

Soaking of bovine hides and its control in the tannery

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The control of soaking of hides in tanneries has had a slow enhancement over the years after trial and error, supported by the expertise of tannery technicians and chemical companies with the aim of consistently achieving better-quality leather. During the last three decades, researchers from several institutes have, by means of sophisticated equipment, collaborated in the improvement of the knowledge of what goes on inside the skin of mammals and which substances need to be eliminated in order to perform a complete and better tanning process. The issue has been how to take these findings onto the factory floor of the tanneries. In this paper, a simple method to follow the evolution and control of the soaking of raw hides with the depletion of non-collagenous materials within the hides is presented.

1. Introduction

It is generally accepted that the soaking of hides is one of the crucial steps in leather making.

Soaking is defined as the process of treating hides or skins with water, sometimes with the addition of an assistant or disinfectant, to cleanse them, remove salt and other soluble matter and to rehydrate and soften them⁽¹⁾.

Observing the soaking formulations of different tanneries, it can be seen that there are lots of chemical products involved, different floats, running times, temperatures and different processing vessels. All in order to obtain a soaked hide that can bear the rest of the tanning process.

Some of the problems that leather technicians face are: when can it be defined that the soaking process is over, when has enough extraction of organic and inorganic soluble matters been achieved, and at what point will the amount of these remaining substances in the hides not interfere with the subsequent steps of tanning?

The interference of these remaining substances in the hide will show in different ways on leather. Some of the basic faults that a defective soaking can produce are: limed or tanned hides showing drawn grain, pronounced growth wrinkles, poor grain, poor handle, scud (stains of remaining epidermis), poor or uneven softness (head and neck stiffer than butts), difficulties in reaching shrinkage temperature in chrome tanned leather and poor physical properties.

A non-optimised soaking, or errors or omissions made here, produce faults that cannot be corrected later; conversely, they may be accentuated and can even be erroneously assigned to other factors.

That is why an optimum soaking is the foundation of beamhouse processes and thus, of leather making.

Among the variety of soluble substances that must be eliminated from raw hides, there are non-collagenous

components existing freely in the interfibrillary spaces, namely:

- Blood in fresh hides or its residues, plasma proteins, albumins and globulins.
- Inorganic salts, sodium chloride from salted hides being the most important.
- Soluble organic matter^(2,3,4,12):
 - Polysaccharides, called glycosaminoglycans (GAGs), with the most important being hyaluronic acid (HA)
 - Proteoglycans, the most important being dermatan sulfate proteoglycan (DS)

In the living animal, these substances control the viscosity of extra cellular spaces of skins, flexibility, plumpness and the passage of substances from cell to cell.

1.1 Hyaluronic acid

Although hyaluronic acid (HA) is a minor component of hides, about 0.2 % w/w collagen content (0.22 neck, 0.17 butt and 0.33 belly)⁽⁴⁾, it is a highly viscous liquid with high molecular weight, occupying a large volume in the interfibrillary spaces of collagen fibres but not bound to collagen, rendering a non-porous hide.

"This gel-like substance, until removed, inhibits the elimination of other non-collagen proteins and slows down the opening up process, one of the main objectives of the beamhouse."⁽⁵⁾

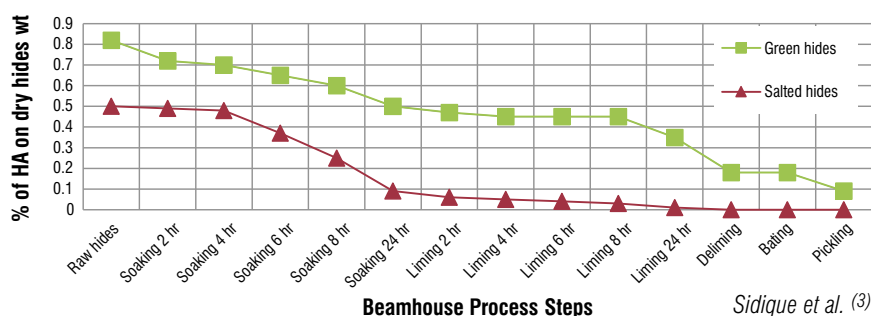
In addition, if HA is not completely removed during soaking and liming, not only will it stick the collagen fibres together, but it may also interact with chromium which would make a difference in the chromium uptake. The result will be less fixation of chromium, variation in its distribution in the cross-sectional layers and low shrinkage temperature.⁽³⁾

Siddique *et al.*⁽³⁾ have measured the HA content in lab samples of fresh and salted hides along the tanning process from raw hides up to chrome tanning.

According to the authors, the tanning process was done individually, from both green and salted hides, following a conventional chrome tanning process. Chemical offer and process parameters were the same for each trial. The residual HA in hides after each beamhouse operation was analysed through bio-chemical analysis assisted by UV-visible spectrophotometry. *Figure 1* summarises this evolution.

1.1.1 Salted hides

These graphs show that the salt curing of fresh hides has the effect, among others, of decreasing the HA content by about 37% (from 0.8 to 0.5 approx.). The removal of this HA and other soluble matter takes place due to the dehydration

**Figure 1: Removal of hyaluronic acid**

effect of sodium chloride in fresh hides.

The highly ionised sodium chloride collapses part of the gel-like structure of HA in fresh hides allowing it to leave the pelt together with other soluble substances.

The elimination of water, salt and other products generates a loss of 18-20% weight by weight (w/w) fresh weight and a decrease of moisture up to about 45% w/w salted weight in properly salted hides.

Simultaneously to the loss of water, there is a sodium chloride increase of about 12-14% w/w salted weight.

1.1.2 Soaking of salted hides

The salt absorbed by the salted hides helps to continue the removal of HA during soaking. After 24 hours of soaking, only 10% of the original HA remains, as shown in the red triangle graph line.

With the soaking process chosen by Siddique (process is not detailed by the authors) there is a two-hour period of low extraction, steadily increasing later on.

Bear in mind that because of the presence of the semipermeable epidermis membrane both in salting as in soaking, the movement of water and products is done from the flesh side of hides; this fact gives the opportunity to emphasise the importance of fleshing green hides before both salting or soaking.

All in all, between salting and soaking, 90% of original HA is extracted.

In the following steps of unhairing and liming, the remaining 10% nearly disappears.

1.1.3 Soaking of fresh hides

When coming to fresh hides, the picture for soaking is different. Since there is not enough sodium chloride present, the collapsing of the gel structure of HA is not possible unless

salt and other soaking aids are used.

Conventional tanning processes generally imply the use of soaking aids, which is why the extraction of HA from fresh hides shows a slope in the green squares graph line, but less pronounced than that in salted hides.

After 24 hours' soaking the extraction reaches about 37%, matching the extraction of sodium chloride in the curing of fresh hides.

The use of different and new soaking aids, especially enzymes, temperature, pH and mechanical action speed up the extraction.

However, at the end of soaking, fresh hides show a higher content of HA than salted stock.

1.2 Dermatan sulfate proteoglycan

Dermatan sulfate (DS) is another minor component of hides, about 0.5% w/w collagen content weight (0.49 neck, 0.47 butt and 0.58 belly)⁽⁴⁾. It is also a cementing substance with high molecular weight but, contrary to HA, it is strongly bound to collagen fibrils. This condition is the most probable cause for the lack of removal of DS during soaking⁽⁴⁾.

DS is extensively removed from hides under alkaline conditions of sulfide unhairing and liming^(6,7). This progressive degradation of DS is related to the opening up of the fibres and the production of softer leather. Nevertheless, this opening up is difficult to get in the neck region because of the greater thickness of the necks but also because of the fibre structure of this region, in which the fibre bundles are surrounded by very pronounced sheaths of reticulin⁽⁴⁾.

After 18 hours of conventional liming there are still considerable amounts of DS in the hides. However, the removal of remaining and degraded DS can also continue during the depletion of the hides that accompanies deliming and

bating. Alkali-stable enzymes can be used to deepen and speed up DS removal.

In order to get all this information, researchers used specific analytical methods and sophisticated instrumental analysis.

1.3 Soaking control

According to the information above, it is interesting to notice that both HA and DS are useful indicators of the effectiveness of soaking and liming, respectively.

Under practical tannery conditions there are various methods to follow up the evolution of the removal of HA in hides and baths which are discussed below.

This is not the case of DS, since liming is associated with unhairing that produces a considerable number of by-products in the floats, generating a complex mixture, as a result of the degradation of hair and epidermis. At present, it is not easy to directly or indirectly determine the remaining DS in hides in the tannery.

2. Materials and methods

Regarding soaking, as it was in early times of leather processing, it can still be labelled as an equilibrium process.

There are three main methods to control the reaching of equilibrium of soaking:

- Weight increase of hides
- Baumé degrees or density of floats
- Refractive index of floats and internal fluids of hides.

2.1 Weight increase

The weight increase is a good method for doing trials or research in the laboratory since successive weighings must be performed with the same piece of hide, something very difficult to do in the tannery with full or half hides within drums.

2.2 Density of floats

The measurement of density or °Bé is a good and extensively used method used in tanneries, but it is an indirect measurement method and it has several disadvantages.

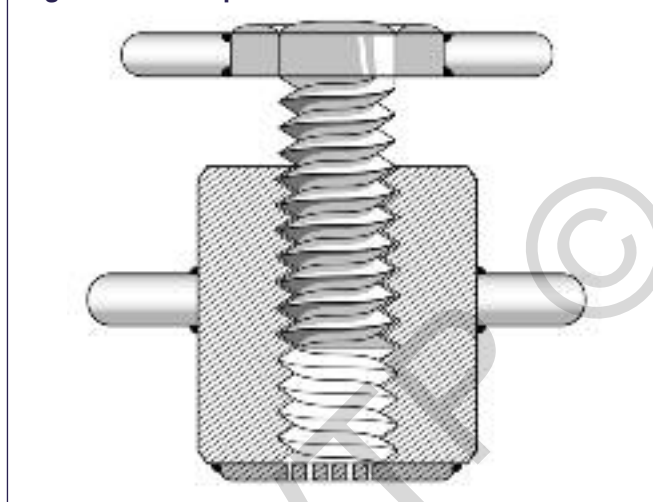
- The hydrometers are delicate instruments that must be kept clean to have reliable readings, as well as the graduated cylinders. Whilst this is not impossible to achieve, in general it is



Figure 2: Saccharimeter and display



Figure 3: Hide squeezer



very difficult to implement in the long term in the tanneries, unless the liquids to be measured are carried to the lab, if there is one.

- The hydrometers are very fragile, they break quite easily and in general tanneries have a high rate of replacement.
- They require a large sample.
- The hydrometers in °Bé are easier to read than densimeters but due to the small size of the scale, results

can easily be misread.

2.3 Refractive index

The measurement of refractive index by a hand-held refractometer or saccharimeter, *Figure 2*, facilitates a convenient and rapid measurement of concentration of liquids and solutions, blends, etc. They are robust, reliable and inexpensive optical instruments, used on the factory floor

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by a variety of industries:

- The display can be purchased in Brix degrees or specific gravity
- Only a few drops are required for a sample
- The reading of the Brix degrees or equivalents is simple and immediate
- Easy to clean and to keep clean

In 1975, Altiparmak, Hakimoglu and Sharphouse,⁽⁸⁾ stated that "Measurement of soluble matter in soak liquor is a useful check since it consists chiefly of salt and to much lesser extent proteins and dirt. It can be quickly measured by pocket sugar refractometer". Unfortunately, their proposal did not have many followers at the time.

2.3.1 Procedure for measuring the soaking bath

The procedure for control purposes is very simple: take just a few drops of the bath, put them in the prism and do the reading. If it fits the standard range, proceed to the next step, otherwise make the established corrections.

But this instrument is also very helpful to further study a standard soaking, how it works with different types of raw hides (weight grading, origin) and/or to test the effect of different or new soaking aids.

For these types of studies or investigations, the small amounts of liquid sample needed by the refractometer allows the technician to follow the evolution of soaking not only

through measuring soluble matter in the baths but also measuring the internal juices of the hides, by means of a hide squeezer as the one shown in *Figure 3*.

2.3.2 Procedure for measuring hides internal fluids

This squeezer is a homemade device that can be made with a nut and bolt of one inch, with a perforated bottom cap, and handles or hexagonal wrenches for screwing.

The hide samples taken from the thickest parts of hides must be thoroughly dried with absorbent paper. Eventually flesh them with a sharp knife of excessive conjunctive tissue and dry them again. Generate deep cross cuts on the flesh side taking care not to perforate the epidermis of the hide. Place the sample in the squeezer and squeeze until internal fluid starts to flow.

Place the first drops in the refractometer prism and take the first reading. Clean the prism. Increase the pressure of the squeezer and take a second reading and repeat until the maximum or steady readings have been achieved.

In a batch of hides, at least six hides must be sampled randomly, generally from the necks or cheeks. Proceed with the readings as above and take the average of readings as the mean value of internal fluids, at fixed times.

At the beginning of soaking the readings are high but they decrease as the soaking progresses until becoming steady when soaking reaches equilibrium.

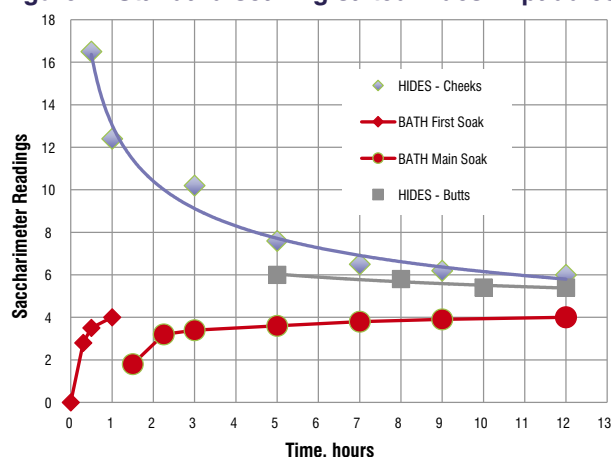
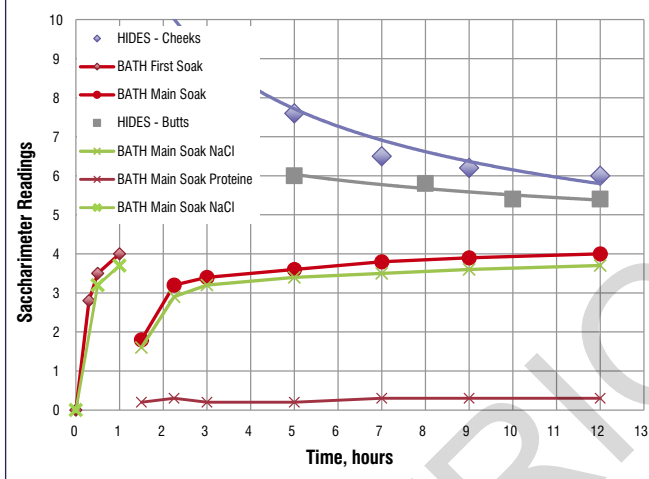
Generally, the readings made during the first hour or so from initiation of soaking, show that this stage is the most

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**Figure 4: Standard soaking salted hides in paddles****Figure 5: NaCl and soluble organic matter evolution, in the bath**

difficult one in terms of extraction of internal fluids due to the low moisture of hides. As soon as the hides start to hydrate, the procedure becomes easier.

The refractive index (RI) of internal fluids is composed by the RI of sodium chloride and the RI of the mixture of soluble proteins present in the hides. Up till now, it is not possible to separate both values in the tannery lab.

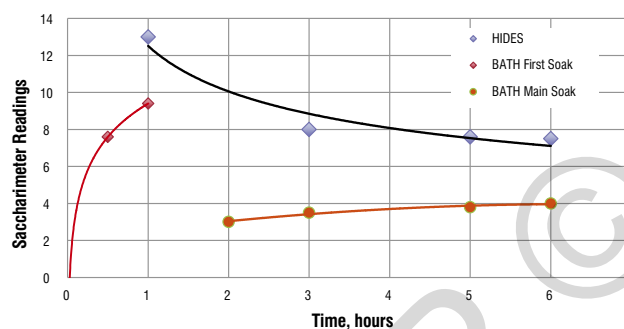
2.3.3 Procedure for complete monitoring of soaking

The procedure to monitor the evolution of the products that migrate from the skin to the bath is far simpler.

With just a few drops of the float the RI of the bath can be measured. The bath is composed chiefly of salt and to a much lesser extent by GAGs and proteins. With a larger sample, the concentration of sodium chloride, by means of the Mohr's method, can be measured in the tannery lab.

Knowing the concentration of NaCl in g/l the equivalent in Brix degrees can be calculated by means of a conversion table⁽⁹⁾. It is always advisable to previously calibrate the saccharimeter with a solution of NaCl of known concentration⁽¹⁰⁾. Bear in mind that for diluted solutions, Brix degrees are proportional to g/l.

The difference between the Brix reading of the bath and the Brix reading equivalent of NaCl calculated from the NaCl analysis, will account for the soluble proteins and GAGs.

Figure 6: Standard soaking salted hides in drum

3. Results

3.1 Monitoring of standard soaking

Figure 4 shows the monitoring of the standard soaking of a given tannery by means of a refractometer. The technicians wanted to study the evolution of soaking of a certain category of salted hides under their standard procedure but extending the soaking time from seven to 12 hours. Later, they evaluated the resulting crust leather against that under normal production with seven hours of soaking time.

The blue rhomboid points represent the evolution of the Brix readings of the internal fluids of cheeks. The grey square points represent the evolution of the fluids of the butts, being thinner in substance, can reach equilibrium faster in the bath. The red dots stand for the Brix readings of the bath main soak. The evolution of Brix readings for the pre-wash bath during the first hour are shown with the red rhomboid points. After draining it, the new bath starts with low readings, slowly increasing up to an asymptotic trend.

3.2 Monitoring the NaCl behaviour

The evolution of NaCl in the soaking bath was measured in the same trial following the procedure mentioned above.

Figure 5 is an enlarged view of Figure 4 for better appreciation of the readings. The green X points represent the evolution of NaCl in the bath found by the Mohr's method, expressed as Brix readings. The brown X points are the results of the difference between the readings of the bath—red dots minus the readings of NaCl green X points—accounting for the total of soluble organic matter transferred from the hides to the bath.

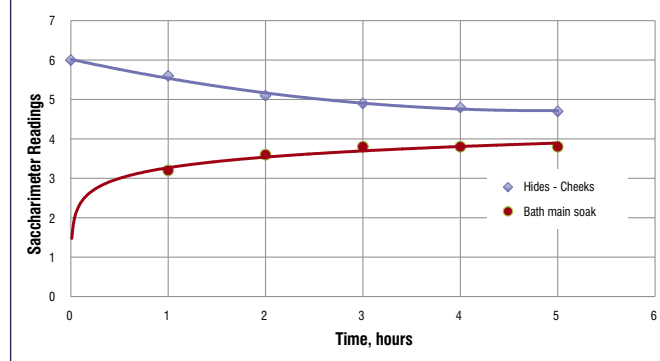
These values are fairly stable meaning that after a few hours no more transfer of organic matter from hides to bath took place, but only small amounts of NaCl were transferred.

As it can be seen in Figures 4 and 5, the normal soaking was preceded by a pre-wash that ended with a reading of 4° Brix. This wash was drained off and the main soak was done with the same percentage of water.

3.3 Monitoring salted hides in a drum

Figure 6 shows the results for soaking of salted hides in a drum. As can be seen, the effect of the drum in the one hour run of the first soak is much more pronounced than that for the paddle. In this case, in addition to the higher mechanical action of the drum, the float of the first wash was half the amount of that of the main soak. Both changes account for the high increase of extraction of solubles that allows shortening the time of the second soak and lower the consumption of water, compared to paddles.

Figure 7: Standard fresh hides soaking in paddles



3.4 Monitoring fresh hides in paddles

Figure 7 shows the results of soaking fresh hides in a paddle.

In general, the readings of internal fluids of fresh hides range around 6° Brix.

As mentioned before, it is more difficult to extract HA and other soluble organic matter from fresh hides than from salted ones. Therefore, a well-balanced mix of soaking aids such as sodium chloride, surfactants, enzymes, pH regulators, and others, are needed. The other variables to consider are mechanical action, temperature, etc.

4. Discussion and conclusions

"Measurement is the first step that leads to control and eventually to improvement."

H. James Harrington, american engineer, author and business consultant

When it comes to controlling the end of soaking, there are several subjective and indirect ways to do it:

- For many years and still valid today, the hydration of dry and salted hides, the measurement of salt concentration in soaking baths, and the cleanliness of the pelts and softness, are checked by feel only.
- More recently, the pH measurement of the baths was introduced with pH indicator paper or pH meters and the inspection of hides by means of Universal pH indicator solution added to the cross-sectional cut of hides.

This method was an important advance since it allowed viewing of the evolution of penetration of the bath products into the cross-section of hides.

4.1 Actual proposal of direct measurement on hides

During the 1980s, in the hands of BLC researchers⁽⁴⁾, the role of HA and GAGs as mentioned in the Introduction of this paper started to become known. Their studies were continued by several other researchers^(3,5), all of them using sophisticated and expensive analytical equipment, beyond the means of the average tannery.

The present work demonstrates that refractometers are instruments with which what happens inside hides with HA can be followed in an indirect way, measuring their internal fluids. These control instruments are sturdy, inexpensive, fast, reliable, easy to use and maintain. Handheld refractometers, as in the case of saccharimeters, are ideal control instruments to be used, not only for soaking but also for other processes.^(8,11)

The soaking of hides and skins is a crucial process in leather making, ensuring a standard outcome being of the utmost importance.

In rather clean fresh hides, the initial Brix readings of internal fluids will be similar among different batches and also to the final readings. Dirty fresh hides, carrying dung for instance, will offer more difficulties, but advantages can be taken from the more extended process to eliminate dung, to deplete the HA and finalise the soaking with readings in the hides lower than those on clean fresh hides. The Brix readings of fresh hides are ideal to see the effects of variables of the process that lead to an increase in the extraction of HA, improving and optimising it.

4.2 Proposal of control method for the soaking process

In addition to the control methods for soaking mentioned above, a complementary method with the introduction of refractometer readings for floats and hides is presented here.

This will ensure a standard, smooth and trouble-free production.

The routine control procedure consists of establishing for each type of raw hide used in the tannery and for any type of processing vessels:

- The checking of the Brix readings of the initial soaking bath, after the addition of all chemicals.
- Establishing the upper and lower limit values of saccharimeter readings for the final bath of the soaking process.
- Establishing the upper and lower limit values for hides at the end of each production batch, taking the average value of samples taken from six different hides in their thickest part.
- If over soaking is detected, identify the lot to be examined for the rest of the process, especially in the crust state.
- If under soaking is detected, extend the running time up to reaching the standard Brix values. (Please refer the list of possible consequences of over and under soaking below).

This procedure must be done with the same rigorousness as routine checks are performed at the end of each chrome tanning batch.

5. Appendix

The following list was partially extracted from the paper of Basford⁽¹³⁾, Part 1 of 3, from the series "The Soaking, Unhairing and Liming Process" and complemented with practical experience from the author.

5.1 Problems associated with under soaking

- Limed or tanned hides showing badly drawn grain and or pronounced growth wrinkles resulting from a greater swelling of the outer areas than the inner layers of the hide or skin during the liming process.
- Limed hides with scud (remains of epidermis, partially destroyed hair) in thickest parts of hides, proving lack of penetration of the soaking bath.
- Difficulties in reaching shrinkage temperature in chrome tanned leather.
- Poor penetration of subsequent chemicals, probably generating process delays.
- Lack of dye penetration, a fine white line just below the grain indicating also poor penetration of soaking bath.



- Brittle, cracky grain due to possible grain overload of chemicals.
- Crust leather with poor or uneven softness, heads and necks stiffer than butts and bellies. This is often incorrectly blamed on problems during the fatliquoring process.
- Low physical properties due to remains of HA that stick the fibres together and prevent them from aligning under physical stress.

5.2 Problems associated with over soaking

- Empty leather, prominent veins, lack of substance, looseness and even abraded (sueded) grain mainly associated with delays in curing or in beginning of processes, or long and warm soaks that promote the proliferation of bacteria causing loss of hide substance. These faults are almost impossible to correct during retanning. ☹

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