

Observations: Temperature related relaxation within liming and other wet processes

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It is well known that by liming at higher temperatures, say, 29°C instead of 25°C, that hides and skins are softer, show less draw and growth marks, and appear less swollen. In addition, after fleshing there is a greater loss of fine wrinkles in the belly areas, and visually the skins are flatter and more extended. This may in part be attributed to a greater breakdown of the structure but, if packs of hides are limed at a given temperature, then control washed at different temperatures, similar observations can be made. This indicates the presence of an additional mechanism.

To record these effects investigations were made on pilot scale. A conventional soak was followed by fleshing, then conventional liming and unhairing at 27°C for 20 hours. After siding and separation into two lots, one received two closed drum washes at 18°C of 300% water + 0.5% lime (as solution/suspension to avoid osmotic effects), and similarly the second lot but at 28°C. The outcome was typical of observations made in bulk manufacture, and is recorded in the following photographs where:

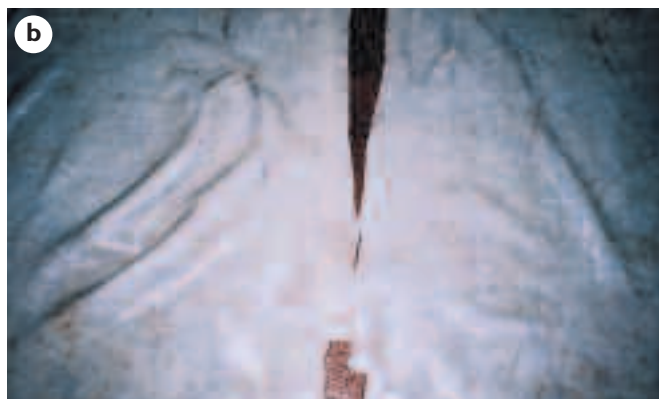
Photograph (a) shows a sided hide after liming and (b) after washing the left side at 18°C (x 2), the right at 28°C (x 2). In these two photographs the sides were simply placed on the floor, whereas (c) and (d) shows the effects of manipulation while trying to flatten the pieces.

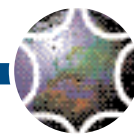
In addition to this general relaxation and flattening as a result of the warmer wash there was a minimisation of growth in the neck and draw in the belly area. These differences do not show clearly as a record due to the translucency of limed hides.

A warmer wash produces a softer, more relaxed, and apparently deswollen substrate, but careful weightings stage-by-stage could not detect any temperature related weight differences. It is seen that these effects stem from a softer structure rather than any changes in total water content.

Temperature related softening

Insight into these effects can be easily observed by subjecting a sample to constant load using a sensitive arrangement similar to that used for detecting the shrinkage temperature of leather, but





Panel I

Temperature-associated softening and dimensional change

Temperature related softening and extension under constant load has been reported on wet blue leathers. Using simple apparatus, increases in length averaging 0.4% were recorded by raising temperatures from 30°C - 60°C. To place this in context, when temperatures were raised within commercial chrome tannage from an average final temperature of 30°C - 57°C, both an increase in area and a grain smoothing were observed. Process adjustments were required to take benefit from the considerably improved chrome uptake, nevertheless, these could not fully account for an area gain in the order of 3.0%. This was measured over a considerable time period, accompanied by a significant reduction in blue split yields⁽¹⁾. This was seen as the result of tanning a temperature-softened hide under stresses induced by drum rotation. In effect, the chrome became fixed within a hide that was being stretched more than usual, the leather becoming set in this extended form.

At higher temperatures (60°C - 240°C) dimensional change under load at various moisture contents have been reported on final leathers. In this case a series of sharp changes in gradient were noted as leathers first extended then shrank⁽²⁾.

Softening as a temperature related effect is well known in materials science, and the effects—especially under conditions of high moisture content—are employed in lasting and forming in footwear and leather goods manufacture. The levels of extension in forming are far greater than inferred by simple test methods, and this appears to apply to observations made within wet processing.

Any natural fats present in a skin will soften with rising temperatures, and this should cause some lubrication and softening. However, the fundamental reasons for these effects are not clear.

It is stated in literature that temperature affects the degree of swelling in liming, but these observations were not supported by measurement. In contrast, work performed at Lederinstitut Gerberschule Reutlingen⁽³⁾ found no reduction in total water content due to increased liming temperatures, although there was a softening effect.

Changes in bound water are also advocated as significant. In this situation it appears that increased lubrication at molecular level may be brought about by the release of bound water from the collagen structure due to temperature change. Within the normal range of process temperatures this could lead to greater relaxation, but not necessarily with any change in total water content⁽⁴⁾. But these mechanisms are very difficult to measure, although visual and tactile change may be clear.

Recent findings, however, throw new light on these effects. It now appears that a reorientation of parts of the collagen backbone occurs under conditions of increasing temperature and load. These softening are sensitive to changes in moisture content, there is a permanence to extensions made under load, and detailed measurement shows the effects as very significant⁽⁵⁾.

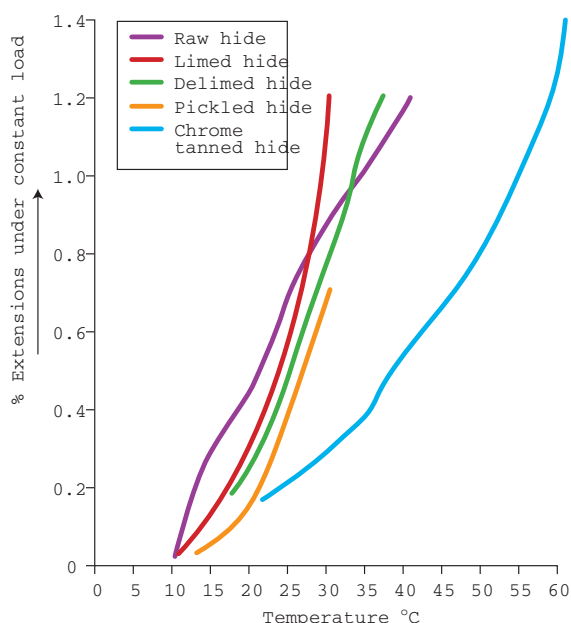
measuring changes in sample length as the temperature is raised.

In conjunction with the investigation described, samples of hide were taken from the butt after soaking, liming, deliming (not bated), pickle and tannage. A constant load of 1050 gm was applied to each strip at 1 x 10 cm, being based on a load of 150

gm/mm of soaked/fleshed substance. The solutions that the samples were immersed in were from each process stage i.e. final lime liquor for liming strips, final pickle liquor for pickled strips etc. The temperature was raised in +3°C steps from a low of 10°C to a high as appropriate. The samples were maintained at these rising temperature steps for 10 minutes before changes were recorded, and the average of four readings is given in Figure 1.

This indicates that over and above effects that might be attributed to chemical change, other significant changes occur that are temperature associated. These effects can be found throughout wet processing, and, in conjunction with applied stress—such as received by skins in rotating process vessels—can be permanent and of benefit in terms of a more relaxed grain and dimensional change such as area extension.

Figure 1: Extension vs Temperature under constant load



These extensions are largely maintained on return to ambient temperatures

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