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Abstract

The following paper describes technology for the recovery and recycling of unused chemicals from both the unhairing/liming and pickle/tanning processes for chrome tanned leather. The technique was investigated by BIOSK at pilot scale of 40 hides/load, then on full scale production in their own tannery, before introduction to tanners in 2009.

The objective was to avoid the high waste of chemicals in manufacture, without endangering the properties or quality of the wet blue, and eliminate chrome discharges. It is now widely used by tanners in China for the manufacture of bovine and sheep skins leather on large scale, but also by small size enterprise.

Keywords

- Advanced recycling systems in commercial wet blue manufacture.
- Elimination of waste waters from unhairing/liming and pickle/chrome tanning processes.
- Minimised effluent treatment.

1. Introduction

The manufacture of wet blue leather centres around the use of very basic chemicals and controlled manufacturing techniques. New products or techniques may be advocated for high chemical uptakes or environmental reasons, but these inevitably change the product, and carry issues themselves. In addition, the techniques may become more complex and difficult to manage.

Normally, the end-floats from these processes are discharged for various options within waste water treatment. But they still contain a considerable amount of unused chemicals, where the inorganic components contribute heavily to the total dissolved solids component. Sulfide containing waste waters may be manageable, but need treating separately, and are of concern regarding toxic emissions and odour.

Chromium is a different matter. The limits set on Chromium in waste water discharges are very stringent, and failure to comply can end in closure. Treatment demands separation of tanning end-floats and washes from the other waste waters, then demand more chemicals and plant to produce solids suitable for disposal. This waste is classified as hazardous. It is possible, via further chemical treatment, to produce a tanning product from this waste. However, this introduces variations into the quality of the final wet blue.

The technology described takes a different approach. It follows traditional leather manufacture, but with more focus on the management of end-floats from unhairing/liming and pickle/tanning. In this situation, these solutions containing unused chemicals are introduced back into process. This significantly reduces the environmental impact of the tannery, and minimises chemicals consumed.

2. Materials and Methodology

The techniques developed are used by manufacturers of bovine and sheepskin wet blue leathers, but with amendments mainly in the areas of pickle and tanning to suit individual plant requirements. They apply to large tanneries with a long-established layout, within small-scale manufacture, and in the new-build situation. Overall, the processes can be viewed as managed in four different sections as follows:

2.1 Soaking and preparation for unhairing/liming.

Hides and skins are soaked conventionally, and within these operations they are green fleshed to remove as much unwanted material as possible. This provides a clean and uniform structure of accurate weight for liming and unhairing process.

All used floats and washings are discharged for effluent treatment.

2.2 Hair removal and liming.

A conventional hair saving approach is used to minimise the organic load on effluent treatment. This requires the controlled discharge of processing floats after hair loosening for hair separation and compacting. The filtered float is then returned to the processing vessel for the process to continue.

However, the process starts where the initial float comprises a solution of unused chemicals recovered from previous processes. These are drawn from a holding tank where the end-floats from all of the processing vessels have been delivered. These are blended together for uniformity, then temperate adjusted (via heat exchanges) to ensure an accurate starting temperature.

The chemical offers are reduced in line with the unused unhairing/liming chemicals in the recovered solution, and savings from the first three tanneries adopting the technology are set down in Section 3.2 as Figure 1. The process continues as normal, with an addition of fresh water when hide swelling is required after complete chemical penetration. At the end of the process, the hides are discharged with the end-float, and delivered directly to limed fleshing.

There are no fresh water washes. The undiluted end-floats are delivered to the main holding tank to mix and balance with discharges from the other liming vessels. In addition, all draining from the adjacent floor areas and delivery routes are collected for re-use.

The hides after liming are flat and well extended, and there is no extra or irregular swelling from fresh water washes. The limed fleshing operation removes both flesh and any residual float from each hide before delivery to limed splitting.

There are no discharges of end-floats or washings for effluent treatment.

2.3 Deliming and bating processes.

These are managed as normal practice. The deliming and bating may take place in the same float, or be separated. The washings can vary, but all salts and residual materials are released from the structure on deswelling, then washed away.

All used floats and washings are discharged for effluent treatment.

2.4 Pickling and chrome tanning

The process is based on a conventional salt/sulfuric pickle, but combined with a pre-chroming. This is followed by a chrome tannage, with a second chrome offer at raised temperature.

Both the combined pickle/pre-chrome, and the second chrome offer uses solutions containing unused chromium compounds as recovered from previous pickle/tanning operations as follows:

- At the end of tanning, the hides and floats are discharged without any washings. The hides are stacked to drain, with all draining's contained in the department by bunding.
- All of these weak chrome solutions are filtered, then delivered to two holding tanks where they mix with discharges from the other tanning vessels. They are temperature adjusted in the first tank (No.1) to suite the pickle process, and the second tank (No. 2) to 55 – 75C (according to tanners' requirements).
- In preparation for pickle, the goods are given a very low float with fresh water, salt added, then a small addition of formic acid. This is sufficient to acidify the grain and avoid chrome staining.
- The pickle commences with a sulfuric acid offer diluted with solutions from tank No.1, and at the same time more solution from tank No.1 is pumped into the drum to increase the float to 50%.
- The main chrome tannage follows as normal, but at reduced chrome offer. After basification, the float is increased by a further 100% using the recovered chrome solutions from tank No.2. This high temperature addition ensures a high chrome uptake, so the concentration at the end of process is suitable for unload without any washings.
- The hides are stacked to drain before selections in a bunded area.

There are no discharges of end-floats or washings for effluent treatment.

3. Results and Discussion

3.1 Water management within closed systems

This high efficiency technology offers a significant reduction in water use. At the end of liming, any end-float that remains on the surface after delivery to fleshing is pressed, squeezed and slicked from the hides at the time of fleshing. This means that water-washes on completion of liming can be avoided. Similarly, the chrome uptake is sufficiently high to eliminate the need for washes to avoid staining.

At the same time there is significant movement of water within these two processes to avoid a high build-up of neutral salts.

As an example, consider an unhairing/liming process that starts with an offer of recovered float at 80% of the input weight. Here, the soaked/fleshed hides already contain fresh water held within the structure – approximately 60% on in-put weight - and this is increased by a 20% addition of fresh water. The total amount of water in the system is therefore 160%, half being introduced as fresh water, and half as recycled chemicals in solution.

At the end of process, as a result of alkali swelling, the hide-bound water containing chemicals consumed has increased from 60% to 80%. This hide-bound water, with used chemicals and solublised proteins/fats etc. is then released in the deliming/bating process - as within conventional processes.

Similarly, fresh water held in the delimed/bated/washed hides is introduced to the pickle, with a small addition of fresh water to assist the distribution of salts and formic acid. On completion, the water held in the tanned leather is removed from the system.

These appear to be closed-loop processes, but involve significant water exchange. Continuous additions of fresh water are made to both unhairing/liming and pickle/tanning systems, with equal volume removals at the end of each operation. This prevents a continuous build-up of unwanted salts, and both the liming and tanning procedures achieve equilibrium.

3.2. Chemical savings

Saving vary according to the processes used by the tanners before change to this technology. The values from the first three tanneries that adopted the technology are set down in Figure 1:

Figure 1

Savings in Chemicals and water

Chemical savings	Percentage
Sodium sulfide and hydrosulfide (combined)	18 to 50
Calcium Hydroxide (lime)	17 to 43
Common salt (pickle)	57 to 71
Chrome tanning agent (only one exact value)	29
Water	Up to 50

Stated but not measured

- Considerable reductions in water, and in the energy required to temperature control this water.
- Lack of odour in the tannery and effluent treatment areas.

3.3 Environmental advantage

There are significant advantages involving issues of logistics and sustainability:

Unhairing/Liming operations:

- Elimination of waste waters from unhairing/liming.
- No segregation of sulfide containing floats at the end of processing.
- No sulfide oxidation treatment.
- Significant lack of odour in plant and external.

- Reduced BOD, COD, Nitrogen, Solids and TDS.
- Recovered hair - compact and chrome free
- Significant savings in chemical savings.

Chrome tanning:

- Elimination of chrome discharges from wet blue manufacture.
- No segregation required of chrome containing floats at the end of process and washings.
- No processing of chrome containing waste waters.
- No high chrome solids as hazardous waste for disposal
- No collection and reprocessing as a (variable) chrome tanning agent.

In general:

- Reduced volume of waste waters in terms of volume and concentrations for effluent treatment and site discharge.
- A smaller effluent treatment plant required.
- Savings in energy (lower requirements for biological treatment and no sulfide oxidation)
- Significantly lowering of neutral salts (TDS).

3.4 Leather Technical

Advantages can be summarised:

- Flexible and adaptable technology to meet individual tanners needs.
- Stable and consistent manufacture.
- A flat and well relaxed wet-blue leather.
- Fine grained, clean and free of stains, and uniform colour.

4.0 Conclusion

The technology offers the total elimination of waste waters from both the unhairing/liming and pickling/chrome tanning operations in wet blue manufacture. This high efficiency processing is based around the use of basic chemicals and control systems, and provides a consistent product to specification.

There are substantial savings in chemicals usage, and corresponding reductions in the quantities of unused chemicals requiring effluent treatment.

Among other environmental advantages, there is the elimination of chrome containing waste waters and solids classed as hazardous waste to address from wet blue manufacture. This is very significant where stringent limits are set based on the chromium content at the point of discharge.

This high value and high efficiency leather making technology is central to issues of sustainability.

6.0 References

- Technology developed by Biosk Chemicals, China
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