



Yield, quality and physical properties of leather

PART 2 of 3: FACTORS WITHIN WET PROCESSES AND OPERATIONS

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In Part 1, published in World Leather, November 2008, yield-related issues were discussed including the accuracy of area measurement, the reliability of yield-related information, and observations on the way that value has often been lost during leather manufacture.

Part 2 continues with a review of the influence of temperature, pH, and mechanical effects during chemical processing and wet mechanical operations, and provides some quantification of effects.

Part 3 will be published in February/March 2009, and discusses the factors that affect yield and quality in drying and post-drying operations.

Over and above the quality and condition of purchased hides/skins, and both the chemical processes and machine operations applied, the following four items are seen as fundamental to achieve the best results in terms of yield and quality within wet processing.

Item 1) MINIMISING GROWTH AND DRAW

Apart from hair removal and the cleanness of the grain, it is very difficult to relate the condition of goods in the beamhouse with quality as finished leather.

A complete fibre rehydration and carefully controlled swelling in liming—sufficient to uniformly open the fibre structure, but insufficient to cause permanent distortion—is required. Before allowing swelling to commence, this is best managed by ensuring:

- A complete penetration of alkali throughout the skin section—especially throughout the dense fibre structure of growth lines in the neck areas.
- The epidermis can be easily scraped from the surface of the grain—particularly in the areas that are prone to drawn lines and fine wrinkling—so that grain-swelling is even and unrestricted.

In addition to the chemicals used in liming, a relatively low float during the alkali penetration phase inhibits any swelling. A subsequent addition of water to dilute the float then allows osmotic swelling to occur, so the degree of swelling is managed by controlling the float levels. The dense neck-growth structure is particularly slow to penetrate, but only if the alkali penetration is complete in these difficult parts—plus some time to enable equilibrium within the growth lines—can the swelling be as uniform as possible. This improves the relaxation in these areas, providing advantage in the final leathers in terms of reduced draw and growth in neck-parts.

The washing of limed leathers also needs close control. The addition of water alone will reduce the concentration of alkali at the surface of the hide or skin and cause secondary osmotic swelling, with the risks of enhanced growth and draw. This can be avoided by adding alkali (lime) within the washing sequence. The less the fibre distortion, then the flatter and more

relaxed the final leathers, with the potential to improve both grading and saleable area.

The deliming process is also very important as the resultant de-swelling provides the only opportunity to remove detritus from within the skin structure. Over and above the deliming techniques used, the process is normally taken as complete when there is 100% removal of alkali as shown via an indicator applied to the cut section. However, this is only an indication of pH, it is not a measure of residual waste materials deep within the hide. Additional processing time is needed for this waste to be released from deep within the structure, and allow full relaxation in growthy parts.

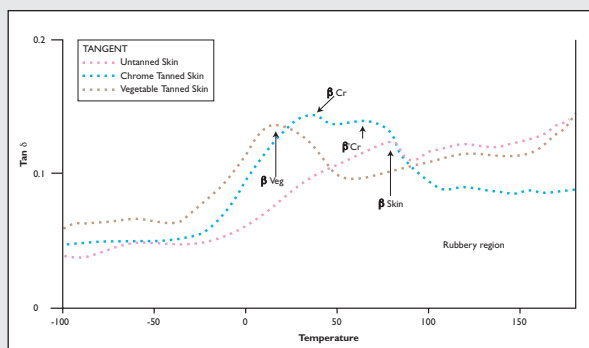
The controlled uptake of tanning agents is especially important to avoid conditions that would cause a contraction of the carefully relaxed hides/skins from beamhouse processing. Too rapid fixation causes grain coarsening, draw in the belly regions, and an accentuation of residual growth lines, and thus quality and area yields can fall dramatically. Similarly, the avoidance of astringent conditions throughout retannage is essential for the maintenance of potential yield gained by good practice in the manufacture of wet blue, wet white, vegetable or other tannages.

Item 2) THE ROLE OF TEMPERATURE WITHIN WET PROCESSING

Temperature and moisture have very significant effects on the physical behaviour of hides and skins throughout all processes and operations. As the temperature and moisture content increase, hides and skins become softer. In addition, there is a shift in the balance between elastic and plastic behaviour towards a more plastic state as set down in *Panel 3*.

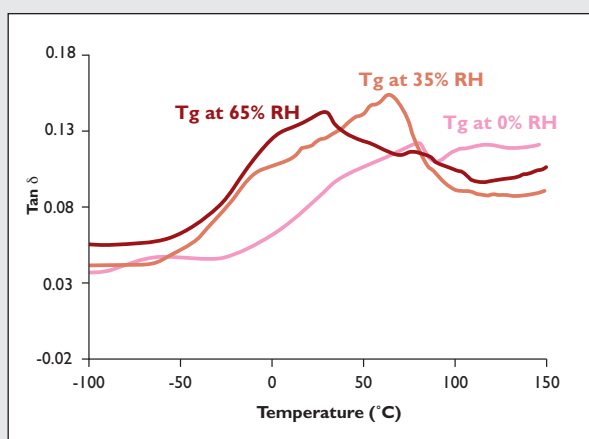
This is due to a reorientation of parts of the polypeptide backbone structure at molecular level as moisture contents and temperatures increase. Within wet processing—when goods are fully saturated—this means that an increase in temperature allows a hide/skin to be stretched more easily. This is shown in *Panel 4*, and, in addition, any extension has a tendency to be retained.

This has profound implications within machine operations, as machinery applies a strong stretching or setting action to wet leathers. These actions can be viewed as combined fleshing/setting, samm/setting, shaving/setting, with the setting component significantly increased by temperature rise.

**Panel 3:****Shifts between elastic and plastic behaviour of leather: the influence of temperature****Item 3/1**

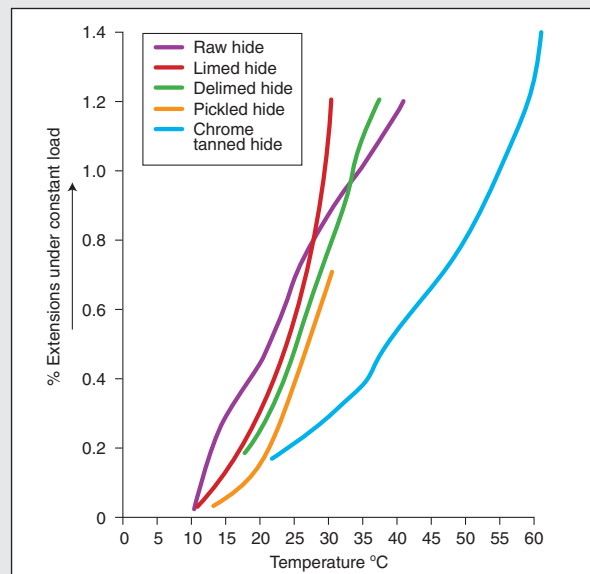
As the temperature of a polymer (collagen) increases, it softens, coupled with a shift from elastic to plastic behaviour. At a point known as the Glass Transition Temperature (T_g) the material may be shaped into a new configuration, with a retention of this new shape on return to normal conditions.

This shift from elastic to plastic behaviour can be measured using Dynamic Mechanical Thermal Analysis and expressed mathematically as Tangent δ . These shifts are shown in Item 3/1 as a function of temperature on samples conditioned at 0%. It is noted that different tannage reduce the T_g of raw skin to different values, and that these temperatures lay within the range of leather processing. It is also noted that the greater the moisture content, the lower the T_g as shown in Item 3/2.

Shifts between elastic and plastic behaviour of skin: the influence of moisture**Item 3/2**

In this figure the loss of tangent ($\tan \delta$) as a function of temperature for dried (acetone dried) skin samples is shown as influenced by moisture content. The higher the moisture content, the lower the T_g . These samples were conditioned in a given relative humidity environment (0, 34, 65% RH).

Credit: Figure from "The glass transition temperature of leather and its implications to the leather industry", Sujee Jeyapalina, World Leather, August/September 2004, pp47-49.

Panel 4: Effects of temperature on the extension of a sample processed from raw state to wet blue under constant load

The samples were taken from the same hide location at various stages of process.

Credit: Modified figure (E5/1) from "Back to Basics: A framework for leather manufacture", Essay No.5, R.Daniels and W.Landmann, World Leather August/September 2005, p44.

Panel 5:**Temperature: effects on mechanical action and chemical uptake**

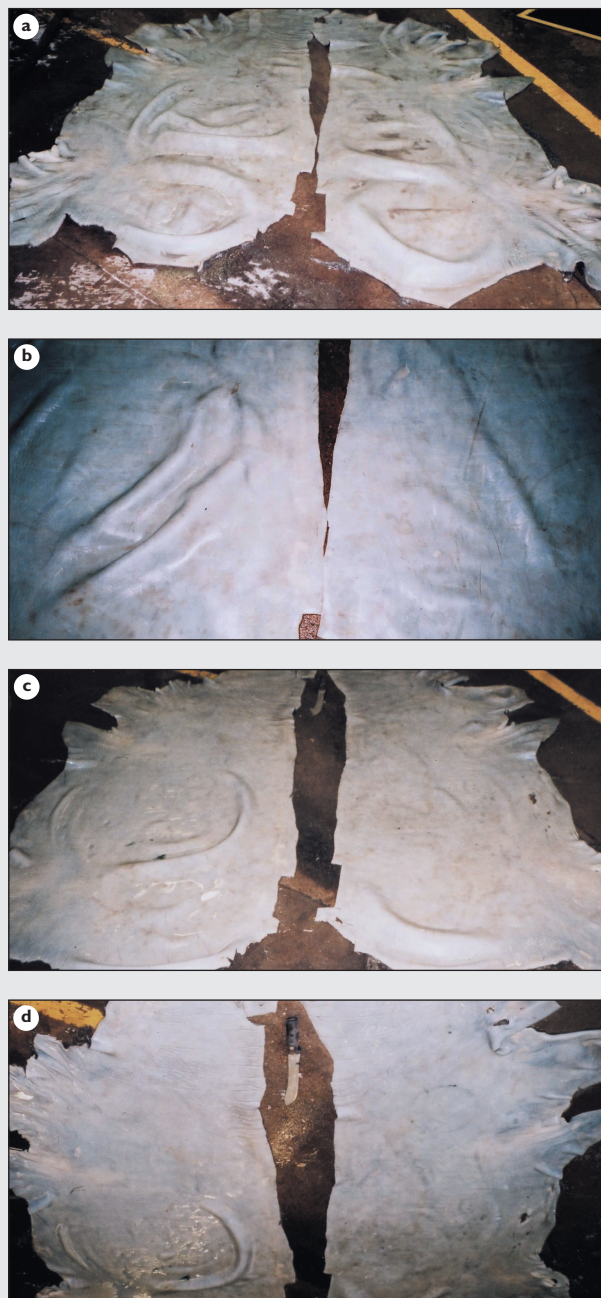
Temperature produces interesting effects in leather processing. Lower temperatures slow chemical reactions, and this favours deeper penetration before fixation. On the other hand, lower temperatures reduce the stretching-relaxation movement of goods in process, and this reduces the rate of penetration. When temperatures have fallen in tannage due to sudden and severe weather conditions, this has resulted in poor penetration before fixation: the centre parts have been undertanned, but with over-fixation of chrome on the grain. In addition, the size of molecular conglomerates and emulsions will also increase at lower temperatures, and in conjunction with reduced stretching-relaxation in chemical processing can lead to an increase in surface deposits.

The influence of lime splitting

Limed splitting is often stated as causing increases in area yields. However, white-liming often follows limed splitting, whereas it is not normal practice when lime splitting is omitted, and this should be taken into account. Also the thinner, more uniform substance and clean open flesh side will enable an easier deliming and release of waste products than when processing full substance hides. And during deliming/bating, pickle and tannage, if the same mechanical forces are applied via vessel rotation as would be applied to full substance, then a greater extension can be expected due to the lower split thickness.



Panel 6: The influence of temperature in the washing of lime hides



Photograph (a) shows a sided hide after liming, and (b) after washing the left side at 18°C, the right at 28°C. In these two photographs the sides were simply placed on the floor, whereas (c) and (d) shows the effects of manipulation while trying to flatten the pieces. Two batch washes of 300% each were used on the pieces, with the addition of 0.5% $\text{Ca}(\text{OH})_2$ to avoid osmotic effects.

In addition to a general relaxation and flattening as a result of the warmer wash there was a softening, and minimisation of growth in the neck parts and draw/wrinkling in the belly areas. These results do not show clearly as a record due to the translucency of the limed pieces.

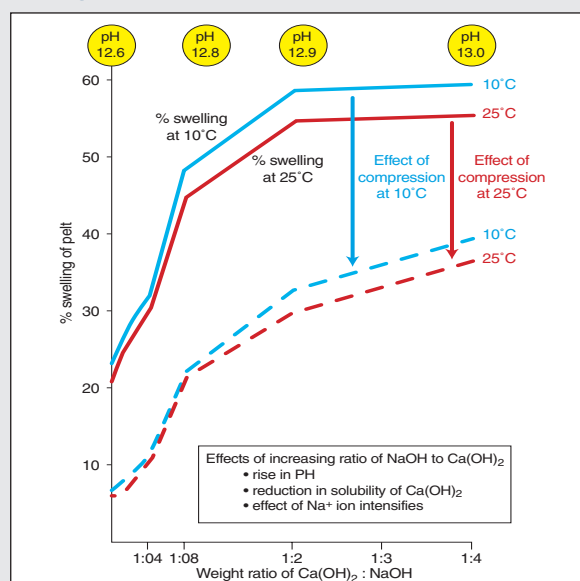
Credit: Images from "Observations: Temperature related relaxation within liming and other wet processes", R. Daniels, World Leather August/September 2004.

After lime fleshing warmer goods lay flatter, are more extended, and show a greater reduction in growth lines and draw/wrinkling when compared to colder goods. Warmer wet blue spreads more readily on samm/setting, with a more uniform release of water and, if the goods are to be split, this means an improved presentation. Similarly, warmer goods improve the setting/stretching action during shaving, and prior to drying the setting action within samm/setting is improved. Warm damp leather offered to vacuum drying can also be hand set more readily than leathers that are cold.

This improved setting component is very important during cutting actions, when goods are fleshed/split/shaved. In particular, wrinkles and growth are better extended and flattened, and by cutting the fibre structure in this strained state, the flattened form tends to be retained. This benefits the next process or operation, so the effects can be synergistic.

Temperature also strongly influences mechanical actions within chemical processing. Pegs, shelves and fins all apply force to the goods as the processing vessel rotates, and the softening caused by higher temperature results in a greater extension of goods as they are stressed. The improved flexing action caused by these cycles of applied stress and relaxation favours both the release of unwanted products from hides and skins and the penetration of chemicals into the structure. In addition, the

Panel 7: The influence of temperature on the swelling of pelts under different conditions of liming

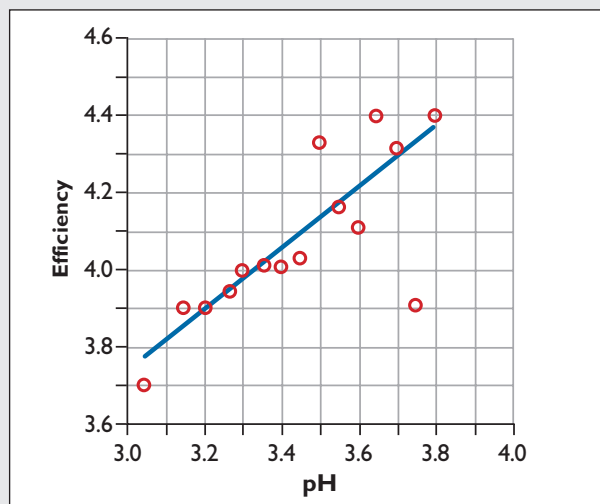


- The solid lines in the graph show the swelling of pelt (measured by thickness) at increasing ratios of $\text{NaOH}:\text{Ca}(\text{OH})_2$ and rising pH values.
- The broken lines indicate how much the pelt samples under these conditions could be compressed by applying standard pressure.
- Higher temperatures produced less swelling and greater softness, as indicated by the lower values in both swelling and compression.

Credit: Modified figure from "The role of bound and free water in the liming process": Summary by A. Landmann. World Leather, Dec/Jan 2004/5, pp23-25. The figure is based on investigations made by Herfeld and associates, Lederinstitut Gerberschule Reutlingen, Germany.



Panel 8: The effect of pH on the substance of the tanned butt at elevated temperatures (final temperature of tannage 58°C (+/- 2°))



The hides used in these investigations were all from the same weight range and source, and the butt substances were based on measurements taken under carefully controlled conditions. The points are means and the correlation is weighted according to the number of packs making up the points. From statistical analysis: Correlation Coefficient = 0.6400. Number of packs analysed = 109.

Credit: "Chrome tannage (part 3): The combined influence of temperature and pH", R. Daniels, World Leather August/September 1994.

chemical fixation and void-filling in tanning and retanning occurs as the hides and skins are in more extended condition. This, combined with a shift towards plastic behaviour, favours the retention of leather in an extended form.

Item 3) THE COMBINED INFLUENCE OF TEMPERATURE AND pH ON SUBSTANCE

Temperature associated effects are also reflected in washing after liming. If the wash temperature is, say 28°C, the goods are more flaccid and relaxed than if washed at lower temperatures. This is illustrated in *Panel 6*.

But in addition to the described temperature effects there are temperature/pH-related changes within chemical processing to take into account.

Investigations by Herfeld and associates showed that at a given pH the swelling of limed pelt is reduced by higher temperatures. This is shown in *Panel 7*: the temperature differentials are higher than found in practice, but these effects can be observed even within changes of a few degrees.

Full-scale investigations also showed that within tannage at elevated final temperature (58°C) a lower pH would cause a significant decrease in substance in the butt area. This is shown in *Panel 8*.

This infers that completing tannage at a lower pH produces flatter and more extended leather, and examination and measurement of these leathers in the finished state confirmed this. In practice considerable area gains were achieved, but it was necessary to shave to higher substances to offset losses in thickness. The higher temperatures employed in these investigations enabled an increase in chrome uptake and more

than compensated for operating to a lower end-pH.

It is also noted that investigations at lower final temperatures (approximately 30°C), did not detect any relationship between pH and the tanned substance, although this might be expected.

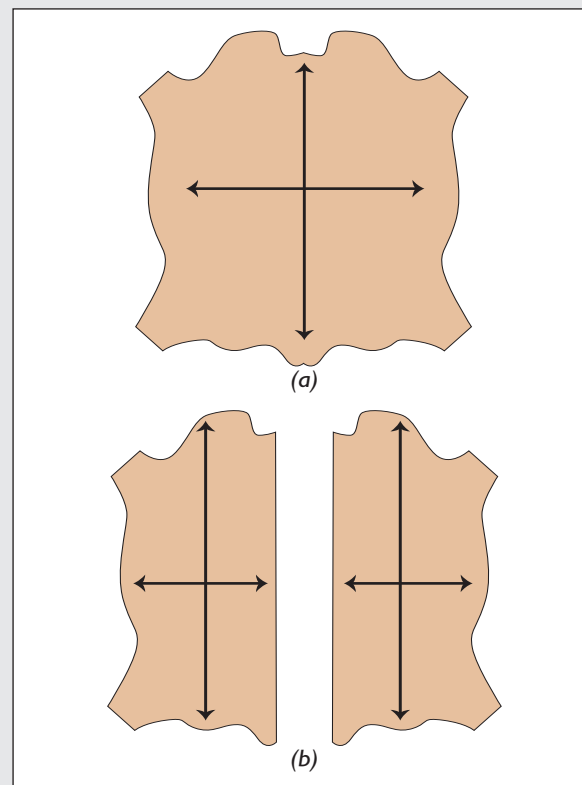
Item 4) BENEFITS FROM PROCESSING HIDES INSTEAD OF SIDES

The greater uniformity of shape offered by processing hides instead of sides provides advantage. More stress/strain is developed in the belly-belly direction by rotation of the vessel during chemical processing. This improves the extension of both wrinkles running parallel to the backbone direction and of growth lines across the neck areas, and is illustrated in *Panel 9*.

In contrast, the processing of sides increases the overall extension in the butt-neck direction and encourages contraction and curvature in the belly-backbone direction. This predominant strain parallel to the backbone encourages the development of any draw-lines that originally formed during the life of the animal, and chemical modifications and fixations substantiate these effects.

These effects are very clear if comparisons are made between sides and hides processed together through soaking, liming and tanning. It is believed that these effects continue to favour the processing of hides through dyeing/retanning and machine operations as opposed to side leather production.

Panel 9: The benefits of processing pieces of uniform shape



a) Balanced tension received by hide during process. Favours a flat and well-extended piece, especially in belly and neck parts.

b) Greater butt-neck stress, and reduced tension across the piece. Creates curling effect backbone to belly and favours rolling. Belly and neck parts are poorly extended, with an increase in levels of draw/wrinkling and growth marks.