



Back to Basics: A Framework for Leather Manufacture

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Dry, flat and extended leathers: Part 1

1. Temperature and moisture-related effects

2. Removal of water from the leather structure

Review of information

The information presented in *Essays 1 to 16* has covered wet processes and operations involved in the conversion of raw hides and skins into leather. There has been very little reference to the chemistry involved in this process, as a vast amount of information is available elsewhere.

The focus has been upon the way that the physical properties of hides and skins change within each stage of manufacture. These changes influence the way that forces are received, and set limits on the forces that can be applied to hides and skins at any time. This provides the boundaries for the safe management of mechanical forces within chemical processes and machine operations. It reveals the areas where chemical processes can play no part; variations that may be incorrectly attributed to machine setting or presentation; and the constantly changing properties of hides and skins as the process develops. The objective has been to reveal the framework that chemical and mechanical events operate within.

Within this series, the development of basic leather properties is viewed as taking place in three major stages:

Stage 1: The modification of the fibre structure, the release of unwanted components, and the removal of unwanted parts of this structure by slicing or cutting.

Stage 2: The amendment of the modified structure by products that are either chemically bonded or physically retained within the matrix.

Stage 3: The formation of a dry, flat substrate in pre-determined shape and dimensions.

The following *Essays* aim to cover events

Definition of terms

Elastic behaviour: When a force is applied, the material will stretch and store the applied energy. On release, the energy causes the material to return to the original form.

Plastic behaviour: When a force is applied, the material will stretch, but use the energy to deform permanently. On release, the material remains in its new configuration.

Strain: Distortion due to forces applied. Relates change in dimension to the original dimension, and for these purposes expressed as a percentage.

Stress: Force per unit area acting on a material and tending to cause strain.

Set: Percentage residual deformation after removal of force and after a period of recovery.

Stretch: this is a general term used when a material is extended. It does not specify extension in terms of uniformity, percentage or direction.

in the third stage, taken as the point in general manufacture when goods have been removed from the vessel after retanning, dyeing and fatliquoring.

Complexities associated with leather drying

The methods used in drying produce very different results. Many refinements within earlier processing—especially concerning the choices in retannage and softening/fatliquoring agents—and machine settings are driven by the required outcome from this stage.

But the drying process does not simply relate to the removal of water from leather. Considerable changes take place in terms of structural deformation, causing a shift in the aesthetic and physical properties. This deformation is dependent upon four elements:

- The temperature of the leather.
- The moisture content of the leather.
- The strain that is developed within the leather.
- The forces that are applied to the leather to develop this strain.

These elements interact to produce a very specific shift in effects, and in the broadest terms it is seen that:

- The temperature and moisture content of the leather determine the shift between elastic and plastic behaviour. This balance influences the strain that can be achieved in preparation, and retained in drying (*Presented in this Essay - Essay 17, Part 1*)
- The strain, stress and temperature determine the way that fibres adhere together as the moisture content of the leather is reduced during drying (*Presented in Essay 17, Part 2*)

These matters are significant. They affect the leather's behaviour through the preparation stages before drying, at the time of presentation to drying, during first-time drying, and then beyond to the crust or pre-finished state. (*Presented in Essay 17, Part 3*).

They can be the cause of major shifts in both physical and aesthetic properties. If used thoughtfully they can provide considerable advantage, and make the behaviour of the final leather more predictable.

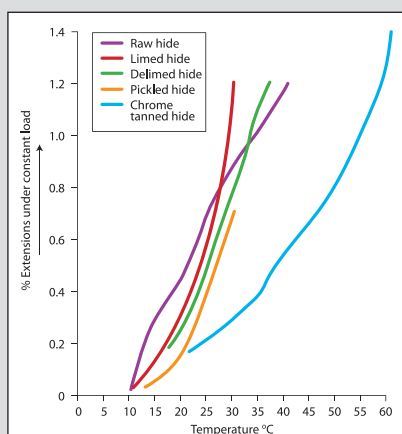
1. Temperature and moisture related effects

At this stage it is useful to reconsider information given in *Essay 5*. For the purpose of discussion within this section, two panels (*E5/1 and E5/2*) from *Essay 5* are re-presented as *Panels E17/1 and E17/2*.



Panel E17/1: This graph indicates that hides and skins under constant load stretch more easily as temperatures rise, and as the raw skin is modified in preparation for tanning. In the example, the samples are fully saturated, and tanning allows higher temperatures to be tolerated. There is a tendency for the samples to remain in the deformed state when temperatures used are higher.

Panel E17/1: Effects of temperature on the extension of a sample under constant load



Panel E17/2: This graph shows the effects of both temperature and moisture on the elastic/plastic behaviour of a raw skin. As the temperature rises there is a shift towards more plastic behaviour, which peaks at the points identified as Tg (the glass transition temperature) where deformation of the stressed sample is largely retained. When the moisture content of the sample is very low, this point of permanent deformation can be close to 100°C. However, if the moisture content is increased, this point can be at a much lower temperature.

Panel E17/3: This graph shows the behaviour of raw, chrome, and vegetable tanned samples at low moisture contents as the temperature rises. This shows that the shift from elastic to plastic behaviour occurs at a lower temperature due to the act of tanning.

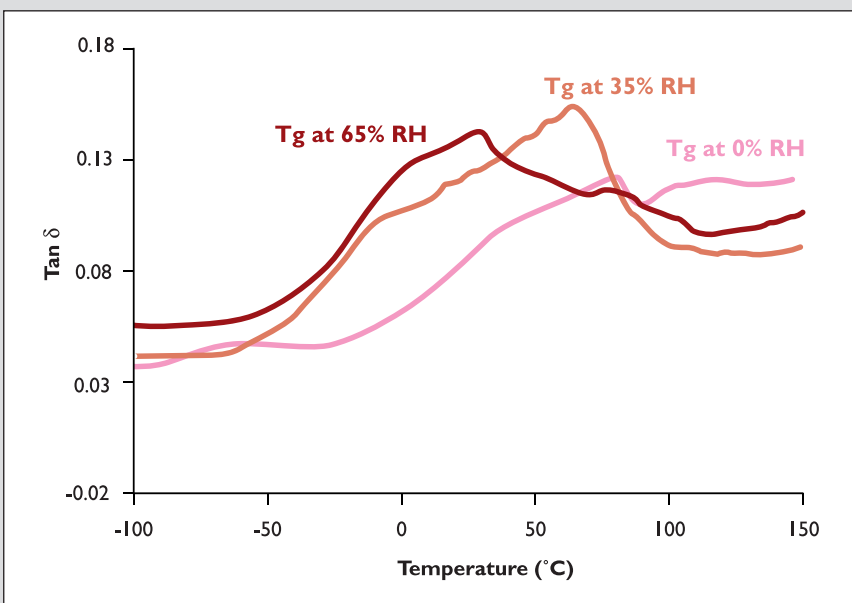
The process of tanning also enables the processed skin to withstand higher temperatures without damage to the collagen structure. It lowers the point of deformation to temperatures that can be readily managed in leather-making, but is dependent upon the type of tannage. As shown in the graph, vegetable tanned leathers can be deformed and maintain

a new configuration more easily than chrome tanned leathers.

Panel E17/1, 2 and 3: These details demonstrate the relationship between moisture content and temperature. Combined they enable shifts between elastic and plastic behaviour towards conditions where a stretched shape can be

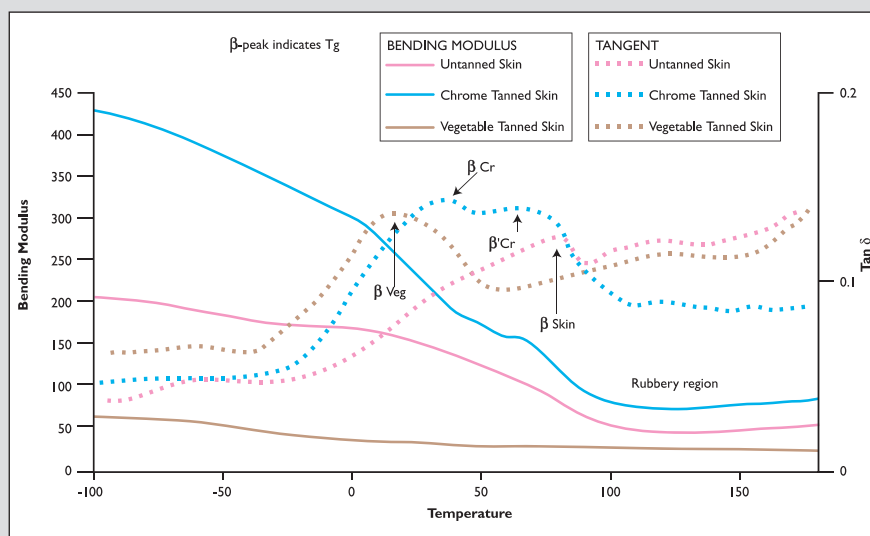
maintained. In practice this means that the tendency to revert to the natural rounded shape of the animal can be broken. Under conditions of elevated moisture and temperature, leather can be strained into a flat and extended configuration. If this shape is maintained, on return to normal temperatures and lower moisture contents, the new form will predominate, i.e. the ➤

Panel E17/2: Loss tangent, $\tan \delta$, as a function of temperature for acetone-dried skin samples pre-conditioned in a given relative humidity environment (0, 35, 65% RH) (See acknowledgements)



The shift from elastic to plastic behaviour can be measured, and is expressed mathematically as $\tan \delta$

Panel E17/3: Change in elastic/plastic behaviour as a function of temperature



The shift from elastic to plastic behaviour - expressed as $\tan \delta$ - as a function of temperature for untanned, chrome, and vegetable tanned skin preconditioned at 0% RH.



Panel E17/4: Migration and discolouration

There can be a considerable migration of substances other than water during leather drying. This can include neutral salts, raw oils, fats and fatliquor components, unfixed tannins and dyestuffs. The higher the temperature the faster this migration. This can cause problems with staining, uneven water absorbency across the grain surface, and changes in other physical properties. Some chemical products are subject to colour change by high drying temperatures. This should be taken into consideration in the selection of chemical products. Possibly the most extreme example where these effects are found is in the drying of vegetable tanned heavy leathers. Very long drying times and low temperatures are required to avoid migration of tanning products. In addition, these materials are photosensitive, so there must be an exclusion of light throughout the drying period.

leather has achieved set.

It also shows that the conditions required to make these changes are affected by tannage, and that different tannages produce different results. Accordingly, all materials that chemically combine with the structure—pre-tanning agents, retanning agents and dyestuffs—will further influence the outcome.

2. The removal of water from the leather structure

Water is squeezed from wet leather within the samm/setting operation. The more water removed by the samming component, the shorter the time required for drying by evaporation.^[Legend 1]

Over and above water physically squeezed from the fibre structure, the removal of water from leather is brought about by evaporation or vapourisation. The rate of evaporation is influenced by the nature of the products incorporated in tanning/retanning/softening processes, and the design of the drying equipment. Drying can be viewed as two phases:

1st-Phase evaporation: A considerable quantity of water is held within the structure on presentation to drying by evaporation, and the leather surface remains wet. Evaporation has a strong cooling effect, so the temperature of the leather is always lower than the temperature of the air used for drying, or the heated plate in contact with the piece.

Panel E17/5: Overview: the effects of variation in drying techniques

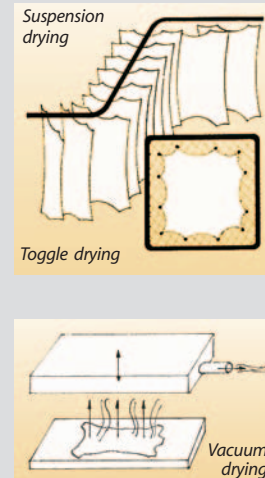
The variations stemming from different modes of drying are considerable. Within the conditions that can be best described as “good working practice”, the following gives an overview into the effects of the major drying techniques. Temperature, moisture content, strain and force as part of pretreatment and during the drying sequence have a considerable effect.

- Suspension drying allows shrinkage and provides the softest of results. A very tight break can be produced, but with a reduction in area, and much of the original rounded animal form can be retained.
- Toggling can cause a massive degree of strain and a flat form, especially if the tension is mechanically actuated. The greater the stress and the tension developed, the higher the temperature and the lower the final moisture content, the harder the leather.
- Vacuum drying enables a flat form to be developed on drying. The direct application of heat to the grain structure not only causes a permanence of grain set, but can also cause compression towards a hard and thin structure.

Vacuum drying can be used to part dry the leathers then be completed with stress-free airing off, or perhaps lightly toggle dried. It can be used on its own if drying temperatures are very low.

- Paste drying allows considerable extension and set. Even so, the quality is dependent upon good plate adhesion and release from the platten, and a paste-free grain surface.

The whole process from preparation to the end of first time drying requires close attention in earlier processing work. This applies in particular to the substance determined at shaving in relation to final leather thickness, and in the properties developed in retanning and fatliquoring processes. Substances change according to the techniques employed, and the strong migration effects of fatliquors must be addressed in both vacuum and paste drying. The more open-structured parts require filling and support from retanning agents, especially in paste drying, and if vacuum drying result in too low moisture contents.



The rate of drying is fully dependent upon the capacity of the drying equipment.

2nd-Phase evaporation: A point is reached where the capacity to remove the water vapour is greater than the rate of migration of the moisture from within the leather structure to the exposed surface. The previously wet surface begins to dry, and there is a considerable decrease in the rate of water removal from the leather. As surface evaporation diminishes, the temperature of the leather rises towards the temperature of the air or contact plate. There is no free moisture on the leather surface, and all of the physically-bound water has been removed.

This change from the wet to dry state does not happen uniformly across a piece of leather. It is governed by the density of the fibre structure, the location and hydrophobic nature of materials within the structure, gravity, and the effects from the preparation stages for drying. This

means that there is a period when the two phases occur at the same time across a piece of leather undergoing drying—easily recognised as wet and dry areas. There is always a variation in moisture content, but as more moisture is removed, there is greater uniformity both across and throughout the skin structure. 🌐

Legend

1. There are also advantages in the retention of strain, but these must be balanced against the problems of an over-compressed fibre structure. These matters are discussed in Essay 17 Part 2.

Acknowledgements

E17/1

Observations: Temperature related relaxation within liming and other wet processes: R P Daniels, pp 44-45, World Leather Aug/Sept 2004

E17/2 and E17/3

The glass transition temperature of leather and its implications to the leather industry: Sujee Jayapalina, pp4749, World Leather Aug/Sept 2004