Closed-loop liming and chrome tanning processing: A solution to pollution

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Abstract

This paper concerns a radical new approach to the unhairing/liming and chrome tanning processes for wet blue manufacture. The technology - developed by BIOSK Chemicals, China – only produces waste waters from soaking operations, and the deliming and bating processes. The technology includes hair recovery and closed loop processing in liming and chrome tanning processes, and totally avoids waste waters discharged from these two major manufacturing stages.
The wet blue leathers produced are of high quality - proven by long term high volume manufacture – with dramatic savings in chemical and water use. The reduction in environmental load is significantly reduced, causing major saving in plant, energy use and operational costs, waste disposal charges and issues associated with chromium compounds.

Keywords: liming, chrome tanning, waste water.

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.
The technology was initiated and developed by BIOSK Chemicals over a five year period before introduction commercially in 2011. By 2016 the technology was being used in full scale production by the following tanneries which provide the basic information for this report:

- Ruisen Leather, Fujian Province, China.
- Xingye Leather, Fujian Province, China.
- Xing Ning Tannery, Jiang Su Province, China.
- Haunghua Defu Leather, Hebei Providence, China.

The production from these tanneries is 18,000: 12,000: 30,000: 12,000 / week respectively of wet salted hides from USA, Australia and Europe to the wet blue state for their own use, sales and contract tanning providing:

- Wet blue hides of high quality and consistency.
- Considerable savings in basic chemicals that were previously unused in processing.
- The elimination of unused chemicals (lime and sodium sulfide/hydrosulfide) from liming/unhairing and (salt, acids and chromium salts) from tanning operations for subsequent effluent treatment.
- Elimination of the sulfide oxidation stage in effluent treatment for used liming floats and wash waters.
- Elimination of problems associated with waste chromium salts - separation, recovery, regeneration/reuse, disposal, or contamination of solid wastes.
- A reduction in solid waste following effluent treatment, and compact hair for potential reuse.
- Savings in water, energy and processing time.

In 2018, a large capacity manufacturer of sheepskin nappa leather for clothing and footwear has changed to the technology. Several large scale bovine tanneries in Hebei Province are presently (2019) in the process of change for both tanning and liming stages.
The technology is not restricted to large tannery production. In the Zhaoyuan leather industrial park, Heilongjiang Province,10 small size tanneries manufacturing small skins and bovine hides to the wet blue state have changed their tanning technology, with the rest of the tanneries in the cluster contracted to change to meet a discharge limit of 0.5 mg/l for Cr.

Development of a technology

There are two key issues that BIOSK addressed when developing this technology:
1] Traditional high uptake processes for wet blue manufacture always left residual

chemicals for effluent treatment and this waste should be eliminated.
2] The leather produced should be consistent and of high quality.
Starting with small scale trials, pilot scale, and then full scale manufacture in a custom built plant the development included the development of biocides, fungicides and a liming assist designed to support the technology(2).

The technology

Central to the technology are two self-contained processing loops. The first is a hair saving liming process, the second a combined pickle and pre-chroming followed by chromium tannage. Other processing stages and operations are conventional, ie:

- A pre-soak (or dirt soak), green fleshing, main soak and washes.
- Lime fleshing +/- lime splitting operations according to the tannery needs.
- Conventional deliming, bating and washes.
- Waste waters discharged for normal effluent treatment.

The technology can be used by tanneries of any size, and their existing processes can be modified to the new procedures.

HAIR RECOVERY AND LIMING PROCESSES

There are two main factor in the BIOSK approach to unhairing and liming that are different when compared to conventional processing:

- All of the processing float at the end of the liming stage is recovered for use in following hair saving liming systems.
- There is a total absence of washes at the end of the liming stage. The recovered float remains a resource of concentrated chemicals for reuse.

The general processing details are as follows:

- No fresh water addition is made in preparation for the hair loosening stage, only recovered lime liquor, and lime and sulfide/hydrosulfide (at reduced offer)
- After hair loosening, the float is filtered for conventional hair recovery and compression, with the float returned to the drum.
- The float is increased for the main liming phase using more recovered lime solution and some fresh water, together with lime and sodium hydrosulfide at reduced offer.
- At the end of the process the drum is drained and the hides unloaded without any washing. All of the float and draining's from the front of the drum and surrounding floor areas are recovered using dedicated drainage.

Managing the hair recovery and liming closed-loop

The processing is managed as follows:

- 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 20-22^{0}C.
- Before re-use this solution is mixed using compressed air to ensure the dispersion of any fine residual solids in suspension.
- At the hair recover stage, as the hair is compressed, it acts as a filter for the residual fine solids. This keeps them at a low level and equilibrium within the ongoing process.
- The float in the main swelling phase is often increased in several offers to carefully manage the swelling.
- In addition to the recovered lime solution some fresh water is needed too. This is because float is absorbed by the hides on swelling, and so water as "free float" is subsequently removed from the system. The volume of fresh water required is the same as the water taken up by hide swelling.
- As set down previously, there are no washings at the end of the process so that the unused chemicals in the recovered solutions remain fully concentrated.

Recovered floats from liming and hair saving processing are held in a single tank fitted with heat exchange systems.

The limed hides from fleshing are clean and relaxed for offer to the lime splitting operation.

The hair recovery operation. The hair is very intact and serves to filter residual solids and fats from the float.

Full release of detritus proteins, fats and salts from within the structure on deliming and bating.

HANDLING BETWEEN LIMING AND CHROME TANNAGE

After liming the hides are tipped into a container set beneath the liming vessel, and delivered directly to the area by the lime fleshing machines where 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 as normal, and residual water cut from the flesh side at the moment of fleshing. Splitting is conventional before offer to the deliming and bating process.

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.

ACID/SALT PICKLE AND CHROMIUM TANNING PROCESS

There are two main factor that are different from conventional chrome tanning systems:

- All of the float at the end of the chrome tanning stage is recovered 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.

The general processing details are as follows:

The recovered chrome containing solutions are used in a combined acid/pickle and chromium pre-tannage process. After the main chrome tannage, a final addition of recovered chrome solution is made at an elevated temperature.

Chemical additions – salt, acid and chrome tanning agents - are at reduced offer, and on completion the bath is of sufficiently low chrome content that a final wash can be

avoided. At the end of the process the drum is drained and the hides unloaded without any washing. All of the float and drainings from the front of the drum and surrounding floor area are recovered using dedicated drainage.

Managing the chrome tanning closed-loop

In general, the process is managed as follows:

- The recovered floats from all of the tanning drums are filtered using a filter press to remove fibres and other fine insolubles from suspension. The chrome solution is then delivered to two containment tanks. One tank is temperature adjusted using heat exchange to 20-22^{0}C, the second tank adjusted to between 55^{0}C and 75^{0}C 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 and a small addition of pre-diluted formic acid 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 20-22^{0}C. 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 between 90 and 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 to suit the tannery needs and to raise the processing temperature
- There are no washings with fresh water at the end of the process. The Cr content is low at 0.2 – 0.3%, and the unused chemicals in in the final float remain at this concentration.
- All of the drainings from the drum areas and stacking areas are collected for reuse as described.

No wash required after chrome tanning as low residual Cr2O3 content in the float. Recovery includes all drainings from stacking areas.

All recovered chrome containing floats are filtered to remove solids and fibres before storage in holding tanks for reuse.

WATER EXCHANGE AND PROCESS EQUILIBRIUM

Within both closed-loops there is a stabilisation in terms of chemical concentrations and neutral salts. This stabilising is due to water exchange: water is added to the system and then removed together with neutral solubles held within the fibre structure at the end of each process as follows:

The liming stage

There are no washing stages, nevertheless there are both additions and removal of water.

It is stated that fresh hides contain 64% moisture[3]. Accordingly, water is introduced to the unhairing/liming process contained within the fully soaked hides. During the processing, a fresh water addition is needed too for the replacement of water absorbed by hide swelling in previous liming cycles.

This means that a considerable volume of fresh water is introduced into the liming process. As the process develops, an equilibrium is established by diffusion between the

water/solubles in float and within the hide structure. On hide discharge from the drum, the large volume of water held within the collagen structure – together with solubles – is taken from the otherwise fully closed system. The level of solubles in this self-contained system builds up over five cycles but then stabilises. This is shown in Panel 1:

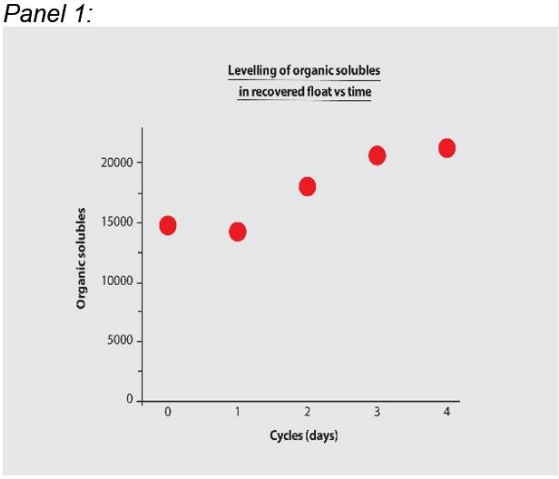
The inorganic content provides useful advantage too as it helps moderate the rate of swelling in the initial liming stages. Instead of a sharp rise in pH on the addition of alkali to process, there is a buffering effect and this appears to moderate the swelling rate when compared to processing using fresh water.

damage to the sensitive grain, or too much surface fixation of chromium.

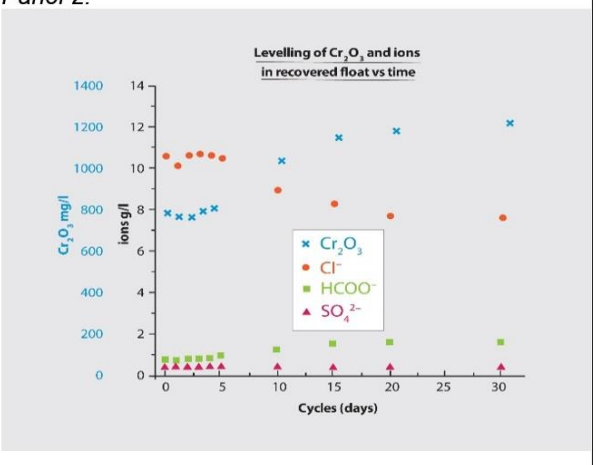
The processing is more relaxed to suit an expensive and delicate structure. The floats tend to be high, and the chemical processing moderate.

As an observation, in liming, the swelling appears slower and more suppressed at the hair release stage, with the hides very relaxed before main swelling. In tannage excessively low floats are avoided, and the temperature rise at the final phase of tanning enables relaxation and hide extension. A high uptake of chemicals is not an objective at the time of liming and tanning as any the active chemicals that remain are fully recovered for reuse.

Panel 1:



Panel 2:



The tanning stage

There are no washing stages, nevertheless there are additions of water as contained in the delimed and bated hides, as a very low free float for the light surface acidification, and from dilution of the formic acid.

During process, diffusion occurs as in normal processing, with the level of solubles building up over twenty cycles and then stabilising. This is shown in *Panel 2*[5]*:*

ADVANTAGES OFFERED BY THE TECHNOLOGY

There are significant advantages in the quality of product, in chemical and water savings, and environmentally as follows:

a] The quality of leather

This is not a typical high chemical uptake approach to manufacture. The processing does not rely on low floats and pH conditions to drive a high chemical uptake. Consequently, issues such as tangling and poor chemical distribution are avoided, together with abrasion

The use of recovered floats provides other advantages too. Tight temperature control of the recovered solutions via heat exchange means that summer/winter variations that are often experienced are avoided.

Also, the chemical composition of these solutions is very uniform. They are not the result of single-pack production, but a blend of all of the previous processing batches. The processing is consistent, and the recovered solutions are the outcome of carefully managed production.

There are also savings in time as many of the washing sequences are avoided, and this can be used to advantage. For example, in liming, to ensure that alkali penetration is complete throughout the structure, and in particular in the folded and creased structure in the neck parts, before main swelling to minimise growth marks. Also - if necessary – to make more time available to ensure a thorough deliming and release of solubles, protein residues and grease throughout the structure before the final washes.

b] Savings in water and chemicals

There are significant savings in water. One of the tanneries visited reported a water reduction of 50% due to this technology. In addition, there is no need to accommodate the reuse of wash waters. For example, the collection of second wash waters for reuse as the first wash as practiced after liming and tanning.

All of the active processing chemicals are completely used i.e. sulfides/hydrosulfides, alkali, and acids and chrome tanning agents. None of these are wasted.

If precipitation of the unused chrome is common practice before disposal, then there is no need for alkali additions to create chromium hydroxide. If regeneration is practice, then there is scope to save the acids used to regenerate a weak chrome solution.

The savings in chemicals are considerable. At the time of site surveys in the first three tanneries to adopt these processes savings were varies, but ranged 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)

c] Environmental advantages

All reactive chemicals are fully used in processing:

- There are no unused active chemicals discharged for waste water treatment from liming and tanning
- There are no sulfide containing waste waters to separate and then oxidise. There is no need for an oxidation stage, the addition of catalysts, or energy requirement for the provision of oxygen.
- There are no neutral sulfites/sulfates arising from oxidation of waste lime discharges. The potential for reduction at a later stage to form hydrogen sulfide with associated toxicity risks is thus eliminated.
- A general lack of odour within the tannery and around the site in general.
- A lowering of neutral salts and inorganic Total Dissolved Solids, discharged to effluent treatment.
- Discharges from liming are at a much reduced levels of BOD, COD, nitrogen and suspended solids.
- Chrome related issues are avoided as there are no chrome containing waste waters from wet blue manufacture. Accordingly, for wet blue units, there is an absence of chromium within the solids generated within effluent processing. The disposal of dewatered solids classified as a toxic waste is avoided, extending the possibility of other uses for these solids.
- The recovered hair is very intact and compact. It is free of chrome contamination with potential for secondary use.
- The water volume is reduced. This offers advantage for longer retention times in existing effluent treatment to further raise standards, or for a smaller and more compact effluent treatment plant.
- Energy saving from reduced air requirements for oxidation and for aerobic biological treatment.
- A reduction in size, energy and running costs for ultra-filtration, reverse osmosis or other advance treatment systems used for tertiary treatment.
- Where zero effluent treatment is required, there are reductions in:
    - Volume of treated effluent for evaporation
    - Plant size
    - Energy use
    - The quantity of recovered salts.
- The volume of solids generated within effluent treatment is reduced in volume and can be chrome free. Recovered hair that is dewatered and uncontaminated.

BIOSK technology offers significant reduction in solid waste from effluent treatment for disposal. Recovered hair is chrome free with potential for other uses.

Provides a reduction in volume and neutral salts for Zero effluent Discharge treatment togethr with reduced energy costs.

This is a significantly different approach to leather making, avoiding many of the issues associated with traditional manufacture. The technology is proven by many years of production of high quality wet blue leathers.Major saving in chemical use are offered. A simplification of effluent treatment, minimisation of solid waste, a reduction in volume of water used and discharged, and a lowering of components for end-of-pipe discharge.

Conclusions

A radical new approach for wet blue manufacture has been developed by BIOSK Chemicals, China that totally avoids effluents discharged from liming and chromium tanning processes. It eliminated traditional environmental problems associated with wet blue leather manufacture, and produces a high quality product.

Thanks and acknowledgements

1] The four tanneries that opened their doors for site inspection:

- Ruisen Leather,Fujian Province, China:
- Xingye Leather, Fujian Province, China:
- Xing Ning Tannery,Jiang Su Province, China:
- Haunghua Defu Leather, Hebei Province, China.

2. Auxiliaries developed by BIOSK to support the technology: ELIPO-L (Agent for liming) ELIPO-D (Agent for tanning), DO-PRO (Liming Assist)
3. Leather Technicians Handbook: J.H.Sharphouse
4. Analysis of liming floats: Qilu Universtiy of Technology, Jinan, China
5. Analysis of Tanning floats Shaanxi University of Science and Technology, Xian, China.
6. Site visits and photographs: R.Daniels.