FELLMONGERY

In the sheep industry fellmongery is the process of removing wool from the skin after it has been removed from the carcass, and treating the skin for eventual conversion into leather.

Fellmongering has four steps:

1. **Depilation**
   Separation of the wool from the skin. The flesh side of the pelt is sprayed with a solution containing Na_2S, NaHS, $Ca(HS)_2$, $Ca(OH)_2$ and Na(OH), (the paint), and the wool is pulled off mechanically.
2. **Liming**
   Removal of remaining wool and the epidermis (top layer of the skin). This is achieved tumbling the pelts together in the liming liquor.
3. **Deliming/Bating**
   Lowering the pH using CO_2 and NH_4^+ ions, modifying protein (elastin) and removing protein degraded during liming, and traeting with enzymes to improve the softness, suppleness and surface qualities of the pelt for the leather industry.
4. **Pickling**
   Preserving the pelt for storing or shipping prior to tanning.

INTRODUCTION

Aspects of fellmongery were briefly covered in the article on tanning (V-B). To demonstrate in more detail a major chemical process within an industry, the fellmongering of lamb and sheep skins is considered in greater depth. This process is the basis on which later tannery processes turn lamb pelts (dewoolled skins) into clothing leathers and sheep pelts into mainly chamois leathers.

New Zealand is a leading producer of lamb and sheep pelts, supplying some 30% of world trade from plants that process 20,000 skins or even 40,000 skins a day. These large numbers of skins are treated chemically to provide slipe wool (chemically removed as opposed to shom) and a pickled pelt that can be utilised by the tanner to produce leather.

Of all the processes carried out alongside a modem meat plant, the one that relies most heavily on chemistry is fellmongering. This is the process in which wool is removed from the skin, and the skin is treated or pickled so that it can be stored or shipped for conversion into leather.

Fellmongering can be divided into four steps:

1 *Depilation* - Separation of the wool from the skin.

2 *Liming* - Removal of unpulled wool and the epidermis (the top layer) of the skin. Opening up the skin-structure by causing its fibres to swell and removing interfibrillary material.

3 *Deliming/Bating* - Lowering the pH, modifying protein (elastin) and removing protein degraded during liming.

The enzymatic treatment improves the softness and suppleness of the pelt and cleans the surface to give a good basis for subsequent treatments, especially leather dyeing.

4 *Pickling* - Preserving the pelt so that it can be stored or shipped for tanning. The acidic condition is also a prerequisite for the tanning chemistry that will be used to make the leather.

DEPILATION

Because the skin is often more valuable than the wool, it is essential that the wool is obtained without damaging the pelt. As is typical of animals, the major solid component of the outer coating is protein and the fellmongers initial problem is to separate two similar substances without damaging either of them. The two main proteins involved are keratin and collagen.

Keratin	Collagen
Main constituent of wool, hair, nails, horns, claws and epidermis.	Main constituent of skin.
Relatively resistant to acids and water and solvents such as alcohol and ether, hence its effectiveness as a protective outer coating.	Insoluble in water, weak acids and alkalis, but is attacked by strong ones.
Rapidly attacked by strong alkalinity and sodium sulphide.	Swells or "plumps" by absorbing water in acid or alkaline solutions.

At first sight the use of sodium sulfide alone would seem to be a simple means of accomplishing the separation of wool and skin. A sodium sulfide solution applied to the flesh side of the skin would soak through and destroy the shaft next to the wool roots without adversely affecting the skin and the wool could be pulled off.

But to be effective within reasonable timeframes, the sodium sulfide must maintain sufficient alkalinity around the wool roots to digest the wool protein, keratin.

Because alkali reacts with collagen (in a nucleophilic substitution reaction) the concentration of hydroxide ions in the sodium sulfide solution decreases as the solution soaks through the skin, which would also absorb water and swell. Thus, the problem is how to get a solution through the skin in a reasonable period of time so that when it reaches the wool roots it has a pH of at least 12.5, bearing in mind that:

- the hydroxide ion concentration is going to drop as it passes through the skin and reacts with the collagen,
- the skin is going to absorb water,
- ions move through the skin at different rates.

These problems are overcome to a large extent by using a strong depilatory solution (a paint to the fellmonger) of sodium sulfide containing sodium hydroxide and/or calcium hydroxide (lime). Calcium hydroxide or slaked lime is traditionally used where the skins can be held overnight to give the depilatory paint time to work. Calcium hydroxide is not very soluble and when added to excess gives a solution of pH 12.5 and in it the equilibrium

$$Ca(OH)_2(s) \leftrightarrows Ca^{2+}(aq) + 2OH^-(aq)$$

is established. As this solution passes through the skin and reacts with it, this equilibrium moves to the right maintaining a steady concentration of hydroxide ions.

Because skins vary in thickness and density and lamb skins differ from sheep skins the strength of the paint must be controlled to prevent damage to thin open-textured skins. One way this can be done is by using other sulfides such as sodium hydrogen sulphide or calcium hydrogen sulphide. These salts behave rather differently to sodium sulphide when dissolved in water.

(i) Sodium sulfide (Na_2S)

$$Na_2S \rightarrow 2Na^+(aq) + S^{2-}(aq)$$

The sulfide ion (S^{2-}) is a strong base, p$K_a(HS^-)$ = 12.9 or $K_b(S^{2-}) = 7.8 \times 10^{-2}$ it reacts with water:

$$S^{2-}(aq) + H_2O \leftrightarrows HS^-(aq) + OH^-(aq)$$

About 50% of the sulfide ions present react in this way. Thus the ions present in the solution are Na^+, OH^-, HS^- and S^{2-}.

(ii) Sodium hydrogen sulfide (NaHS) and calcium hydrogen sulfide ($Ca(HS)_2$).

The hydrogen sulfide ion is a very weak base, pK_a (H_2S) = 7.0 or $K_b(HS^-)$ 1.0×10^{-7}, and very little reaction occurs when these salts dissolve in water. Their solutions have a much lower hydroxide ion concentration than sodium sulfide.

$$NaHS(s) \rightarrow Na^+(aq) + HS^-(aq)$$
$$Ca(HS)_2(s) \rightarrow Ca^{2+}(aq) + HS^-(aq)$$

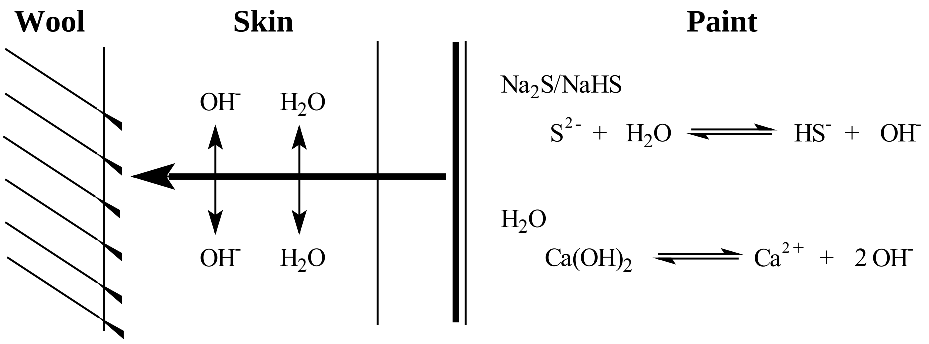
Addition of calcium hydroxide to any of these solutions increases the concentration of calcium ions and hydroxide ions.

As the solution moves through the skin it must remain electrically neutral so the movements of sulfide and hydroxide ions are controlled by whatever positive ions can move with them. Sodium ions move faster than calcium ions, so the presence of sodium ions is necessary for a satisfactory rate of penetration. The ratio of sodium ions in Na_2S, NaHS and $Ca(HS)_2$ solutions of equal concentration is 2:1:0. Sodium sulfide penetrates the skin most readily but it also has the highest pH which has the potential to damage the skins. Mixtures of the different sulfides together with calcium hydroxide can be used to cope with varying types of skin.

The situation is further complicated by the fact that water is absorbed by the collagen as it reacts with hydroxide ions and swells, and this limits the amount of calcium hydroxide that can be carried through.

In today's production enviromnent, companies need to process as many skins through a plant as possible to make efficient use of equipment and minimise costs.

This has led to the use of rapid depilation systems that loosen wool within 2 to 5 hours. These so called LASRA Quikpul systems achieve rapid dewoolling using the same principles of chemistry and the same reagents. The quick result is achieved by increasing the strength of the sulfide solution and/or adding sodium hydroxide into the paint mixture. This is to



provide a greater excess of alkalinity to drive the hydroxide ions through the skin as quickly as possible. The increased risk to the skin is offset by the fact that the period of exposure is greatly reduced.

Under the modem Quikpul systems, the use of calcium hydroxide has decreased markedly in favour of the use of sodium hydroxide and specialised additives are included to help the paint to do the quick job that is required.

In practice the skins are laid wool side down on a conveyor belt and the flesh side is sprayed with the paint from overhead nozzles. They are left for periods of 2 hours or overnight depending on the system being used and then the wool is pulled off by machine.
To summarise:

> Sulfide ions are necessary to attack the wool around the region of the roots.
>
> Hydroxide ions are necessary to provide the optimum pH for sulphide action on the wool protein.
>
> Sodium hydroxide is used to ensure rapid penetration of the skin.
>
> Hydroxide is necessary to provide a suitable pH and maintain it as the hydroxide ions react with the collagen.

LIMING

The skin, as it comes from the wool pullers may have patches of unpulled wool adhering. It will also have the external layer of skin - the epidermis - still present. This has a protein structure similar to wool and very different from the collagen of the true skin.

The amount of paint is applied in such a way that the epidermis, though attacked by the chemicals in the paint, is not totally degraded. In this way, the pulling machines will remove the wool from the skin but will leave the epidermis behind as a film. The reason for this measure is to avoid contaminating the wool with epidermis.

Because its structure is different from the true skin, the epidermis is removed before the skin is prepared for tanning, and this, together with removal of residual wool, is the first objective of the liming process.

The true skin, below the epidermis, consists of two layers:
(1) the grain layer - extending from the external surface of the true skin to the wool roots. It is made up mainly of fibrous protein tissue or collagen, but has large numbers of other structures such as sweat glands, fat glands and wool follicles.
(2) The flesh layer - consists mainly of collagen fibres with interfibrilliary material and nerves and blood vessels.

In both layers the collagen fibres are surrounded by the non-fibrous protein material.

The boundary between the layers is well marked in most lamb and sheep skins and the bonding between them is not strong. Before leather can be produced, non fibrous material must be removed and liming is the first step in achieving this. If the non fibrous material is not removed, it acts like glue when the skin is dried later in the tanning process and the leather ends up stiff and unsuitable for soft/ drapey clothing. Thus, the objectives of liming are to:

- remove excess wool and the epidermis
- open up the fibrous material in the true skin, by the removal of interfibrillary material by the action of alkali and water, which also cause it to swell and plump so that non fibrous protein can be attacked
- cause a reduction in the natural growth patterns on the skin to produce a nice flat piece of leather

As they come from the pullers the skins are in a condition for all objectives to be achieved. They contain sulphide and alkali and a limited amount of absorbed water from the depilatory paint. Liming is carried out in enclosed or semi closed vessels called drums or processors containing the lime liquor. This liquor contains sodium sulphide, calcium hydroxide, sodium hydroxide solution - formed largely from the chemicals dissolved in the skins and carried over with the residual paint used to loosen the wool. Normally this carry-over of chemical is enough to achieve the objectives with only small additions of sodium sulphide or hydrosulphide needed to ensure all residual wool and epidermis is removed. The excess wool and epidermis are removed by the combined action of the hydroxide and sulphide ions and the skins rubbing together as they are tumbled in the drum or processor.

Because of their high pH the skins absorb water and plump immediately they are placed in the solution. This is what is required but as with depilation the process must be carefully controlled. The two skin layers swell at different rates and to different extents and because the bonding between the layers is not very strong they may separate if plumping is too rapid. Gentle and gradual plumping allows the developed strain within the skin to be spread over the whole pelt and not concentrated at one point thus decreasing the chances of the grain and flesh layers separating.

Factors which effect the rate of swelling are:

(i) *pH*
The higher the concentration of hydroxide ions the faster swelling occurs. Excessive hydroxide ions come largely from the depilatory paint due to an excess of sodium sulphide or sodium hydroxide. To keep the pH of the lime liquor at a safe level, the strength of the paint must be as low as possible or the alkalinity in the lime liquor can be reduced by washing the skin with water down to a desired level

(ii) *Mechanical action*
The more the pelts are tumbled the greater the contact between them and the lime liquor and the more rapidly they will absorb water. In addition the plumped pelts are tender and under strain. In this condition they are more susceptible to physical damage by rough treatment. Hence, mechanical action must be just sufficient to keep the pelts moving and only long enough to achieve the objectives.

(iii) *Condition of the lime liquor*
In today's world, all companies strive to minimise the impact of their processing on the enviromnent and to minimise costs of treating waste which can amount to hundreds of thousands of dollars each year.

Increasingly, companies are looking to reuse or recycle processing liquors rather than put them down the drain. Lime liquors are good examples of recycling technology.

Lime liquors that have already been used contain broken down protein and other dissolved material which acts as a buffer, controlling pH. Pelts limed in such a "mellow" lime liquor plump more slowly than those in a fresh liquor.

(iv) *Temperature*
An increase in temperature speeds up water absorption and damage by alkali. The lime process is usually controlled at $21^{o}C$ to $26^{o}C$.

During liming non fibrous protein, which is more readily attacked by alkali than collagen, is broken down and reduced to a soluble state. Much of it is removed during the liming process itself, some remains to be removed at the enzyme-treatment or bate stage.

Each fibre consists of a number of fibrils twisted together like strands of a rope. Liming partly frees the fibrils from each other (splitting - a physical/chemical process) and mechanical action tends to break open the fibril bundles and break them into smaller bundles (separation - a mechanical process). Both of these processes are desirable to a controlled extent in treatment of the pelt.

DELIMING/BATING

Deliming used to be completed before the bating or enzymatic treatment began. Processing today has merged these activities into a single stage. This is possible because the chemicals used to delime or lower the pH can penetrate the skin faster than the enzyme. Enzymes are large molecular species which penetrate skin with some difficulty. The deliming chemicals therefore keep ahead of the enzymes, preparing the way and adjusting the pH conditions to enable the enzyme to do its work.

This is quite a smart way of using different penetration rates to combine two process that once were used separately.

The objectives of the deliming part of the process are to:
(a) reduce the pH of the pelt causing the swelling of the pelt to fall.
(b) help with the removal of the remaining non-fibrous matter.

The limed pelts have alkali both free (dissolved in the absorbed water) and combined (chemically bonded to the collagen protein). You can probably think of two obvious ways of removing this:
(i) washing with water
(ii) adding acid

Both of these have disadvantages. Although water is cheap, it will cause the pelts to swell still more, the pelts would require very extensive tumbling which could damage them and the process of leaching out all the alkali would be very slow. Addition of acid can be successful, but is rarely used since it must be very carefully controlled since alkali is contained within the pelt and reaction would be too rapid. Remember a strong acid and a strong alkali react and give out much heat. This heat would be enough to risk damage to the skin. Hydrochloric acid can be used, but is expensive in New Zealand, although the calcium chloride is very soluble and can be washed out. Sulphuric acid, which is cheaper, produces calcium sulphate which is not very soluble and not easily removed; removal of calcium sulphate is important for good quality leather. Boric acid, a weak acid, is a very effective deliming agent and can also be used but the boron from the acid causes problems in the environment.

In New Zealand, deliming is usually done with carbon dioxide or ammonium chloride or ammonium sulphate. Both ammonium salts react with alkali, but at no stage produce strongly acidic conditions. The reaction is the same one you have probably used to prepare ammonia in the laboratory:

$$2NH_4C1 + Ca(OH)_2 \rightarrow CaCl_2 + 2NH_3 + 2H_2O$$

The pelts are gently tumbled and the temperature kept low in the initial stages of deliming to prevent damage as the pelts are still swollen, but as the reaction nears completion and the swelling decreases, warm water is used to ensure complete removal of non fibrous material.

The carbon dioxide system injects the gas into the liquor. Where sufficient carbon dioxide is injected, the pH falls below 8 and bicarbonate rather than carbonate is formed in solution. Whilst carbonate can leave unsightly marks on the surface of the skin and the leather (because it does not dissolve easily) there are no such problems with bicarbonate. The reaction can be summarised as follows:

$$2CO_2 + Ca(OH)_2 \rightarrow Ca\,(HCO_3)_2$$

Carbon dioxide liming is gaining in favour because it can be easily automated and the technology is very clean.

The problems that could arise with hydrogen sulphide generation from the action of the low pH on residual sodium sulphide carried over in the skin are dealt with by using sodium peroxide to oxidise the sulphide to sulphate and harmless sulphur compounds.

The objectives of the bating stage of the process are:

- to give the pelts a smooth silky feel
- to open up the pelt structure more fully to give softness and suppleness to the pelts
- to ensure the skin surface will dye a bright, even colour

Producing leather from animal skins is a very old process and the term "bating" originally applied to the use of animal dung, generally from hens, pigeons, or dogs, to achieve the required results. As you can imagine, centuries ago the bate shop would have been a filthy and unpleasant place to work in, particularly as the bate liquor was kept for long periods of time and merely strengthened as required with more dung.

No improvements in the conditions of this part of fellmongering were possible until the active substances in the dung could be identified. In the late 1800's, these were found to be enzymes which aid the decomposition of certain proteins. Enzymes are substances found in all living things. Their presence is necessary to allow what can be very complex reactions, generally related to the breakdown of large molecules such as fats, carbohydrates and protein, to take place under very mild conditions. Your digestive tract will not tolerate the high concentrations, pressures and temperatures that must be used to accomplish the same processes in the laboratory without enzymes. They are in effect catalysts. The other feature of enzymes is that they are highly specific. Each enzyme catalyses a particular step of a particular reaction. The enzymes involved in bating are now produced commercially as a by-product of food manufacture or using genetic engineering technologies and can be used without the previously associated unpleasantness.

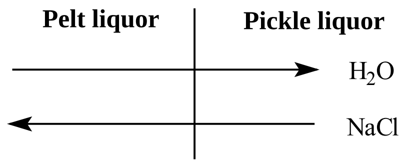
Although enzymes are active in mild conditions, the conditions for greatest activity are critical. The protein enzymes used in bating are most active in a pH range of 8 - 9 and at temperatures between 32 and 38^{o}C. The deliming process reduces the pH from 12.5 to 7 - 9 depending on the deliming chemistry.

Bating is carried out in the same vessel as deliming. Once the pH has dropped to 9 and the temperature increased, the bating enzymes are added shortly after deliming has started. The exact mechanism of bating is still uncertain, but it produces the desired result and that, up to a point, is what matters. Pelts for different kinds of leather require different degrees of bating. The fellmonger aims at a moderate degree of bating and the tanner can use enzymes or other treatments to give the degree of softness or the feel required in the leather.

PICKLING

New Zealand pelts can sometimes be stored for up to a year before being processed by the tanner and it is necessary to preserve them against the action of mould and bacteria for this period.

Bacterial and most mould (fungi) growths are prevented in strongly acidic conditions. The use of acid for preservation is well established. It is a technique used in the food industry, of course. As has been stated before, acid conditions can cause the pelts to swell and can also permanently damage them. Although acid is less efficient in controlling mould, it is safer to use from the point of view of damage. Sulphuric acid is normally employed as it is cheap and effective. The swelling that would be caused by the acid is controlled by the addition of common salt, sodium chloride. The usual procedure is to add salt to the pickle vessel and after the salt has dissolved, put the pelts in. The pelts still contain a considerable amount of water (pelt liquor) and during pickling, diffusion occurs until the pelt liquor and pickle liquor are at the same salt concentration i.e. until equilibrium has been established.



The process results in a decreasing density of the pickle liquor and this is followed with a hydrometer similar to the type used to check the charge of a car battery. At this stage the acid is added and the presence of the salt represses swelling right from the start. Fungicide is needed to prevent fungal growth that can occur even in acidic material. The acid diffuses into the pelt reacting first with remaining calcium hydroxide forming calcium sulphate. A properly delimed pelt should have little lime left and the amount of calcium sulphate produced, although not very soluble, is easily handled because of the large volume of water. Badly limed pelts cause calcium sulphate in the pelt, giving it a rough texture.

Secondly, the acid combines chemically with the collagen in much the same way as alkali does. Thus the acidity of the pelt liquor does not increase, until the two reactions are complete. Then the pH decreases until equilibrium is once again established between the pelt and pickle liquors. Mechanical action or tumbling is continued for about three hours to achieve this. The pelts can then be taken out, graded, drained and packed.

The pickling process is as critical as any other in the fellmongery and the composition of the pelt liquor on packing must be controlled to ensure safe preservation. If equilibrium has been established, the composition of the pelt liquor will be the same as the pickle liquor and this can be easily analysed for salt and acid content.

If you have followed your way through the steps involved in fellmongering, you will realise that most of the chemistry is essentially simple and well understood. However, the animal skin contains a large number of substances and addition of a simple chemical reagent can result in several reactions occurring, not all of which are desirable. On top of this, careless processing in one step may lead to problems in a subsequent step. Hence, each step must be carefully controlled to produce pelts of the highest quality possible.

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