Paper B16

A novel low sulphide process for improved ovine leather quality

Richard Edmonds[1], Tim Allsop[1], Geoff Holmes[1], Sue Cooper[1], Melissa Basil-Jones[2] and Richard Haverkamp[2]
[1]New Zealand Leather and Shoe Research Association Inc. (LASRA®), 69 Dairy Farm Road, Palmerston North, New Zealand, Phone: 64-6-3559028, Fax: 64-6-3541185, e-mail: richard.edmonds@lasra.co.nz
[2]School of Engineering and advanced technology, Massey University, Palmerston North, New Zealand, Phone: 64-6-3569099 x 81056, e-mail: r.haverkamp@massey.ac.nz

Introduction

Developing a process which minimises or eliminates the use of sodium sulphide has been a priority for a number of years, as evidenced by the large number of attempts at low or non sulphide methods described in the literature. (Smidek *et al.* 1987; Wolf 1991; Sehgal *et al.* 1996; Christner 2000; Sundar *et al.* 2006; Rose *et al.* 2007). The reason for this is that sodium sulphide is unpleasant to use and its misuse is both costly and potentially hazardous.

In industry the application of sodium sulphide in the depilation process is usually carried out in a pragmatic fashion without much regard to the underlying chemical processes which are occurring. In this work we seek to examine the depilation process a little further, and through a focussed rational management of the process attempt to determine the minimum amount of sulphide required to achieve depilation. This work is based on the concept that by careful management of the concentration of caustic in painting and liming the amount of sulphide used can be dramatically reduced.

Unmanaged use of alkali during the fellmongering process is risky. Too little alkali can result in incomplete depilation, particularly within a fast acting (less than 4 hour, Quikpul) regime, and increases the risk of release of hydrogen sulphide gas, which begins to occur when the pH of a sulphide containing solution drops below 9.

On the other hand using excess alkali is known to cause significant cost to the processor through excess solubilisation of skin substance, and potential localised alkali damage to skins, increased disposal costs, and effluent handling difficulties with associated compliance failure costs.

Principle of low sulphide depilation

Conventional lime/sulphide depilation relies on keratin solubilisation which occurs through a nucleophilic substitution reaction which requires the presence of both sulphide ions and hydroxide ions. The reaction rate is a function of the concentration of both sulphide and hydroxyl ions. It is a trade off between the two as illustrated in figure 1.

As the pH is increased the amount of sulphide required to dissolve keratin is reduced and vice versa. Note here that the standard conditions of pH 12.5 and sulphide concentrations ranging from 1 to 2 %w/v at the fibre represent only one of the conceivable depilatory conditions. Lowering the pH will increase sulphide requirements or increasing it will decrease the sulphide requirements.

It is worth noting also that the sulphide scale on this graph is a log scale and that a change of one pH unit implies a 10-fold change in the required sulphide concentration. Although the pH and sulphide concentration can be adjusted to different values and still achieve depilation the required change in sulphide concentration is large. If the pH is reduced to 12 then 200g/L sodium sulphide is required, but if the pH is raised to 13 then the sodium sulphide can be as low as 19g/L. If the relationship is

extrapolated to a pH of 13.5 the concentration required for successful depilation at a sodium sulphide concentration of 6.3g/L.

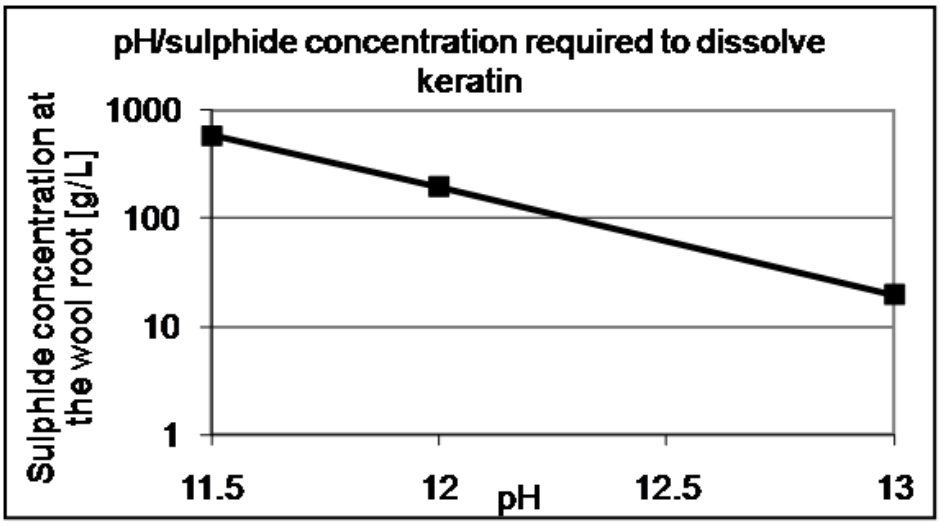


Figure 1: Relationship between the dissolving of keratin under conventional alkaline sulphide conditions and the pH and sulphide concentration. Data displayed here interpreted from (Vivian 1964)

The important point is that by increasing the sodium hydroxide concentration in the depilatory paint the amount of sulphide used can be drastically reduced. However, increasing the sodium hydroxide in depilatory paint places the skins at risk of alkali damage during liming. This is where the measurement and control of sodium hydroxide in liming becomes important. The risk of skin damage from a high level of sodium hydroxide in the depilatory paint can be mitigated by neutralising the excess sodium hydroxide with calcium chloride

Adding calcium chloride reduces caustic alkalinity because it reacts with the hydroxide ions to produce the slightly soluble calcium hydroxide, so removing them from solution. Due to the buffering of calcium ions at pH 12.5, the process is a particularly safe and robust way of reducing causticity without affecting pH.

Calcium chloride is usually supplied as either an anhydrous powder, hydrated crystals, or as a liquid solution. A liquid solution would probably be the most convenient because of ease of use in automated dosing systems. Anhydrous calcium chloride does not store well as it is strongly hygroscopic and reacts with water in a strong exothermic reaction making it difficult to handle. Calcium chloride dihydrate crystals are relatively stable and this is the form of calcium chloride most readily available.

Neutralising 1g of sodium hydroxide requires about 1.7g of calcium chloride.

By measuring the sodium hydroxide content of the liming liquor the appropriate amount of calcium chloride can be easily calculated and added in a solution form to the liming liquor. The dissolved calcium chloride then reacts to form slightly soluble calcium hydroxide. If it is found to be undesirable to have particles of calcium hydroxide in the liming liquor these may be removed by inline dosing followed by centrifugation and recycling of the liming liquor. Alternatively the calcium hydroxide may be kept in solution by the addition of sugar (sucrose). Sugar reacts with the calcium hydroxide to form soluble calcium sucrate.

In order to determine how much sugar would be required to keep all the calcium hydroxide in solution an experiment was carried out. An alkaline solution was prepared containing 40g/L sodium hydroxide and 200g/L flake sulphide (pure sodium sulphide used to achieve 200g/L flake equivalent). A (6%

w/v) solution of calcium chloride (dihydrate) was then used to titrate out the caustic alkalinity. Different amounts of sugar were added to the calcium chloride solution to determine how much would be required to keep the calcium hydroxide precipitate in solution. The results are illustrated in figure 2.

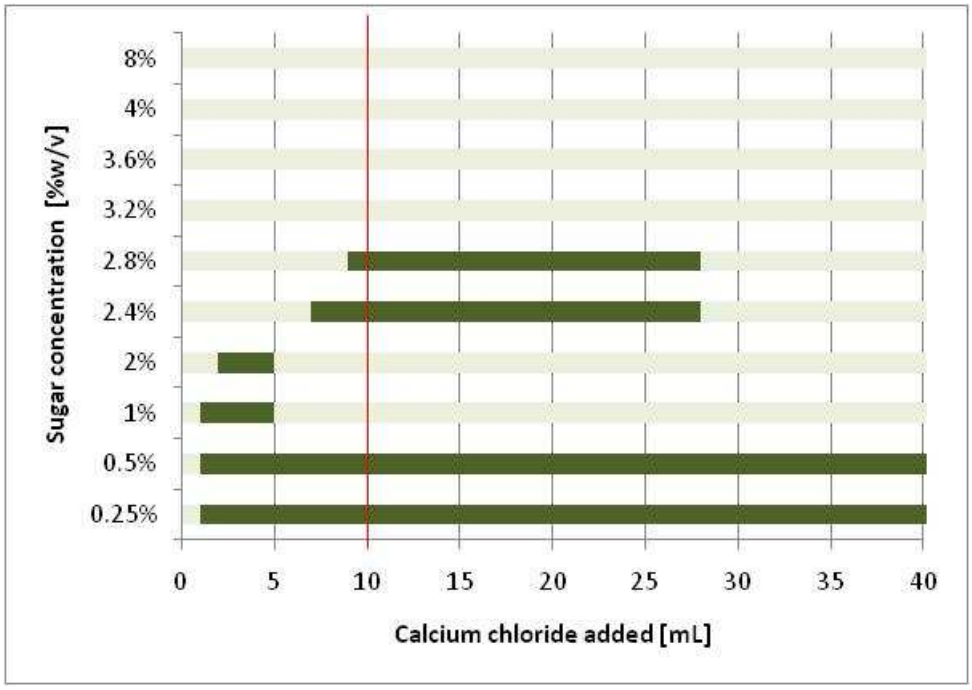


Figure 2: Effect of sugar on calcium hydroxide precipitation. If a precipitate was observed this is illustrated by a dark bar. At low levels of sugar (<1% w/v) the calcium chloride quickly formed a precipitate which did not dissolve. At higher levels of sugar the precipitate took longer to appear. When the sugar was dissolved in the calcium chloride solution at a concentration of at least 3.2% a precipitate did not form.

It should be noted however that the calcium hydroxide precipitate formed is of a different structure to the ground hydrated lime powder normally used in conventional liming and is likely to have a different effect on the grain surface. This is illustrated in figure 3. The precipitated calcium hydroxide formed much smaller crystals which are likely to be less abrasive. Photomicrographs of the two forms of lime are illustrated below.

One of the main risks of using a high alkali depilation process is the swelling caused by a high pH. Previous LASRA research has shown that ovine skins begin swelling at about pH 11 and continue to swell as the pH is increased (Passman *et al.* 2004). Unpublished research at LASRA has however shown that the use of a swelling repression agent will protect skins from excess swelling during the alkaline liming process.

An experiment was carried out to determine if this reagent could be used to reduce the swelling that occurs due to the high pH which is reached in the low sulphide process.

Pieces of green skin were soaked in a 0.1% phosphate buffer solution and the pH slowly adjusted. Pieces were periodically removed from the solution and the swelling measured gravimetrically by weighing the piece and calculating liquid absorption. Results are illustrated in figure 4.

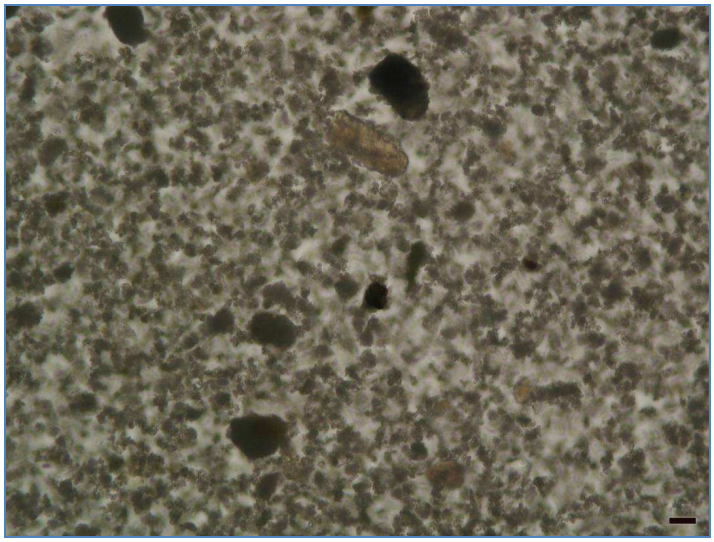


Figure 3a: Conventional hydrated lime for use in depilatory paint thickening (bar 25 µm)

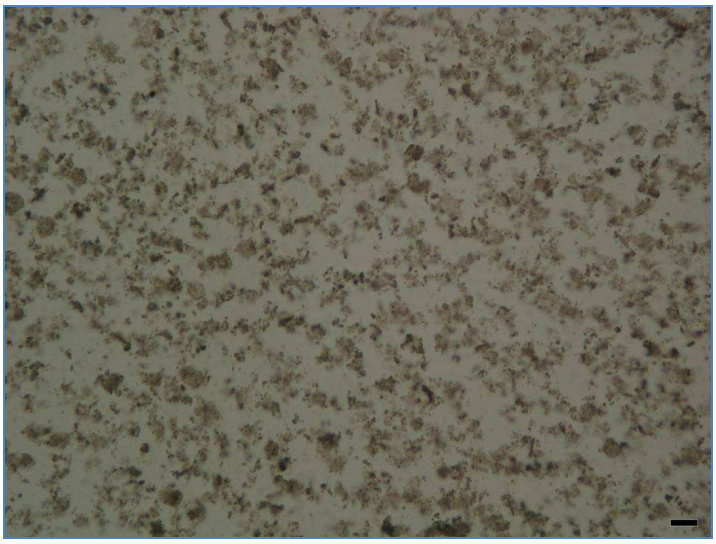


Figure 3b: Precipitated lime from calcium chloride addition (bar is 25 µm)

As expected increasing the pH resulted in swelling of the skin, with a dramatic increase at around pH 11, as noted previously. The addition of a swelling repression agent resulted in some protection against swelling, The addition of 2% of the reagent resulted in a significant reduction in alkaline swelling. This represents a possible way to mitigate the extent of alkali swelling and consequential risk of damage during depilation when using a highly alkaline depilatory.

Since the use of lime as a sole thickener for depilatory paint is known to cause serious damage to the surface of pelts during processing (known as leopard grain) its use for this purpose has declined over the years and most of it has been replaced by starch based thickeners. The remaining hydrated lime acts as a source of alkali and as a thickener modifier. Because, in this work it was necessary to achieve a particularly high pH using sodium hydroxide the use of hydrated lime as an alkali reserve was unnecessary. This meant that the lime could be replaced by an alternative zeolite based thickener.

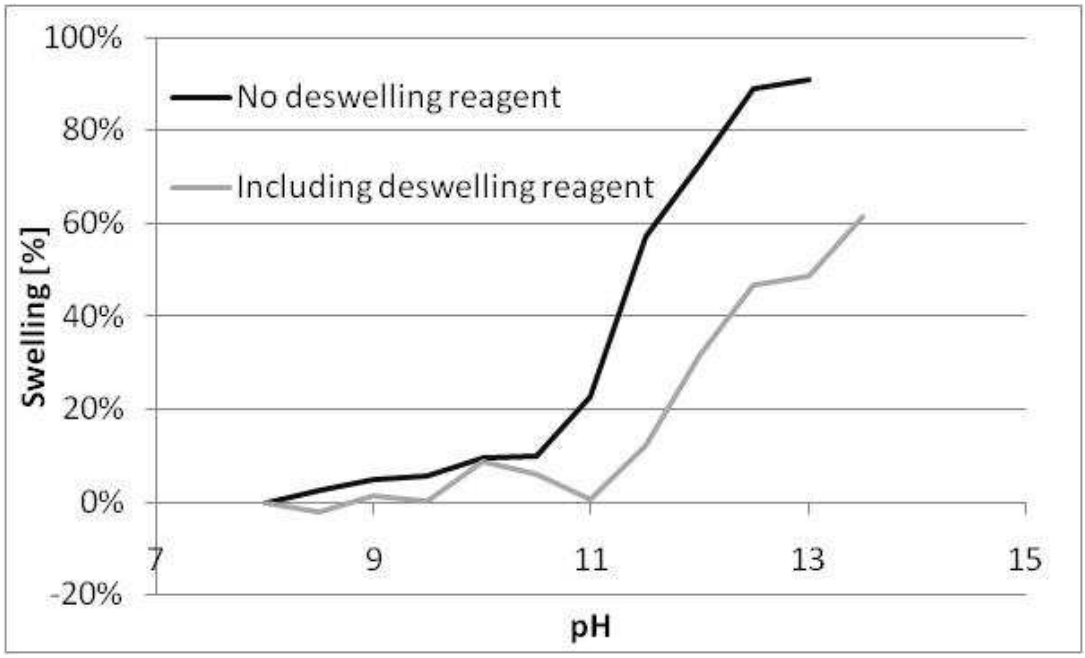


Figure 4: Impact of the use of a swelling repression agent on swelling of lamb skin at high pH

Low sulphide overnight depilatory formulation

The first attempt at a low sulphide, high alkaline, caustic control, depilatory paint formulation was an overnight paint. The formulation was based on a tenfold reduction in the quantity of sulphide used with enough sodium hydroxide added to increase the pH by 1 to about 13.5.
Ten skins were depilated with the overnight low sulphide depilatory and ten skins were painted with the standard overnight formulation. Both sets of skins were well depilated after 16 hours. The conventional skins were then processed through to crust leather using a standard LASRA processes. The novel low sulphide high alkali painted skins were first neutralised in an 80% float containing 210g of calcium chloride per litre of paint used. The skins were processed for 4 hours in this solution before washing out the lime and continuing with the standard LASRA process through to crust leather and testing for physical properties. The results are illustrated below.

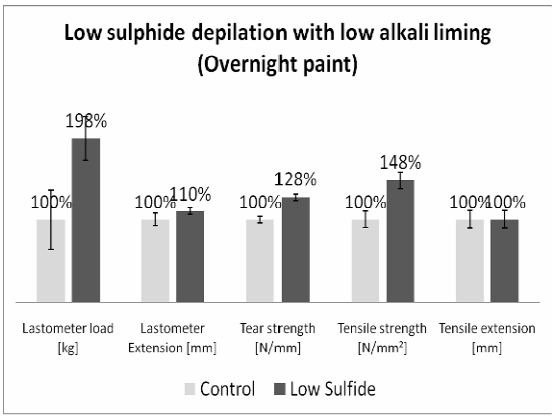


Figure 5: Impact of low sulphide overnight depilation on the physical properties of ovine leather

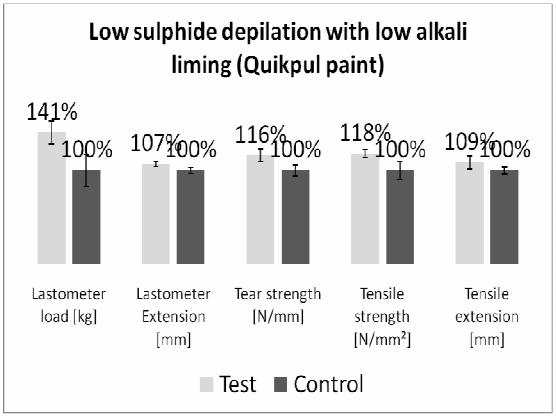


Figure 6: The impact of low sulphide Quikpul depilation on physical properties of ovine leather

The physical test results of the low sulphide depilated pelts were consistently same as or better than, those for the control pelts. The next step was to produce a low sulphide Quikpul depilatory paint.

Quikpul depilation formulations typically require 2 to 4 hours from painting to pulling depending on the strength of the paint used. In this work it was desirable to determine whether a 2 hour pull could be achieved with a significant reduction in sulphide use. An experiment was therefore set up to test the ability of low sulphide high alkali formulations to depilate ovine skins in a short time. The range of reagent formulations is given in table 1:

Pairs of skins were then painted with the 16 different paint formulations and the extent of depilation monitored every hour for 6 hours. After 2 hours the level of depilation was only 65% for the best skins. So it would seem that a 2 hour paint would not work with a significant reduction in sulphide. However the depilation process was allowed to continue and after 4 hours the best skins had reached 85% depilation as illustrated in figure 7.

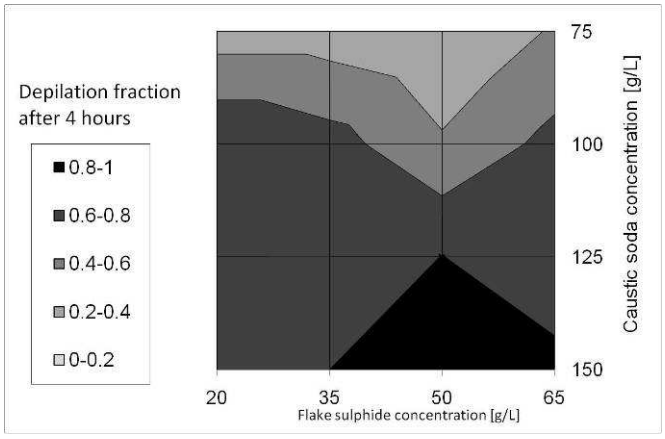


Figure 7: Proportion of skins which depilated 4 hours after application of depilatory paint. Sodium sulphide and sodium hydroxide concentrations are shown on the horizontal and vertical axis respectively and the level of depilation at a given paint formulation given by the gray scale with darker regions indicating a greater level of depilation.

Flake sulphide/ Caustic	20 g/L	35 g/L	50 g/L	65 g/L
75 g/L	1	2	3	4
100 g/L	5	6	7	8
125 g/L	9	10	11	12
150 g/L	13	14	15	16

Table 1: Depilatory paint formulations 1 to 16.

It can be seen from figure 7 that the best depilation at 4 hours occurred with paint containing 65g/L flake sulphide and 150g/L sodium hydroxide. This is still significantly less than the standard overnight sulphide usage of 160g/L and represents a significant reduction in sulphide comparied to a conventional Quikpul formulation containing 200g/L flake sulphide.

This paint formulation was then used in further tests to examine the properties of leathers produced after this depilation. 10 skins were depilated with the Quikpul low sulphide depilatory and 10 skins were painted with the standard Quikpul formulation. The novel low sulphide skins were pulled after 4 hours and the conventional Quikpul control skins were pulled after two hours. Both sets of skins pulled well. The conventional skins were then processed through to crust using standard LASRA processes. The novel low sulphide high alkali painted skins were neutralised in an 80% float containing 272g of calcium chloride per litre of paint. They were processed for 4 hours in this solution

before washing out of lime and continuing with the standard LASRA process through to crust the physical properties of both sets of leather were tested. The results are illustrated in figure 6.
There was an increase in all strength measurements for low sulphide treated skin, confirming what had been seen with overnight paint. We believe the strength is improved because the skins were exposed to highly alkaline conditions in a static state, and once in process the excess alkalinity was essentially neutralised with the calcium chloride. As a result the collagen was protected from further alkali damage during processing. It would seem that even conventional controlled processing results in a weakening of the leather through the action of alkali, in comparison to a process where the excess alkali was neutralised at the beginning of processing.

Understanding improvements in strength

Work is being carried out in New Zealand to produce lamb skins of exceptional strength. It is therefore important to understand the basis of that strength. For this purpose work has commenced investigating the nature of the strength of leather and how it might be optimised and improved particularly in the case of the New Zealand ovine leather product.

Leather is a complex composite material. It is made up of individual fibres of different dimensions and properties which are arranged inconsistently through the bulk structure. Building a description of the strength of leather based on the properties of its component parts is therefore a significant challenge and is the subject of this investigation.

Early work in understanding the properties of leather based on the structure involved measuring the stretch and alignment of individual fibres (Mitton 1945). By assuming a random distribution of fibres and measuring the rheological properties of an individual fibre a reasonable estimate of the properties of bulk leather could be made. The nature of the tools at the time limited the ability to include the range of distributions of fibre orientations and the range of fibre thicknesses which exist throughout a typical sample of leather. This work highlighted the importance of a consistent test environment. Due to the high surface areas involved with individual fibres they are highly susceptible to temperature and humidity changes in the local environment.

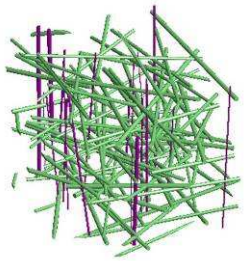
More recently work been completed where the distribution of collagen fibre orientation has been modelled (Jor et al 2007) and the same convention for reporting the orientation of fibres in leather has been incorporated in the work reported here.

By adjusting the parameters for the angle of weave and the distribution of fibres around that angle it is possible to generate models of leather that describe the observed variations in angle of weave as shown below

"High angle" "Well distributed" "Low angle"

σ_x=0.1 σ_z=0.1 σ_x=0.8 σ_z=0.8 σ_x=0.1 σ_z=0.8

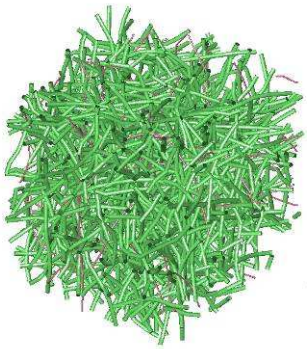
σ_x and σ_y represent the distribution around the average angle of weave in each of two spatial dimensions. Different protein types with individual fibre orientation distributions have also been incorporated into this descriptive model as shown below:



Collagen (σ_x=0.1 σ_z=0.8, green)
Elastin (σ_x=0.1 σ_z=0.2, red)

However we know that collagen and elastin are fibres and not rods so this aspect was also included in to the model.

The incorporation of fibre undulation has been carried out in which the undulation of the fibre along its length is reported as its persistence length (Stein *et al.* 2008). The use of persistence length allows a more realistic representation of a leather composed of fibres rather than rods. Inclusion of two protein fibres with varied orientation distributions is illustrated below:



Collagen (σ_x=0.1 σ_z=0.8, green)
Elastin (σ_x=0.1 σ_z=0.2, red)

The next step of the modelling will be to incorporate the fibrillar split up nature of the fibres in leather. The impact of splitting up is an important determinant of the physical properties of the final leather and so should be included in a complete description of the leather structure.

Once the structure is modelled the next step will be to study the impact of each of the physical parameters modelled on the properties of the bulk leather including rheology and ultimate strength. With this understanding we will then incorporate the impact of different processing and tanning regimes on that structure. The techniques for measuring these effects are being developed alongside the modelling work and will provide vital information about the input values to any modelling system.

Property measurement

Our approach is to systematically study the effects of conventional lambskin processing on the physical strength and chemical composition of ovine skin from raw material to final leather. This baseline information will be used to compare alternative treatments and novel additives and crosslinks on fibril strength and other relevant properties of the leather. This knowledge will then be used to develop ovine leather of improved strength for use in footwear leather.

A range of techniques for the determination of these changes are being investigated in the first part of the work. Literature investigations have indicated that small angle X-ray scattering (SAXS) may be a useful technique for investigating underpinning structural descriptions of leather related to strength in bulk samples including collagen type and the distribution of the angle of weave. Confocal microscopy was identified as a useful tool for investigating and describing the relationship between protein types and structure and strength in leather, and staining techniques have been successfully developed for this purpose. Atomic force microscopy was identified in the literature as a means by which rheological and strength properties of individual fibres could be determined and a device for measuring such properties incoporating environmental control is being developed for this. Proteomic tools including 2D electrophoresis and 2D-LCMS are being investigated for their ability to identify qualitative differences in proteins from skins of different strengths. The literature in this area and preliminary studies by the team have found that minor protein levels may have a large influence on the bulk properties of the resulting leather (Edmonds *et al.* 2008) and differentially stripping the major collagens from the samples is likely to amplify the relative response of the proteomic techniques in order to show how the stronger skins differ from the weaker ones.

Work on these methods is continuing with analysis of relevant samples in order to validate findings to date.

Conclusions

The aim of this work was to determine if significant reductions in sulphide use could be achieved through the controlled use of sodium hydroxide in the depilation step followed by neutralisation at the beginning of processing.

Not only was it possible to achieve good levels of depilation with significant reductions in the use of sodium sulphide but skins processed while controlling the alkalinity of liming resulted in leathers that were significantly stronger than conventionally depilated skins.

It was postulated that the reduced alkalinity in processing was the reason behind the increase in strength. This interesting phenomenon will be investigated further using funding from the New Zealand Ministry of Science and Innovation.

Acknowledgments

The author wishes to acknowledge the assistance of Hayley Looner in the processing and assessment of the leathers in this trial and MSI funder under project LSRX0801 and LASRA membership.

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