



Waterless processing

ILM Consultant Technical Editor Karl Flowers looks at three water-saving processes in chromium tanning and the importance of conserving this precious resource.

The use of water in the tannery is a constant source of concern for any leather producer. Figures for the consumption of water vary from 15 L/kg of hide to 60 L/kg (Buljan and Král, 2015, Flowers, 2017). With true conservation of mass in mind, the water used by the tannery may be polluted, but it is generally remediated and returned to a natural water source for further use by the ecosystem.

Regardless of whether it is bona fide water, or an alternative solvent (solid or liquid), the role of a solvent in the wet end is irrefutable; a tanner needs something. Some experts have predicted that 2030 is the earliest year in which serious water shortages begin, and some countries officially run out of fresh water. The fundamental role of water that the solvent plays in the process needs to be understood so that it can be minimised, replaced or made to be more effective (Benjamin, 2010; Flowers, 2018).

At the top of the waste hierarchy, elimination of a waste stands out. Tanneries must eliminate water, more than ever, if they are to remain competitive (Richey et al., 2015). Tanners are finding ever newer methods of eliminating water from the process. The latest focus of attention appears to be the tanning step.

The incentive, however, has not only been for sustainability reasons; there appear to be process efficiency and quality reasons. The focus of all the technologies has been to cut out added process water and to use that concentration and mechanical action increase to allow better, more efficient penetration of the chromium tanning salt.

A simple fact is that the lower the water, the higher the concentration of chemical and the faster the diffusion into that substrate will take place. The chemicals will be limited by their solubility into water and, for some chemicals, lowering water to almost nothing could be problematic; vegetable tannins – due to the quantities added, can result in saturated solutions. In the 1990s it was not uncommon for tanneries to be using 100-150% floats for chromium tanning, together with 8-10% chromium sulfate (26% Cr₂O₃). The concentration of chromium as g/L may not have changed, but the amount of water certainly has, with modern tanneries using 0-50% (*0% - it is highly unlikely that all water in between leather folds will be removed; some tanners count the amount of water in a tanning drum never to be below 20%), together with chromium additions being 4.5-5.5%.

Another important factor to consider with the new water awareness is that the time/cost savings and general process efficiency is increased. A low float means chemical, water and electricity cost reductions. The high mechanical action means the drums can turn much slower than they would be with high float volumes. If the tanner does not take these mechanical force increases into account when using a low float system, then the damage to the leather may be significant. Drums that use a combination of deep shelves and low- or free-of-water systems can turn the drums at 3-6 RPM for normal tanning. That could be as much as 3-6 RPM lower than normal systems. Those power savings have big cost implications. ▣

The three most interesting low- or free-of-water technologies that are currently being used commercially are:

Xorbs - Qualus

Qualus, (the leather division of Xeros Cleaning) has been using Xorb technology since 2012, with the patent published in 2014 (Xeros, 2014). The use of plastic beads in the tanning drum has allowed the tanning operators to drastically reduce the amount of water to as low as 10%. The negative effects of low floats in the Qualus technology appear to be avoided through the fact that the Xorbs do partitioning effects, in a manner very similar to that of water (resisting compression, see Flowers, 2018). Claims about the micro-abrasion cleaning effects are also made, but no conclusive scientific proof (pointing to exactly that action) has been published. Effects demonstrated through overall scientific evidence have shown quality enhancements. Rapid and even penetration of the tanning agents are evident.

Waterless chrome tanning (WCT) - CLRI

A technology that is two years old is the water-free technology from the Central Leather Research Institute that claims no effluent is generated. However, the patent states that after pickling the liquor is drained off (CSIR/CLRI, 2017). It is not clear, from the patent, as to whether that pickle float is re-used, which may be the way that the effluent-free part of the claim is maintained. The material is pickled using 0.5-1.5% organic acid, the pH does not go below pH 4.8, after which it is treated with a cationic fatliquor.

The chromium salts are then added at 5-8% into effectively a

dry drum. Like the technology listed below, there is still water inside the hides and this water acts as the solvent for the dissolving of the tanning agent. The pH of the drum will fall to between 3.4 and 4.4 as the chromium salt hydrolyses. Total chromium tanning time is six hours. The drum is emptied after quality checks and little to no effluent will result.

DriTan - Ecco

Another low-water process that has appeared in the last few months is the DriTan technology that Ecco has been using. In this technology, the hides are sammyed and then the dry chromium salts are added to the drum, with some pickle if necessary. The low float results in the rapid penetration of the salts into the hide. Unlike the WCT process, the Ecco technology makes use of a basification process or makes use of self-basifying chromium salts. Effluent is minimised with claims of up to 25 million litres of water saved annually as a result of the low water processing.

Conclusion

These three examples are going to be the floodgates opening on new technologies that may or may-not be protected. The intellectual property (IP) shown in these patents does tie down many areas of development, but processes are notoriously hard to protect (unlike engineering and chemistry), because a very subtle behaviour tweak can get around the protections, as can be seen by these three companies moving around each other's IP.

The next few months will see new developments on water-saving, closed loop systems or tan recycle/recovery technology in the area of chromium tanning. ■

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