A radical new approach within liming and chrome tanning technologies

DIRECT REUSE OF CONCENTRATED USED FLOATS IN WET BLUE MANUFACTURE AVOIDANCE OF EFFLUENT FROM LIMING AND TANNING PROCESSES

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A revolutionary approach to liming and tanning practices has been successfully developed by BIOSK (SQ) Chemicals, China. Concentrated floats from liming and tanning are retained in self-contained cycles and reused in processing. This results in:

- *100% use of chemicals required in liming and chrome tanning processes*
- *Savings in chemicals and water consumed*
- *Virtual elimination of all effluents from liming and tanning processes*

Among manufacturers who are using these techniques are three major tanneries who between them process some 60,000 wet salted hides a week to the wet blue state.

Full scale manufacture using these techniques commenced in 2011, and this report is based on detailed information given by these tanneries during site visits by World Leather *in June 2016.*

1. Introduction

Following five years of investment in development, large scale pilot trials and refinement by BIOSK Chemicals Co. Ltd[1], direct recycling systems of undiluted used floats from liming and unhairing, and chrome tanning are now established in full scale operation for the manufacture of wet blue leather. To create this report three major tanneries in China were visited:

- Xing Ning Tannery, Jiang Su Province
- Ruisen Leather, Fujian Province
- Xing ye Leather, Fujian Province

The input as wet salted hides from USA, Europe and Australia for footwear leather and some sales of wet blue were 30,000, 18,000, and 12,000 hides per week respectively. The recycling systems commenced in the tanneries in 2013, 2011, and 2011 repectively.

In the BIOSK approach—named as "BIO-cycle" technology by the company—used and concentrated floats from the liming and tanning processes are recovered and directly used in subsequent batches. The hides are discharged without any washings after these processes, and good systems for transporting hides and their management ensure ease of movement and

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handling within machine operations.

An absence of any washings means that the unused chemicals in the recovered floats remain at a high concentration, and thus in the optimum state for reuse. Both the liming and tanning operations become self-contained, and the chemicals offered to process are used completely, without losses of any residual chemicals.

The absence of washing results in considerable savings in water, chemicals and processing time. Moreover, there are no contaminated wastewaters from either of these two difficult process stages for effluent treatment.

Of the tanneries visited, all three are using the technology both within liming/unhairing and chrome tanning processes. An outline of the way that these self-contained systems operate is described in this report.

2] Recycling: liming and unhairing

Hides are limed using a hair recovery process that directly uses recovered concentrated floats from earlier liming/unhairing procedures, replacing fresh water.

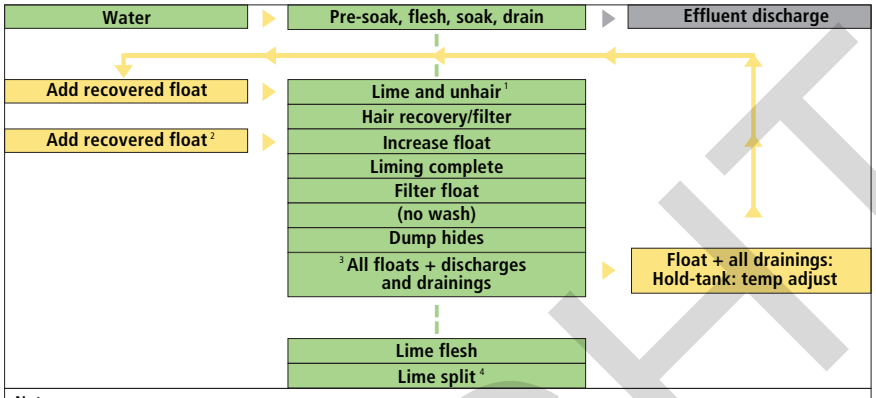
2.1 FLOAT RECOVERY FROM LIMING / UNHAIRING OPERATIONS

The liming process includes a hair recovery filtration step. At the end of the liming/unhairing process the used float is drained and filtered a second time to remove any remaining hair debris. These concentrated used floats are then pumped using dedicated pipework to a recovered lime-holding tank. There is no washing sequence at the end of the liming process.

Instead, the limed hides are dumped into stainless steel watertight trucks, together with some remaining float. Any overspill is collected in the drainage gully that is dedicated to the liming section only. Spillage from a wider area in front of these drums can be brushed into this gully, too, then pumped to the recovered lime-holding tank.

The hides are transported by forklift truck into the limed fleshing area, where the remaining float in the trucks assist the hides flow onto the floor. As the hides spill onto the floor they separate, and can be easily hooked onto a line conveyor for delivery to the lime fleshing operation. There is no contamination by other floats in this area, so the spillage and drainings are collected via drains and pumped to the recovered lime-holding tank. This area is mainly surrounded with rubber bunding of sufficient height to contain this spillage but low enough to allow the easy movement of forklift trucks.

Panel 1: The liming process: direct reuse of used floats and chemicals in a self-contained loop [3]



Note: [1] Reduced chemical offers (chemicals in recycled float made up to required quantity)
[2] May be several additions: can include water and chemicals
[3] No effluent discharge: floats and chemicals retained in a self-contained loop
[4] May remain as full substance

The recovered lime holding-tanks are of sufficient capacity to hold and blend more than one day's discharges from the whole liming section. They are fitted with heat exchange systems and heat pumps for adjustment to a required temperature between 20-25°C before direct use in subsequent liming processes. To ensure that the recovered liquor is fully homogeneous—especially the unused lime particles that would otherwise settle out—a small volume of compressed air is introduced for mixing purposes at the time of offer to the liming operations.

2.2 THE LIMING / UNHAIRING PROCESS

Previously the hides have been pre-soaked and green fleshed, then loaded into the liming drums for the main soaking operation. The process starts with the drums being thoroughly drained after the main soak.

The recovered lime liquor (temperature adjusted) is pumped directly from the lime-holding tank as the float. Additions of chemicals and liming auxiliaries are made as required for the process.

After two hours the hair recovery takes place. Here the float is recirculated over a 30 minute period through the hair filter, then pumped back to the drum.

A second addition of recovered lime liquor together with some water is added after four to six hours, with the process finishing some 10 hours later. The float is then discharged for recovery and reuse as described in section 2.1. A schematic outlining the recovery and reuse system is given as *Panel 1*.

After lime fleshing the hides are trimmed, lime split and drum loaded for the deliming and bating procedures.

2.3 OBSERVATIONS

- The appearance of the limed hides at limed fleshing showed normal swelling with necks well extended. After splitting there is more relaxation and a clean grain.
- All of the used floats are completely recycled in the concentrated form. There is a total absence of washings of drained limed goods to cause any dilution within the system or surplus for treatment in the effluent treatment plant.
- The process is almost self-contained. The float is "topped up" with some fresh water, but this is to make up a loss caused by the water taken up by the hides due to swelling. The residual chemicals in the used float are also "topped up" in the liming process, but with much reduced chemical offers. The use of these chemicals and float is complete. Everything is used and there is nothing to discharge.

3. Recycling: chrome tanning

This process is based on an acid pickle with a chrome pre-tannage using recovered chrome liquor. This is followed by a chrome tannage, supported by a second addition of recovered chrome liquor

3.1 FLOAT RECOVERY FROM CHROME TANNING OPERATIONS

At the end of the tanning process there is no washing stage. Some of the float is drained from the drum using conventional draining gutters and pipework for delivery to a chrome reception sump. The hides are

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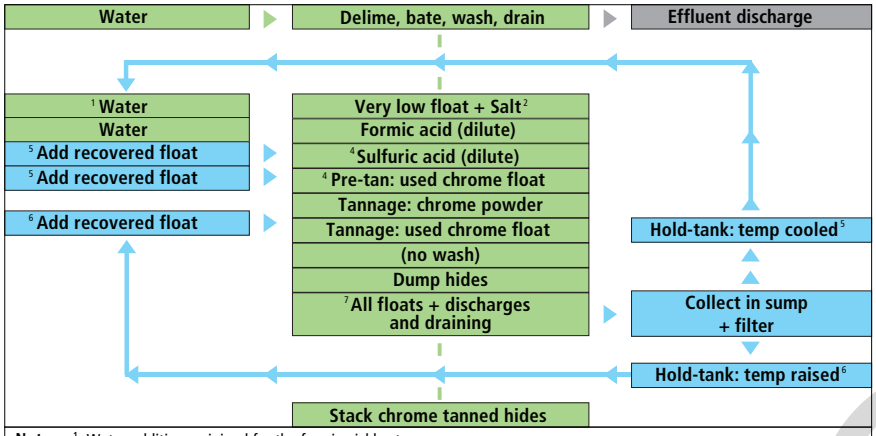
Panel 2: The chrome tanning process: direct reuse of used floats and chemicals in a self-contained loop [7]



Note:
[1] Water additions minimal for the formic pickle stage
[2] Low salt offer: build up of sodium sulfate/chloride from recycled chrome floats
[3] Float minimum to dilute formic acid
[4] Acid and pre-chrome tanning solution added together: avoids chrome stains
[5] Temperature reduced for pickle and pre-tannage (20°-22°C as required)
[6] Temperature raised for main tannage (55°-65°C as required)
[7] No effluent discharge: floats and chemicals retained in a self-contained loop

then dumped directly into watertight trucks, with the spillage draining from the area also flowing to this sump.

The hides are delivered to a wet blue stacking and grading area, and discharged from the trucks together with the residual float. This area is isolated and can be bunded, with the drainings also flowing onto the chrome reception sump.

Next, the recovered used chrome liquors are coarse screened, then fine screened using a wedge wire filter followed by delivery into a shallow tank for removal of any floating solids. Alternatively, a conventional filter press is used.

The recovered liquors are then delivered to two holding-tanks:

- One tank (a) is used for holding recovered chrome liquor for use in the pickling stage. Here the temperature is reduced by heat exchange to a defined temperature between 20°C and 25°C.
- The second tank (b) is for use in the tanning process, and an adjustment is made to a required temperature between 55°C and 65°C.

3.2 THE CHROME TANNING PROCESS

The techniques vary, but a generalised procedure is given:

- After deliming and bating the drums are completely drained. As an alternative, the deliming and bating processes can take place in separate drums, followed by dumping into trucks and loading into tanning drums. The objective is to transfer the minimum amount of water into the pickle/tanning process.
- If there is no remaining float, then a little water may be added.
- An addition is made of between 1.0% and 3.0% salt.
- An addition of 0.5% formic acid diluted in water is made.
- Run the drum for 10 minutes.

Two containers may be used for the acidification stage, one being for the feed of formic acid. The second is used for the dilution of sulfuric acid using recovered and chilled chrome liquor (from holding-tank a) to replace water.

- The next stage is a combined pickle and chrome pre-tannage where recovered and chilled chrome liquor (from holding-tank a) is pumped into the tanning drum. At the same time, the diluted sulfuric acid is blended with this chrome liquor addition using a metering pump. This addition takes about 10 minutes.
- Run 90 – 120 minutes.
- Chrome powder is then added for tanning, the weight being calculated so that the total offer as chromium will be to specification.
- Run 4 hours.
- An addition of recovered and heated chrome liquor is then made (from holding-tank b), and the drum is run for a further 4 hours. This includes a basification stage.
- A final float of 150% is produced.

At the end of the process, the float is discharged for recovery and recycling as described in section 3.1. A schematic outlining the recovery and reuse system is given as *Panel 2*.

3.3 OBSERVATIONS

- The wet blue leathers showed a smooth and fine grain. The necks were well extended, with a lack of draw in the belly parts.
- The hides were clean, with no signs of chrome stains or residual hair.
- The process is virtually a self-contained loop similar to the liming stage and is "topped up" with chemicals and water.
- The salt offer can be very low due to the build-up of sodium sulfate from previous additions of chrome powder, and the recycling of sodium chloride.
- Chrome and acids are added to the system, but there are no effluent discharges.

4. The tanneries

- These are modern and well equipped tanneries. The processing drums are 4.2 x 4.5 metres in size and fitted with deep shelves. The input is between 450 and 500 hides in each drum load, with a limed split weight (may remain full substance for special requirements) for tanning between 8.0 – 9.0 tons.
- The pre-soak, soak, lime, delime and bate, and tanning drainage arrangements are completely separate. This avoids any cross contamination of the recovered liquors. In some situations, the drainage pipework can be opened and cleaned inside with cleaning rods and detergent.
- The plants are clean, spacious, have good floors and are efficiently managed. There are time-saving benefits due to the absence of conventional washing cycles. The unloading of drums and movement of goods by forklift trucks and other handling operations is fast and very effective.
- It appears that the recycling of the large volumes of recovered floats and materials and the temperature control, ensures a high consistency of the wet blue leather.
- The recycling is said to take between 5 – 10 cycles before the process fully reaches equilibrium.

5. Advantages using BIOSK technology for wet blue manufacture

The technology can be easily implemented, and it only needs a small investment and modification of equipment. Moreover, there are considerable savings that can be achieved.

5.1 SAVINGS IN WATER AND CHEMICALS

Over and above a consistent, well extended and clean grained wet blue

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Hides are given a short pre-soak, then unloaded for green-fleshing.

All of the holding tanks for the recovered used floats are fitted with heat exchange coils and heat pumps to raise or lower the temperature as required.

Before recycling as a complete replacement of water in the liming process, the recovered used floats are thoroughly mixed to ensure that any residual lime is in suspension.

The hair is recovered after a two hour process time, and is substantially intact and well compacted. The float is filtered a second time before final discharge and collection.

leather, there are reductions in the amount of chemical offers and water use. These vary between the tanneries but can be set down as minimum and maximum savings on hide weight as:

- 200 - 300 litres of water per hide.
- 0.4 - 1.5% sodium sulfide and sodium hydrosulfide combined.
- 1.0 - 3.5% lime.
- 3.0 - 4.0% salt.
- 1.0 - 2.5% chrome powder.
- a reduction in acid requirements in the pickle stage.

These savings when based on the original process requirements, can be expressed as:

- Up to 50% water (excluding savings that can be made by reuse of used soak liquors - see *Panel 3*).
- 18 - 50% sodium sulfide and sodium hydrosulfide combined.
- 17 - 43% lime.
- 57 - 71% common salt.
- More than 29% chrome tanning powder.

Panel 3: The reuse of used floats from soaking operations for pre-soak

One of the tanneries is reusing floats from the main-soak process. These are collected and held in a pair of soak-holding tanks for temperature adjustment, then used as a fresh water replacement for a pre-soak (dirt soak). At the end of this process they are discharged to the effluent plant as normal practice.

5.2 SAVINGS IN EFFLUENT TREATMENT

Discharges remain from the pre-soaking and soaking processes, and from deliming and bating, but there are radical difference in terms of effluent treatment between this and conventional technologies. This is due to:

- The absence of discharges and washings from the liming/unhairing process with the attendant sulfide for oxidation, and the heavy load of suspended solids, COD, BOD and nitrogen from hair burn.

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The liming process and subsequent lime fleshing operations produce clean and well extended hides for offer to the lime splitting operation.

All floats and drainings from chrome tannage and from stacking areas are collected in a common sump. They are then filtered to remove any solids and grease, and delivered to holding tanks for recycling.

- Advantage gained from the hair recovery process as the hair remains very intact. A well dewatered, compact, fibrous and uncontaminated by-product is produced with scope for reuse. This is in contrast to high volume sludge for removal within effluent treatment that results from hair burn processes, and avoids the problems created by a mixed and contaminated sludge for dewatering and disposal.
- A rationalised chrome tannage process. This avoids issues associated with conventional practice where the large volumes of low concentration chrome containing wastewater requires either chrome precipitation and disposal, chrome recovery, or a large volume of chrome contaminated solids from effluent treatment for final disposal.
- A lower level of salts to address, especially sodium chloride as produced from conventional acid/salt pickle.

Over and above these significant advantages, there are other gains within existing effluent treatment plants due to the longer retention times that are provided by the reduced volume and load as this can result in improved performance.

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Two tanks are used to hold the recovered chrome solutions. One is for use at pickling and pre-tanning stages, the second as part of tannage. Two tanks are needed because of different temperature requirements at these two stages.

The final wet blue leathers are well extended, especially in the neck parts. The grain is smooth, fine and clean, and show no signs of staining.

For a new plant there are reduced investments required as the plant size and footprint can be significantly smaller than normally needed.

Legend

- *BIOSK Chemicals Co Ltd specialises in the research and promotion of leather production technology. It produces different types of products required in leather manufacture including liming auxiliary Do-Pro, and tanning auxiliaries Elipo L and Elipo D, respectively a bactericide and fungicide. To support the technology described:*
  - *Elipo L is used at 0.15% offer in the liming process.*
  - *Elipo D is used at the beginning and end of pickle/tanning at 0.25% total offer.*
- *The company also manufactures hair filtering machinery for hair recovery purposes, and provides technical support and services for the industry.*
- *The technology as described in this overview is patent protected in China, Australia and New Zealand.*

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HIGHLIGHTS

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