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Mr. Robert F. White, *Journal Editor*, 1314 50th Street, Suite 103, Lubbock, TX 79412, USA.
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Closed-loop Liming and Chrome Tanning Systems in Full-scale Wet Blue Manufacture. Operational Management, Technical and Environmental Advantages

by
Richard Daniels,[1] Jiasheng Su,[2] Falei Zhang[2] and Zhuangdou Zhang[2]
[1]*Greentech + Associates,*
Northampton, UK
[2]*BIOSK,**
Shangqui City, Henan Prov., China

Abstract

Closed-loop liming/unhairing and chromium tanning systems are now established for the full-scale manufacture of bovine wet blue leathers. The technology ensures full recovery and reuse of the concentrated used processing floats, and four major tanneries are now producing some 72,000 hides per week as high quality wet blue leathers from salted American, European and Australian wet salted hides. These are for their own use, sales, and contract tanning.

In practice there are no discharges or washings for effluent treatment from either the liming/unhairing or the acid/salt pickle and chromium tanning processes. Accordingly, there is no chemical wastage from these two major stages within leather making. There are significant saving in processing chemicals – lime, sodium sulfide/hydrosulfide, salt, acids, chromium tanning agents and water too. The problems associated with treating waste waters from these two environmentally difficult stages are thus totally avoided.

Based on independent on-site surveys[1] within each of these four tanneries, this paper shows how the technology is managed in practice. In particular it shows how the process stabilizes within these processing loops, and how a continuous increase in neutral salts is avoided.

Introduction

The unhairing and liming, and chromium tanning process are the two most important leather making stages. They are also inefficient in terms of chemical use and uptake, resulting in considerable waste as unused chemicals for subsequent effluent treatment. In particular, the unhairing stage produces a high load within effluent treatment in terms of BOD, COD, Nitrogen and suspended solids, and a significant quantity of contaminated solid waste for controlled disposal.

Rationalization is limited because of the sensitive nature of the raw bovine hides. The quality and characteristics of the final leathers can easily be affected, and changes that might appear useful in environmental terms within these two major stages can have profound negative effects on quality. These may be observed at the wet blue stage, but often remain undetected until final leather assessments.

Many attempts have been made to rationalize these processes. This has included sensitive high efficiency systems, the use of low floats and more mechanical action, and various forms of recycling and regeneration of used chemicals. But the basic processes have remained largely unchanged for decades.

With the objective of reducing waste at source, and to maintain or improve the quality of wet blue and the subsequent final leathers, a five-year investigation was set up by BIOSK Chemicals.

Central to these studies was process rationalization with recovery and reuse of discharges from the major processing stages. This involved small scale studies, then the creation of a purpose-built pilot plant capable of processing loads up to 40 hides input, and finally a commercial scale facility fitted with full scale drums and whole hide fleshing machines. Because the technology included the retention of recovered floats, a series of collection sumps were constructed in the floor of the building during its construction.

*BIOSK e-mail address: support@biosk.com
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This whole development was spread across five years. Once the objectives had been met in terms of practicality and quality of the wet blue and final leathers, the technology was introduced to industry.

The technology was adopted as full-scale production by the first tannery in in 2011 and is now being used for all production by four major tanneries in China. These process wet salted hides from the USA, Australia and Europe to the wet blue state. This leather is subsequently used by these tanners for in-house manufacture to the final leather state, sold to other tanners for processing, or manufactured under contract for customers. The detail of these tanneries is listed in Figure 1:

Methodology

The process is modified from a guideline process according to the tannery needs. It uses basic chemicals together with auxiliaries[3] developed by BIOSK as tanning and liming assists and has been introduced into these tanneries in two stages:

i] The process was first applied, evaluated, and then established as a hair saving process with complete recovery and reuse of the used lime float. The drainage systems enabled full collection of used floats and ensured that the recovered floats remained uncontaminated.

ii] Once the hair recovery liming process was established, and experience gained by practical management for several months, then rationalization of the chromium tanning process commenced. This also involved collection of all of the draining's at the end of the tanning process. The tannage was modified around a combined acid/salt pickle with a pre-chroming stage, followed by the main tannage.

Central to the technology is the absence of fresh water washes at the end of these two processes. This ensures that the used floats remained undiluted, with the residual chemicals in the most concentrated state, hence in the most suitable state for reuse. This results in significant savings in water use, the energy required to heat wash waters, and operational time.

Figure 1
Manufacturers of wet blue using BIOSK-technology[2]

Tannery/location	Wet salted bovine hides Input/week	Commence manufacture
Ruisen Leather, Fujian Province, China	18,000	2011[1]
Xingye Leather, Fujian Province, China	12,000	2011[1]
Xing Ning Tannery, Jiang Su Province, China	30,000	2013[1]
Haung Defu Leather, Helel Province, China	12,000	2016[2]

Site survey/report: [1] 2016, [2] 2017.

Technology: Liming and Hair Recovery Stage
The technology is based around a hair-saving and liming system that is best described as self-contained.

The process commences with salted bovine hides first receiving a short dirt soak, followed by fleshing. The hides are then fully wet-back in the main soak, with the used floats discharged to the effluent treatment plant as normal practice

The hides then enter the unhairing/liming process where recovered floats with residual chemicals in solution are used to replace fresh water. There are five key factors:

- There are no washes at the end of the liming stage before the drum load is discharged
- All of the recovered floats remain fully concentrated.
- At the time of unloading all of the floats are collected. This includes all draining from the drum, the floor and handling areas.
- Dedicated drainage is used to avoid contamination.
- The recovered floats from all of the liming drums are held within a single storage vessel.

These recovered floats are used in subsequent limings to replace fresh water. Before use they are thoroughly mixed by aeration, and carefully temperature adjusted. This is performed by heat exchange using stainless steel coils set within the vessel. This is particularly useful for cooling in summer periods where a temperature adjustment to 20 – 22^{0}C is employed. It is noted that after many cycles these recovered floats remain of good color, of low viscosity, and without the development of odor.

The process starts with preparation for a hair immunization stage where the normal water addition is replaced with an offer of recovered float only. Chemicals for immunization and loosening are added as normal, but at a reduced offer, and after two hours the hair is loose but intact with the hides clean and flaccid.

The hair recovery operation then commences. The float and residual hair are drained through the drum ports via collection troughs to a hair filtration unit, with the filtered float returned to the drum. As the intact hair is filtered from the float the mass acts as a filter and removed fine particles too. This hair is very intact and compacts well.

The main liming process continues with an increase in float to induce alkaline swelling. This requires a second addition of the recovered lime float, but also some fresh water, and can take place in several stages. Liming chemicals are added at this stage, but at a reduced offer due to the recovered chemical content. Once the process is complete, the float can be refiltered, and the hides dropped. All of the float drained from the drum, from hide-drop, and the draining's is collected for reuse.

The hides then receive a conventional lime fleshing. The hides are well drained on line-delivery to the operation, with scud and grease squeezed from the grain as usual practice. The hides are clean and are handled conventionally on lime fleshing and splitting.

The hides are then delimed and bated. Here salts, protein residues and grease from within the collagen structure are released as normal. Because of the time-savings created by omitting washings after liming and tanning, the deliming can be particularly thorough. All draining's and washings following deliming are delivered to the effluent treatment plant.

Technology: Pickling and Chromium Tanning Stage

The technology is based around an acid/salt pickle combined with a pre-chroming process, followed by a two-part chromium tannage.

At the end of the tanning process, the float is high with a low chromium content, and a final wash can be avoided. In a similar manner to the technique used in the liming cycle, all of the chrome containing draining from drum discharge, the area around the drum, and from hide stacking areas are recovered for reuse. These draining's are carefully segregated to avoid contamination and are screened/filtered to remove fine solids from the recovered float.

These solutions are held in two storage tanks. One tank is temperature adjusted to 20 – 22^{0}C for use in pickling and for a pre-chroming. The second adjusted to between 55 – 75^{0}C (according to the requirements of the individual tannery) for use as part of the main tannage.

The process starts with either a completely drained float after deliming or bating, or with hides transferred from deliming and bating in dedicated drums to the pickle/tanning drum.

A small amount of water is introduced, just sufficient to disperse a low salt offer then followed by an offer of formic acid diluted with water. After a short run the main pickle commences in combination with a pre-chroming.

Here, sulfuric acid diluted with recovered chromium float at 20-22^{0}C is pumped into the drum. At the same time the float is increased by 50% but replacing water with recovered float at 20-22^{0}C. Chrome stains are avoided as the hides are slightly acidic from the pre-pickle with formic acid, and because the sulfuric acid and the chrome float is pumped into the drum over the same time period. The running time is normally 90 minutes but is increased if the hides are full substance.

The main tannage starts with an addition of chrome tanning powder, but at a reduced offer in line with the amount of chromium available due to the recycling technique. The tannage takes four hours and included a basification stage. A final addition of recovered chromium is then offered to the process from the second holding-tank at 55-75^{0}C.

This is a high volume addition and helps protects the hides from too much mechanical action. The elevated temperatures ensures good fixation, but also allows the hides to relax and spread within the tanning process.

Mechanisms within the Liming Cycle

With the water content of hydrated hides at approximately 64%,[4] and with a fresh water addition in the main swelling phase, a considerable amount of free water is introduced into each unhairing/liming cycle.

By diffusion, the concentration of chemicals gradually reaches an equilibrium between the float and the hide structure at the

Figure 2. Inspection of delimed and bated hides. Time saved within the processing allows optimum time in deliming/washings for the maximum removal of Inorganic salts, solubilized proteins and fats from deep within the fiber structure.

end of the lime process. On hide discharge, water held within the swollen hides together with solubles is removed from the system.

This water remains within each hide through fleshing and splitting but is finally released from the structure during de-swelling in the deliming and bating process. Salts and solubilized protein/fats are thus released from the structure in the same way as conventional processing, then washed away as normal practice. There is no build-up of these components within the process to carry forward in to the tanning operation.

In the next liming cycle, more fresh water is introduced from within the soaked hides. The recovered used lime float provides most of the float, but some fresh water is required too. This is added after hair removal, the volume required matching the amount of water take up by hide swelling in the previous liming cycles.

This continuous addition of fresh water, coupled with removal as held within the swollen hides in each cycle, avoids a continuous build-up of salts and other solubles. In practice the system reaches equilibrium in 5-cycles.

There are additional benefits with this technique too. The increased level of organic matter in the float provides a buffering action, and although the level of residual protein is low it is sufficient to avoid a sharp pH rise at the start of the hair immunization stage. In addition to any swelling repression caused by neutral salts in liming, this slower pH rise moderates the early grain swelling.

Mechanisms within the Chromium Tanning Cycle

There are similar mechanisms with the tanning cycles. Fresh water is introduced as held within the delimed hides and in the diluted formic acid addition.

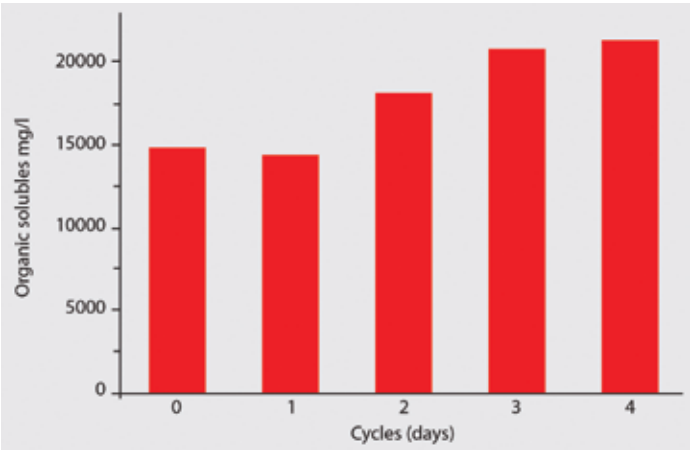

Figure 3. Equalization of the organic content in liming.[5] The graph shows a levelling of organic components within the liming process where equilibrium is reached within 5-cycles.

However, there is a small amount of swelling between the delimed and tanned states causing a water loss from the system. More fresh water is thus required, and this is added to the tannage with the addition of the recovered float at 55-75^{0}C.

Equilibrium is established by the end of tannage at the time of drum discharge. The removal of solubles contained in the hide-contained water also prevent a continuous build-up of formate, chloride and sulfate ions in the system. In practice equilibrium is reached in 20-cycles.

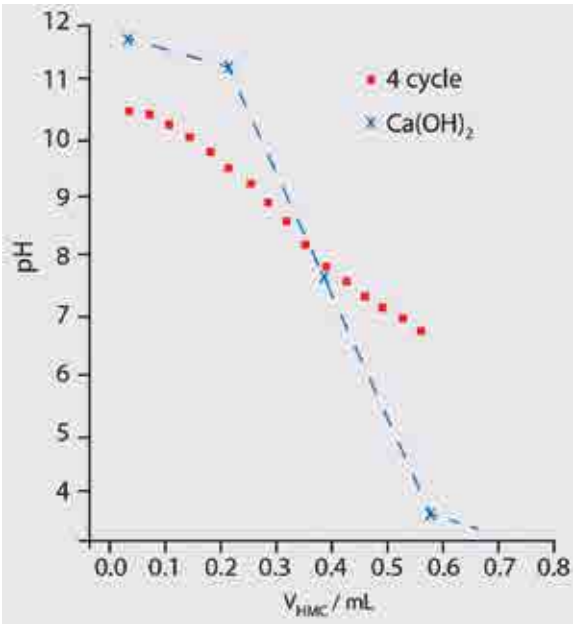

Figure 4. Buffering effects of the organic content in liming:[5] $Ca(0H)_2$/water x 4-cycle. The presence of the organic content in the self-contained approach provides a moderation of swelling in the early processing stages when compared to fresh water float.

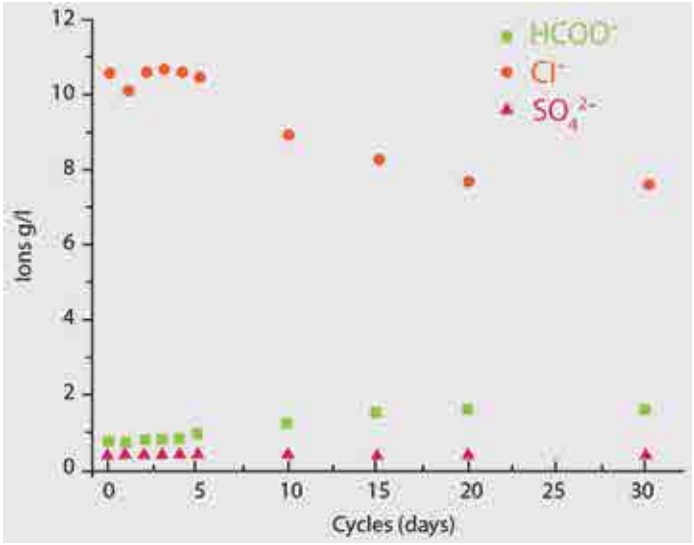

Figure 5. Equilibrium of formate, chloride and sulfate ions in chromium tanning cycles.[5] The graph shows a levelling of formate, chloride and sulfate ions in the chromium tanning process with equilibrium reached within 20-cycles.

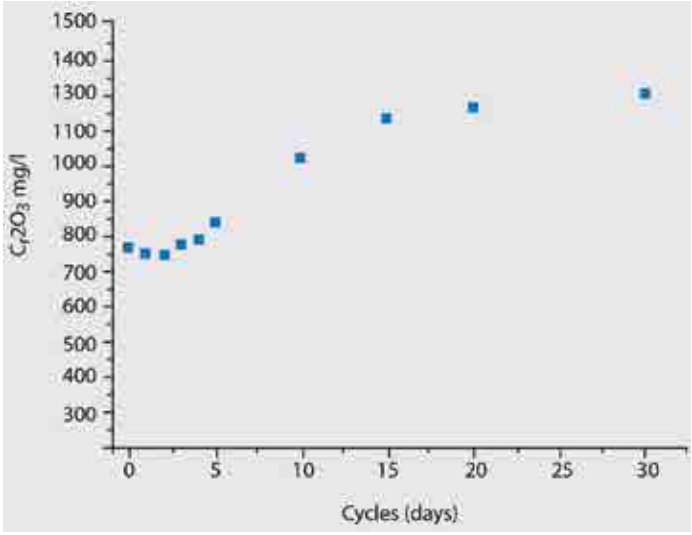

Figure 6. Equilibrium of chromium as Cr_2O_3 in chromium tanning cycles.[5] Similar to the levelling of ions shown in Figure 5, equilibrium of chromium ion expressed as Cr_2O_3 is reached within 20-cycles.

Results and Discussion

There are three important areas:

Advantage: Environmental
There is a total elimination of waste waters from liming and chromium tanning stages. This means that:

- There is no sulfide for oxidation, and hence no oxidation step within effluent treatment. Any residual sulfides carried over to deliming and bating can be treated within the process as normal practice.
- It is observed that there is an absence of odor as frequently found near to effluent treatment plants.
- There is no increase in the sulfate effluent component arising from oxidation of sulfides as found in normal effluent treatment. This plays part in an overall reduction in salts/ TDS in the treated effluent.
- There are no high-volume chrome containing waste waters to segregate and treat. There are no issues with precipitation, dewatering and disposal of chromium hydroxide as hazardous waste, with regeneration of chromium solutions for re-use. or within subsequent processes.
- No unused reactive chemicals are discarded for effluent treatment. There is complete uptake within the self-contained systems.
- The use of neutral salts in process is reduced to a minimum. with a corresponding reduction in TDS.
- Discharges for effluent treatment are at a much-reduced level of BOD, COD, nitrogen and suspended solids due to the hair saving component. The volume is reduced too as the water washes at the end of liming and tanning are eliminated.
- There is a significant reduction in the levels of solids for disposal due to the hair saving approach. It is observed that the hair is very intact and uncontaminated and offers potential for secondary uses.

Advantage: Chemical and Water Use
There is a significant saving in chemical required for processing. These savings differ between the tanneries, but within the first three tanneries studied these fall between the following values:

- 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)
- Up to 50% water savings (1 measure value)

Advantage: Technical and Product
The usual approach to reduce waste and pollution is to use high efficiency systems - such as low floats with high mechanical action, high chemical concentrations, and pH conditions that favor high uptake. But this approach carries problems associated with tangling and poor circulation of products between the hides - staining, grain abrasion/scuffing, and accentuated growth and draw.

In contrast, this technology uses more moderate conditions. Higher floats ensure that the mechanical action is gentler and a good chemical distribution. The technology does not demand a high uptake of chemicals at the time of processing - the unused chemicals are recovered and reused!

Moreover, the combination of a relatively high float - and elevated temperatures in tanning - enable the hides to become relaxed and extended.

The temperature control is very tight too, so summer/winter variations that are often experienced can be avoided. The chemical composition of the recovered floats held in the common holding tanks is very uniform too. It is not the result of a single-pack production but is a blend of all of the previous processing batches. It is consistent and the outcome of carefully managed production.

There are also savings in time due to the absence of washing used in traditional processing. This is significant as this can be used to good advantage. For example, ensuring that the penetration of chemicals before lime swelling is complete, and to provide additional time within deliming to ensure maximum removal of solubles and grease throughout the hide structure.

Conclusions

This advance recycling system is well-established for hair-saving liming and chromium tanning within commercial wet blue bovine manufacture. The technology enables significant chemical savings, avoids water waste, and eliminates the difficult sulfide oxidation and chrome recovery stages in effluent treatment. There is less waste for treatment, and less solids from effluent treatment for disposal.

In liming, there is a reduction in grain swelling in the early process stages, with equilibrium reached after 5-cycles. In chromium tannage a levelling of formate, chloride and sulfate ions occurs within 20-cycles. There is a time saving element too which can be used for process benefit.

The technology offers an alternative to the sensitive high efficiency approach to manufacture which can be so easily affected by small change. The moderate processing conditions offered by this self-contained technique is part of the manufacture of uniform and high value bovine wet blue leathers.

Acknowledgements/References

1. On site tannery surveys: Richard Daniels
2. The four major Chinese tanneries who opened their doors and gave permission for this study: Ruisen Leather, Fujian Province, Xingye Leather, Fujian Province, Xing Ning Tannery, Jiang Su Province, Haung Defu Leather, Hebel Province.
3. Auxiliaries developed by BIOSK for this technology: ELIPO-L (Agent for liming) ELIPO (Agent for tanning), DO-PRO (Liming Assist)
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5. Analysis of liming and tanning floats: Qilu University of Technology, Jinan, China and Shaanxi University of Science and Technology, Xian, China.