



Swelling within the leather manufacturing process

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Swelling is the increase of volume (*hence size*) of a material due to the absorption and/or retention of a solvent, by structural changes, or heat. The word implies a shift from the norm, or a comparison to a less distended state.

Mature collagen is insoluble in water, but like most polymers it is able to swell^[Legend 1]. The degree of swelling is determined by the extent of crosslinking, and is affected by both animal species and age.

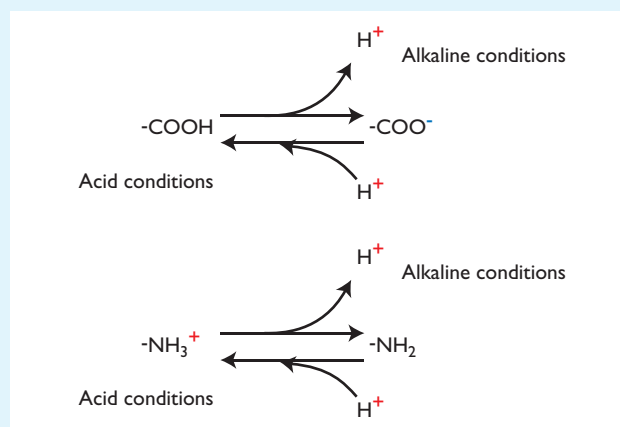
Swelling occurs in many more places than first expected in the manufacture of leather. The conventional references to swelling under alkaline and acid conditions in leather making should theoretically include the rehydration of hides and skins, and the wetting back of dried or part-dried leathers. Processes that impart filling, such as vegetable tannages and heavy retanning processes also bring about swelling of some form. However, the dramatic swelling which occurs during liming and are addressed in acid pickle are as a direct result of pH changes and collagen's ability to act as a polyelectrolyte^[Legend 2].

What causes swelling

There is no single cause for swelling, and in practice several effects can take place at the same time.

Panel 1: The addition and removal of hydrogen ions from amino and carboxyl groups

The addition of hydrogen ions (protonation), and their removal (deprotonation) to amino and carboxyl groups can be represented as follows:



DIFFUSION: A TWO-WAY PROCESS

Materials swell in the soaking and wetting back processes due to diffusion, being described as "the intermingling of particles as a result of their kinetic motion". During diffusion, there is an effort for events to balance out. In practice this means that areas of low moisture content would increase in moisture content, and vice versa.

But similarly, the ionic strength of the system seeks equilibrium. All salts, common salt or sodium chloride being the most common example, are ionic compounds composed of cations (*positively charged particles*) and anions (*negatively charged particles*). Just as water seeks equilibrium as part of the diffusion process, areas of low ionic strength seek an increase in ionic strength, and vice versa. This process is fully dependent upon charge, and is independent of the chemical nature of the salt.

In the soaking of salted hides, we therefore get the migration of water from the float into the hide, and salt out of the hide into the float in an attempt to 'balance' the concentrations of each. This is essentially a two-way process, but with the overall effect of the water moving into the hide and the salt moving out. If the volume of water moving in is greater than the volume of salt moving out, then the hide swells^[Legend 3].

OSMOSIS UNDER ALKALINE AND ACID CONDITIONS: A ONE-WAY PROCESS

Within the leather-making process, the skin structure acts as a semi-permeable membrane. This inhibits the movement of large molecules, but allows the passage of smaller molecules—such as water, salts, common acids and alkalis.

Osmosis is a selective diffusion process, where particles wish to move from areas of high concentration to those of low concentration and establish a 'balance', but where the movement in one direction is hindered.

Osmotic swelling under alkaline conditions

During liming at pH 12.5, collagen is well above its pI (*isoelectric point, or iep of pH 6 to 8*) and carries an overall negative (*anionic*) charge. The increase in pH causes a removal of hydrogen ions from amino and carboxyl groups as indicated in Panel 1.

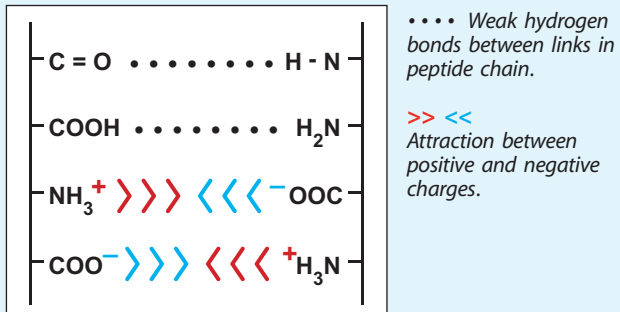
However, the negative ionic charge produced is attached to the collagen and therefore cannot migrate. This creates the presence of a high ionic strength and a comparatively low water concentration in a hide. ➤

This paper - "Swelling within the leather manufacturing process" - is a complete work. However, information that complements this important subject is provided by the paper "Protein and leather charge," J.Guthrie-Strachan and K.Flowers, British School of Leather Technology, The University of Northampton. This was published in World Leather December/January 2005/6, p19-23.

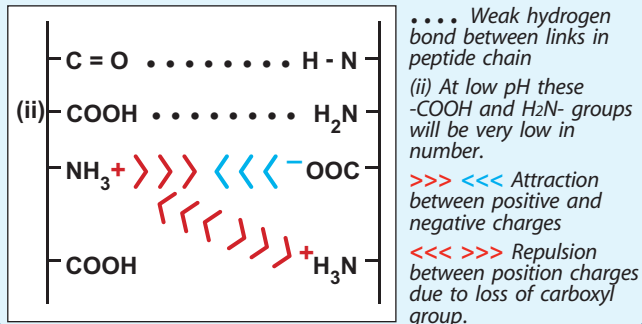


SWELLING WITHIN THE LEATHER MANUFACTURING PROCESS

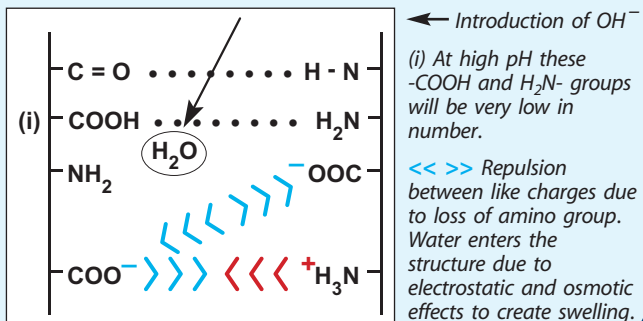
Panel 2: Charge at the pI (IEP)



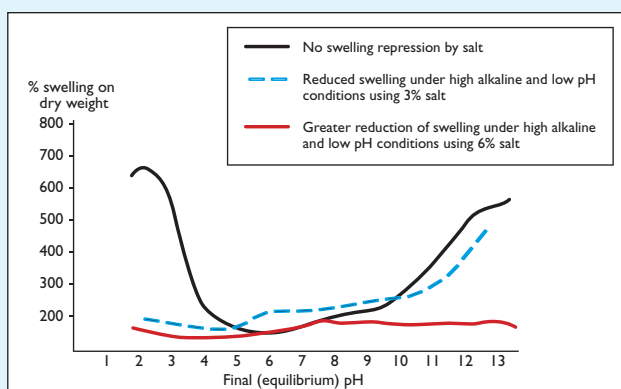
Panel 4: Charge after the addition of H⁺



Panel 3: Charge after introduction of OH⁻



Panel 5: Swelling of the skin as a function of pH and repression by addition of salt



If the lime float has a lower ionic strength and a higher water concentration than the hide, water will flow into the hide to balance out the concentration. However, this is a one-way process, as the ionic charge on the collagen is fixed and cannot migrate out. This results in the net flow of water into the hide, thus swelling occurs.

The differences in charge at the pI and at high pH as found within liming are indicated in *Panels 2 and 3*.

Osmotic swelling under acid conditions

Similar effects can be seen at pHs below the pI (*during pickling*) where collagen carries an overall positive charge.

During acid pickle at pH 3.5 - 3.0, collagen is well below its pI (*approximately pH 5*) and carries an overall positive (*cationic*) charge. The reduction in pH causes an addition of hydrogen ions to amino and carboxyl groups (see *Panel 1*). However, the positive ionic charge produced is attached to the collagen and therefore cannot migrate.

This creates a high ionic strength and a comparatively low water concentration in a hide. If the acid float has a lower ionic strength and a higher water concentration than the hide, water will flow into the hide to balance out the concentration. This is also a one-way process, as the ionic charge cannot migrate out. This results in the net flow of water into the hide, thus swelling occurs.

The charge at low pH as found within acid pickle are indicated in *Panel 4* and may be compared with the charge at pI and high pH as given in *Panels 2 and 3*.

THE SUPPRESSION OF OSMOTIC SWELLING

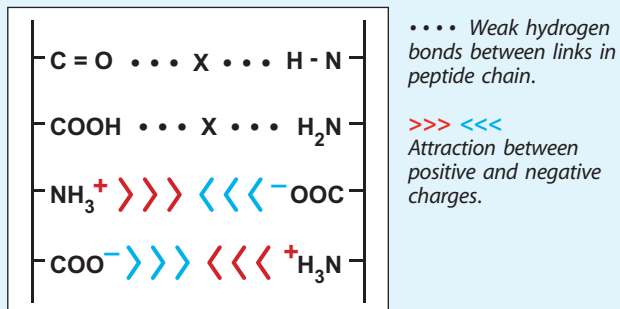
Both osmotic swelling effects and diffusion are at their lowest at the pI of collagen, that is approximately pH 7.0 for raw hides and skins, and pH 5-6 after conventional liming and deliming.

Under alkaline and acid conditions, swelling occurs as described previously, but this swelling can be reduced by the addition of common salt (*sodium chloride*) to the processing bath. This is because the ionic strength (*or ionic concentration*) of the float is increased in comparison to the conditions within the hide.

In effect the osmotic effects that require a flow of water into the hide as a result of a high or low pH can be diminished or even counter-balanced. The swelling of skin as a function of pH is shown within *Panel 5*. This also shows the effect of the addition of salt to a float as a 3% and 6% solution.

This shows that the 6% salt solution has a greater inhibition on osmotic swelling than a 3% solution. However, there is an increase in swelling at 3% concentration under neutral pH conditions, but this may be associated with lyotropic effects.

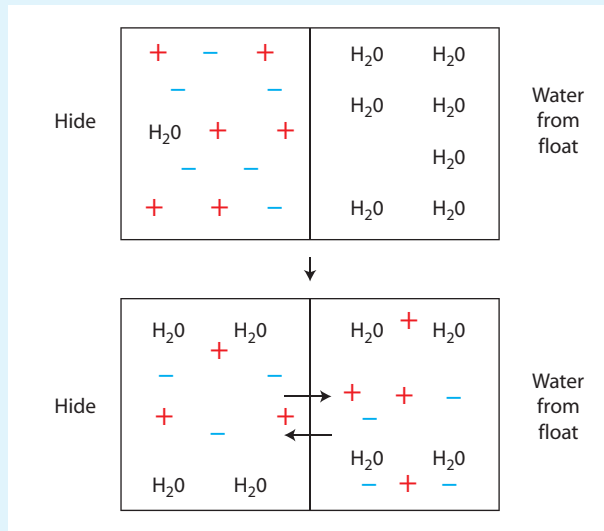
Panel 6: Lyotropic swelling at pI due to breaking of hydrogen bonds



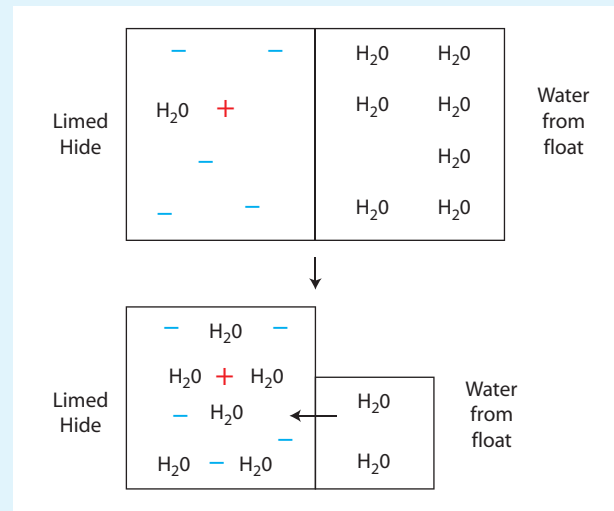


Panel 7: Summary of swelling within the leather manufacturing process

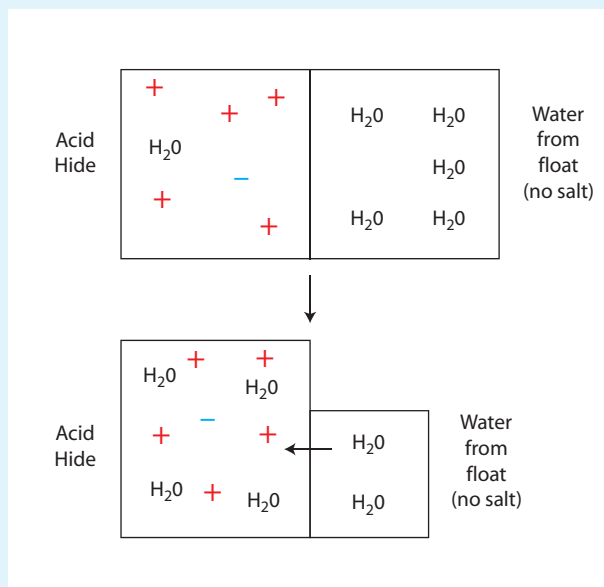
7/1: Diffusion in soaking



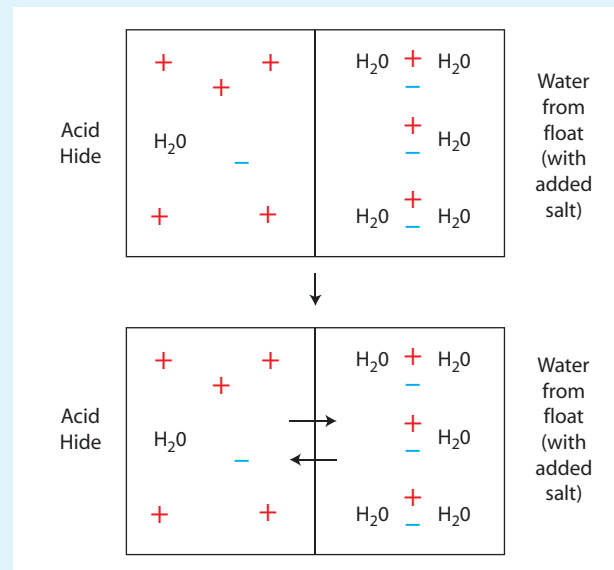
7/2: Osmosis under liming conditions.



7/3: Osmosis under acid-pickle conditions. Without salt.



7/4: Osmosis under acid-pickle conditions. With salt.



LYOTROPIC SWELLING: IONIC COMPOUND AND MOLECULAR EFFECTS

Lyotropic swelling is defined as the "uptake of water by, and swelling of, a protein, produced by neutral salts and due mainly to the interaction of ions and molecules with non-ionic bonds, probably crosslinks of the hydrogen bond type, leading to lessened cohesion⁽¹⁾".

This means that many neutral salts can block or disrupt attractive links within and between the collagen peptide chain. Although these bonds are weak, they are many in number and are significant in helping to retain the integrity of the

collagen/fibre structure. This effect is illustrated in *Panel 6*, which indicates a breaking of the hydrogen bonds, and subsequent swelling effects at pI. This can be compared directly with the hydrogen bonding indicated in *Panel 2*, but the same loss of cohesion would apply under both alkaline, neutral and acid conditions (*Panels 3 and 4*).

In theory diffusion and osmotic swelling is completely reversible, but this is not always the case for lyotropic swelling. Lyotropic swelling occurs at high ionic strengths of ionic compounds according to the Hofmeister series of anions and cations⁽²⁾ as shown:



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thiocyanate < iodide < bromide < nitrate < chloride < acetate < sulfate < citrate

lithium < sodium < potassium < calcium < strontium < barium < hydrogen ion < aluminium

Care should be taken when using large concentrations of ionic compounds that all combinations of cations and anions are as low as possible on the Hofmeister series. Sodium and chloride are both low on the Hofmeister series, but high sodium chloride concentrations used to prevent osmotic swelling can, at the same time, cause lyotropic swelling. The overall effect on a gross scale at high and low pH conditions can be such that swelling is suppressed.

It is important in leather-making practice to note that the lyotropic effects of calcium hydroxide are manageable and beneficial as a result of its low solubility in water. However, a high ionic concentration of calcium ion—that might result from the inclusion of calcium chloride into a process—may cause strong lyotropic breakdown. Sulfuric acid is also a very strong lyotropic agent.

How is swelling managed?

Swelling is a complex issue. Effects that encourage swelling can take place, while at the same time de-swelling effects can occur. In practice both osmotic and lyotropic swelling can occur at the same time. It is possible that lyotropic swelling could occur, but counterbalanced by osmotic effects. Many of these effects are theoretical and are not always practical in terms of leather manufacture^[Legend 4]. It is clear, however, that the control of swelling in leather manufacture is vital^[Legend 5].

It is normal practice to generate a slow and stepwise increase in pH during soaking to minimise the pH jump in the initial liming stages. Swelling can be encouraged by salt, where, after the initial contaminated soak liquor is drained, some salt is carried over to the main soak. A degree Baumé (°Bé) of 2 actually encourages swelling, although higher values will suppress osmotic swelling.

Lime swelling is highly desirable as it assists in the opening up of the fibre structure and separation of fibre bundles. Osmotic swelling, however, generates large strains (*osmotic pressure*) which can damage the skin structure if it is not managed properly. Rapid and uneven swelling during soaking and liming can generate powerful localised straining which is able to distort the structure, resulting in excessive growth in neck areas, drawn grain and area loss.

Historically, where processing was limited to high floats, such as found in pits and paddles, and basic drum systems, there were often many additions of alkali to control osmotic swelling. Salt was often added to minimise initial swelling effects, or used lime liquors were included in the bath. Part of the benefits of recycling these used unhairing/lime liquors was the increase in ionic concentration within the float, thus the inhibition of swelling.

Today, where drum systems can operate at selected float levels, the differences in concentration that can be managed between the float and the hide are used as part of swelling control. The osmotic swelling caused by high pH can be almost fully suppressed at the start of unhairing/liming by the high concentration of solubles in a low float. Subsequent dilution of this float in carefully managed steps can create differences in the ionic concentration, hence controlled movement of water into the hide that results in a carefully managed swelling.

It is noted that hides are extremely susceptible to mechanical damage when they are in a swollen state as the fibres are already stretched to their limits. Many animal types (*fish*) and immature animals (*calf skin*) possess a lower amount of crosslinked Type I collagen and are naturally more fragile during the liming operation. With some exotic species, not only is it necessary to minimise mechanical action, but the increase in float levels may take place in as many as four steps.

Conventionally, a °Bé of 6 (1°Bé is equivalent to a 1% sodium chloride concentration) is required to suppress acid swelling and ensure a flat and relaxed substrate for tanning. However, although not generally encouraged, a slightly lower °Bé may be used to allow superficial swelling for the retention of hair or wool. It has also been employed where low quality hides and skins are being used as the slight swelling helps to create a hard and tightened grain that would otherwise be loose and show a poor break. In this situation the tanned skins tend to show a glassy grain appearance, are firmer, and taken to excess by low pH, produces a weakening of the structure and lower tensile strength.

In vegetable tanning, salts are used in a conditioning process. In this situation a high salt concentration can be used to dewater or de-swell a hide as part of the preparation for tanning. This is to reduce an osmotic shift of water from the hide into the concentrated vegetable tanning bath during tanning. This minimises the dilution of the tannins, and thus helps to maintain the efficiency of the tanning process.

Once tanning is complete swelling is no longer considered dangerous. However, it should be recognised that swelling still occurs in the dyeing, retanning and fatliquoring process, and in the wetting of leathers after drying. It is also an important factor in the finishing of leathers where grain swelling is a well-known phenomenon. ☉

Legend

- 1) If we refer to polymers in general, it is common knowledge that water and other solvents that reduce or eliminate intermolecular forces in thermoplastic or lightly crosslinked thermoset polymers result in swelling. Crosslinking, on the other hand, reduces a polymer's ability to expand and absorb solvent. ➤
- 2) A polyelectrolyte is a polymer with many chemical groups on it, which may become positively or negatively charged.
- 3) It is theoretically possible for a material to swell in volume but reduce in mass.
- 4) It is noted that in addition to the effects discussed, heat swells collagen in a conventional manner up to a point when the protein becomes denatured and shrinking starts to occur (up to 15°C below T₃). Surfactants, solvents and molecules like urea are all able to cause swelling to some degree.
- 5) It is important to note that swelling of raw material/pelt/leather is conventionally measured as an increase in weight (due to the absorption of water). This is a gross measurement, which gives little information as to what is happening on a microscopic level.

References

- [1] http://www.iultcs.org/leather_terms/
- [2] K. Bienkiewicz, *Physical Chemistry of Leather Manufacture*, 1983, Robert E. Krieger Publishing Company, Malabar, USA.