



In Part 1, 'Practicalities of the soaking process', of this three part series (World Leather, November 2006), detailed guidelines for the successful soaking of bovine hides were presented. This covered the different requirements of fresh, salted and dried hides, with close focus on the use of the auxiliaries that can be applied in this first important stage of leather manufacture. On the basis of good soaking procedures, this second paper provides detailed information on the key aspects that underpin good practice within commercial unhairing/liming systems.

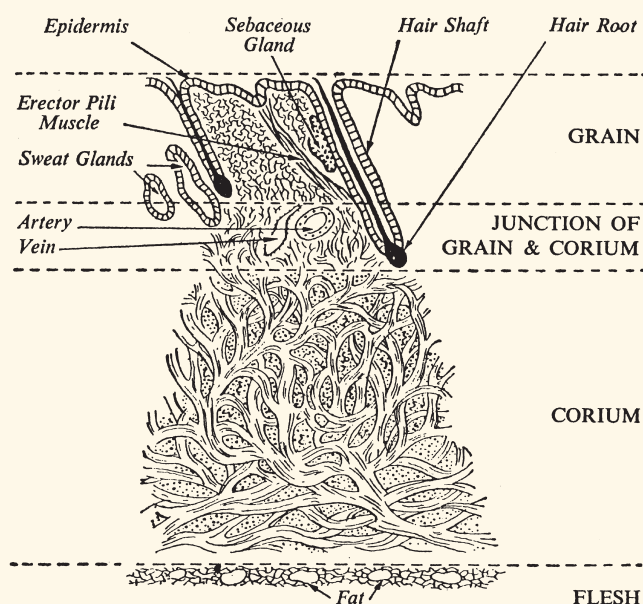
The soaking, unhairing and liming process

Part 2 of 3:

The practicalities of the unhairing/liming process

John Basford⁽¹⁾

Panel 1: Cross section of skin⁽²⁾



When hides and skins are clean and hydrated, the liming process can begin. The structure of the skin is important in understanding the principles of liming. When examined under a microscope, skin sections show three major layers as illustrated in *Panel 1*: the epidermis, the corium, and the flesh. The epidermis is very thin and is of no use to the tanner, and the flesh is cut away by machine before tannage. The remaining grain and corium is the structure that is made into leather.

Objectives of the liming process

The aim of liming is to remove the unwanted parts—the hair,

epidermis, and the interfibrillary proteins—and prepare the hides (*or skins*) for the removal of flesh and fatty tissue by fleshing machine. Interfibrillary proteins fill the voids within the fibre bundles, and these are removed during the opening-up of the fibre structure that occurs during liming. If the opening-up is poor, then the penetration of tanning materials and fatliquors will be prevented. This encourages the fibre bundles to stick together when dried. Without this separation the production of soft leathers cannot be achieved.

Liming processes are as diverse as the raw material itself and the technical people involved. There are options to use hair-save or hair-burn systems, to green flesh or lime flesh if the ➤



THE PRACTICALITIES OF THE UNHAIRING/LIMING PROCESS

equipment is available, or a combination of both. The vessels used can be as varied as those available in any particular tannery, including pits, paddles, drums large and small, mixers (*so called hide processors*), and stainless steel Y-compartment drums.

While the majority of tanners use lime and sodium sulfide for unhairing, the environmental impact of this system is very high. This has led to new chemicals being developed to minimise the effect of wastewater pollution, as well as solid waste disposal.

The unhairing and liming process

The alkaline unhairing process involves a chemical assault on the disulfide bond of the hair keratin, but this action is reliant on a number of factors:

- The pH. This must be high enough to swell the keratin and break the disulphide bond.
- The temperature used during processing.
- The amount of time allowed for the chemical reactions to take place.
- The degree of mechanical action applied. This is related to the equipment available.

Most tanners of hides work on a 48-hour process, from soaking to wet blue. Using lime alone it is impossible to achieve unhairing within the normal available time. Only if the pH is raised above pH13.0 coupled with process temperatures above 30°C is hair dissolution possible using lime alone, but these conditions are highly damaging to the hides, in particular the grain enamel.

This grain enamel, although a very thin structure, is the most expensive part of the skin, on a weight basis. Any damage to the enamel will devalue the leather produced. To achieve safe unhairing, a lower pH and temperature are essential, and this requires the addition of sodium sulfide or another sharpening agent to assist the breakdown of the disulfide bond.

As with soaking, it is difficult to directly assess problems caused during liming with faults in the finished leather. But we can say that poor liming can contribute to:

Loose empty leather with low tensile strength:

This is caused by processing too long or at too high a temperature. Excess quantities of lime, or running too long or too fast when swollen, can also cause this problem.

Firm/bony leather:

This is caused by insufficient opening-up during liming. This is due to poor penetration of chemicals or insufficient quantities used.

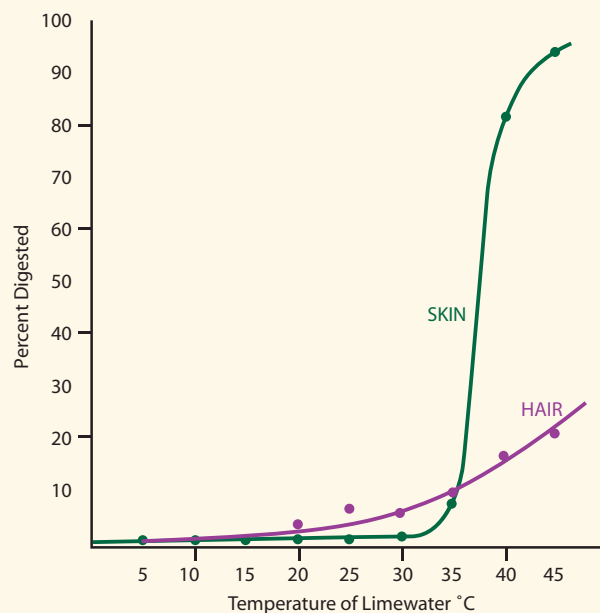
Drawn grain:

This can be caused by plumping too early in the process, so allowing the surface to swell more than the inside of the hide. When swelling takes place in the total thickness of the hide, a flatter and smoother grain surface occurs. Excessive sodium sulfide and caustic soda offers, insufficient removal of interfibrillary matter, and under soaking can also cause drawn grain.

Dirty grain:

This is mainly related to the poor removal of the epidermis and/or hair roots. Commonly called scud, this can also be caused by swelling too early in the process, by insufficient running times, or poor chemical penetration before swelling has started.

Panel 2: The breakdown of collagen and keratin at pH12.5 as a function of temperature⁽²⁾



This graph indicates the breakdown of collagen and hair in a lime-only solution. In practice temperatures must remain below 29°C to avoid damage to the grain, and unhairing agents added to increase the rate of hair breakdown.

Variables within the liming process

The process used for liming will depend on the type of raw material and its expected end-use. Considerable variations in leather characteristics can be achieved by varying this process.

There are many different types of leather, but as cattle hides are the main source of raw material, so the processing of cattle hides is central to this paper.

With cattle hides the hair is normally destroyed in the drum and disposed of in the liquid waste. Nevertheless, there are now processes available for hair recovery to minimise the solid matter in the effluent. These hair-save processes need special equipment for filtering the hair released from the hide while the lime liquor is being circulated, but otherwise conventional equipment is used. Even with cattle hides there are numerous liming variations available, allowing the tanner to adjust the end result to his own requirements.

THE LENGTH OF FLOAT

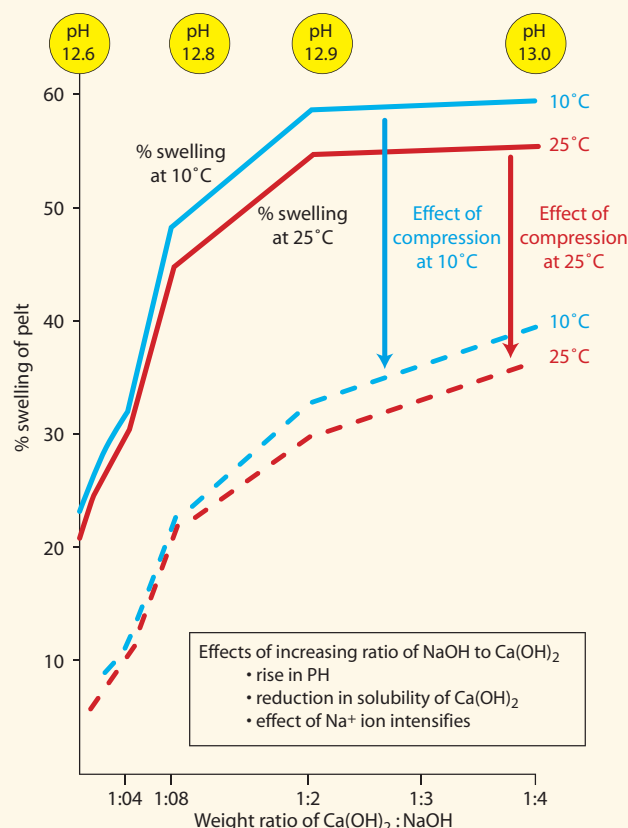
By using a drum or hide processor for liming, it is possible to adjust the amount of water used within the process. This means that the concentration of chemicals, and the degree of swelling, can be carefully controlled at all times.

By initially working in a low float—say 30-50%—it is possible to destroy the hair and epidermis without swelling. This system has been called 'Drum Painting'. However, after the full penetration of the alkali throughout the hide structure, swelling can be induced by increasing the float. The swelling, as a result of this technique, will be more regular throughout the substance and will result in reduced draw and growth wrinkles.

The amount of float used has a direct effect on the degree of mechanical action that is needed, and enables reduced running times during processing. ➤



Panel 3: The swelling of pelt due to increasing ratios of NaOH:Ca(OH)₂ at different temperatures⁽³⁾



The graph shows that:

- At the same pH, sodium hydroxide provides more swelling than lime-based swelling.
- The higher the pH the greater the swelling.
- The higher the temperature, the less the swelling.
- Within working practice, the greater the swelling, the firmer the final leather and the greater the risk of fibre distortion.

THE TEMPERATURE OF PROCESS

The temperature of processing must be carefully controlled.

In the highest range for liming—that is 28/30°C—the plumping effects of liquors containing lime are reduced. But at these temperatures there is a clear risk of grain damage. In experience, temperatures above 26°C are too dangerous for every day use, but the advantages of liming at 23/25°C are considerable.

What is more important is the consistency of the liming temperatures, particularly during the overnight automatic running period. If temperatures are allowed to drop overnight, a clear reduction in opening-up will result.

THE PROCESS TIME

When using wet salted, brined or fresh/chilled/iced hides, it is normal to work on a 20/22-hour system for soaking and liming. This allows unloading and reloading within the 24-hour cycle, thus giving regular and standardised daily production. Dry or dry salted hides demand longer times for soaking, so the 20/22 hour liming cycle can only be started after pre-soaking is complete.

It was common to give a further time in a white lime solution for certain types of leather, such as upholstery. This white-liming was generally performed after fleshing and before lime splitting. This practice has fallen out of favour due to time restraints, and more efficient liming processes. These provide an increased opening-up of the structure as required for producing modern soft leathers in the 20/22-hour system.

THE MECHANICAL ACTION

When the hides are in their swollen condition, excessive mechanical action can cause damage. Drum running speeds and running times, therefore, must be strictly controlled.

Traditionally, all liming drums were restricted to 1/2 rpm to minimise any damage. However, with drums of 3-metre diameter and above, this slow speed gives insufficient mixing of the chemicals. A faster speed is needed, so most large liming drums have two speeds, being 2 and 4 rpm. This allows the tanner to obtain the best mixing and mechanical action possible at each stage of the process.

A further advantage is provided by the possibility of alternate running/reverse cycles. This helps to open the bundle of hides in the middle of the load, so improving hide contact with the chemicals.

The addition of liquor recirculation to liming drums further helps the tanner, as the increased mixing obtained often allows a reduced chemical offer. Where this recirculation is available, it is possible to include filtering systems to remove hair from liquor suspension, so that hair-saving processes can be installed easily. This considerably reduces both the strength and solids content of the used liquors carried over into the effluent.

The chemical additives

The chemicals most commonly used can be divided into two groups:

Those that assist and accelerate the unhairing process:

This includes sodium sulfide, sodium hydrosulfide and amines such as dimethylamine, which can partially replace sodium sulfide. Thiols, such as the sodium salt of thioglycolic acid and mercaptoethanol, can be added to this group.

Those that actually complete the swelling and opening-up of the hide:

This comprises lime, being mostly used in its hydrated form, and caustic soda (sodium hydroxide).

SODIUM SULFIDE

Sodium sulfide will increase the pH due to hydroxyl ions produced on mixing with water, and will therefore cause an increase in swelling. The early use of sulfide in the liming process is not recommended. This is to avoid excess surface swelling—hence reduced chemical penetration—in the unhairing/liming process, and the possibility of a reduction in quality of the final leather.

SODIUM HYDROSULFIDE

Sodium hydrosulfide, at the start of hair removal, can rapidly penetrate to the hair roots, especially when assisted by wetting agents. Due to a moderately alkaline pH, this will take place without either grain swelling or hair removal, and this allows ➤



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for the possibility of an extended running time to ensure good penetration. This penetration is enhanced if enzymes have been used to accelerate the soaking process.

After this penetration, lime and sodium sulfide are added to increase the pH. This results in the hair roots being dissolved, and the release of the hair into the liquor. This leaves a clean, scud-free pelt.

It is noted that while providing a lower pH—so less swelling—sodium hydrosulfide will still increase the total alkalinity of the system.

AMINES

Historically, it was well known that the unhairing action of lime liquors could be increased by the addition of old liquors, that is, from the previous day's unhairing. The active ingredient that caused this improvement was identified as amines, being produced in this situation from the amino acids that were broken down in the highly alkaline liquors. Commercial production of amines for the leather industry concentrated on dimethylamine in its purest form, as it was found impure products had a pronounced disagreeable odour.

The use of dimethylamine in unhairing has been shown to minimise the plumping and destructive action on collagen, as well as speed up the unhairing. When used, it is normally added to the unhairing float in amounts of 1.0% to 1.5% on the hide weight.

While sodium hydrosulfide contains no caustic soda, some caustic soda is formed whenever sodium salt is added to a liquor containing lime. Hydrosulfide produces less alkalinity than sodium sulfide, but still enough to increase the plumping. This does not occur if amines are used, so the grain remains flat and the hides have fuller flanks.

Amines still offer the tanner the opportunity to reduce sulfide usage, but because of developments in hair-save processes their use has largely been replaced by thiols.

THIOLS

Because of cost, these products seldom completely replace sulfides for unhairing. They are more commonly used in combination, with the aim of reducing the more environmentally problematic sulfide component of effluents.

More importantly, thiols are very useful in hair-save processes where they are normally added before the hair immunisation stage. At this point they will penetrate the epidermis, and partly attack the pre-keratin of the hair root without affecting the keratin of the hair shaft. The reduced swelling obtained by using these auxiliaries is a further advantage.

LIME

Lime is only sparingly soluble in water but provides a reserve of alkalinity, maintaining or buffering the pH around 12.5. This pH is ideal for safe opening-up of the fibre bundles. In the past up to 5% of lime was often offered, but due to its limited solubility this is unnecessary and caused problems of removal during deliming, and in waste treatment. Today between 3.0-3.5% is normally used.

Lime slowly breaks down the soluble proteins between the collagen fibres, which would normally act as adhesives if not removed before tanning. This explains why the longer hides are left in lime containing liquors, the softer the resulting leather.

CAUSTIC SODA

Caustic soda, or sodium hydroxide, will increase the alkalinity and so accelerate the liming process. Caustic soda must be used in the liquid form, and creates heat when being dissolved. It is

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difficult to handle from a safety point of view, and its use is not common. When sodium sulfide is used in lime containing floats, hydroxyl ions are produced similarly to caustic soda, and this is normally sufficient to provide the swelling as required.

Liming control

To establish consistent liming on a day-to-day basis, checks need to be carried out at various process stages. By recording these findings, a picture can be built up of how constant the liming is. It should be remembered, however, that the only true test is how the liming has affected the finished leather.

UNHAIRING

When the process has commenced using a low float—30 to 50%—and before an increase as part of a controlled swelling, the hides must be inspected for hair and epidermis removal. If any of the epidermis is left on when the hides start to swell, then distortion of the grain layers will occur. This will cause drawn grain and/or looseness, which is difficult to remove in later processing.

At this inspection stage there is still little swelling, so an extra running time is possible to help correct any problems. When the hair and epidermis removal is satisfactory, the float can be increased by adding water, then run intermittently overnight. This is essential to ensure an even osmotic swelling and opening of the fibre structure.

PLUMPING

The amount of plumping and smoothness of the grain should be assessed before washing starts the following morning. While little can be done at this stage to increase or reduce the swelling, the comparison between batches produced on previous days is relevant when assessing any problems that might arise from a production load.

The amount of plumping or swelling during liming has been associated with the degree of opening-up being achieved. Opening-up covers both the osmotic swelling and the reduction in cohesion of collagen, and both result in increases in water uptake.

It is now accepted that swelling is not the cause of opening-up, but a side effect of this process. By using enzyme soaking aids and low swelling auxiliaries—such as thiols—opening of the fibre bundles can be obtained without excessive swelling.

ANALYSIS OF USED LIQUORS

The alkalinity of the waste liquor will give an indication of its plumping power, and the sulfide content will help check the accuracy of chemical additions. To avoid excess swelling—and so reduce drawn grain and neck wrinkles—the final liming should range between pH 12.3 - 12.8. If there is an excess of lime, there should be a buffering at pH 12.5. ⚙️

Legend

- 1) John Basford has worked in the tanning industry for more than 50 years, first as a tanner, but mostly as a technician for a chemical company. He has travelled and worked extensively in numerous parts of the world, and has substantial experience in the beamhouse on many different raw materials.
- 2) Image courtesy of 'Leather Technicians Handbook', J.H. Sharp house.
- 3) This information is based on extensive investigations performed between 1963 and 1967 by Herfeld and Associates, Lederinstitut Gerberschule Reutlingen, Germany. The graph in this form is presented in 'The role of bound and free water in the liming process', summarised in World Leather, November 2004.



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