

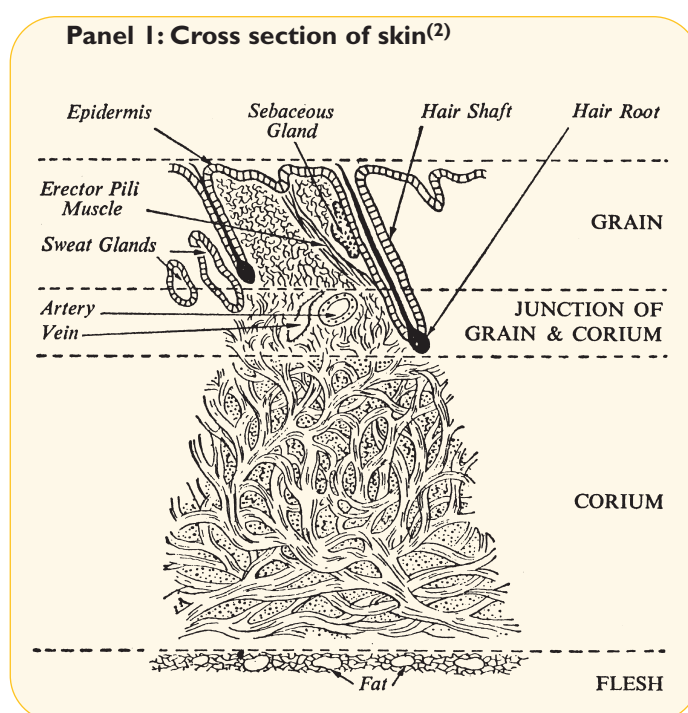


The soaking, unhairing and liming process

Part 1 of 3:

The practicalities of the soaking process

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The soaking, unhairing and liming processes, when complemented by deliming and bating, isolate the leather-making protein chemically, and modify the structure of the hides or skin physically. It is very difficult to assess the effectiveness of these processes, as problems encountered at the time of soaking and liming do not appear to relate directly to the problems found in finished leather. This is due to the dissimilarity of limed pelt to finished leather, and the enormous range of processes needed to convert one to the other.

Although vast improvements have been achieved in the areas of retanning, dyeing, fatliquoring and finishing since the 1990s, the chemical processes for soaking and liming still rely on the use of lime and sulfide—often in excess. And these processes are the most polluting within the tannery. Vast amounts of contaminated water and solid waste are produced, being at best expensive to treat and dispose of, and with an uncertain future.

Due to these environmental pressures, many in-depth studies have been made since the 1990s. The extensive research carried out by research associations, chemical manufacturers and tanners, has produced new ideas to assist and improve the conversion of hides and skins to pelts ready for tanning. This has changed the way this area of leather-making is perceived.

Raw materials

In most cases hides and skins are by-products of the meat industry. Traditionally, the curing processes were performed away from the abattoir for hygiene purposes. However, the delay between kill and cure caused by taking the hides off-site often creates quality problems.

At the point of slaughter the hides and skins are already contaminated with bacteria. Any delay between kill and cure allows rapid growth of these bacterial colonies. To reduce any damage the cure must be carried out as quickly as possible.

In controlled tests in New Zealand, it was found that sheepskins showed considerable bacterial growth just six hours after the kill. At this stage the stacked skins, which had not been cooled, had a temperature of 30°C. After twelve hours this temperature had increased to almost 40°C, due to bacterial activity, while bacterial growth was found throughout the skin substance. After twenty hours, hair-slip—indicating bacterial damage in the hair root—was found on all of the skins.

This problem is much worse on sheepskins than bovine hides due to the high bacteria levels found in the wool, even when the animal is alive. But these figures give an indication of the speed of bacterial growth. Clearly, it is very important that hides and



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skins are cooled as quickly as possible following the kill to keep this growth to a minimum. Curing should also be carried out as soon as is practically possible.

Salt preservation: Salt is traditionally used for preservation, but causes problems within both solid and liquid waste treatment and disposal. While salt is unlikely to disappear as a cure, as it is suited for the storage and trading of hides and skins, it is a fact that fresh, chilled and iced hides have become an accepted starting point for many tanneries.

Fresh hides: There are high amounts of bacteria contained in fresh hides, and these will multiply rapidly if they are not cooled quickly after the kill. But the big disadvantage of cooling is that the effects are very short-term. The reliance is upon the abattoir cooling the hides, and applying ice—and bactericide in many cases—before packing them into watertight containers (*needed to restrict any contaminated run-off during transport*). However, when this type of treatment is carried out correctly, it produces the best quality leather.

Dry and dry-salted hides and skins: In many countries, the raw material is different to the hides and skins found in Europe or the USA. Africa has a predominance of dry or dry-salted hides and skins, so more work must be done during soaking when using these raw materials to achieve satisfactory results.

Hides and skins that have been over-dried are difficult to wet back and require longer soak times. This in itself causes problems during processing, with increased bacterial action. In addition, quick drying in direct sunlight will cause the outer layers to become over-dried, often leaving the inner layers with enough trapped moisture for bacterial growth to continue. Although these hides only look over-dried on receipt, they often disintegrate during soaking.

Both quality and conservation play a large part in the characteristics of the finished leather. While the type and quality of the cure is outside the tanner's influence, the inspection and rejection of sub-standard material can identify good suppliers with whom to concentrate purchasing. The hides and skins can also be sorted for size to avoid the processing problems caused by a mix of different weight ranges. Although this operation becomes more difficult with fresh or iced hides, the time and effort spent with this will quickly pay for itself in increased quality.

Soaking

The problems stemming from this stage are often difficult to relate to the outcome in fully processed leathers. However, they can be set down as:

PROBLEMS ASSOCIATED WITH UNDER SOAKING

The following characteristics can be found:

- A hard handle to the leather. This is often incorrectly blamed on problems within the fatliquoring process.
- A badly drawn grain. This results from a greater swelling of the outer areas of the hide or skin within the liming process than the inner layers.
- Cracky grain. This is due to poor penetration and possible grain overload of subsequent chemicals.
- An empty flat leather.

PROBLEMS ASSOCIATED WITH OVER SOAKING

The following characteristics can be found:

- Empty, rag-like leather. Some types of raw material inherently have this problem, but it can be caused in hides and skins that might otherwise be satisfactory due to excessive splitting of the fibre structure. It can also be due to extreme bacterial damage caused by long warm soaks.
- So-called sueded grain. This has many causes, but results from tender grain, mainly caused by bacteria, both before curing or during soaking.
- Prominent veins. These are often increased by any large loss of substance during soaking. The vein walls are partly digested and collapse on subsequent machine pressure allowing the indentation to show on the grain side during finishing.
- Lack of substance. This can result from loss of hide substance by excessive soaking, or from insufficient opening-up during liming. These faults are almost impossible to correct during retannage.

The objectives of the soaking process

Soaking is the first process that takes place in the tannery. The objective is to reverse the curing process and prepare the hides and skins for the unhairing/liming process. The main aims are to:

- remove chemicals, including salt used for cure.
- re-hydrate the hides and skin.
- remove extraneous matter such as blood, dirt and dung.
- remove soluble interfibre proteins. These are mainly polysaccharides and disaccharides (*sugars*) that must be removed to allow penetration of the chemicals.

Variables within the soaking process

THE VOLUME OF WATER

The removal of salt, and in particular soluble proteins and other soluble matter, needs multiple changes of water. If water is restricted, there will be a rapid increase in soluble matter in the float. This inhibits the further diffusion of soluble materials from within the hides. If taken to the extreme, the non-removal of soluble protein will restrict the penetration of liming chemicals, and thus the degree of softness that can be achieved. Low floats also give a poorer distribution of chemicals, and restrict the physical opening-up and movement of the hides.

It is common to first use a dirt soak to reduce some of the soluble matter. Due to the heavy bacterial contamination on the hides, a biocide is frequently added to this bath. The temperature of the water can be adjusted to allow the hides to reach optimal temperature for soaking of 24–26°C. This is especially important for iced and chilled hides.

If preservation has been done by salting, it is common to desalt the hides in a rotating cage. This desalting machine will also remove any residual ice from iced hides, as well as loose dung.

THE TEMPERATURE OF PROCESSING

An increase in temperature will increase the rate of rehydration. However, It has been proved that soaking below 20°C will reduce the bacteria activity, whereas higher temperatures or extended soaking times will encourage this activity.



Collagen is also very sensitive to temperature, particularly in the presence of alkalines during and after liming. It has been found that grain damage starts to accelerate when the temperature reaches 60°C at pH 7.0, but at pH 12.0 this process starts at 45°C. At pH 13.0 the temperature only needs to be in the 30°C region before degradation becomes noticeable. A common fault in leather is so-called 'sueded grain', being the description of the surface of the grain when the the enamel is damaged. This type of damage can be caused by temperatures as low as 30°C during liming and deliming. It must be remembered that the solubility of collagen also increases with temperature. At 10°C solubility is only 2% but at 30°C this increases to 10%. It can be seen that the temperature of soaking, liming, and washing must be strictly controlled in order that losses in substance of the final leather are minimised.

In practice the temperature employed in soaking is between 25/26°C. However, for extended soaking, such as is needed for dry hides, the temperature is normally reduced to 20-22°C.

THE TIME OF SOAKING

Extra time given to soaking will minimise the use of soaking assists, but has several obvious disadvantages:

- The production is reduced.
- Increased bacterial levels may cause damage.
- The cleaning is poor as, unless the float is changed, eventually the dirt in the liquor will equal the dirt in the hide.

THE MECHANICAL ACTION

Increased mechanical action will improve the rehydration rate, but friction can also increase the temperature and so assist bacterial growth. Excessive mechanical action before the hides are fully softened, can also cause fibre damage due to over-flexing, and is often the cause of loose leather.

There are a number of factors that influence the mechanical action other than running times. Drum speeds, float levels and load levels, the use of pegs or shelves within drums, and the vessel type. Vessels used for soaking in place of traditional pits range from paddles, drums, mixers, and Y-type vessels. All of these vessels have different mechanical actions, and care is needed when introducing a new process to ensure the speed of running and float levels are suitable.

The chemical additives

Chemicals that are commonly used during soaking include:

BIOCIDES

As soaking returns moisture to the hide it releases soluble protein, and thus additional nutrient is made available for the proteolytic bacteria. This bacterial growth often results in hide damage. Accordingly, it is common practice to use biocides in the soaking process to protect the hides. Any damage already done will not be reversed, but the addition of biocides will prevent further damage.

With a generally poor standard of cure, the use of biocides is essential. As it is with the longer soaking time associated with dry and dry-salted raw material. Simple economics necessitates the tanner to do all that is possible to maximise the leather-making substance.

By coupling the biocide with a strong emulsifier in the soaking bath, most bacteria that cause problems can be eliminated. If the

emulsifiers in this soaking auxiliary are selected and blended carefully the biocide will quickly penetrate to the hair follicle, being the main problem area.

The choice of biocide itself is very important, as soaking enzymes are now widely used to minimise soaking time. Any biocide used must, therefore, not interfere with subsequent enzymatic treatment. In the case of fresh, chilled and iced hides and skins, it should be possible to use both chemicals in the same bath.

Environmental problems associated with salt, the subsequent reduced charges arising from salting, and reduced lead times, has increased the use of fresh hides and skins. Where fresh hides and skins are being processed, the use of biocides during soak becomes essential.

Many of the commercial products available have been developed for this purpose. This development has been in response to problems that customers have experienced due to delayed receipt of fresh hides into the tannery.

NON-IONIC WETTING AGENTS

These assist the rate of rehydration and cleaning. Their use begins the emulsification of the natural fats in the hide, although the amount of non-ionic wetting agents needed to fully emulsify the entire natural fat in the hides would make its use impractical.

Excessive use of these products can cause problems later in processing. In this event, the amount of grease removed from the hide makes the consequent emulsion unstable. This unstable mixture is deposited on the hair and surface of the hide or skin, and cannot be discharged with the soak liquors. Subsequently, the dispersion and penetration of unhairing/liming chemicals is restricted by this surface coating of partly emulsified fat. In this situation, increases in the running time and chemicals are needed before hair removal is complete. Generally, better results are obtained when the amount of wetting agent/emulsifier is kept to the minimum during soaking, with the removal of the natural fat concerned during the deliming and bating process when the float temperature is more controlled.

ALKALIS

Alkalis increase the pH of the float and cause the hide to swell and take up more water, thus improving the rate of rehydration. Sodium carbonate, sodium hydroxide, and sodium sulfide are all used extensively for this purpose.

Excessive swelling, however, must be avoided as this can trap the hair roots, causing problems with unhairing and the subsequent grain cleanliness. It is common to aim for a pH 9.5 - 10.0 in the float, ensuring this pH is through the hide or skin substance by the end of the soak. The increased pH will also minimise the pH jump when lime is added during the following unhairing/liming process.

ENZYMES

The use of enzyme soaking agents is almost the norm. These products are biological catalysts, and are used to accelerate the soaking process. They are widely used to reduce soaking times, as part of achieving soaking and liming in a maximum of 22 hours.

Enzymes work by partially hydrolysing the fatty substances at the hair root, so assisting the penetration of the unhairing/liming chemicals. These selective enzymes will not break down the soluble proteins, as they cannot degrade the side chains. However, they do help by degrading the albumins and ►



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globulins, so making them easier to remove.

Similar to bacteria, enzymes penetrate mainly from the flesh side, as the epidermis acts as a barrier. And this penetration can be slowed by natural grease in the hide. For this reason, many enzyme products are marketed combined with efficient fat dispersants. This ensures quicker distribution of the active substance through the hide or skin.

Initially, there was considerable resistance to the use of enzymes for soaking as, when biocides were not used, increased grain damage was common. But experience gained from many different countries shows clear advantages when using an enzyme assisted soaking. As long as the raw material is pre-treated with a compatible biocide, the use of enzymes will not increase any bacterial damage that has already occurred. Naturally, it should be recognised that care must be taken when working with raw material with high bacterial levels. In these situations, when an enzyme product is used, the use of a compatible biocide is indispensable.

This type of enzyme product is at its most active in the range of pH 9.5 to 10.0. In combination with an alkali such as soda ash (*sodium carbonate*), it is proven to give a vastly superior result when compared with a non-enzyme soak.

The use of an enzyme, in combination with biocide and non-ionic wetting agents, will improve the removal of the interfibrillary material and partly emulsify the natural fat during soaking. The more thorough opening-up achieved with soaking enzymes not only allows the tanner to reduce soaking time, but also reduces the liming time because of the faster penetration of chemicals. In addition, there are advantages in reduced chemical use, as well as a smoother and cleaner grain. Area gains are also possible, with area increases of up to 3% not uncommon.

The role of mechanical operations

Mechanical operations also affect the rate of soaking

THE FLESHING OPERATION

It is a considerable advantage if the hides and skins can be pre-fleshed during the soaking process. If they are fleshed when they still have a certain firmness, a better result is obtained. If this operation is left until soaking is complete it will have a limited effect, as the hides or skins will be too flaccid for good flesh removal.

When using wet-salted hides, this green fleshing is often done after only 60 to 90 minutes of time in pre-soak. If this is performed the day before they are put into processing for the main soak and unhairing/liming, the use of a biocide will ensure that bacterial activity is kept under control.

The effect of green fleshing goes further than just removing any flesh and fat tissue. It can be considered more of a breaking operation as it also opens up the hide structure. This subsequently allows better penetration of chemicals thus producing a much more uniform result. It is then normally followed by a further fleshing after liming.

The problem when processing salted or dried hides and skins is that the weights are really guess weights. The moisture content is never determined, and that this can vary considerably according to the weather and length of storage. Green fleshing and processing on a known fleshed weight is the basis of a more regular result.

THE SOAKING VESSEL

In practice soaking can be carried out in any available vessel. On wet-salted raw material drums or paddles are usual, with unhairing/liming normally carried out in the same vessel after

Panel 2

Problems associated with fresh hides

It has been suggested that soaking aids are not really relevant when using raw materials direct from the abattoir. Experience, however, has shown that fresh raw material has different problems to salted hides, and these need to be addressed.

During salting, water is removed from the hide due to the dehydrating action of the salt, but other interfibrillary matter is also removed with this water. These components comprise unstructured proteins that fill the spaces between the collagen fibres and the lack of removal can hinder the production of soft leathers.

Natural grease presents another problem when processing fresh hides, as this is normally partially broken down during salting and storage, making it easier to remove during beamhouse operations. With fresh hides this retained grease slows the chemical distribution and penetration, restricting the opening up of the collagen structure, and causing over-swelling of the grain. This causes a distortion at the junction of the grain and corium, and hence drawn grain.

soaking is complete.

For dry and dry-salted raw material a static soak is needed if damage is to be avoided. This is normally carried out in a pit, but drums or paddles can be used.

There are other factors which dictate which vessel is to be used, such as hair or wool length. Long hair or wool will tend to matt together in a drum giving problems of penetration later in the processing; this type of raw material is, therefore, mainly processed in paddles or Y-compartmental vessels.

Soaking control

An assessment of the soak should be made and controlled each day. This includes:

- The condition of the soaked hides and skins in terms of the softness and cleanliness: the tightness of hair or wool is essential. Even the best processes will give varying results on different raw stock. Extra running or generally longer soaking must be given if thought necessary. It is better to delay the start of unhairing/liming rather than produce an inferior quality because of an insufficient soak.
- The measurement of salt concentration after soaking can also be used for control purposes. This is normally taken as a Baume reading. It is important as salt can be carried over from soaking and this can affect the level of swelling in liming. In the case of a high concentration, a further wash must be given. Controlling the salt concentration to a maximum of 2% in the liming process will enable regular swelling results. 🌐

Legend

- 1) John Basford has worked in the tanning industry for more than 50 years, firstly as a tanner, but mostly as a technician for a chemical company. He has travelled and worked extensively in numerous areas of the world, and has substantial experience in the beamhouse, working on many different raw materials.
- 2) Image courtesy 'Leather Technicians Handbook', J.H.Sharphouse.