



Innovation

Part 1: Recycling and regeneration

Twenty world standard tanneries have opened their doors for in-depth study as part of Tannery of the Year Awards 2009 and 2011. Considerable technical information has been published in *World Leather* following these visits, and there has been an emphasis on environmental aspects.

It is clear that throughout all of the manufacturing sequences used within these companies, very careful thought has been given – and considerable time and money invested – in ways to reduce the environmental footprint. This is particularly noticeable in wet processing, where the technical aspects of leather manufacture are fully entwined with techniques to minimise pollution and waste. Some general shifts that have taken place are set down in *Panel 1*, but also specific innovation to save water use, to reduce the chemical demand, and to reduce the quantity of pollutants offered is being applied.

Minimising water and chemicals consumed in leather manufacture

The following techniques are being used by some of the tanneries that participated in these studies.

RECYCLING USED LIME LIQUORS

Used lime liquors and washings are being segregated from the other wastewater streams and delivered via gullies fitted with simple bar screens to a recycling plant. From collection in an open sump, the liquor is pumped to an elevated rotary screen that removes solids down to 1mm size, followed by settling. Any surface scum/grease is skimmed from the surface, and the final supernatant stored in an open sump which acts as a reservoir. This recovered supernatant is used for soaking fresh hides, and all of the liming floats.

THE REUSE OF DELIMING LIQUORS

The deliming liquors are collected in a sump, then pH adjusted to pH 8.0 (using regenerated pickle liquor – see the reuse of pickle liquors). This is followed by filtration using a self-cleaning disc filter of one micro size, with delivery into a second sump that serves as a reservoir. This treated deliming liquor is used as the float within the liming process.

THE REUSE OF PICKLE LIQUORS

At the end of the pickling process for hides, the drums are completely drained, and all of the pickle liquors are collected in an external sump and allowed to cool for 24 hours. Samples are taken for salinity analysis and pH measurement, and the acidity adjusted at this stage using sulfuric acid.

The pickling process for the following batches of hides commences by adding salt and sodium formate. Formic acid is then added as the first stage of acidification, followed by the sulfuric acid addition in the form of the regenerated used pickle liquor.

RECYCLING USED CHROME AND PICKLE LIQUORS

All of the used chrome liquors and drainings from the wet blue and samming are segregated from the other waste water streams and delivered via gullies fitted with simple bar screens to the recycling plant. The liquors are allowed to settle and balance in a sump, and then flow from the surface into a second sump, which acts as a reservoir. The retention time is extended as this enables the liquors to cool from the final tanning temperatures.

These liquors are used for the dilution of sulfuric acid used in picking, and within the pickle and tanning baths. The chrome balance is made up with fresh chrome liquor.

The operation is managed by taking samples of the used chrome bath and analysing for chromium, calcium and total acid content. This establishes the balance between sulfuric and formic in the system and avoids a build up of calcium salts.

The system is carefully monitored with the objective of recycling 90% of the chrome that is discharged from tanning. The residual 10% is dosed with calcium hydroxide and allowed two days to settle. The supernatant is discharged to primary effluent treatment, and the chrome sludge dewatered before removal from the site by a specialist company.

RECYCLING USED RE-CHROME LIQUORS

Stainless steel tanks are situated above each drum in the retan/dying department (as shown in *Panel 2*) for the collection of exhaust float from a re-chroming process. This recovered chrome solution is then made up to strength and used for the next rechroming process. This is repeated five times before discharge, then starting a new cycle.

Panel 1: Recycling used re-chrome liquors.



CREDIT: XINGYE LEATHER TECHNOLOGY COMPANY, FUJIAN PROVINCE, CHINA



Panel I: General shifts in manufacture

Not only are considerable savings being made in water use, but by separation of wastes, or use of alternative chemicals in process, new opportunities arise as the various by-products and waste streams are relatively uncontaminated.

These shifts in approach to leather making are well known, but they record changes in manufacture that can now be considered as established in practice.

A SHIFT FROM SALTED TO FRESH HIDES IS TAKING PLACE

The trend towards collection/delivery of fresh hides is significant. This calls for very rapid transport times from abattoir to the tannery. Where chilled/refrigerated transport is not possible, collection distances have to be short, and sometimes deliveries take place at night as the temperatures are lower. This all requires very close linkages and trust between suppliers and tanners. A high level of quality monitoring at the earliest stages possible is required by the tanner, with fast feedback to the supplier.

These actions mean that the problems caused by salt are avoided. These hides require a minimum soaking time before unhairing and liming, and the option of a clean fleshing before soaking means that a more uniform opening in liming is possible. The fleshings yield better quality oil upon rendering.

SURPLUS SALT IS BEING REMOVED FROM HIDES AND SKINS BEFORE COMMENCING MANUFACTURE

For many reasons salted hides are used by tanners. There is often an excessive quantity of salt on the hide, and this is removed by slow tumbling in an open cage. This is collected as a solid, and minimises the salinity of the final effluent.

HAIR SAVING PROCESSES ARE BEING USED

Screening is used to either save as much hair as possible from a true hair saving process, or to remove hair from the float before it is completely dissociated. In both events, the load on the effluent treatment plant in terms of COD, suspended solids, and nitrogen is reduced. The recovered hair is uncontaminated from other chemicals used in subsequent processing, and sometimes composted with other wastes then used for land conditioning.

ALTERNATIVES TO AMMONIUM SALTS IN DELIMING ARE ESTABLISHED

Ammonium salts are still used, but often in reduced amounts and in association with speciality chemicals and carbon dioxide. Also, many deliming systems are entirely based on carbon dioxide or speciality chemicals. This reduction of ammonium salts in waste waters reduces odour, and costs in terms of energy input within effluent treatment and plant requirements.

ALTERNATIVE TANNING SYSTEMS TO CHROME TANNING ARE UNDER INVESTIGATION

Chromium remains the major tanning system, but considerable efforts are being taken to segregate chrome-containing wastewaters from the main effluent streams. This means the level of chromium in the general screenings and final sludge from effluent treatment is very low or absent, and this reduces the problem of disposal of these wastes, or even finding a useful outlet.

Over and above wet white production based on glutaraldehyde, tanners are seeking chrome-free alternative processes. Options being developed include WetGreen based on leaves from olives, and various types of "white" new-generation tannages are under evaluation. Of considerable importance, there is the possibility of salt elimination from the conventional acid/salt pickle. In this situation, coupled with an input of fresh hides, the problems of salinity can largely be eliminated.

These final leathers do not have the same heat resistance under wet conditions as chrome leather. However, it is considered that many opportunities for alternative tanning systems have been missed in the past. This is because an unnecessarily high standard for shrinkage temperature for many uses of leathers has become accepted. ☉

RECYCLING OF WATER FROM WETTING BACK WET BLUE LEATHER

Floats from wetting back wet blue leathers are collected, settled, screen filtered to remove solids, then skimmed in a flotation tank to remove grease. The reclaimed wash waters are then reused together with fresh water for wetting back subsequent batches of wet blue stock.

CHROME RECOVERY FROM USED CHROME LIQUORS

There are several variations to chrome recovery and reuse. In general all of the exhaust chrome liquors from tanning are segregated from the tanning drums, coarse bar-screened, then fed into a collection sump. They are then fine-screened using a wedge wire screen, and delivered into a mixing/settling tank where the pH is raised to pH 8.5.

If sodium hydroxide or sodium carbonate solution is used for pH adjustment, then the sludge formed is dewatered using a centrifuge or filter press to form solids at approximately 20% / 40% solids content respectively. The filtrate is discharged and the solids added to sulfuric acid in a reaction vessel.

If magnesium oxide/calcium hydroxide is used, then the rate of pH change is dependent upon the particle size of the base, and several hours' stirring are required. The solids are allowed to settle in the reaction vessel, and form a very dense viscous sludge of 7-8% solids content. The supernatant is discharged from above the sludge, and sulfuric acid added to dissolve the chrome sludge.

The final pH of the regenerated chrome liquor is pH 3.2-3.4, basicity 33%, and the chrome content up to 10% Cr₂O₃. This is used for tanning both lime splits and skins with new 33 basic chrome added to make up the required chrome offer.



Panel 3: Innovation at Josef Heinen GmbH & Co Kg, Germany

Considerable innovation has been applied within manufacture to minimise the water consumption. This has been achieved by careful water metering using Huni systems, recycling of wash batches, and the recovery and reuse of water following chemical dosing treatment. This has resulted in an unusual and highly effective system. The key elements are outlined:

- Fresh hides are used to minimise salinity generated from process. Very occasionally salted hides are used, but this is following consent from the local authorities as there are tight limits on end-of-pipe salinity.
- The waste water discharges are segregated into two streams. One comprises discharges from soaking, liming/unhairing and deliming/bating. The second is specific for acid waste streams – pickle liquors/used tanning baths, and washings from retannage/dyeing/fatliquoring.
- The acid waste streams are pumped to a chemical dosing plant located next to the beamhouse where the wastewaters are

stirred, and the pH raised slowly to pH 10.0 using common lime. This is then dosed with ferric chloride and polyelectrolytes to remove colloids and solubles that can be precipitated.

- The treated waste water is then settled to remove the suspended solids, creating a clear supernatant that contains less than 1 mg/l insoluble chrome.
- This supernatant is stored in a holding tank for reuse in processing.
- Water is drawn from this holding tank for the main soak.
- The waste water discharged from the main soak is collected, settled in an inverted cone to clarify, and then reused for the dirt-soak. When the dirt-soak is complete, this float is discharged to the effluent treatment plant.
- The liming process draws water from the holding tank, and after liming the wastewater is discharged to the effluent treatment plant.
- The final wash after liming uses fresh water. This is recovered, and used for the first-time wash, then discharged to the effluent treatment plant. ☺

CHROME RECOVERY FROM CHROME SHAVINGS

Chrome shavings are processed using alkali at high temperature to form a hydrolysate, and the hydrolysate and chromium hydroxide allowed to separate by settling. The settled chromium hydroxide sludge is discharged from the base, and then centrifuged to produce a dry cake. This is added to a reaction vessel where it is dissolved in sulfuric acid, and adjusted to form a chrome solution at 33% basicity.

THE REUSE OF WASH WATERS

There are examples of reuse of wash waters, where water from a second wash is segregated and used for a first time wash. This is most commonly found in washing after liming. An example of a very complex system for the reuse of wash waters and discharges from processing is detailed in *Panel 3*.

REDUCING THE VOLUME OF ABSTRACTED WATER USED IN MANUFACTURE

Over and above methods used to minimise the volume of water used in leather manufacture, many tanners are seeking ways to reduce the volume of water that they receive from municipal supply, or abstract from the ground. There are two main methods being used, and sometimes both are employed on the same location.

RAINWATER COLLECTION AND USE

There are many examples of rainwater collection and use. Generally all or part of the roof area is used to collect water, and this is then discharged into collection sumps, or held in small reservoirs. These holding areas may serve as water for fire fighting in an emergency, or if there is a surplus, then used for irrigation of the area surrounding the tannery. In some cases this water is used for wetting back wet blue leathers, and sometimes blended with water from bore holes or municipal supply for general leather processing. This can generate very significant water savings.

REVERSE OSMOSIS (RO) AND PERMEATE REUSE IN PROCESS

This is successfully applied after very high-quality effluent treatment. A very low suspended solids content is essential to

avoid blockage of the membranes used for filtration. This ensures a long life before membrane replacement as this is an expensive technology.

In general, a plant operating with a mixed input of salted hides and wet blue can expect to recover 50-75% of the treated effluent as high-quality permeate that can be used for leather processing, or raw water for boiler feed. If the input is wet blue hides and skins, then this may rise to 75-85% permeate for reuse.

The lower-volume concentrate may contain up to 30,000 mg/l as Total Dissolved Solids (mainly common salt, but also residual compounds – often coloured – as hard COD). If the tanneries are close to the sea then marine discharge via pipeline/canals may occur. Where the tanneries are inland, there are examples where the concentrate is evaporated in shallow lagoons by spray drying as shown in *Panel 4*. The solids that are recovered are stored at government-approved locations. ☺

Panel 4: Spray evaporation of concentrate from RO



CREDIT: TATA INTERNATIONAL LEATHER BUSINESS UNIT, DEWAS, MADHYA PRADESH, INDIA.