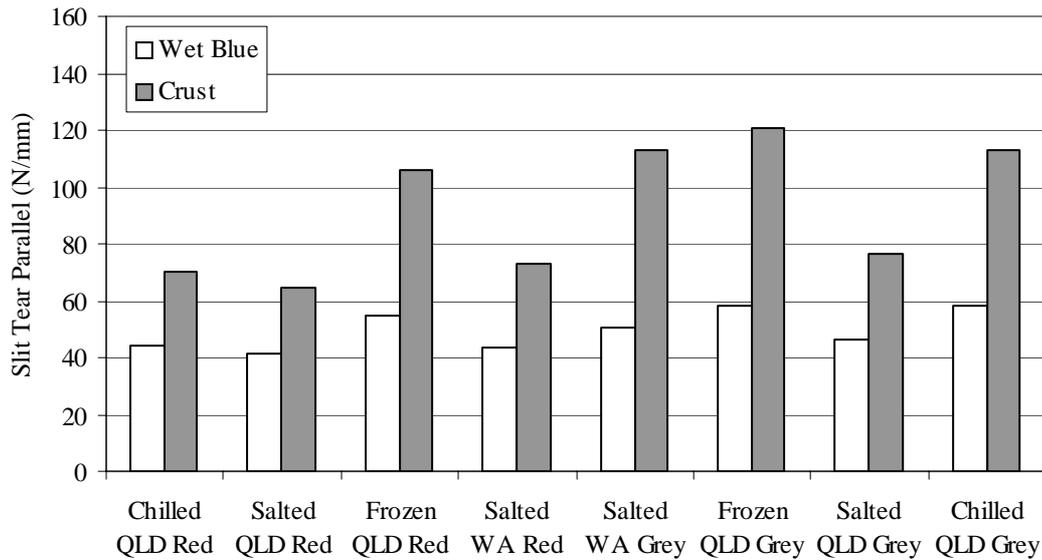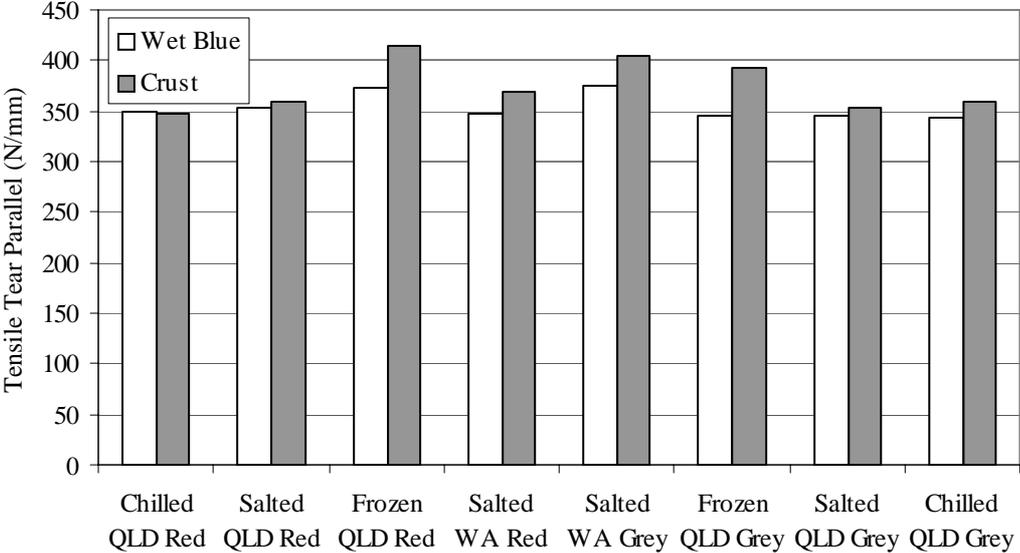

Figure 3.10. *Comparison of Wet Blue and Crust Tensile (N/mm) results parallel to the backbone for Summer Harvested skins.*
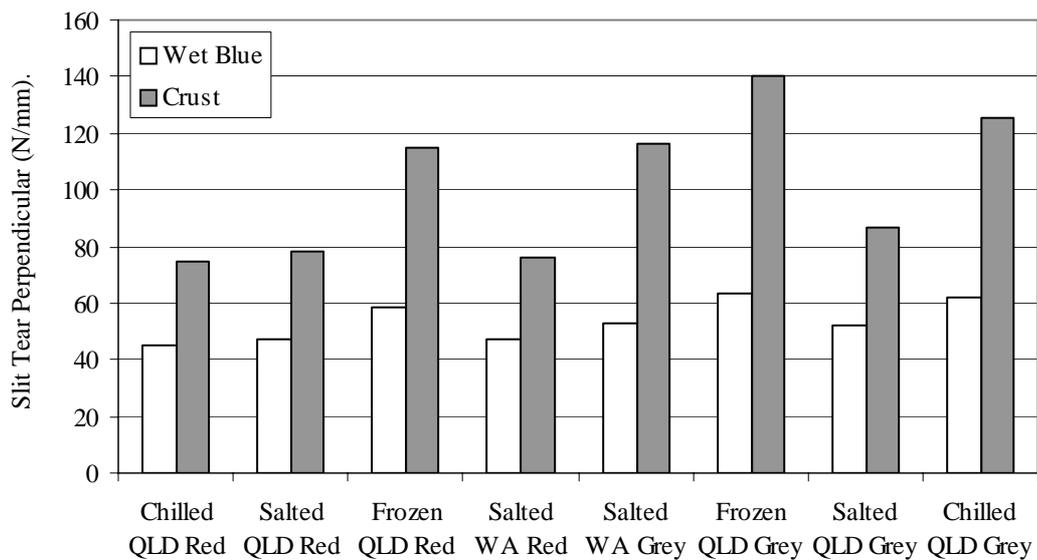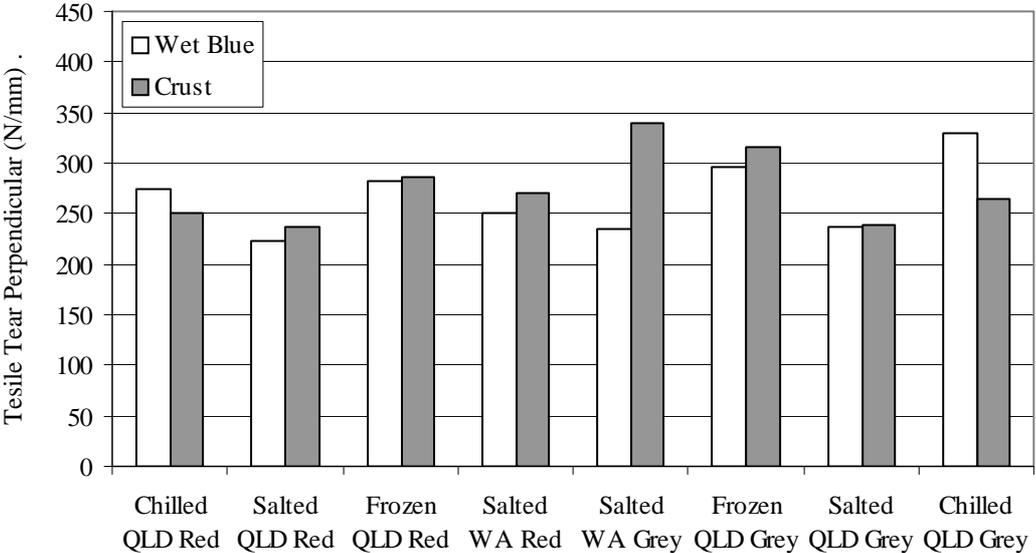

Figure 3.11. *Comparison of Wet Blue and Crust Tensile (N/mm) results perpendicular to the backbone for Summer Harvested skins.*

3.2.3.4 Explanation for frozen red and salted greys

The unusually high tear strength for the frozen red skins from the summer series appeared to be due to a number of skins in the set with different properties to those expected for this type of kangaroo (Table 3.2). Identification of different species of kangaroo is usually carried out prior to processing (identification is usually done on the basis of key differences between red and grey kangaroo relating to fur). Red kangaroo has a thin coating of soft fine fur, which is easily distinguishable from that of the grey kangaroo with its course thick fur. Species identification becomes more difficult after hair removal, but an experienced person can detect differences at the pickle stage by looking for certain

grain effects. At the wet blue and leather stage the differentiation between the red and grey skins becomes more difficult and accurate classification requires the use of microscopic techniques.

Table 3.2. *Individual skin data from the Frozen Queensland red group pack showing the spread of values*

Harvest Season	Summer Harvest Skins N/mm	Winter Harvest Skins N/mm
Skin 1	43.87 (*)	31.39
Skin 2	32.01	27.61
Skin 3	35.56	31.80
Skin 4	50.75 (*)	27.87
Skin 5	38.58	25.68
Skin 6	68.66 (*)	27.36
Skin 7	37.60	26.96
Skin 8	60.80 (*)	29.52
Skin 9	78.18 (*)	29.75
Skin 10	69.61 (*)	27.09
Average	**51.56**	**28.50**
SD	**16.58**	**2.02**
% RSD	**32.15**	**7.08**
* denotes the skins from the "third" species – see text below for more detail		

The set of frozen reds skins were examined using light microscopy and compared to skins from the Queensland chilled reds and grey skins. The chilled red skin is characterised by the high number of follicle groups in a unit area. In Figure 3.12A, there are approximately 390 follicle groups in the grain, with mainly one or two follicles present in each group. Grey kangaroo have a lower number of follicle groups in the sample area but each group consists of 3-5 follicles (Figure 3.12C). All of the skins from the frozen red group with higher tear values, have a consistent grain pattern, an example of is shown in Figure 3.12B. The initial observation is that it appears to be intermediate between the red and grey skins. The sample area contains approximately 190 follicle groups. It appears to have less follicles per group than the grey kangaroo but the texture of the grain surface is not as coarse as the grey and appears to be flatter like red kangaroo. The microscopy of the remaining skins from the frozen red pack, are consistent with images for the chilled red skins. We have identified that the skins from the frozen red pack in summer, with the unusually high tear strength, do not appear to be red kangaroo. Although their strength properties are more like that of the grey kangaroo, there are still some differences to suggest that they are not the same species. One possibly explanation is that the unusual skins in this pack could be Euros or *Macropus robustus.,* which may be found in regions where frozen kangaroo skins are harvested. This commercial species is the same size as a medium kangaroo and is found in drier regions and can have red colourings. The summer conditions may change the fur of the Euro enough that they are mistaken for red kangaroo. The skins with high strength all contained levels of tick and pock damage whereas the other red skins were relatively unmarked.
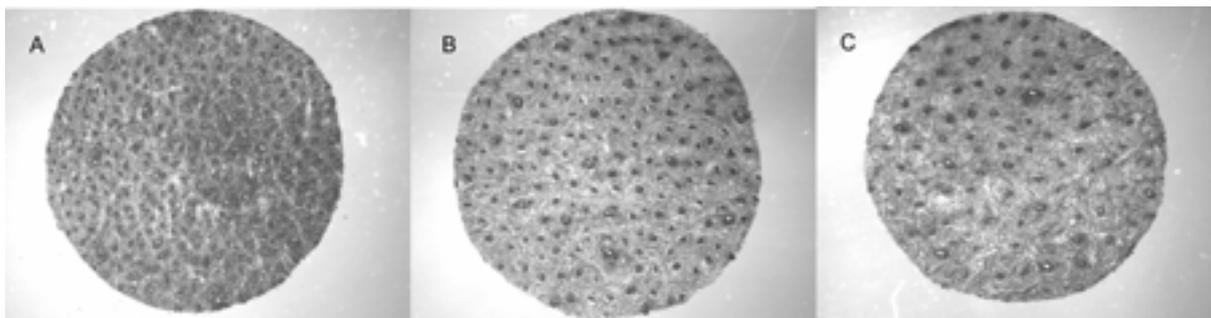
Figure 3.12. *Horizontal sections of A. typical red kangaroo, B. "third" species, C. typical grey kangaroo.*

The salted grey skins with the unexpected low tear strength were examined by microscope and confirmed as grey kangaroo. The low tear strength, which is for this group of 10 skins, could be due to degradation from poor preservation.

The tear strength results for the frozen reds and salted greys from Queensland did not appear to fit the trends from the winter study. Although preliminary work showed that not all of the skins in the frozen reds appeared to be of that third species, the explanation for the salted grey results was not due to species.

This area of the project was extended to include a third set of skins harvested from the summer of 2000/2001. Four skins types were collected and processed using the standard conditions. The chilled red and grey skins were chosen as reference along with the frozen red and salted grey.

The chilled reds afforded an average tear DIN strength of 28.8N/mm, which is similar to the previous summer value of 30.5N/mm. The standard deviation for this set of skins is small at 2.89, which also includes a particularly low skin value of 23.4N/mm. The frozen reds have an average value of 37.6N/mm, but there are three of the ten skins with strength values over 50N/mm. The average value for the seven skins in the "expected range" is 30.4N/mm with the remaining skins averaging 54.6N/mm compared to the previous summer value of 51.6N/mm. As in the first summer period the frozen red series still appears to have a mixture of the two species indicating the difficulty of selecting skins.

The Queensland chilled grey skins averaged 46.5 and the salted skins 39.3N/mm with strengths in both groups ranging form 25N/mm to 56N/mm. The Queensland salted grey skins still appear to be significantly lower than the Queensland chilled grey skins as in the first summer series.

3.3 Effect of Storage at Pickle

3.3.1 Introduction

A key intermediate product in the processing of kangaroo leather is pickled skins. Pickling is a treatment with acid and salt to bring the skins to the desired pH for either storage or tanning.

Like sheepskins, pickled kangaroo skins can be stored for long periods before processing into leather, without obvious structural damage. There have been numerous studies on the effect of pickle storage on sheepskin structure. Factors such as high temperature and longer storage times[31-34] have been found to be detrimental to the skin structure.

As a high performance product, kangaroo leathers need to meet stringent strength criteria to satisfy customers. A loss in strength of as little as 10 % can pose a problem for the tanner in meeting the

strength requirement. It is therefore crucial to understand how the strength of final leather is affected by pickle storage conditions to ensure that productions will fall within strength requirements.

Matched side trials were set up to study the effect of pickle storage time at two different temperatures on the final strength of kangaroo leather. This study includes the same eight different types of pickled skins over two harvest seasons, including winter and summer as in Section 3.2. A batch of skins harvested in winter was placed in storage as described below. Six months later, a second batch, harvested in summer, was similarly placed in storage. Skins were divided into sides. Left halves were stored at ambient temperature at the tannery (Queensland) and right halves were stored at constant temperature in a cold room at 4°C (CSIRO-Victoria). At six monthly intervals, matched sides were tanned, retanned and tested.

For economical reasons, pickled kangaroo skins are normally stored at ambient temperatures. The ambient temperature in a shed environment can vary considerably between time of day and season of the year. Therefore the temperature profile was logged continuously throughout the trial.

3.3.2 Results

Skins stored under ambient conditions experienced temperatures up to 45°C with an average of approximately 22°C for the 18 month time period (Figure 3.13). The first summer was hotter than the second. The winter skins were sampled at six months but only minor changes to performance were observed so it was decided to take the first sample from the summer skins at the 12 month point. At the end of each six month period, the moisture content of the pickled skins was measured prior to tanning.

During the 18 months storage period at ambient temperatures the skins decreased in moisture considerably, with the average moisture content falling from 53% at 6 months to 25.5% and then 17.9% at 12 and 18 months respectively (Table 3.3) for the winter harvest skins. The situation is not quite as severe for the summer harvest skins (Table 3.3) with a fall in moisture to 46% and 30.7% for 12 months and 18 months respectively. This is in contrast to the cold stored pickled skins which maintained their moisture content at approximately 60% for all skins throughout the storage time. This indicates that the loss in moisture content of the ambient stored skins is due to evaporation and not to drainage. The lower overall drop in the moisture for the summer skins compared with winter skins stored for the same time may be due to the different storage temperature profile experienced by the two sets of skins, or because the summer skins were not sampled at the six month point and were thus not exposed to the air as much.

Table 3.3. Average Moisture Content (%) of Pickled Skins after Storage

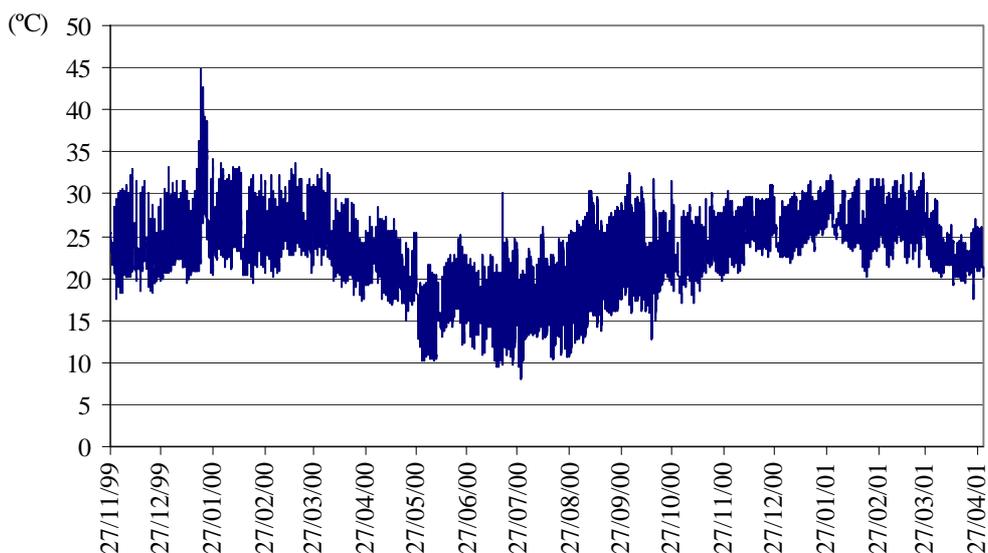| Storage Time	Winter Harvest		Summer Harvest	
	Chilled	Ambient	Chilled	Ambient
6 months	60.4	53.0	-	-
12 months	60.4	25.5	61.8	46.0
18 months	60.4	17.9	61.9	30.7

Figure 3.13. *Recorded temperatures for the pickle storage at Packer Tanning, Narangba QLD, from November 1999 to April 2001.*

The pH of the pickled skins (Table 3.4) was determined from an aqueous extract by the method outlined in Section 2.3.2. After storage at the different temperatures for six months, there was a slight difference in the pH of the aqueous extract of the winter harvest skins for the chilled and ambient skins, with values of 2.53 and 2.61 respectively.

Table 3.4. *Changes in pH of Pickled Skins due to Storage at Different Temperatures.*

Time Period	Winter Harvest		Summer Harvest	
	Chilled	Ambient	Chilled	Ambient
6 months[†]	2.53	2.61	-	-
12 months [†]	2.61	2.75	2.63	2.80
18 months [†]	2.75	2.91	2.71	2.88

† The lower moisture contents of the sides from Packer Tanning compared to the matched sides at CSIRO was taken into account during the test

The pH of the skins stored at ambient temperature continued to rise during the last 12 months of the storage time, with the final values for the skins reaching 2.91 at 18 months. The skins stored at 4°C were found to also increase in pH during the 18 months, with the pH of aqueous extracts increasing from pH 2.53 at 6 months to a final value pH of 2.75 at the end of the 18 month storage period. Packer Tanning has since shown that the pH of the aqueous extract from the commercial kangaroo pickle starts at pH 2.34 but increases to pH 2.41 in the first month and only reaches a pH of 2.6 after 6 months storage at ambient temperatures.

The results in Table 3.4 for the pH of the aqueous extract from the summer harvest skins show a similar trend to that of the winter skins. At 12 and 18 months the chilled skin values were pH 2.63 and 2.71 respectively which correspond well with the winter values at the same time (pH2.61 and 2.75). In the case of the Packer Tanning skins, a similar trend is also observed with the pH values of 2.80 and 2.88 at 12 and 18 months respectively corresponding to the winter values of pH2.75 and 2.91.

Tear testing (DIN) of the crust leather after 6 months of pickle storage of winter harvest skins showed only minor differences in relative strength (Newton/mm) between the chilled and ambient skins (Table 3.5). The decrease in tear strength of the ambient stored skins compared to the chilled averaged over the 4 packs, was 5% for red and 3% for grey kangaroo. After 12 months, the average decrease in the tear strength of the ambient skins was 11% for red and 14% for grey kangaroo. The difference in tear

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strength (N/mm) between the matched sides increased significantly, after 18 months, with the skins stored at ambient being approximately 38% and 40% lower in strength than the corresponding chilled sides for the red and grey skins respectively.

Differences between place of origin (Queensland and Western Australia) and preservation technique (salted, frozen and chilled) appear to be minor and so averages over the 8 packs are reported to identify the trends.

The matched sides were further tested for tensile strength. It was found that the overall decrease in tear strength observed in the ambient skins compared to the chilled skins in the tear testing was repeated in the tensile results with an approximate loss of 39%.

Interestingly, it has been found that crust leather produced from ambient stored pickle was found to have a reduced extractable fat content (25% less by DCM) compared to the leather from the chilled matched sides which had been retanned in the same drum.

There were thickness differences between ambient winter harvest and cold stored skins. Although the quoted difference in the strength measurements have taken thickness into account (ie. N/mm), it should be noted that the skins stored at ambient temperature gave crust leather that was thinner in all cases compared to the chilled skins. The decrease in the thickness of the leather made from Packer Tanning stored pickle skins at 18 months was approximately 8% relative to the CSIRO skins.

The tear DIN strength (Table 3.5) of the summer harvest skins at 12 and 18 months shows only a slight decrease in strength for the ambient skins. After 12 months, they had marginally decreased in tear strength relative to the chilled skins with red kangaroo lower by 3% and 6% for grey kangaroo, similar to the winter 6 month series values. After 18 months the difference between the ambient skins and the chilled skins is similar to that observed at 12 months, with the red kangaroo lower in strength by 2% and grey kangaroo by 8%. The decrease in tear strength was again duplicated in the tensile results.

Table 3.5. *Tear DIN results for crust kangaroo leather produced from pickled skins stored at different temperatures.*

Storage Time	Low Temperature storage (4ºC)		Ambient temperature storage		% decrease in strength	
	N/mm	N	N/mm	N	N/mm	N
Winter Harvested Skins						
Red						
6 months	28.5	40.0	27.1	36.6	5	9
12 months	33.0	43.6	29.6	38.	11	15
18 months	27.5	34.6	17.1	21.3	38	63
Grey						
6 months	53.3	101.4	51.7	90.6	3	12
12 months	54.4	92.1	46.9	72.4	14	27
18 months	47.1	73.9	28.2	41.6	40	77
Summer Harvested Skins						
Red						
12 months	29.6	40.3	28.6	35.8	3	13
18 months	24.9	34.3	24.5	31.0	2	11
Grey						
12 months	48.0	75.4	45.1	65.8	6	15
18 months	43.7	70.7	40.2	59.4	8	19

The winter harvest pickled sides stored at ambient temperature for 12 and 18 months were found, when processed to wet blue, to have a coarser raised grain and a distinctive darker blue colour than the corresponding matched sides from chilled skins. A reference to similar observations in acid damaged pelts attributed this effect to increased chromium uptake.[33] However, relatively small differences (<5%) in total chromium content were found between the ambient and chilled sides. Where a difference in the chromium content was observed, the ambient skins were always slightly higher in value. Although the yellowing of pickled skins during prolonged ambient storage may be contributing to the colour difference, the main factor must be that the chrome reacts differently with the ambient skins than with the cold stored skins. A difference in cross-linking, and colour, may be due to an increased number of carboxyl groups from protein degradation[34] in the pickled skins stored at higher temperatures.

Although the 18 month ambient stored skins have a 40% loss of strength, the hydrothermal shrinkage temperature, T_s, of the wet blue is higher than for matching chilled skins. T_s measures the stability of wet blue, which is related to the degree of cross-linking within the collagen matrix. These results indicate that T_s does not correlate with the strength of wet blue, particularly for skins affected by long term storage.

3.3.3 Discussion

The finding that leather strength decreased by 40% for the winter skins stored for 18 months at ambient conditions compared to the skins stored at 4ºC shows the risk associated with prolonged storage. These skins were stored for two summers with the first summer having many days with temperatures over 30ºC and the skins dried to18% moisture during storage. The strength of the leather from the summer skins decreased by less than 10% during storage for two winters and a cool summer. The skins dried out to 30% during storage. The storage temperature and the drying of the skins both appear to contribute to loss in strength. The collagen degradation increases with low skin moisture content and high storage temperatures. The evaporation of moisture from the skin would concentrate the acid in the skin and in combination with the elevated temperatures of the summer period provide the right combination for skin degradation resulting in significant loss of strength in the skins.

Winter and summer harvested pickled skins both show similar increases in pH during storage with greater increase at ambient temperatures than at 4ºC. The increase in the pH of aqueous extracts from sheepskins during storage has been reported by several workers.[31-34] However, the big differences in skin strength with similar pH increase over the same storage time period show that pH of aqueous extracts of skins is not an accurate measure for predicting potential loss of strength in skins on storage. The results suggest that the acid is hydrolysing peptides and proteins that are not significant to structural integrity. The hydrolysis consumes acid, which increases the pH but does not necessarily damage the collagen of the skin.

In addition to loss of strength, long term storage of pickled skins can result in other problems. The winter harvest pickled sides stored at ambient temperature for 12 and 18 months had an unacceptably coarse raised grain and dark colour in wet-blue. The dark colour of the skins would result in variable dye shades, especially with light colours.

3.4 Conclusions

The study has identified a number of significant issues:

- Grey kangaroo leather is stronger than red. It appears that a different species, possibly the Euro, is sometimes classified as red kangaroo.

- Retanning significantly increases the tear strength of kangaroo wet blue. The properties of wet blue cannot be used to predict the final leather tear strength.

- For summer skins both freezing and chilling produced stronger leathers than salting.

- The tear strengths of samples taken perpendicular to the backbone were stronger (10-23%) than the corresponding parallel samples.

- The tensile strength of wet blue was not changed significantly during the retanning process.

- The tensile strength of the perpendicular samples was lower than the parallel samples.

- If pickled kangaroo skins are to be stored for long periods they should be stored at low temperatures and moisture loss from the skins should be minimised.

- High storage temperatures (>30°C) in combination with drying out of pickled skins can decrease leather strength by as much as 40%.

- Increase in pH with storage time is not a reliable indicator of loss of skin strength.

- Shrinkage temperature of wet blue is not an indicator of loss of strength from pickle storage.

- Degradation caused during prolonged pickle storage affects the quality of the leather (strength, thickness, feel and colour).

4. Tanning

4.1 Introduction

Since its discovery in 1858, chromium has become the most widely used material for tanning hides and skins. Reaction with chromium (III) salts produces tanned leather, commonly termed "wet blue" which, due to stabilisation of the collagen fibre, has excellent long term preservation, high thermal stability and resistance to bacterial attack. For small skins such as lamb and kangaroo, it is convenient to process in two steps, first from the raw state through to a "preservation pickle" at which point skins can be graded and stored relatively safely or they can be traded. Pickled skins can then be selected on size and/or quality to suit a particular type of leather before being committed to the relatively expensive tanning step. This approach is impractical for bovine hides, which are usually processed straight through to wet blue where they can be stored, graded and traded. The tanning of pickled skins through to wet blue involves several in-drum processes (Figure 4.1). It is important to soak skins to rehydrate them, particularly if they have dried out during storage, to prevent unwanted fibre damage in the initial part of the process. Skins can then be fatliquored or pretanned, using a variety of tanning systems, prior to the addition of chrome tanning reagent.
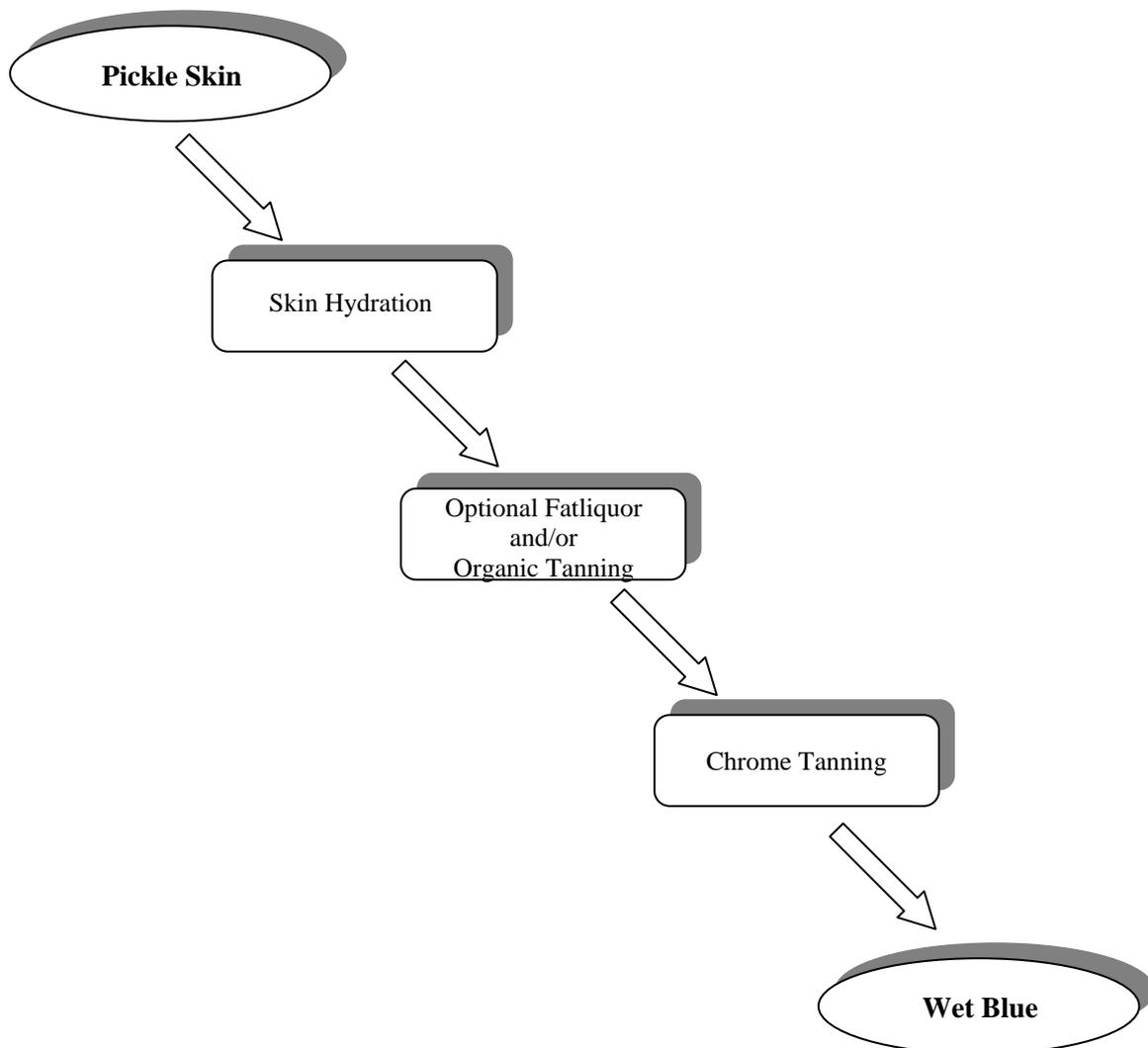

Figure 4.1. *Process for conversion of pickled skins to wet blue.*

Chrome tanning involves treatment of skins with a solution of chromium (III) salts below pH 3 which allows penetration, followed by a pH adjustment to pH 4, which promotes binding of the metal atoms to the collagen. The chemistry of chrome tanning is complex, with several competing reactions occurring. Factors including the condition of the skins, basicity and concentration of chromium salt used, pH, temperature and mechanical action can all affect the properties of the leather.[35-37] In addition, lubricating agents (fatliquors) and organic tanning agents such as aldehydes and resins, added prior to or in conjunction with the chromium, can also substantially affect the strength, handle and appearance of the final product. There is little product differentiation up to the tanning step, since the main aim is to produce wet blue on a large scale that provides a consistent starting material for use in the retanning, dyeing and fatliquoring (RDF) process. *In this chapter we report how certain chemical modifications in the production of wet blue kangaroo from commercially pickled skins affect the strength of the crust leather.*

4.2 Effect of pretanning variables on strength

4.2.1 Fatliquors

The use of fatliquors are important in the processing of pickled skins to wet blue as they improve hydration of the skins in the drum, assist in the penetration of other reagents and start to introduce some of the properties required in the final leather. It is also considered important to commence the lubrication of the collagen fibres to improve strength and softness of the leather.[38,39] Although there is a wide range of commercially available fatliquors, we have chosen two systems to study: a sulphated hydrocarbon stable to the high electrolyte levels of pickle solutions and a modified fatliquor based on a traditional fish oil offering good softening and lubrication properties.

4.2.1.1 Modified fish oil
The addition of the modified fish oil (2%) prior to the chrome tanning salts was found to have no significant effect on the strength of the leather. The results showed that the addition of the fatliquor decreased the strength by 1%, which is within error determined for matched side trials (Section 2.3.1). Increasing the level of the fish oil to 4% resulted in crust leather with a slight decrease (3%) in tear measurements in comparison to leather with no fish oil, which is still not significant (Figure 4.2).
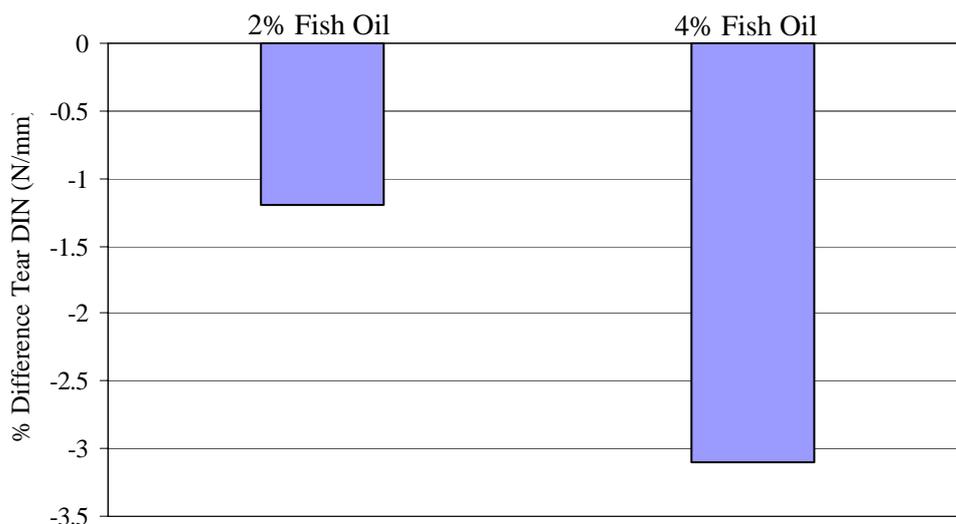

Figure 4.2. *Effect of modified Fish Oil fatliquor on the tear strength of crust kangaroo leather. The % difference Tear DIN (N/mm) values are quoted relative to no added fatliquor.*

4.2.1.2 Sulphated hydrocarbon fatliquors
Commonly, certain types of sulphated hydrocarbon fatliquors are used in the processing of pickled skins that have partially dried out during prolonged storage to assist in their rehydration and improve the slipping action in the drum. These electrolyte stable reagents are also considered to offer additional benefits to the final wet blue properties such as good penetration of other fatliquors, improved shaving and prevention of drying out of skin edges. The effect on the strength of crust leather due to these reagents and the possible interaction with the modified fish oil was examined (see Figure 4.3). When sulphated hydrocarbon was added to the process with no fish oil, the resulting tear strength of the crust leathers was similar indicating that the sulphated fatliquor had no effect on the strength. Sides containing both fish oil and sulphated hydrocarbon added at two different levels (2 and 4%) were prepared and the difference in strength, relative to sides prepared with no fatliquors was determined. The results from these trials indicate that even the higher fatliquor levels of 4% afforded no significant difference in tear strength. These experiments indicated that the use of fatliquors at this stage of processing does not appear to influence the strength properties of the resulting crust leather to any degree although these reagents may contribute other benefits to wet blue and crust leather.
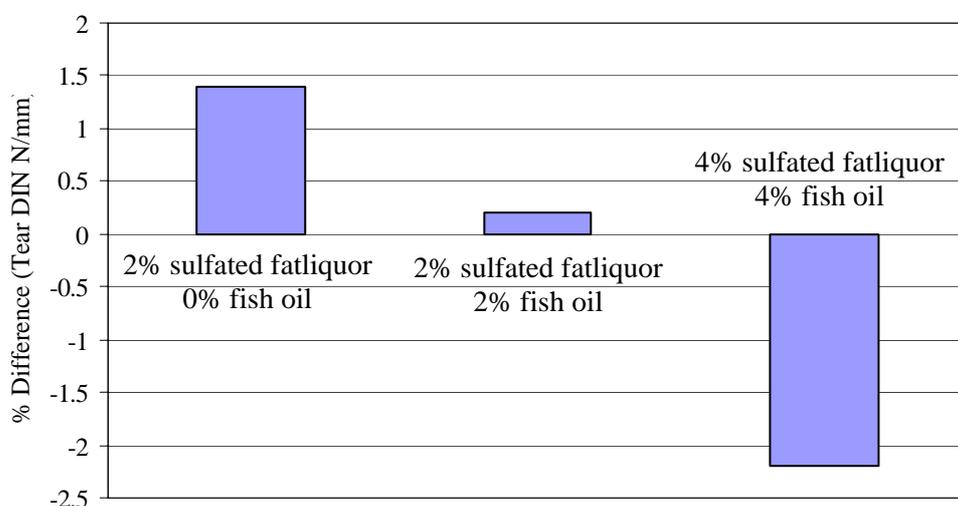

Figure 4.3. *Effect of modified Fish Oil and sulfated hydrocarbon fatliquor agent combinations on the tear strength of crust kangaroo leather. The % difference Tear DIN (N/mm) values are quoted relative to no added fatliquor*

4.2.2 Auxiliary Tanning Agents

The use of organic tanning agents in combination with Chromium (III) salts is common in the manufacture of leather to produce a wide range of leather products. Organic tannages fall into several categories including aldehyde, vegetable and synthetic polymer or syntan based systems. These auxiliary or pretanning agents are normally included for their beneficial effect on a range of finished leather physical properties. However, due to the fact that these materials are tanning agents in their own right, and form crosslinks with collagen that are in addition to those formed with the chrome tanning agent, they offer the possibility of having beneficial effects on leather strength. For this reason, examples of two of the categories of auxiliary tanning agents were compared to a control tannage having no pretannage to identify their potential for improving strength.

4.2.2.1 Aldehydes
The most widely used aldehydes in tanning are glutaraldehyde and modified glutaraldehydes. When a modified glutaraldehyde tanning agent was added, prior to the chromium (III) salts, it resulted in an 8% increase in the tear strength of the crust leather produced compared with a standard process having no pretannage (Figure 4.4). However, doubling the levels of reagent gave only half the increase in tear

strength of the leather. Surprisingly the addition of a solution of glutaraldehyde (50% solution) afforded crust leather, with a significant decrease in the tear strength (11%) compared to the expected strength with no added pretanning agent. Doubling the level of glutaraldehyde in the process resulted in a further decrease (23%) in the tear strength of the leather.

4.2.2.2 Amino resins

Certain amino resins used in the retanning of bovine wet blue, because they offer considerable advantages in the filling of the hides, also offer improvements in the strength.[40] However, achieving the penetration of these resins can be difficult, particularly in thick hides, due the size of the molecule and its reactivity with the collagen. It is thought that if resins could be used as a pretreatment before tannage then this might avoid the reactivity problems and give penetration before fixation in the following chrome tanning step.[40]

The addition of a dicyanamide resin (1.7%) during the tanning step was reported to produce softer, fuller, more compact leathers with a tighter grain for bovine leathers.[40] Also, the resins potentially offer improvement in the chrome uptake from the bath. Addition of the dicyanamide resin system into the kangaroo process prior to the chrome tanning step was found to give comparable improvements in tear strength to that obtained with the modified glutaraldehyde reagent, representing an 8% improvement over the systems with no additives. This improvement in tear strength in kangaroo was similar to the reported increase in the tear strength of the bovine hides (12%).[40] However, care is required when applying resin systems prior to the chrome tanning step as undesirable precipitates can form due to interaction between the residual resin in the bath and the chromium salt added during the tanning step.
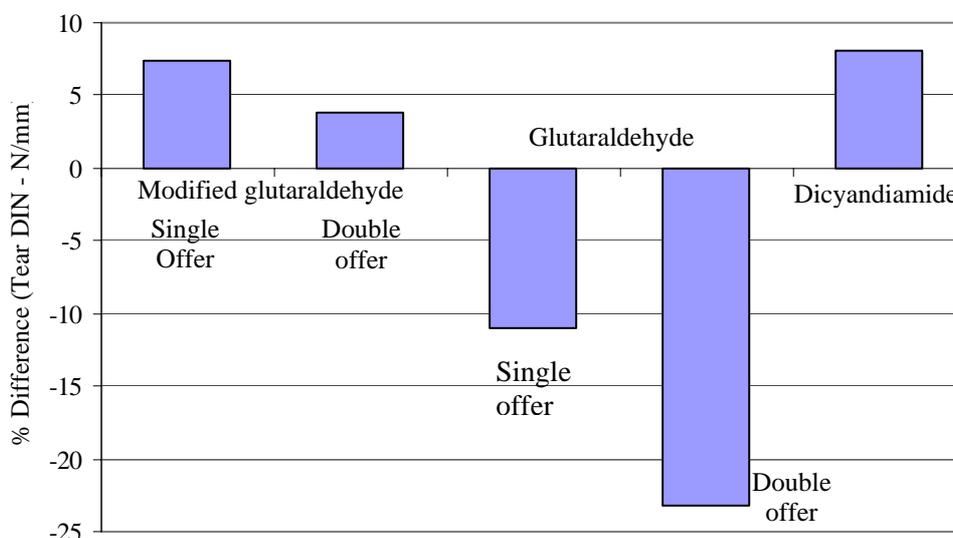
Figure 4.4. *Effect of auxiliary tanning agents on the tear strength of crust kangaroo leather. Values are quoted as % difference (Tear DIN – N/mm) from leather produced with no organic tanning agent.*

4.3 Chrome Tanning

Although, it is reported[36] that the strength of chrome tanned bovine leather decreases as the chrome content is increased, there are no reports of any corresponding study on kangaroo. It has been suggested that chrome oxide levels of 5 % dry weight, is the critical limit above which bovine leather strength decreases, although no detailed study has been carried out to substantiate this claim. Kangaroo skins are generally tanned with higher levels of chromium (III) salts than bovine hides, and

often resulting in chrome oxide levels over 5%. Therefore, a study of kangaroo wet blue to determine the effect of varying chrome oxide content on the strength of crust leather was carried out.

Commercial pickled skins were processed as matched sides to wet blue with varying levels of chromium oxide (Cr_2O_3). One side of the skin was processed using the chromium offer from the standard process, 4% of the normal chromium (III) sulfate (33% basicity 26% Cr_2O_3) plus 5% of a self basifying chromium (III) salt (52% basicity, 21% Cr_2O_3). The other side of the skin was processed with varying levels of chromium (III) salts, but approximately maintaining the ratio between the normal and self basifying chromium (III) tanning reagents (~4:5). During the course of this work, effort was made to maintain the same specific gravity, temperature and pH between the experiments.

The final chromium oxide content in the kangaroo skins was found to range between 1.89-5.11% resulting from initial chromium powder offers in the processing bath ranging from 2% of the normal chromium (III) reagent plus 3% of the self basifying chromium (III) reagent through to 6% of the normal chromium (III) reagent plus 8% of the self basifying chromium (III) reagent (Figure 4.5). Offers of 9% normal chromium (III) reagent and 9% of the self basifying chromium (III) reagent alone were also made for comparison.
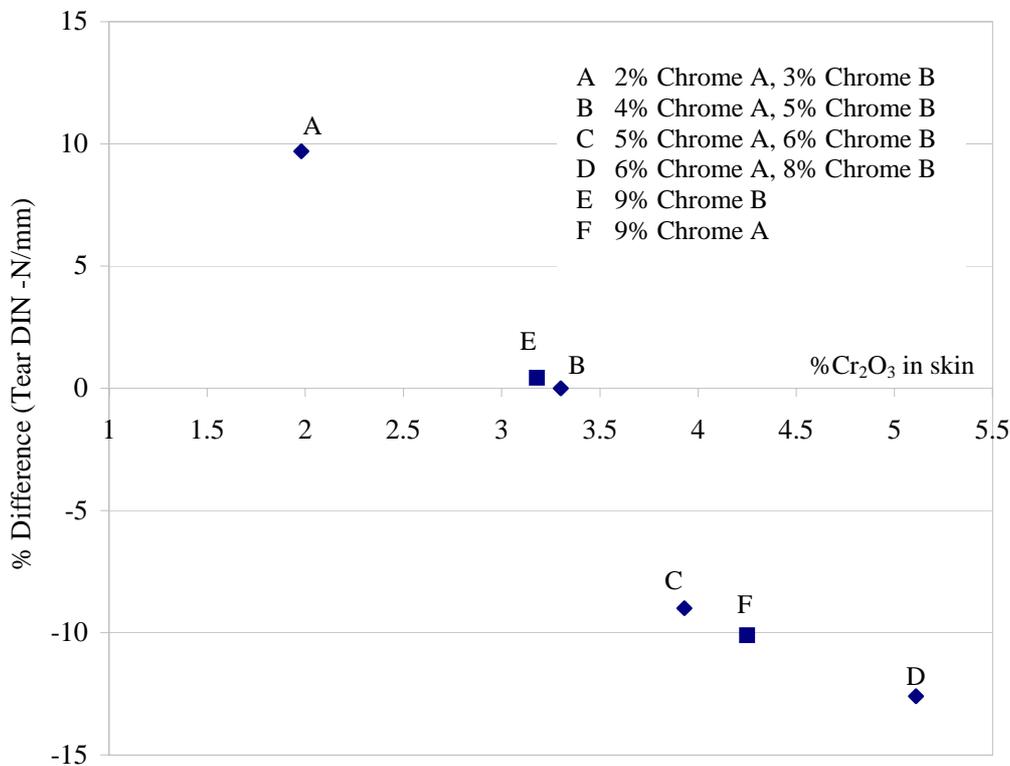
Figure 4.5. *Effect of %Cr_2O_3 in the skin on the tear strength of crust kangaroo leather. % Difference in Tear DIN (N/mm) are quoted relative to the control value of 35.06N/mm. Chrome A refers to normal chromium (III) sulfate (33% basicity 26% Cr_2O_3) and Chrome B refers to self basifying chromium (III) salt (52% basicity, 21% Cr_2O_3).*

For kangaroo skins, it was determined that there was a relationship between chrome content and strength over the range studied from 1.9 to 5.1%. Increasing Cr_2O_3 levels in the skins from 1.89 to 5.11 % results in decreased tear strength of 23% (Figure 4.5). The tear strength of the sides processed with 4% normal chromium (III) reagent plus 5% self basifying chromium (III) reagent averaged 35.06N/mm and a Cr_2O_3 value of 3.3%. Increasing the Cr_2O_3 content in the skins to 5.11% resulted in decreased tear strength (13%) relative to the standard.

The relationship between Cr_2O_3 content and shrinkage temperature was also studied (Figure 4.6). The standard conditions of 4% normal chromium (III) reagent and 5% self basifying chromium (III) reagent afforded an averaged shrinkage temperature of 99.1°C. The graph shows that the gain in Ts is only 7% going from 3.3% to 5.11 % Cr_2O_3 compared the 13% gain in T_s going from 1.89 to 3.3% Cr_2O_3. The shrinkage temperature is an accurate method to determine the stability of the leather to heat. Another procedure used in industry is the boil test where leather is dropped into boiling water and the time recorded before it undergoes irreversible damage. A time of 2-3 min minutes before any signs of change would be considered acceptable in this type of test. A shrinkage temperature of 99°C would be high enough to pass the test. It should be noted that the shrinkage temperatures of these samples were determined 7 days after processing of the wet blue. Wet blue with Ts values of 99.1°C after one week will increase to approximately 103°C on further ageing.

The results were confirmed in a further trial where matched sides were processed with chrome powder offers of 9%, the left side was processed with 9% normal chromium (III) reagent and the right hand side with 9% of self basifying chromium (III) reagent. The chromium oxide content of the wet blue samples and the tear values of the crust leather correlated well with the graph shown in Figure 4.5. This indicates that kangaroo strength decreases with increasing chromium content. In addition, the Ts and Cr_2O_3 content values fitted with the graph shown in Figure 4.6.
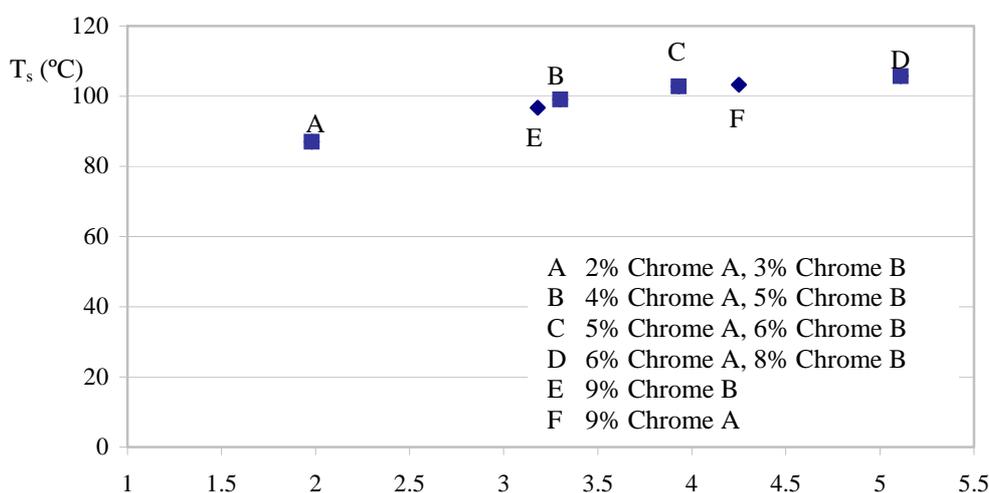
Figure 4.6. *Effect of %Cr_2O_3 in the skin on the shrinkage temperature, T_s(°C) of crust kangaroo leather. Chrome A refers to normal chromium (III) sulfate (33% basicity 26% Cr_2O_3) and Chrome B refers to self basifying chromium (III) salt (52% basicity, 21% Cr_2O_3).*

4.4 Conclusion

A certain level of chrome oxide is required in the skins to ensure adequate long term preservation and acceptable shrinkage temperatures but it was found that the amount of chromium (III) salts taken up by the skins can have a significant effect on the strength of the kangaroo leather. If the trend observed from the 40 litre drums extrapolates to commercial processing, there appears to be an opportunity to improve the strength of the leather by reducing Cr_2O_3 levels in the wet blue. However, reducing the Cr_2O_3 content in the skins to maximise tear strength has to be balanced with the corresponding loss of T_s and any changes in the handle of the leather.

Although the addition of fatliquors during the tanning process is commonly believed by the industry to be important for improving the lubrication of fibres and hence the strength of leather, in our work with two fatliquors, it was found that they do not improve the tear strength of the final crust leather. It should be noted that the fatliquors will influence other properties important for the leather such as softness. The addition of other tanning agents in conjunction with the primary chrome tannage was

found to significantly influence the tear strength. An indication of the difficulty in predicting the effect these type of reagents will have on the properties of the leather is demonstrated by the glutaraldehyde results. Glutaraldehyde was found to have a significant detrimental effect on the tear strength with a decrease of >11%, but a modified glutaraldehyde reagent can offer a moderate improvement in the tear properties of the leather. However, some of the benefit is lost if a larger offer is made. A similar level of improvement was found with the use of an amino resin reagent. The dicyandiamide resin, generally used in retanning processes, was found to afford an 8% increase in strength, comparable to the modified glutaraldehyde system.

5. Production of Crust Leather from Wet Blue

5.1 Introduction

The tanning of skins and hides with chromium salts is critical in stabilising the collagen fibre to resist bacterial attack and increase the temperature stability. However, the material from this process does not possess the physical and aesthetic properties required for the range of products made from leather. Therefore wet blue from the chrome tanning process is converted to useable leather in a series of chemical and mechanical operations (Figure 5.1).
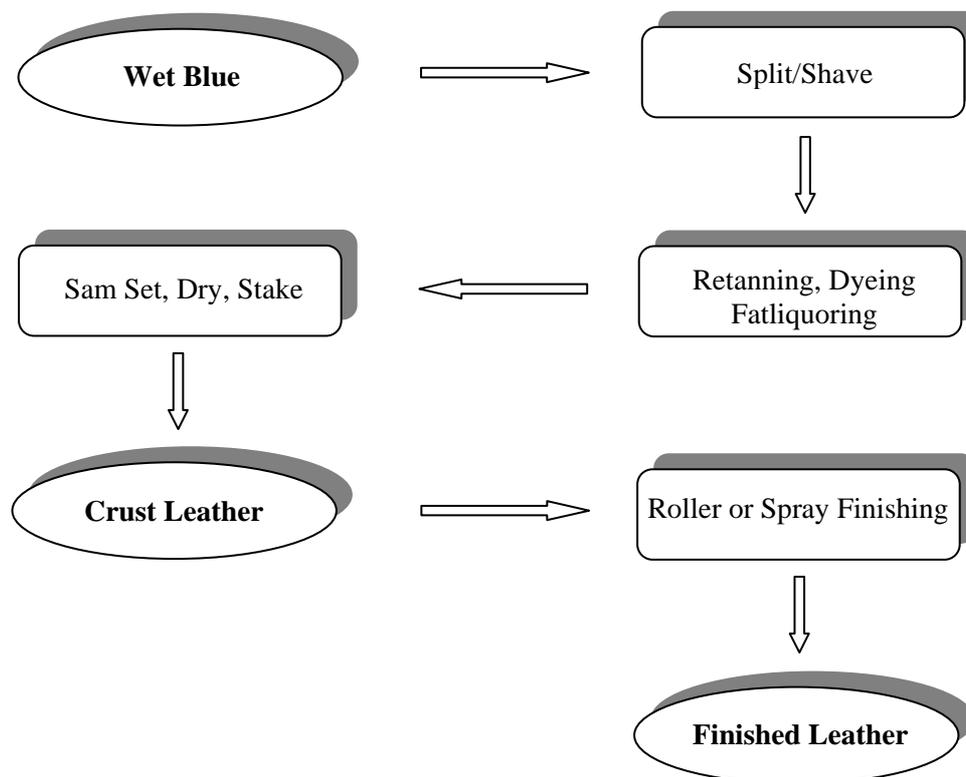
Figure 5.1. Outline of physical operations and chemical processes in the conversion of wet blue to crust.

Starting from one type of wet blue, it is possible, through the appropriate choice of various dyes, fatliquors, vegetable and organic tanning agents, to produce a selection of leathers with very different aesthetic, physical and chemical properties which have been tailored to suit particular applications. The final step in production for most types of leather is the application of polymeric finishes using spray or roller coating techniques. The finishes contribute to the durability of the leather and can be used to help cover undesirable defects or blemishes in the grain. Although the finishing is an integral part of the manufacturing process, it falls outside of the scope of this project. *The aim of the work described in this chapter was to determine the factors during the chemical and mechanical operations that influence leather strength during the production of crust leather from wet blue.*

5.2 Chemical Processes
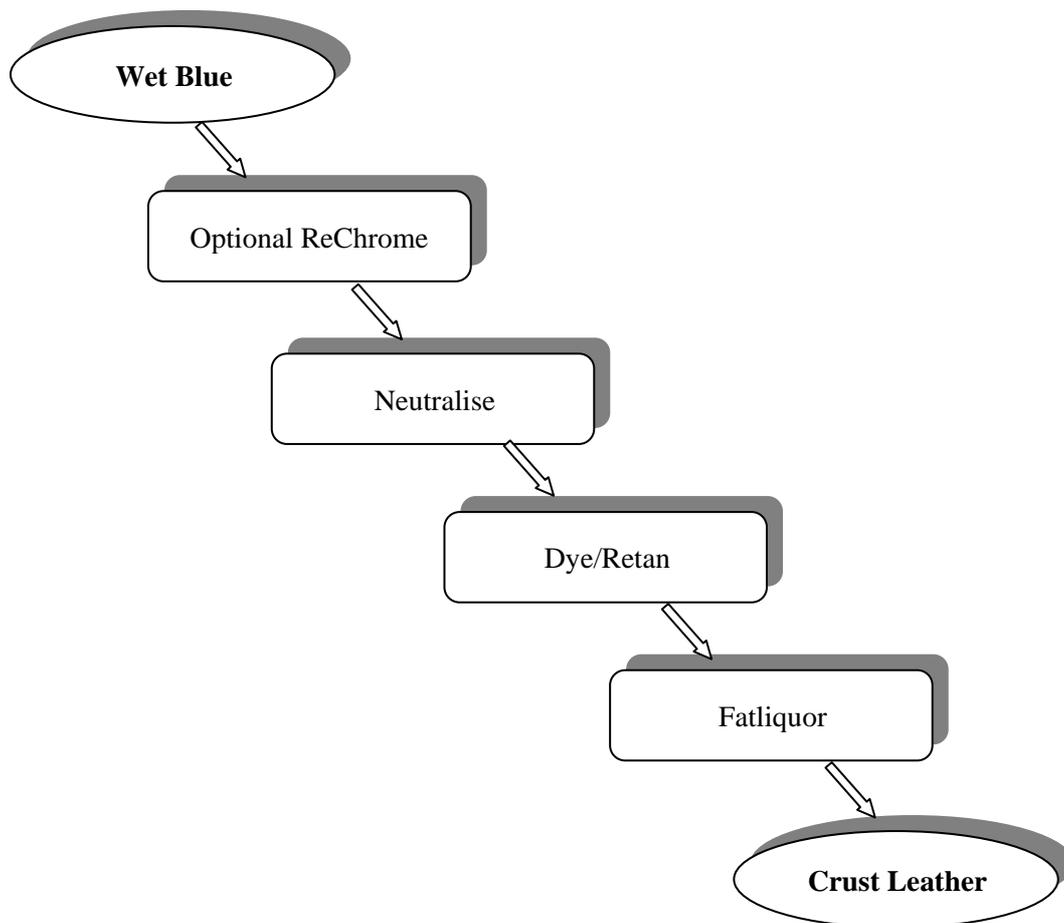
Figure 5.2. *Outline of the chemical processes from wet blue to dyed crust, principally involving retanning, dyeing and fatliquoring (RDF) steps.*

The highly complex chemical processing of the wet blue involves a number of well defined steps including retanning, dyeing and fatliquoring (RDF) (Figure 5.2). The wet blue is washed to reduce salts levels, remove loose fibres (generated during shaving) and to rehydrate the skins prior to the commencement of retanning. Some tanners rechrome the wet blue, a process involving the addition of chromium (III) salts or chrome-syntan complexes. This is considered important if the wet blue has been stored for a long periods or if the tanner uses wet blue from different suppliers.

The retanning dyeing and fatlquoring (RDF) process commences with the step known as neutralisation, where the pH of the material is raised to over pH 4.8, so that anionic tanning materials, dyestuffs and fatliquoring agents, used in this stage of processing, are not bound too quickly or superficially and can evenly penetrate into the leather. This stage of the process is carried out at low temperatures (<40ºC) and at high chemical concentration to aid the penetration of the reagents. Towards the end of the RDF stage, the temperature is raised, usually to 60-65ºC, and acid is added to decrease the pH to approx 3.6-3.8, in order to fix the reagents to the collagen.

5.2.1 Neutralisation

The effect on the strength of the leather due to modifying the neutralisation time and pH were investigated. The purpose of neutralisation is to raise the pH of the wet blue from approx pH3.6-4.0 to pH4.8-6.5, by the addition of mild alkaline reagents such as neutralising syntans or inorganic salts eg sodium bicarbonate, sodium formate, ammonium bicarbonate. The proper neutralisation of the wet blue enables even distribution of the RDF chemicals and is considered important for producing quality leather. A careful balance must be achieved so that the anionic reagents used in the RDF process can penetrate efficiently but still be weakly attracted to the leather fibres. If the pH of neutralisation is too low, the leather remains highly reactive towards anionic retanning agents, dyestuffs and fatliquors, leading to surface precipitation or poor penetration and uneven distribution into the fibre structure. High pH values provide good distribution and penetration but results in slow fixation of reagents. If the pH during neutralisation is allowed to go too high, it can increase the risk of leather damage including coarse grain, thin flanks, looseness and draw, although draw is less of a risk with kangaroo skins than other skin/hide types. The optimum pH for neutralisation needs to be determined for different processes, as it can vary for the different types of retanning agents.
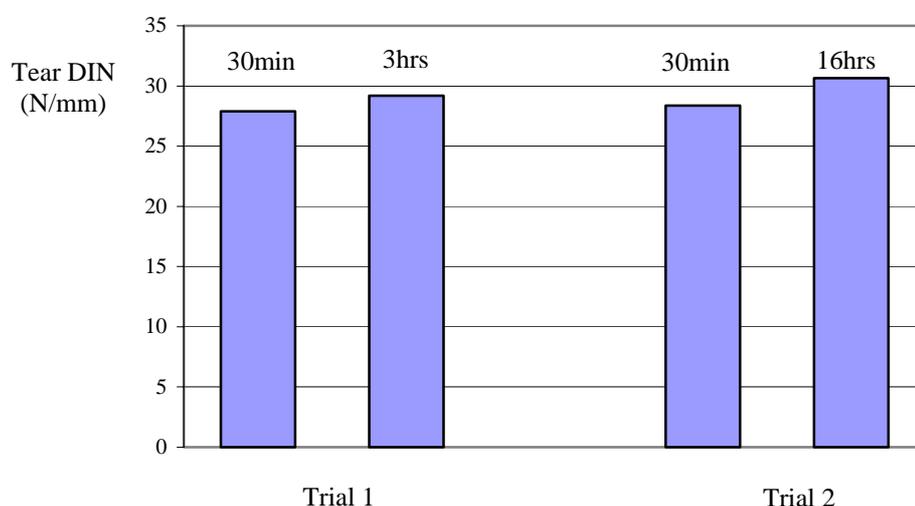
Figure 5.3. *Effect of neutralisation time on the tear strength of crust kangaroo leather, compared to control (30min).*

5.2.1.1 Effect of neutralisation

The neutralisation time was increased from 30 min to 3 hours and 16 hours to determine the overall effect on the strength of leather. The time of 3h was considered to be the practical upper time limit that industry would use for this part of the process. The prolonged neutralization time of 16 hours was carried out to indicate what potential benefits could be obtained if the skins had adequate time to fully stabilise to the pH conditions. The results shown in Figure 5.3 indicate that an increase in neutralisation time from 30 min to 3 h appeared to offer no significant improvement of (4%) in the tear strength of the leather. The extended neutralisation time of 16 h resulted in a further improvement in the tear strength, with an 8% increase in strength of the crust leather compared to the control. Although, the moderate neutralization time (3 h) may offer a slight increase in the tear strength this has to be considered against the potential problems that might arise for industry from a longer processing time. The improvement in the tear strength due to the extended neutralisation time (16 h) could be associated with an increased uptake of fatliquor, as it was determined that there was a 7% increase in total extractable fats from the leather compared to the control skins.

5.2.1.2 Effect of pH during neutralisation on strength

This area of work was extended to determine if the pH during the neutralisation step has an effect on the tear strength of the final leather (Figure 5.4). A series of trials were carried out using the standard neutralisation time of 30 min with the pH values recorded prior to the addition of the fatliquor. The pH of neutralisation in these trials was altered by changing the amount of the two neutralising salts (Section 2.2.2). A trial comparing the pH of 5.1 with 7.55 (F), points considered to be the two extremes for the neutralisation process, showed that there was a 6 % increase in the tear strength as the pH of neutralisation was increased. However, further trials looking at small increments in the pH range from 5.1 to 7.5 (Figure 5.4) indicated a non-linear relationship in the effect of increasing the pH of neutralisation on tear strength. It was found that the tear strength decreased by 10%, as the pH of the neutralisation bath was increased from pH 5.05 to 5.30 (A). When the pH of neutralisation was increased from 5.35 to 5.85 (B), the tear strength of the resulting crust leather was found to marginally decrease.   A similar small decrease was observed by increasing the pH from 5.65 to 6.05 (C). An increase of 4% in tear strength was observed as the neutralisation pH increased from 5.85 to 6.40 (D). This value would be a combination of a small drop going from 5.85 to the pH representing the lowest strength value and then an increase in strength going to 6.40. A further increase in the pH from 6.2 to 6.45 (E) afforded a significant increase in the tear strength (16%) of the crust leather. This series of experiments illustrates the potential complexity of the neutralisation step.   Across the pH range normally associated with the neutralisation step, we found in this experiment that the difference in tear strength can be significant, with a minimum value near 5.85-6.00 and optimum strength near the two extremes, pH 5.00 and pH 7.5, with the latter affording the higher values. Further work in this area would be required to determine if this effect occurs with other processes. Although we have examined the effect on strength during to the variation of the neutralisation pH, the changes in other properties of the leather would also need to be determined.

The chart shows % Difference (Tear DIN - N/mm) on the y-axis (ranging from -15 to 20) for bars A through F.

Legend:
A pH 5.05 vs 5.30
B pH 5.35 vs 5.85
C pH 5.65 vs 6.05
D pH 5.85 vs 6.40
E pH 6.20 vs 6.45
F pH 5.10 vs 7.55
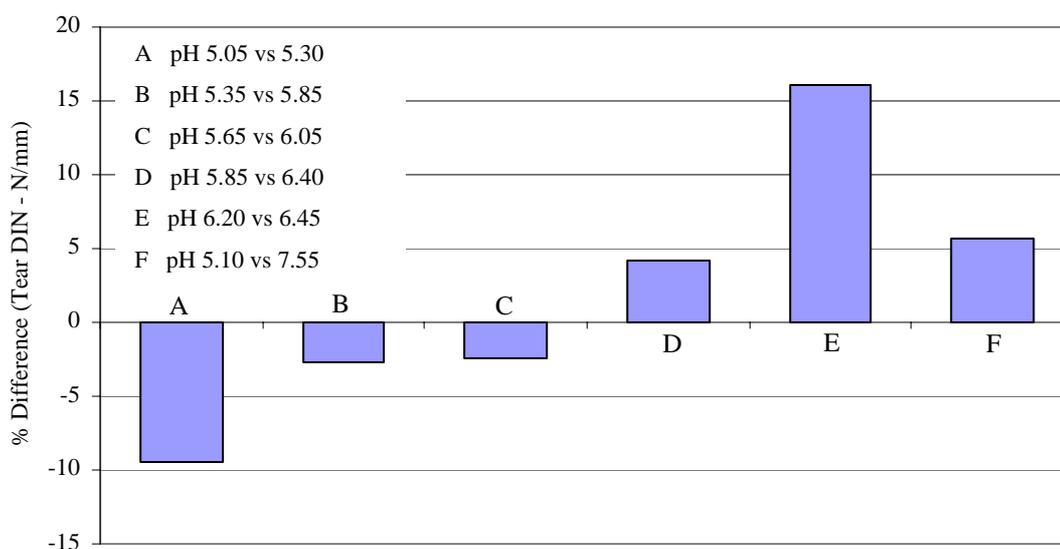
Figure 5.4. *Effect of neutralisation pH on crust leather strength. Values quoted as % difference Tear DIN (N/mm)*

5.2.2 Effect of Fatliquoring Agents

Fatliquoring is considered an important contributing factor to leather strength but it also affects many other leather properties such as softness, touch (dry, greasy), fullness, grain firmness or looseness, smell, adhesion properties, water uptake or release, and water repellency.[41] It has been suggested that fatliquors penetrate into the collagen structure and then spread evenly over the fibril surface preventing adhesion of fibres and providing lubrication for maximum leather stretch and flexibility. Fatliquors can be added at various stages in the RDF process not only in the main fatliquoring step but

also during neutralisation and the retanning/dye stage. It has been reported that tear strength increases with addition of marine based fatliquors up to a limit of 10%. [41]

This section of the work aimed to determine the effect on strength of kangaroo leather due to various fatliquors added at different points in the process and with different levels of application. Initial work in our study demonstrated the importance of the fatliquors for strength in the leather. A Matched side trial comparing the standard process with sides produced with all fatliquors removed resulted in the unfatliquored skins being 50% weaker in tear strength.

5.2.2.1 Modified Fish Oil Fatliquors

The fatliquor work commenced with a modified fish oil, as they are believed to be a good general purpose reagent for softness and lubrication for strong leather. It was added at the level of 2% in the neutralisation stage followed by a standard RDF process and compared to crust leather having no fatliquor in the neutralisation. The addition of the modified fish oil fatliquor (2%) results in a 11% increase in the tear strength compared to leather prepared with no fatliquor added in this step (Table 5.1). When the level of fatliquor added at this stage is increased to 4%, only a marginal further increase in the tear strength (3%) of the crust leather was found when compared to leather produced with 2%.

Table 5.1. *Effect of a modified Fish Oil fatliquor addition during the neutralisation step of the RDF process. Values quoted as % difference Tear DIN (N/mm).*

	Neutralisation time	% Modified Fish Oil	Time of Fatliquor after Neutralisation	Total Time	% Difference Tear DIN (N/mm)
LHS	30min	0	30min	1hr	-11
RHS	30min	2	30min	1hr	
LHS	30min	4	30min	1hr	3
RHS	30min	2	30min	1hr	
LHS	30min	2	2.5hr	3hr	8
RHS	30min	2	30min	1hr	
LHS	30min	2	2.5hr	3hr	10
RHS	2.5hr	2	30min	3hr	
LHS	30min	4	2.5hr	3hr	13
RHS	30min	2	2.5hr	3hr	

The effect of a longer time for penetration of the fatliquor during neutralisation, prior to the addition of other RDF chemicals was examined. Increasing the time for fatliquor penetration from 30min to 2.5hr resulted in a 8% increase in tear strength. This result indicated that there could be some advantage in increasing the time for penetration. However, it had to be confirmed that this improvement in strength was due to the extended time for penetration and not to the benefits of prolonging the neutralisation time. Therefore a trial with a total time of 3hr for both the neutralisation and fatliquoring steps was conducted. Skins with neutralisation (30min) followed by a long fatliquoring step (2.5hr) resulted in a 10% increase in tear strength compared to a long neutralisation time (2.5hr) with a short fatliquoring time (30min). This experiment demonstrated that increasing the time the fatliquor can penetrate into the skins, after neutralisation, can improve the tear strength of crust leather. The benefits in adding fatliquor in the neutralisation step can be slightly enhanced by doubling the fatliquor concentration to 4% with a long neutralisation time (2.5hr), which led to a 13% increase in tear strength.

5.2.2.2 Effect of alternative fatliquoring agents

There is a wide range of fatliquoring compounds based on natural fats or synthetic analogues available to the tanner. A selection of these systems was examined during the course of this work to determine how these systems influence the physical strength properties of the kangaroo leather (Figure 5.5). Natural fats/oils, which make up a significant proportion of fatliquors are derived from a range of animal, marine and vegetable sources. Although it was not possible to examine every type of fatliquor

during the course of the project, it was considered important to determine what differences, if any, could be expected from using fatliquors derived from different sources. Fatliquoring systems based on the traditional fish oils are considered to be the most effective and popular types of reagents used in fatliquoring leather. The reagents used in this work are commercial formulations available from chemical suppliers to the industry. During processing, the reagents were diluted in hot water prior to addition.

It was found that a different modified fish oil fatliquor (A), from that used in the study above gave similar strength results for the crust leather. However, a slight decrease in the tear strength was observed for a fatliquor based on fish oil combined with lanolin (B). One of the most widely used fatliquors prior to synthetic systems was neatsfoot oil, obtained from cattle hooves. Neatsfoot oil (C) modified to assist in penetration, resulted in a decrease in the tear strength of 8% compared with the fish oil. Similar decreases in tear strength were observed for the systems based on sulfated triglycerides (D) and sulfited oxidised natural oil (E). However, the sulfited vegetable oil (F) afforded an increase in tear strength and was found to be the only reagent tested that improved the tear strength relative to the fish oil in the standard process. Systems based on paraffin (G, H) were evaluated with both resulting in decreases in tear strength, the chlorinated reagent (H) having the greatest negative effect (18%).
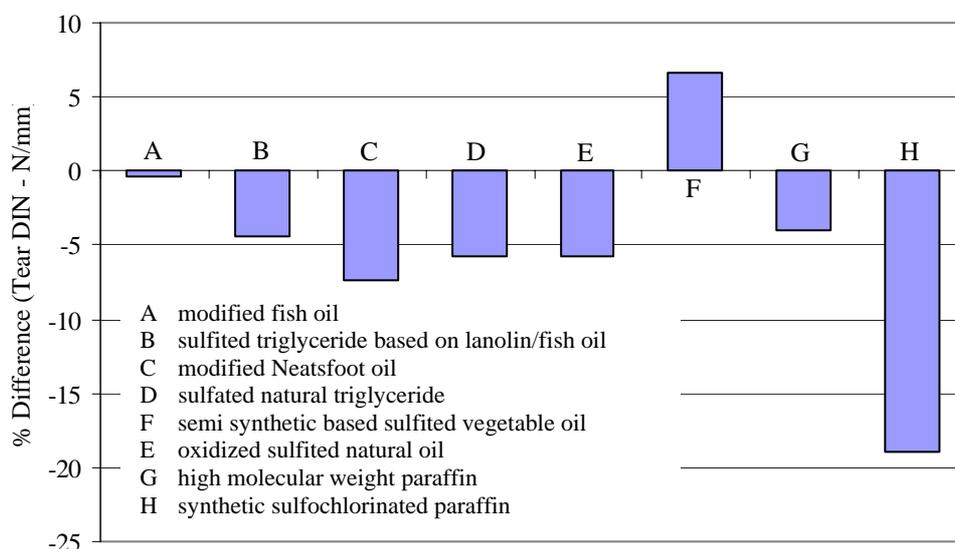

A   modified fish oil
B   sulfited triglyceride based on lanolin/fish oil
C   modified Neatsfoot oil
D   sulfated natural triglyceride
F   semi synthetic based sulfited vegetable oil
E   oxidized sulfited natural oil
G   high molecular weight paraffin
H   synthetic sulfochlorinated paraffin

Figure 5.5. *Effect of replacing modified fish oil with a range of fatliquors from natural and synthetic sources. Values quoted as % difference Tear DIN (N/mm) with respect to 2% modified fish oil.*

5.2.2.3 Waterproofing Fatliquors
The work examining the effect of alternative fatliquoring agents was extended to include a range of synthetic systems based on phosphate esters, siloxanes and acrylics currently used in the leather industry as waterproofing agents. Most of these reagents tend to be added late in the retan stage with a second addition in the fatliquor step to obtain the best waterproofing performance. In this part of the work we compared the effect of the waterproofing agents against a second type of fatliquor used in the commercial process, based on natural fat and oils, which is added in the process at the same stages recommended for most of the water proofing systems (2% in retan step, 1% fatliquor step).

Unlike earlier waterproofing treatments, which depended upon complete blockage of the leather structure with oils or fats, modern systems are based on the theory that the fibres and fibrils are coated with the water proofing agent providing a hydrophobic surface which reduces the ability of the water to pass through the leather. However, as only the fibres are coated it allows the leather to remain

porous maintaining the natural high water vapour and air permeability. The purpose of this work was to determine if the waterproofing systems, due to this efficient coating of fibres, can also act as suitable lubricants considered necessary for ensuring good strength in leather.

Table 5.2. *Effect of waterproofing fatliquoring agents on the tear strength of crust kangaroo leather. Values quoted as %difference (Tear DIN – N/mm) from the commercial process.*

	Waterproof Agent	% offer in retan	% offer in fatliquor	% difference (Tear DIN – N/mm)
1	Paradol WPR	2	1	-7
2	Paradol WPM	4	1	-9
3 4	Perfectol QX/QT	2 (QX) 2 (QX/QT)	1 (QX/QT) 1 (QX/QT)	-14 -11
5 6	Perfectol WR/HQ	2 (WR) 2 (WR/HQ)	1 (WR/HQ) 1 (WR/HQ)	-8 1
7 8	Lubritan SP	2 (Pre retan) 4 (Pre retan)	1 1	11 19
9 10 11 12	Lubritan WP	2 (Pre retan) 4 (Pre retan) 2 (Post retan) 4 (Post retan)	1 1 1 1	-1 -5 13 22
13 14 15	Densodrin CD	2 6 6	1 1 4	10 8 33
16 17 18 19	Cutafob HAS	2 4 6 8	1 1 1 1	3 23 15 26
20 21 22 23		2 2 2 2	1 4 6 8	3 22 43 54
24		8	8	62
25		8	8 Cap	-4

The results for the water proofing reagents examined are shown in Table 5.2. The Paradol WPR, Paradol WPM, Perfectol WR/HQ and Perfectol QX/QT systems were found to cause a decrease in the tear strength when added in both the retan and fatliquor stages (Entries 1-6). The results for Lubritan SP afforded moderate improvements in tear strength when added after the neutralisation step at 60ºC, with an 11% increase (Entry 7) or a 19% increase when the amount of water proofing reagent added in the process was doubled (Entry 8). When Lubritan WP was added to the process using the same conditions as SP, it was found that addition of 2% of the reagent did not affect the strength, doubling the amount of reagent added resulted in a marginal decrease in strength (5%) (Entries 9-10). The Lubritan WP at 2% was found to give good improvement (13%) in the tear strength if it was added at the end of the retan step (Entry 11). Increasing the amount of reagent added from 2% to 4% increased the tear strength from 13 to 22% (Entry 12).

When Densodrin CD, a siloxane and wax based material, was added in the process, at 2% in the retan step and 1% fatliquor step, it increased the tear strength of the leather by 10% (Entry 13). Increasing the Densodrin CD levels in the retan step up to 6% had little effect on the strength (Entry 14) but significant improvements in the strength (33%) were found when the addition of the reagent was increased in the fatliquor stage from 1% to 4% (Entry 15).

Cutafob HAS, a mixture of an acrylate and a phosphoric acid ester, gave the best results for increasing tear strength. Although the initial conditions of 2% in the retan step followed by1% in the fatliquor step gave a marginal increase in the strength (Entry 16), the improvement upon doubling the retan offer to 4% was significant (23 %) (Entry 17). Further increasing the level of reagent used in the retan step had mixed results with 4 and 6% affording 15 and 26 % increases in tear strength (Entry 18-19).

The main benefits in strength for Cutafob HAS occur when it is used at higher levels in the fatliquor step. Maintaining the level of Cutafob HAS added in the retan step at 2% and increasing the levels in the fatliquor from 4% to 8% resulted in the improvements in the tear strength increasing from 22% to 54% (Entry 21-23). A further gain in strength can be obtained from a combination of 8% added in the retan and 8% added in fatliquor, which resulted in a 62% increase (Entry 24). Capping the above trials, with 33% basicity chromium sulphate, required to optimise the water proofing performance, resulted in the loss of all gains in tear strengths. An example is given in Entry 25.

5.2.3 Retanning agents

Tanning or retanning agents are used in the RDF process to introduce specific characteristics into the leather including aesthetic properties such as feel, handle, in conjunction with other chemical and physical properties. They are based on inorganic salts, organic molecules and organometallic complexes. Their properties include filling action for equalizing consistency, strengthening the grain, dispersing and fixing other syntans and dyes etc. There have been some reports specifically looking at the effect of retanning agents on the physical properties of leather. However, none of these published studies is extensive and they cover work on ovine as well as bovine leather but not kangaroo.[42-45] The aim of this area of the current study was to determine the effect on strength for of a range of retanning agents.

5.2.3.1 Chromium and Chromium based syntans
In the production of leather, the main use of chromium (III) salts is in the tanning of pickled skins and hides, but it can also be used in several stages during the RDF process. In the retanning step, chromium (III) salts are commonly used as a pre-treatment (rechrome) or, in more recent times, as part of the new waterproofing technology. The chrome retanning at the start of the RDF process provides an opportunity for the tanner to reduce any differences due to thickness and grease variation in the wet blue being used. It is also important in production in helping to reduce the differences in the final leather, which may arise from using wet blue sourced from different suppliers or incorporating stock that has been stored for long periods. It has been reported that bovine hides which have been chrome retanned give leather which is weaker in strength, but no quantitative study has been carried out. The use of chrome salts to "cap" a leather after retanning is common with certain water proofing systems where the optimum water resistance is only obtained from reaction of the hydrophilic groups on the waterproofing reagents in the leather with the metal salt.

In the present study, addition of 2% chromium powder (33% basicity), based on wet blue weight, prior to the neutralisation step resulted in a 10% decrease in the tear strength of the crust leather compared to the standard process (Figure 5.6). A similar drop in strength (9%) was also observed when a 3% offer of chromium reagent (33% basicity) was added after the final fatliquoring step.
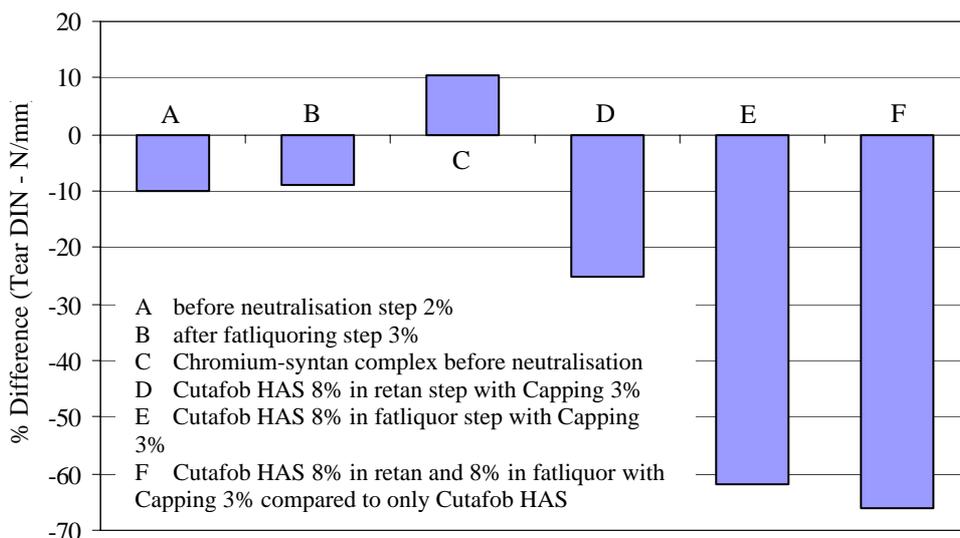
Figure 5.6. *Effect of chromium (III) sulfate (33% basicity), addition in the RDF process, on the tear strength of crust leather. Values quoted as % difference Tear DIN (N/mm) from control process with no addition of chromium tanning powder in the RDF process unless otherwise stated.*

In skins prepared with waterproofing agents, where one side is treated with chrome powder at the end of the process (D, E, F), it was found that the gains in strength due to the use of the waterproofing systems (20-66%) were lost due to the addition of the chromium salt. The complexation between the waterproofing agent and the chrome must interfere with the ability of the fibres to slip past each other after lubrication

5.2.3.2 Syntans and Resins
The commercial syntans and resins available to the tanner have changed dramatically over the years as the field of polymer chemistry has developed. Originally syntans were based on the condensation products from phenol and naphthol sulfonic acids and formaldehyde. These aromatic polyacids, which are referred to as auxiliary tanning agents, were found to combine irreversibly with collagen.[41] In chromium tanned leather, it is believed that these type of syntans react with the chromium salt to form a complex containing the syntan molecule. Resins fall into two types: styrene-maleic anhydride copolymers and methylol compounds based on nitrogen bases. The latter systems include the amine resins from melamine, urea, and dicyanamide condensation products with formaldehyde. In recent times it has become difficult to clearly separate these two areas as it is common to find resin systems that incorporate the original syntan functionality of a phenol sulfonic acid. The importance of the resin on strength is demonstrated by preliminary work which showed that the removal of all syntans/resins from the commercial process increased the tear strength by 32%.

In this area of the work, resin/syntan systems were evaluated against a general styrene maleic anhydride naphthalene sulfonic acid resin added in the retan step, to reduce possible thickness differences in the crust leather which can arise due to the known filling action of the amine resins. When the general resin was compared against a polyphenolic sulfonate incorporating a polyamine sulfonic acid we find that low levels of this syntan gave an increase in the tear strength of 5% (Figure 5.7). Doubling the levels of reagent causes a overall 10% drop with the crust leather from this resin now 5% lower in strength then the standard leather.

When the dicyanamide resin described in Chapter 4, which afforded a 7% increase in the tear strength of the leather, is now used in the retanning step, we found that low levels afforded a significant increase in strength (18%) of the crust leather. Once again, higher levels of resin in the process resulted in a decrease in tear strength compared to the control. Another derivative of a dicyanamide

resin (Figure 5.7D), this time including urea, was evaluated and found to afford slightly lower tear strength. A modified melamine formaldehyde resin gave an increase in tear strength of 8% for normal offers and 6% for higher levels in the process. A sulfited melamine resin showed marginal improvement (1%) at low levels but increasing the amount of reagent resulted in a 5% decrease in tear strength compared to the control. The best result in this area was due to use of a polyamidecarboxylic acid derivative which increased the tear strength of the leather >20%, at the levels used.
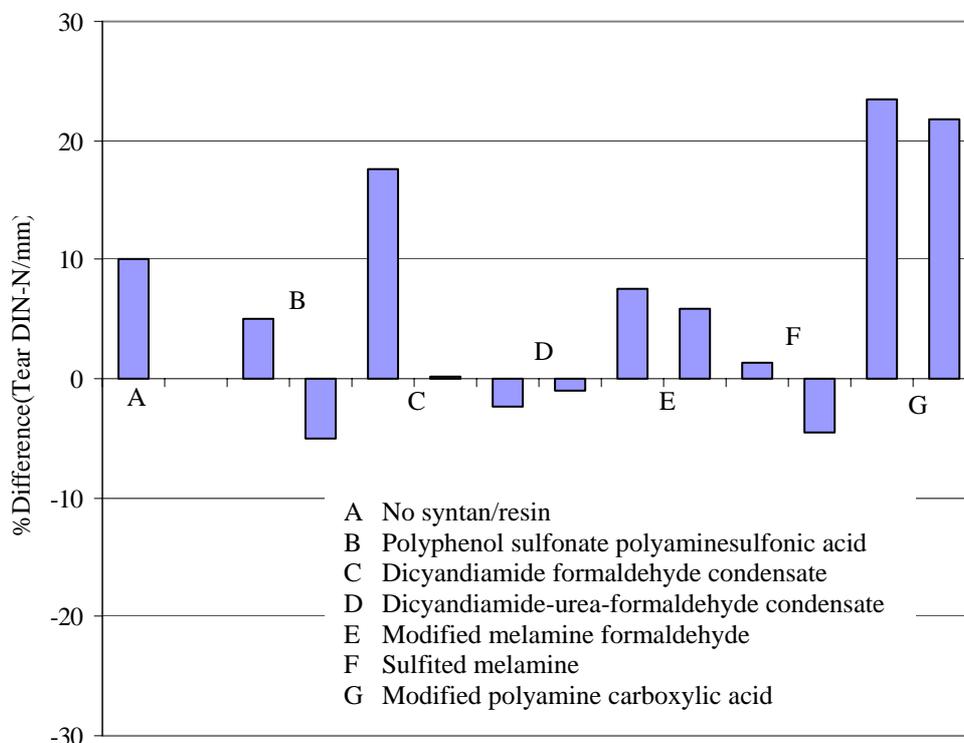

A No syntan/resin
B Polyphenol sulfonate polyaminesulfonic acid
C Dicyandiamide formaldehyde condensate
D Dicyandiamide-urea-formaldehyde condensate
E Modified melamine formaldehyde
F Sulfited melamine
G Modified polyamine carboxylic acid

Figure 5.7. *Effect of syntan/resin in the retan step of the RDF process. Values quoted as % difference Tear DIN (N/mm) from a control syntan of polyphenol sulfonate polyamine sulfonic acid. Except for the first column (A) all other data are grouped in pairs, indicating trials with low and high levels of offer respectively.*

5.2.4 Dyes and Pigments

All leather is dyed to meet fashion demands with the majority finishing up as dark colours such as black and brown. The coloured leathers are usually achieved by a combination of dyes and pigment added in the RDF process, although some additional pigmentation can be added in the finishing coats. It has already been observed that some dyes used in leather processing can have undesirable effects on the leather properties such as water resistance.[19] It was found during the course of this work that the dyes and pigment also have a dramatic effect on tear strength (Figure 5.8).

Crust leather produced with a mixture of dyes and pigment was found to have decreased in tear strength by 24%. The effect of only adding pigment to the process caused a 9 % decrease in strength. Even a small addition of a single dye component still results in an ~5% drop in strength. The results for this section of work indicate that high levels of dyes and pigments in the process, commonly used to produce dark colours need to be evaluated to determine their effect on other properties of the leather. Although the removal of dyes and pigments from the process is not a viable option, it was found that changing the order of addition of the chemical reagents, by adding the dyes and pigment just prior to acidification in the retan/dye step can increase the strength of the leather by 6% over the standard process conditions. The leather in this case still appeared to have complete penetration of the colour.
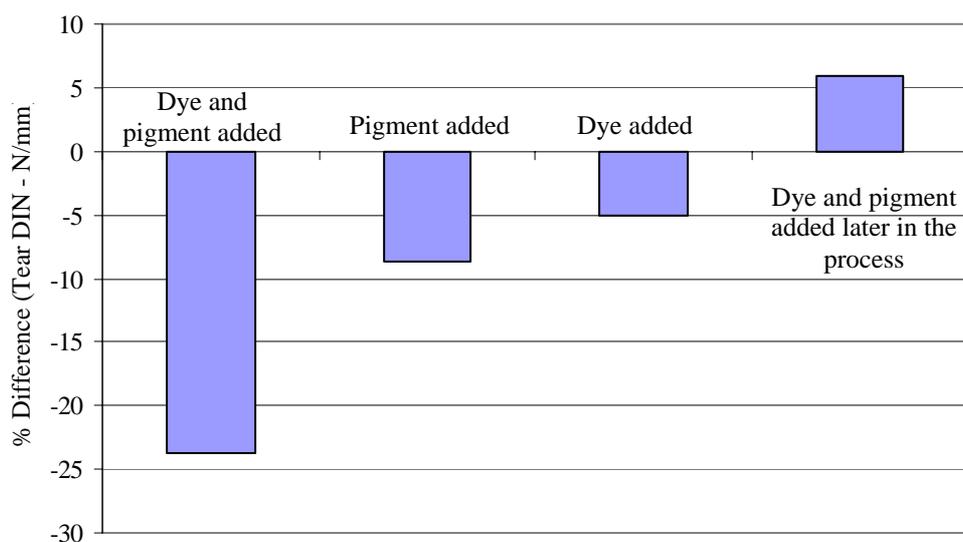
Figure 5.8. *Effect of adding dye and pigment, in a process, on the tear strength of crust kangaroo leather. Values are quoted as % difference Tear DIN (N/mm) from a control process which has no dye or pigment present.*

5.2.5 Additive effects in improving tear strength

In all of the work described in Chapter 5, we have only looked at changing one variable at a time to determine its effect of the strength of the leather. The potential exists to gain improvements in strength by changing several factors during the course of the process. For example, the dicyandiamide resin reagent increased strength by 18% in Section 5.2.3.2 and a waterproof agent increased strength by 43% in Section 5.2.2.3. A combination of the resin and waterproof agent produced a 60% increase in tear strength compared to the standard process. This value is comparable to the combined total of the two individuals trials and demonstrates the potential gains that could be achieved by small modifications to several parts of the process rather then one major change that might have a bigger impact on other properties of the final leather. The challenge for the tanner is to balance the factors producing increases in tear strength against all the other aesthetic, chemical and physical properties in their final leather.

5.3 Mechanical Operations

The manufacture of finished leather from wet blue requires a combination of chemical and mechanical operations to give the desired physical and aesthetics properties in the final product. Although most leather research focuses on modifications to the chemical process, the importance of the mechanical operations on the physical properties of the leather should not be underestimated. So the effect on strength due to the common mechanical operations used in kangaroo leather production was studied. The first of these operations is the shaving of the wet blue, prior to the RDF process, to the desired thickness required in the final leather product. The wet processing of leather is followed by a series of mechanical operations designed to contribute specific properties into the final leather. The leather is subjected to the operation referred to as sam/setting. The physical pressing between rollers is designed to spread the leather (setting), which flattens and increases surface area of the leather. In addition, during this action, excess water is removed from the leather (samming). The moisture content of the leather is further reduced by drying using a combination of heat and vacuum. The final step, prior to finishing by roller coating or spraying, is the mechanical softening of the leather (staking), which separates fibres and gives the required degree of softness to the leather.

5.3.1 Shaving

Shaving is the key adjustment to the kangaroo leather thickness at the end of wet blue before commencing the RDF process. Usually for thick skins/hides thickness adjustment is made by a combination of splitting and shaving. In the case of bovine leather splitting is the key method for reducing thickness. It efficiently removes the majority of the excess material which is usually of some value (as split or suede leather) but usually only gives you the approximate thickness, which can then be reduced by the shaving process. However, the splitting of thin skins is uneconomic if the residue ("drop split") is too thin to use or has no value and shaving is adequate for the amount of material to be removed. The splitting of kangaroo skins is difficult due the natural contours in the skins Therefore skins are only shaved, mainly to remove loose fibrous material from the underside of the skin and to even out the thickness over the whole skin.

A comparison of kangaroo skin and bovine hide has been published indicating that morphology, ie angle of weave and fibre size distribution is substantially different.[6] This results in a higher tensile strength for lightweight kangaroo leathers than bovine leathers. Previous literature referring to bovine indicated that reducing the corium layer of bovine leather results in a decrease in strength.[4,46] No similar report has appeared in the literature with regard to kangaroo skins. The aim in this section of work is to determine what effect shaving has on the strength of kangaroo leather.
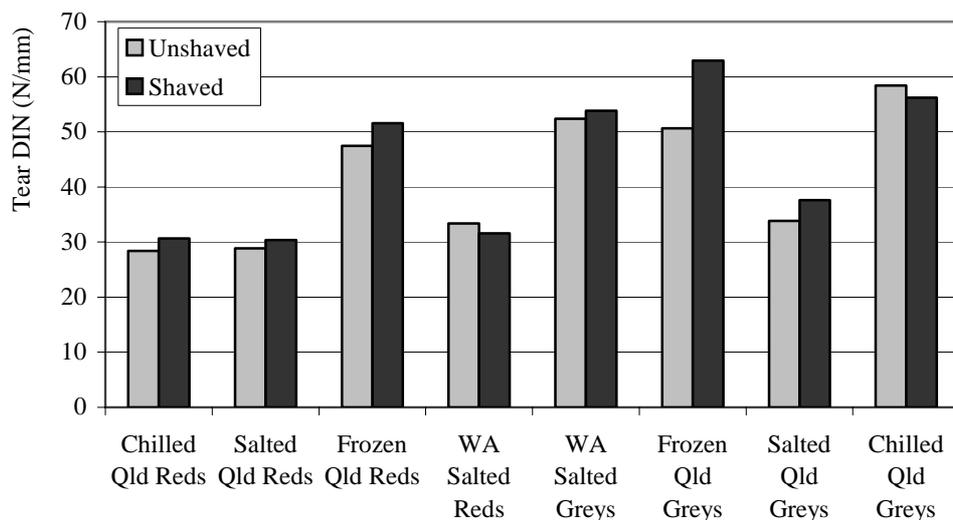

Figure 5.9. *Effect of shaving on the tear strength of skins for Red and Grey species and the various preservation techniques.*

A comparison of shaved and unshaved tear results for the skins are shown in Figure 5.9. The shaving certainly does not appear to cause the significant decrease in strength that is reported for bovine.[6] Overall the shaving, used in the commercial process, has resulted in a 7% reduction in the thickness of the skins. The slight increases observed for the red (4%) and grey (8%) skins is considered to be due to the loose fibrous material found on the skins which, after removal by shaving, would cause a reduction in the thickness but would not be considered to be influencing the strength significantly. The individual results from the strength testing are variable with two of the 8 packs showing a decrease in strength due to shaving. The differences between the shaved and unshaved skins across the packs ranges from a decrease of 3.9% to an increase in strength of 24%.

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5.3.2 Drying of Leather

Drying is one of the most important operations affecting leather quality. At the end of the RDF process, the leather contains large amounts of water, which needs to be removed for the leather to acquire its final texture, consistency and flexibility. For bovine, mechanical pressing (samming) of this material is used to remove excess moisture but the lowest water content which can be attained is about 55%.[47,48] The use of higher pressure will potentially damaged the fibre structure. A number of drying methods such as air drying, vacuum drying and microwave or radiofrequency have been developed over the years involving convective, conductive or radiation processes.[49] In recent times, vacuum drying has become one of the most popular methods in leather manufacturing.[50] Compared to conventional air-drying, vacuum drying is preferred due to its faster drying speed and limited space requirements. In this process, wet leather is spread on a heated metal plate and covered with an airtight hood forming a vacuum chamber. The chamber pressure is reduced thereby lowering the water boiling point. Water is removed in a few minutes from the leather by evaporation.

Although the theory of leather drying and modes of drying have been reviewed by a number of authors[35,47,48] there have been only a limited number of scientific papers related to vacuum drying.[50-53] In some of these reports, the effect of variation in the drying conditions and its effect on the physical properties of the leather including softness and strength have been determined. However, reports of the relationship between drying conditions and the effect on strength of the resulting leather are contradictory. For example, it has reported that tensile strength[41] is diminished by higher drying temperatures. Other workers[54] have observed that drying temperature has no apparent influence on softness or strength. Lucchese et al.,[52] similarly concluded that drying and stacking did not affect physical properties such as lastometer, tensile and tear strength. There appear to be no reports related to the vacuum drying of kangaroo, therefore we were interested in determining the effects of drying temperature and time on the strength of kangaroo leather.
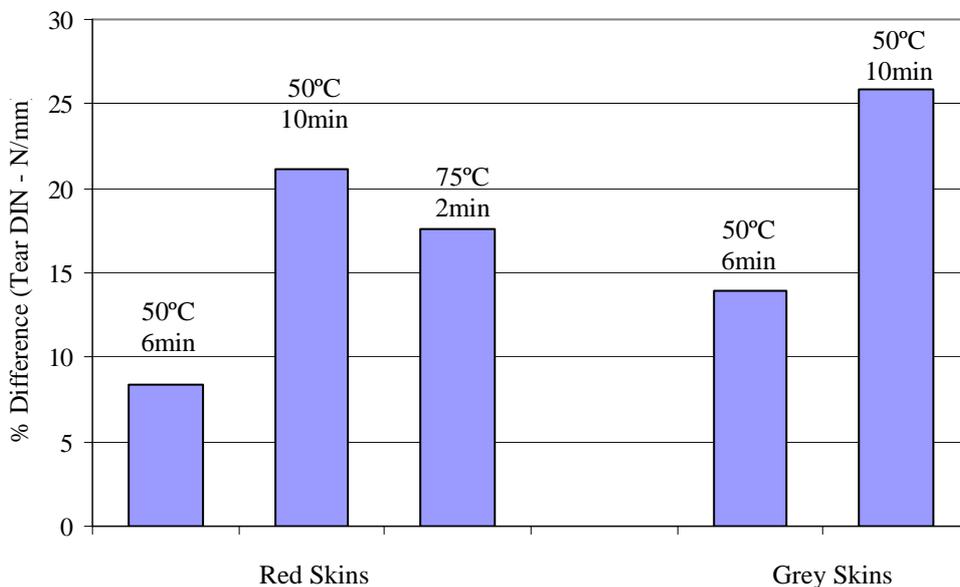

Figure 5.10. *The effect of increasing drying time, at a constant temperature of 50ºC, on the tear strength of Red and Grey Kangaroo crust leather. Leather was not sammed prior to vacuum drying. Values are quoted as % difference Tear DIN (N/mm) from a control of 50ºC 2min.*

Initial work compared the drying of red and grey kangaroo skins at higher temperatures (75ºC) and longer times (4-10min) relative to the standard conditions (50ºC, 2min). It was found that increasing drying times at 50ºC, for both skin types, increases the tear strength (N/mm) as seen in Figure 5.10. The intermediate time (6min) in the study shows that the red and grey skins have increased tear strengths by 9% and 14%, respectively, compared to the control of 2mins. This increase in tear strength was also observed for the longer drying time of 10min, with strength improvements of 18%

and 26% being determined for the red and grey skins. The increase in tear strength appeared to be always slightly higher for grey skins than red skins. The overall effect on the tear strength with increasing drying times is best illustrated in the set of results for the grey skins (Figure 5.11). Increasing the time of drying from 4min to 10min results in a gradual improvement in tear strength starting from 10% to 26% compared to the standard 2min conditions.

It was found that the increased drying times also causes a reduction in skin thickness compared to the sides dried for 2 min. Although this decrease in leather thickness would influence the differences in strength (N/mm), examination of tear strength (N) for the matched sides generally showed increases in tear strength, 9% and 8% for red and grey skins at 6min respectively, due to the longer drying times. In addition, there appears to be some difference in how the skins compress during drying. The red skins have a similar decrease in thickness at both 6 and 10min with values of 16% and 14% respectively. The decrease in thickness of the leather for the grey kangaroo is dependent upon the drying time, with a loss of 7% in thickness for 4 and 6min, but increasing to values of 10% and 19% for the 8 and 10min drying times. The effect of increasing the temperature from 50ºC to 75ºC resulted in an improvement in the tear strength of 18% but these conditions were found to give rise to a significant loss in thickness of 19%. It was also noted that the feel and look of the leather altered with the changing drying conditions.
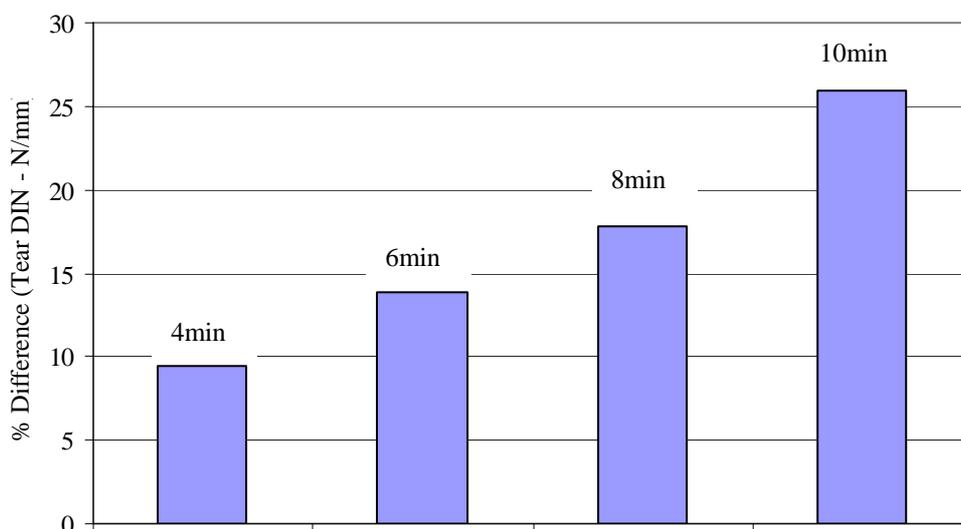

Figure 5.11. The effect of increasing drying time, at 50ºC, on the tear strength of Grey Kangaroo crust leather. Leather was not sammed prior to vacuum drying. Values are quoted as % difference Tear DIN (N/mm) from a control of 50ºC 2min.

During this initial drying study, Liu and DiMaio,[50,53] published their work investigating the relationships between vacuum drying time and temperature on mechanical properties such as tear strength (N/mm) for bovine hides. Their conclusion was that lower drying temperatures, shorter drying time and initial water content (54±4%) are favourable conditions to produce stronger and softer leather. However they also noted that samples with higher initial water content yielded better tear strength with drying temperatures above 60ºC. Their results, based on bovine prepared by a short retannage using only fatliquors, covered a very broad range of conditions including high temperatures (80ºC) and long times (30min). Our concern was that the conclusions were based on conditions outside the drying parameters normally used by industry. In view of the differences of our results to this recent study it was decided to extend the drying work. Due to time constraints and as this additional work was not part of the original project, we aimed only to identify possible causes for the contradiction in our preliminary results and those in the extensive study by Liu and DiMaio.

Samples from bovine and kangaroo skins were prepared based on the Liu and DiMaio's experimental condition, using the basic fatliquoring retannage. A second set of skins were processed by the standard process used throughout this study. All hides/skins were sammed to a moisture content of ~55% and conditioned for two weeks prior to testing. Our bovine results showed that increasing the drying time from 4min to 10min at 50°C or 70°C decreased the tear strength, sometimes by ~20%, is in agreement with the published results. Increasing the temperature of vacuum drying appeared to result in little variation in tear strength between 50 – 70°C for 4min but the longer drying times cause a decrease in tear strength. The observation that increasing temperature of drying causes a decrease in the strength could be a result of the longer times used in the reported trials (up to 30min). Overdrying of the leather is already evident in our work, as the sample from drying at 70°C/10 min increased in weight in the first couple of hours after drying suggesting moisture contents in the samples below the 18-20% immediately after vacuum drying. Although we have repeated only a small part of the extensive study reported by Liu and DiMaio, the results suggest that we are seeing similar trends for bovine with decreasing tear strength for increasing vacuum drying time and temperature.

Commercial kangaroo wet blue was retanned using the bovine procedure and sammed to a moisture content of approximately 58%. Only one skin was used for each trial in this part of the work, and further work is needed to confirm the results. The vacuum drying results for these kangaroo skins suggest that either increasing time or temperature afford increases in the tear strength. These results follow the trend detailed in the initial kangaroo work detailed in Figure 5.10 and 5.11. The skins prepared using the complex commercial process were sammed to a moisture content of 50% and tested after two weeks of conditioning. These skins have undergone the same retanning procedure as those in Figure 5.10 and 5.11 but have the reduced moisture content prolonged conditioning time detailed in DiMaio's study. The results suggests that increasing drying temperature does improve the tear strength of the skins but in this case the longer drying times only increased tear strength at the higher temperature (70°C).

The results from these two sets of kangaroo leather show similar trends to that observed in our initial work (Figure 5.10 and 5.11). It appears that longer drying times and higher temperatures increase the strength of the kangaroo and the trends seem to be independent of the type of retannage. If these trends are correct, then it would suggest that kangaroo generally behaves differently from the reported findings for bovine which found that increasing time and temperature decreases the tear strength of the leather. Drying is complex and the preference for lower drying temperatures is in part due to the increasing demand for softer stronger leather, but our preliminary work has shown that it may not be appropriate to extrapolate the findings for bovine to kangaroo. Although the kangaroo was retanned in a similar fashion to the bovine, the possibility that the differences observed could be related to variations in the commercial tanning of these two materials cannot be ignored. Time restraints prevented a more detailed study being carried out on this area and further work is required to confirm our initial findings and determine how variations in the tanning may affect the drying behaviour and the leather quality such as look and feel.

The two retannages used in the drying study were compared to determine how these very different processes affected the tear strength. Matched sides were produced, one side using the fatliquor only process of DiMaio and the other side was processed using the commercial process. The results show that the fatliquored sides produced leather with approximately 79% increase in tear strength compared to the commercial leather. This highlights the overall effect the range of chemical reagents have on the strength of the kangaroo leather and indicates the possible gains that can be made in improving the tear strength of the leather.

5.3.3 Staking

Chemical lubrication using fatliquors is the main mechanism to introduce softness to meet increasing demand from the market for this type of leather. However, during drying, there is the potential for fibrils within the leather to adhere to each other forming fibre bundles which adversely affects the softness introduced chemically by fatliquors. After drying, the leather can be mechanically softened by

the procedure called staking which, by repeatedly stretching leather by small amounts, breaks up the thick fibres formed in drying into thinner ones. Over stressing of the leather can occur due to excessive mechanical stress softening which pulls the fibres apart potentially breaking them introducing looseness leading to an overall decrease in leather strength.[55-57]

The effect of the commercial staking operation was determined by analysing skins which were processed and halved after drying and one side staked using standard conditions. The initial observation is that the staking decreases the thickness of the crust leathers, with the red kangaroo skins (13-14%) compressed more than the grey skins (8%). Overall the strength of the leather did not decrease due to staking, in fact in some cases slight increases in the tear strength were observed. This apparent increase in strength corresponds to the decrease in leather thickness.
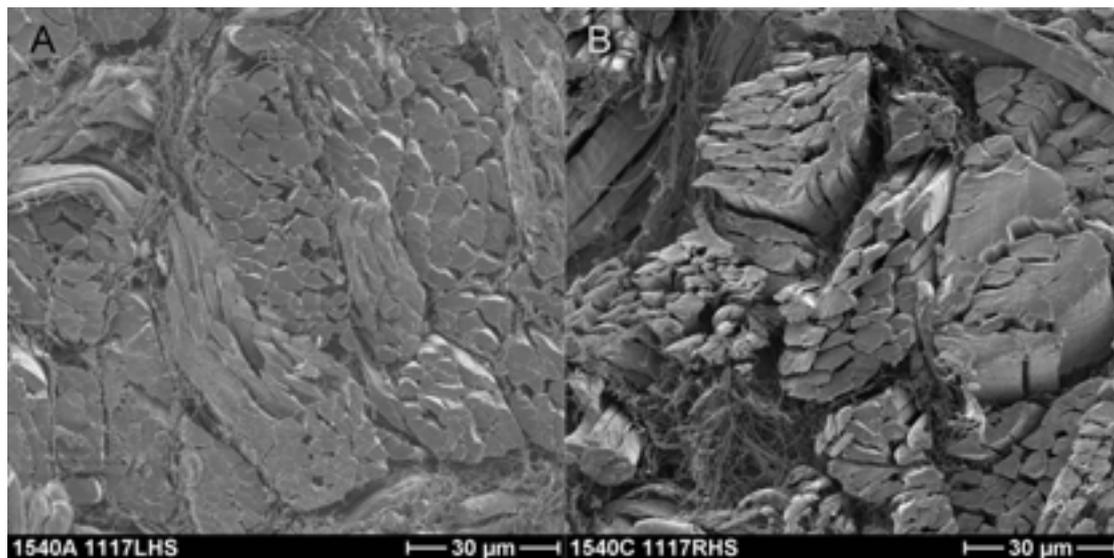

Figure 5.12. Effect of staking on fibre structure. a) commercial leather unstaked b) after staking.

The changes in leather structure due to mechanical stress softening can be seen in the images from scanning electron microscopy for the matched sides sampled under identical conditions.
The images in Figure 5.12 show that in both samples (unstaked and staked) the fibril bundles are clearly defined within the fibre. In Figure 5.12.A. the sample appears to be tightly packed and it is difficult to identify the individual fibres (30mm). The surface is fairly flat and there appears to be little disruption of the structure due to the cutting of the sample. After staking, the tight packing within the structure has been broken up and individual fibres are easily distinguished from each other. In some cases, the fibres have been pulled out of the surface during the sampling indicating that they can move relatively freely within the sample (Figure 12.B). However, it is clear from the two views in Figure 5.13 that no apparent damage to the fibril bundles has occurred with the appearance similar in both images. This would be consistent with no decrease in the leather strength due to staking although there does appear to have been considerable disruption to the sample between the fibres and in the separation of the fibre intro fibril bundles.
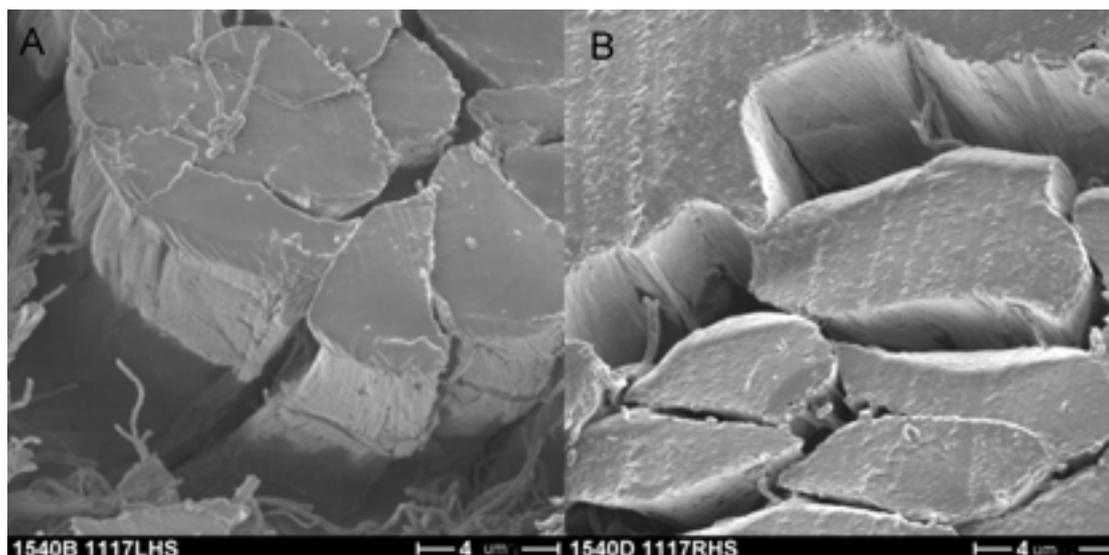
Figure 5.13. *Effect of staking on fibre structure. a) commercial leather unstaked b) after staking.*
Enlargement of Figure 5.12 showing fibril bundles more clearly.

5.4 Conclusion

The complexity and diversity of the chemical processes associated with the manufacture of leather from wet blue make it difficult to accurately relate properties to specific reagents. Our work in this area aimed to determine how different types of chemicals used in a standard process influenced the strength of kangaroo leather. Whereas the tanner takes a holistic approach, addressing all of the properties required by their customers, the main objective of our work was to identify factors affecting strength and the other leather properties were not evaluated. Most of the work described in this chapter was aimed at broadly looking at different reagent types in a predetermined standard process to determine if any of these reagent types can significantly influence the strength of the crust leather. In addition work was also undertaken to determine the effect that mechanical operations had on the tear strength. Results suggests several areas where substantial benefits can be obtained.

- Improvements in strength may be obtained in the neutralisation step by modifying the pH and time for the neutralising salts and allowing sufficient time for fatliquors to penetrate. The pH of neutralisation affects the penetration of other regents in the process and any subsequent differences in the final leather properties will need to be determined.

- Without lubrication of the fibres by fatliquors in the RDF process, the tear strength of resulting leather was found to be 50% weaker than the commercial leather.

- Some waterproofing fatliquor reagents were found to offer significant improvements in tear strength when used in the commercial process. However, the potential gains in tear strength are lost if chrome capping is applied to improve water repellency. Increasing amounts of waterproofing agents reagents added during the retanning stage of the process can increase tear strength by 20%. Increasing levels added in the fatliquoring step can improve tear strength by >50%. Some fatliquors such as sulfochlorinated paraffins were found to have a detrimental effect on tear strength.

- The use of chromium salts at any stage of the RDF generally decreases tear strength up to 10%. The results further support the observation, in section 4.3, that increasing the amount of chromium in the tanning of skins decreases the tear strength. The use of a chromium syntan complex, as opposed to chromium salts, increased tear strength.

- Organic based resins and syntans gave mixed results with most systems lowering strength. However there were some exceptions which provided increases up to 20%.

- The combination of several factors identified in the study could result in significant improvements in the tear strength beyond those possible from one single factor

- Colourants, dyes and pigments added to the RDF were found to decrease tear strength up to 24%.

- Preliminary work on the effect of drying on tear strength, suggests that the behaviour of kangaroo towards longer times or higher drying temperatures is different from the behaviour of bovine leather.

- The staking and shaving conditions examined generally cause a decrease in thickness but do not cause any significant change in strength of the leather.

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