CLOSED-LOOP LIMING AND TANNING SYSTEMS
LARGE AND COTTAGE SCALE MANUFACTURE

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Abstract. Residual floats from liming and chrome tanning processes are being recovered as chemical solutions for re-use within many tanneries in China, presently producing approximately 120,000 wet salted hides/week from USA, Europe and Australia in eight major tanneries. The closed-loop approach in these two major processing stages can now be considered as an established alternative to conventional processing of wet salted hides to the wet blue state. Advantages include chemical savings, reduced water use, simplification of effluent treatment and solid waste disposal with associated cost savings. Being the outcome from carefully controlled processing, these filtered solutions are consistent in composition. The techniques used provide good quality and uniform wet blue though-out the year. Soaking and deliming/bating processes are managed conventionally, with all washings and discharges delivered to the effluent treatment plant. However, the hair saving/liming and tanning stages omit the washing sequences. This results in concentrated solutions for reuse, with no discharges from for effluent treatment. This means an absence of both sulfide and residual chromium salts for treatment/recovery in subsequent effluent treatment. This approach to manufacture is found in established tanneries, but also in a new generation of wet blue units that by November 2018 were at advanced stages of construction. Moreover, the technology has made the technological transition from bovine hides to the manufacture of full grain wet blue sheepskins to the scale of 10,000 skins per day. And for small scale operations – bovine hides, bovine bellies, sheep and goat skins – chrome tannage is taking place in many tanneries too, the process having been adapted to the various conditions and tanners requirements.

Key Words: Closed-loop liming and tanning

1 Introduction

Closed loop processing for manufacturing hides and skins to the wet blue state is now firmly established in full scale manufacture. This comprises two closed-loops for the full recovery and reuse of processing floats at the end of liming and chromium tanning in the eight large scale tanneries who allowed site inspections to provide the information for this report. The technology was initiated and developed by BIOSK Chemicals over a five year period before introduction commercially in 2011. Now approximately 120,000/week of wet salted hides from USA, Australia and Europe are being processed to the wet blue state for their own use, sales and contract tanning.

Fig. 1. High quality bovine wet blue manufacture: High volume manufacture using closed-loop technology.

2 Development of a Technology

There are two key issues that BIOSK addressed when developing this technology:

- Traditional high uptake processes for wet blue manufacture always left residual chemicals for effluent treatment and this waste should be eliminated.
- The leather produced should be consistent and of high quality.

Central to the technology are two self-contained processing loops. The first is a hair save liming process, the second a combined pickle and pre-chroming followed by chromium tannage. Three auxiliary products developed by BIOSK are available to support the processing, and the technology is being used by tanneries of all sizes where their previous procedures have been modified to the new procedures.

2.1 The Hair Recovery and Liming Closed-Loop

The processing is managed as follows:

- All of the processing floats and drainings at the end of the liming stage are recovered for use in subsequent hair saving liming systems.
- There is a total absence of washes at the end of the liming stage. The recovered floats remain a resource of concentrated chemicals for reuse.

The recovered floats from all of the liming drums are delivered to a single holding tank. This is fitted with heat exchange, with the temperature raised or lowered to 20-220C.

- Before re-use this solution is mixed using compressed air to ensure the dispersion of any fine residual solids in suspension.
- Only the recovered solutions, and lime and sulfide/hydrosulfide (at reduced offer) is used within the hair loosening stage
- After hair loosening, the float is filtered for conventional hair recovery and compression, with the float returned to the drum.
- As the hair is compressed on recovery it acts as a filter for the residual fine solids. This keeps the suspended solids at a low level equilibrium within the ongoing process.
- The float for the main swelling phase is often increased in several offers using recovered solutions to carefully manage the swelling.
- At this stage some fresh water added too. In practice, this volume matches the water taken up by hide swelling.

2.2 Handling Operations

On discharge from liming the hides are tipped into a container set beneath the liming vessel, and delivered directly to the area by the lime fleshing machines. Here they are hooked onto a line-conveyor for feed to the fleshing operation. On offer to lime fleshing the hides are well drained and clean.

Scud, grease and residual surface water are squeezed from the grain by the action of the grip rollers at the time of fleshing. At the time of offer to splitting, the hides are clean and dry, and handle as usual.

In the deliming stage the swelling water, together with salts, residual protein and grease contained within the hides are released from the structure. At the end of this process these unwanted products are discharged, followed by fresh water washes as conventional practice.

2.3 The Chrome Tanning Closed-Loop

In general, the process is managed as follows:

- All of the floats and drainings at the end of the chrome tanning stage are recovered from the drums and stacking areas for use in subsequent pickling tanning systems.

- There is a total absence of washes at the end of tannage. The recovered solutions remains a resource of concentrated chemicals for reuse.
- These recovered floats are filtered using a filter press to remove fibres and other solids from solution, and become a resource of concentrated chemicals for reuse.
- These solutions are delivered to two containment tanks. One tank is temperature adjusted using heat exchange to 20-220C, the second tank adjusted to between 550C and 750C - as required by the individual tannery.
- Salt at reduced offer is added to delimed and bated hides. The float level is the minimum possible to enable distribution of the salt.
- A small addition of pre-diluted formic acid is added for a light surface acidification.
- This is followed by a simultaneous main pickle and pre-chroming stage. Sulfuric acid is diluted as normal but using recovered chrome solution at 20-220C. This is pumped into
- the drum, but recovered chrome solution at the same temperature is pumped in too over the same time period. This increases the float as required to 50%.
- These simultaneous additions onto the lightly acidified hides prevent chrome staining and provide a moderate float for the chrome tanning stage.
- After 90 to 120 minutes (according to split/unsplit substance), the chrome tanning agent is offered but at a reduced offer, followed by basification as conventional processing.
- A third offer of chromium is made as recovered solution from the containment tank at elevated temperature. This offer may be as high as 100% float as suits the tannery needs, to raise the processing temperature and improve chrome fixation.
- There are no washings with fresh water at the end of the process.

3 Water exchange and process equilibrium

In the liming stage fresh water is introduced as contained within the fully soaked hides, and as a fresh water addition within the swelling stage. As the process develops, an equilibrium is established by diffusion between the water/solubles in float and within the hide structure.
On hide discharge, the large volume of water held within the swollen collagen structure – together with solubles – is removed from the otherwise fully closed system. In practice, this continuous shift of hide-contained water through in this otherwise self-contained system allows a build-up of solubles that stabilises over five cycles.

In the tanning closed-loop there are no washing stages. Nevertheless, there are additions of water as contained in the delimed and bated hides, as a low float for the light surface acidification and from dilution of the formic acid, with hide-contained water removal at the end of process. In a similar manner to the liming closed-loop, as the process develops, an equilibrium is established by diffusion between the processing solutions and water within the hide structure. In this case, the level of solubles building up over twenty cycles and then stabilising.

4 Large and small scale manufacture

The technology is now being used in three quite different situations and for different leather types:

4.1 Large-Scale Bovine Manufacture

The process has been successfully introduced by BIOSK into many large scale manufacturers of bovine wet blue leather. Most of these tanneries have accommodated the technology by careful segregation of pipework and drainage. Essentially, the collection and recovery systems from both

liming and tanning are isolated from the rest of the tannery drainage systems. Holding-tanks are employed – either within or adjacent the work areas – for collection and temperature adjustment of the recovered solutions.

In some situations, the tanners have made a fresh start. These tanneries have been completely rebuilt from the foundations up around individual processing zones, each with their own systems for used-float management.

Here, both the liming and tanning departments are completely isolated, all floats being recovered, stored and reused with no provision for discharge to the ef fluent treatment plant.

Floats and drainings are kept in complete isolation and free from contamination.

Shows an isolated liming zone in a new-build tannery complete with holding tank.

Fig. 2. Existing and new-build tanneries.

The soaking departments are kept apart from the liming and tanning zones, with their drainage arrangements directly feeding the effluent treatment plant. In addition, these tanneries are performing the deliming and bating processes in isolated areas too. Here, the hides as unloaded and drained at the end of washings are delivered to the tanning zone for pickling, tanning and stacking. These separated zones and their management are illustrated as Figure 3:

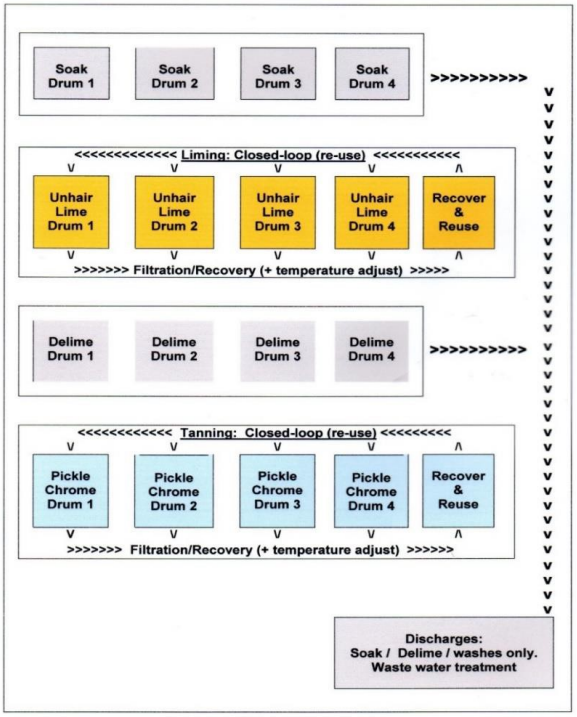

Fig. 3. Segregation: Management of closed-loop recovery and waste water discharges.

4.2 Large-Scale Sheep Skin Manufacture

In 2018 the technology was adopted for full grain sheepskin manufacture on scale up to 10,000 skins per day. After painting, wool removal and liming, the liming floats are recovered and reused in a closed-loop liming suited to sheep skin production. In a similar way to bovine manufacture, the closed-loop approach is used for sheep skin tannage. There are differences in float levels, somewhat higher pH levels during tanning, and slightly lower temperatures in pickling/pre-chroming and the final tanning stage.

Samples showing wet blue sheep skin leathers. Float recovery at the rear of the drum row before filtration and storage.

In this situation, the two chrome holding tanks are set in a sealed enclosure adjacent the tanning department.

Fig. 4. Closed-loop applications in large-scale sheep skin tanneries Samples showing.

4.3 Small-Scale (Cottage) Manufacture

The technology is not restricted to large scale manufacture, and is now being used for a variety of leathers. In November 2018, six small scale tanneries processing wet salted bovine hide butts (small scale fleshing machines limits the piece size), bovine bellies, nappa sheepskins and goat skins had adopted the technology for chrome tanning. There were many variations with the techniques used, according to the different plant and equipment and leather types, end-uses being footwear, bags, clothing and various leather goods. These tanneries are in a group of 30 tanning units and 30 retan/finishing units. Here, the waste waters are being processes in a CETP where they intend to achieve a discharge limit of 0.5 mg/l Cr. The remaining 24 tanneries have undertaken to the group management to convert their tanning departments under licence by BIOSK by June 2019.

Tanks used for holding recovered chrome solutions with temperature adjustment via heat exchange. These are new to specification as shown, but are often adopted from other uses.

Full hide manufacture is limited by the width of the fleshing machine, hence specialist belly leather processing. Air dried/tension free, these leathers are ideal for bags and leather goods.

Fig. 5. Closed-loop applications for small scale enterprise.

5 Advantages

There are significant advantages offered by this technology:

5.1 The Quality Of Leather

This is not a typical high chemical uptake approach to manufacture. The processing does not rely on low floats and sensitive pH conditions to drive a high chemical uptake. Consequently, issues such as tangling and poor chemical distribution are avoided, together with abrasion damage to the sensitive grain, or too much surface fixation of chromium. The processing is more relaxed to suit an expensive and delicate structure.

Also, the chemical composition of the recovered solutions is very uniform. They are a blend from the previous processing batches, the recovered solutions the outcome of carefully managed production.

5.2 Savings In Water And Chemicals

The savings in water and chemicals are considerable. The first three tanneries to adopt this processing found savings ranging between:

- 18 – 50% Sodium sulfide/hydrosulfide combined
- 17 – 43% Calcium hydroxide (slaked lime)
- 57 – 71% Sodium chloride (common salt)
- 29% Chrome tanning Powder (1 given value)
- A water reduction of 50% (1 given value)

5.3 Environmental Advantage

- No unused active chemicals discharged for waste water treatment from liming and tanning
- No sulfide containing waste waters to separate and then oxidise.
- No neutral sulfites/sulfates arising from oxidation of unused sulfides.
- No chromium salts discharged, hence no chrome precipitation/dewatering/regeneration plant needed.
- A lowering of neutral salts, Total Dissolved Solids, chemical oxygen demand and nitrogen for effluent treatment.
- Reduced water requirement. Provides advantage for longer retention times in existing effluent treatment to further raise standards, or for smaller and more compact effluent treatment plant.
- Energy saving from reduced air requirements for oxidation and for aerobic biological treatment.
- Reduced volume of solids generated within effluent treatment and can be chrome free.
- Uncontaminated compressed recovered hair.

6 Conclusions

This is a significantly different approach to leather making that avoids many of the issues associated with traditional manufacture. The technology is proven by many years production of high quality bovine wet blue leather, and is spreading to other leather types at all manufacturing stages and levels of sophistication

Major saving in chemical use are offered. A simplification of effluent treatment and higher standards for discharge, minimisation of solid waste, a reduction in volume of water use, and a relaxed high quality product.

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References

1. *For greater detail on this technology, see the paper "Closed-loop liming and chrome tanning systems in full-scale wet blue manufacture: Operational management, technical and environmental advantage". JALCA, Vol.113, 2018.*