The Elimination of Effluent from Liming, Acid/salt Pickling and the Chromium Tanning Processes

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Abstract

It is acknowledged that within the chemical processing of hides into chrome-tanned leather that the liming, acid pickle and the tanning processes are the major contributors of pollutants. This is in terms of biological load, suspended solids, sulfide, nitrogen, chromium, salinity and the resultant sludges for disposal.

This loading includes unused chemicals that are discharged from these processes due to their poor process efficiencies. Many attempts have been made to lessen this waste at source, but technologies in common use have basically remained unchanged for decades.

Solutions to these problems are far reaching, and the details set down in this paper describe a technology that addresses and resolves these matters. This information was compiled through independent on-site studies within three major tanneries, where approximately 60 000 wet-salted US, European and Australian hides per week have been processed since 2013. Accordingly, this paper describes in detail this radical new approach to leather manufacture.

The initial investigations and developments of this technology by BIOSK involved the building of a full scale wet-blue manufacturing plant, and five years of developments before introduction to industry. The practicality and value of this technology has since been verified by continuous full scale manufacture by tanners that commenced in 2011.

The technology involves the complete retention and recycling of used floats from liming, pickle and tanning in self-contained loops, and eliminates associated washing cycles. This is the base for the complete uptake of processing chemicals, a significant reduction in water use, and zero effluent discharged from these critical manufacturing stages.

1. INTRODUCTION

Conventional liming, acid/salt pickling and chrome tanning processes are inefficient in the use of chemicals, and create considerable pollution that has to be addressed within wastewater treatment. This effluent is high in biological load, nitrogen, sulfide and suspended solids from the dehairing and liming processes, together with neutral salts and chromium as residual chemicals from tanning. Difficult high volume sludges are also created for disposal.

A five year investigation was undertaken by BIOSK to seek the most effective way to make full use of the chemicals used in process, avoid wastewater pollution, and optimise the management of unwanted solids. These objectives were achieved by creating an advanced recycling system – known as BIO-cycle[3] – which resulted in no wastewaters being discharged from unhairing/liming, acid/salt pickling and chromium processes. This technology was subsequently introduced to industry in 2011 for full scale manufacture.

The information set down in this paper is based on details provided by independent on-site studies in three major tanneries[1,4] that have since 2013 processed between them 60 000 wet-salted USA, European and Australian hides per week

2. METHODOLOGY

From initial small scale trials it became clear that the way towards high efficiency liming, pickling and chromium tanning processing would be based on re-using floats recovered from previous processes that remained undiluted by washing cycles. The technology was then developed in a custom built experimental plant fitted with three drums of size 1.8 x 2.2m diameter for loadings of 40 hides per load, and a series of collection sumps for holding recovered floats from the process.

These findings were refined one year later in a purpose built full scale pilot plant. This included three stainless steel processing drums 5.8 x 6.3m diameter working with loadings of up to 600 hides/load, two whole hide fleshing machines, and 15 sumps each of size 16 x 3.3 x 2.5m. These sumps were built into the fabric of the plant during its construction for holding various recovered floats and wash waters from wet-blue manufacture, to optimise their collection, delivery and re-use (Fig.1).

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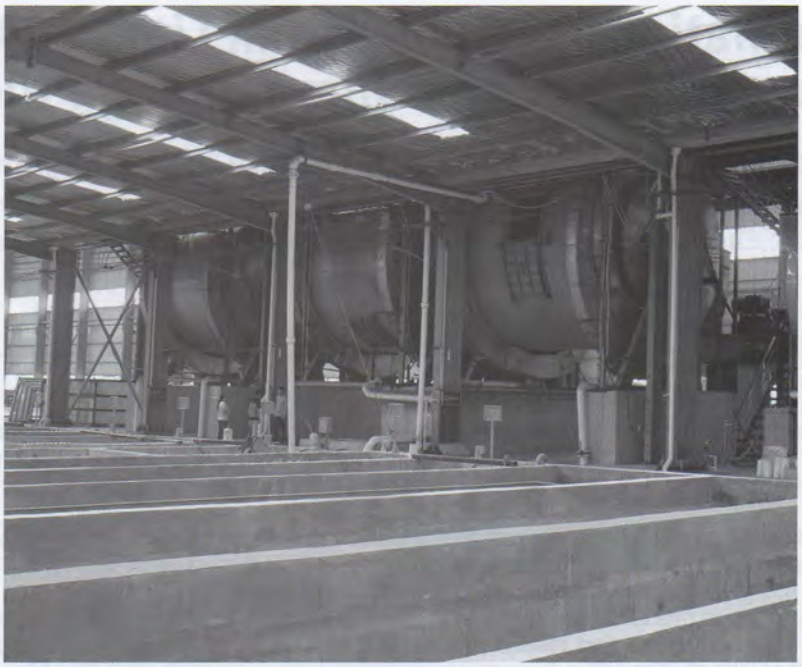

Figure 1. The BIOSK development plant.
Collection sumps for holding the various waste water discharges from wet-blue manufacture are shown in the foreground. In tanneries using the technology,[4] floor-mounted holding tanks are used instead of sumps.

The technology was considered suitable for use on commercial scale one year later, and it was then offered to industry. This included the three tanneries[4] where information for this paper was sourced in June 2016 that were manufacturing 60 000 hides per week combined at the time of the study (Table I).

TABLE I
Tanneries as sources of information[4]

Tannery	Wet-blue production. Hides/week	Date of commencing full-scale manufacture
Xing Ning Tannery, Jiang Su Province, China	30,000	2013
Ruisen Leather, Fujian Province, China	18,000	2011
Xinge ye Leather, Fujian Province, China	12,000	2011

The outcome is high-quality high-volume manufacture of chromium-tanned hides for sales as wet-blue, contract tanning, and in-house processing for finished shoe upper leathers. Central to the system are two self-contained loops:

- A liming recycling process that includes hair recovery
- A pickling and tanning recycling process that includes a combined acid pickle and chrome pre-tanning stage.

Furthermore, there are no washing cycles following either of these procedures. Both loops rely on the continuous re-use of concentrated used floats that are collected from previous processes without any dilution with wash waters. Accordingly, due to the absence of washing cycles, there are no residual wastewaters for treatment from either of these two loops. In practice, the technology has been amended by each tannery to suit each individual needs, but details that follow present an accurate summary of the working process.

2.1 The technology for wet-blue manufacture from wet-salted hides

The processing vessels are conventional wooden drums, loaded with between 450-500 wet-salted hides. These hides receive a dirt soak, with the used float being discharged for wastewater treatment. After green fleshing, the hides receive a main soak, with the used float being either discharged or recovered, and re-used for the dirt soak.

2.1.1 The application of BIO-cycle technology in the liming process

The technology follows these basic steps;

- The collection of undiluted used lime floats that have been filtered and mixed in a holding vessel (the lime-holding tank) that serves all of the liming drums.
- The re-use of these recovered floats as a replacement for the fresh water normally used as float for conventional liming and unhairing
- The addition of chemicals for a hair recovery process.
- After two hours the hair is filtered from the float and the filtered float returned to the liming drum.
- The float is increased using recovered lime liquors from the lime-holding tank, followed by water for controlled osmotic swelling. This stage can be performed in several additions.

• When the liming process is complete, the float is re-filtered to remove residual hair.
• The load is discharged without any washing, and delivered to a dedicated area for loading onto a line-conveyor for feed to the lime fleshing operations. This is followed by lime splitting.
• All of the spillage and drainings from these procedures are collected using dedicated drainage and delivered to the lime-holding tank for re-use in subsequent operations.

There are no washing cycles at the end of the liming process, so the recovered floats remain undiluted. Moreover, it is noted that they are free of odour and hair residues.

The chemicals offered to the process are conventional – lime, sodium sulfide and sodium hydrosulfide – although auxiliary products[5] can be included. These additions are at a reduced level when compared to conventional processing due to the presence of unused chemicals that are retained in the recovered liming floats.

2.1.2 The application of BIO-cycle technology in acid/salt pickle and chromium tanning

After lime splitting, the hides are delimed and bated, then drained and washed as conventional practice, with the washings discharged for normal wastewater treatment. The hides may be unloaded from the deliming vessels, then loaded in to the tanning drums. However, if they are delimed in the tanning drums they must be thoroughly drained before the pickle stage. The technology then follows these basic steps:
• A minimum volume of fresh water is added as float for the distribution of salt and acid in an initial pre-pickle stage.
• A small amount of common salt is added, then an acidification using 0.5% formic acid diluted with water.
• Sulphuric acid is added that has been previously diluted with recovered chrome float.
• At the same time recovered float from previous chromium tanning processes is added to the process.
• The sulphuric acid and the recovered chrome float are pumped into the drum at a metered rate to ensure that both two additions are delivered over the same time period.
• The hides are then run for 90-120 minutes according the weight range in this simultaneous acid pickle and chrome pre-tannage.
• The main tannage commences with an addition at reduced offer of standard chromium tanning agent, and run for another 4 hours. This includes a basification stage.
• More recovered chromium float is added, then run for a further 4 hours.
• The hides are dumped without any washing and then delivered to a dedicated area for stacking before blue samming.

All of the chromium containing spillage and drainings are collected using dedicated drainage, screened/filtered to remove suspended solids and grease, then delivered to two holding tanks. One tank is for re-use in subsequent acid dilution and for the pre-tanning step. The second tank is for the offer of recovered used chrome float that follows the main tannage operations.

3. RESULTS AND DISCUSSION

3.1 Managing the technology

Outline processes for both unhairing/liming, and the pickle/pre-tannage combined and chromium tannage are given as Tables II and III.

It is emphasised that these are generic formulations, and have been amended by each of the three tanneries that have provided the details for this paper to suit their individual operations and market requirements. However, over and above any detail of the actual processing, there are practical aspects to address to ensure that this technology works correctly:
• The plant must be clean and well managed. All of the pipework and drainage arrangements need to be separate for each stage to avoid any contamination.
• The collection tanks must be of sufficient size to hold all of the used floats that are recovered daily from the processing drums. These tanks are fitted internally with coils for heat exchange, and the temperature adjusted precisely using heat pumps. Typically, the recovered lime floats are adjusted to 22°C, the recovered chromium float used for pickle and pre-chroming to 22°C, and the recovered chromium float for tanning to between 55-65°C. These temperatures vary according to the individual tanners requirements and to accommodate summer-winter variations.
• This is a hair recovery system, and the hair recovered is very clean and compact. Being fibrous and largely intact it is easy to manage and dispose of when compared to the contaminated sludges following conventional effluent treatment. This hair can be composted and has potential to be used in higher value products.
• An addition of fresh water is required in the later stages of the liming process. This is because as the hides swell in liming, when subsequently removed, some of the float is taken from the otherwise closed-loop system. The volume of the used lime float that is recovered and available for subsequent processes is therefore always less than required for subsequent batches being processed. This balance is made up by water within the controlled swelling phase after hair removal.
• The pickle/tanning system works in a similar way. The hides swell with water from the delimed state to the final chromium tanned condition. This water contained within the hides is thus removed from the system, hence needs replacing with fresh water in the following pickle/tanning cycles.

3.2 Managing the salinity within processing

Within the unhairing and liming component of this technology, there is a significantly reduced offer of chemicals (see Tables II and III). However, because of self-contained nature of the system there is an inevitable increase of solubles, and this appears to

TABLE II
Hair-saving Liming Process: BIO-cycle technology
Material: Wet-Salted Bovine Hides: USA, Australia, Europe

Pretreatment	First time soak in preparation for green fleshing. Green fleshed and return to liming drum. Main soak. Drain.		
Process	%	Liming procedures	Time
Add float	100	Recovered used lime float at 22°C	
Hair loosening	0.15	ELPO-L[1)]	
	0.8	DO-PRO[2]	
	0.8	Calcium hydroxide	
	0.5	Sodium hydrosulfide	Run 30min / lay 30min
Hair removal		Hair screening/filtration	Run 30 – 60min
Liming continued	0.5	Sodium sulfide	
	0.8	DO-PRO[2]	Run 15min / lay 15min x 2 times / total 60min
	1.0	Calcium hydroxide	Run 30min / lay 30min
	0.3	Sodium sulfide	Run 5min / lay 25min x 6 times / total 3.5h
Add float	80	Recovered used lime float at 22°C + water to make up 80% offer[3]	Run 10min / h overnight
	0.4	Calcium hydroxide	
Drain only DO NOT WASH Discharge hides		Recover float from drum, screen, together with all drainings from unloading/handling for limed fleshing: Hold for recycling.	

[1] BIOSK bactericide product.
[2] BIOSK liming assist product.
[3] The recovered lime liquor is temperature adjusted to the designated temperature.
Fresh water is required to make up the volume as replacement of water taken up by hides in previous process cycles.

cause a repression of swelling in the initial swelling and hair immunisation stage before the hair recovery step. Swelling repression of skin under alkaline conditions due to neutral salts is well known, and is indicated in Figure 2.

It may be that any repression of grain swelling acts as an assist for clean hair removal from the hair shaft, and it is observed that the recovered hair remains fibrous and very intact. This raises the question that an improvement in the integrity of recovered hair might be linked to a greater neutral salts content or inorganic-solubles. However, no research in this speculative area is known.

However, once the hair has been fully released from the hides and recovered, the osmotic swelling of the hides is managed by additions of recovered used lime

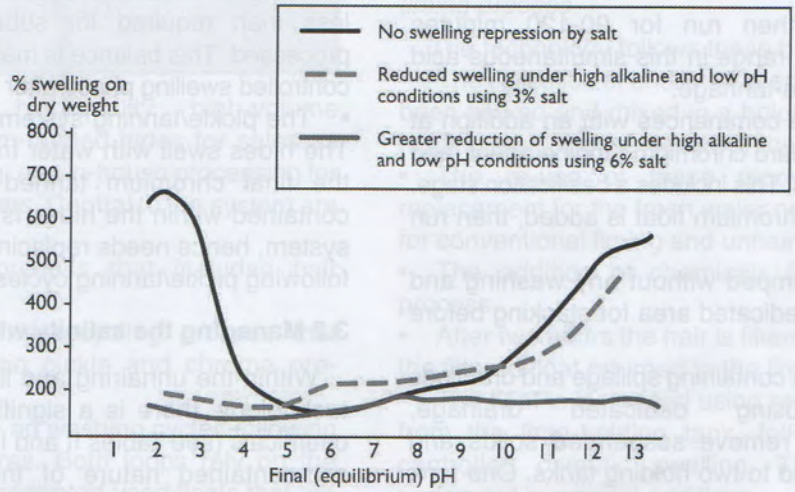

Figure 2. Swelling of a skin as a function of pH and repression by addition of salt.

floats and fresh water. The recovered lime float may be added first and directly followed by water. Alternatively, this stage may be managed using several additions of the recovered lime float followed by water additions.

The process appears to reach stability after approximately five cycles. Here, a continuous build-up of soluble material is avoided because some water and solubles are removed at the end of each cycle. This removal is equal to the volume of water taken up by the hides as they swell from the soaked to fully limed state, and the quantity of solubles contained within that volume.

These solubles are eventually released from the hides in the deliming process as the hides de-swell. Here the washing sequences are as conventional processing, so the removal of unwanted salts and residual products from within the hides is as complete as in normal beamhouse processing. However, the salts formed and subsequently released in total using the BIO-cycle approach are less than generated and released within conventional liming processes. They are in direct relation to the reduced chemical offers in the liming/unhairing phase.

Similarly, the build up of solubles – mainly sodium chloride and sodium sulfate – in the pickle/tanning operations appear to reach a stable level. Here, the salinity is largely maintained by re-use of the recovered chrome tanning floats, and the sodium sulfate present within the chromium tanning agent that is offered in the process. An addition of common salt is required at the beginning of the pickle stage, but this offer is significantly less than the salt additions made in conventional pickling/chromium tanning systems.

A continuous build-up of salts is avoided due to the removal of water and salts in solution held within the tanned hides as they are discharged from the system. This is somewhat similar to the mechanisms within the liming cycle, making use of the swelling that occurs as hides progress from the flaccid delimed state to the final wet-blue product.

These salts are released during further processing of the wet-blue leather, but the salt offer in total is reduced. This ensures that the total salinity generated is always less than experienced with conventional chromium tanning (see Tables II and III).

TABLE III
Pickle, Pre-tannage and Chromium Tannage: BIO-cycle technology
Material: Wet-Salted Bovine Hides: USA, Australia, Europe

Pretreatment	Hides after hair-save liming and lime fleshing. Hides either lime split or full substance. Delimed and bated, drained and without float.		
Process	%	Tanning procedures	Time
Add float		Water minimum possible[1]	
	2.0	Common salt	
	0.2	Bactericide	Run 10min
Acidification	0.5	Formic acid (1:10 dilution with water)	Run 20min
Combined pickle and pre-tannage	1.0	Sulfuric acid (diluted with recovered used chrome bath at 22°C[2])	
	50.0	Recovered used chrome bath at 22°C[2]	Run 60 – 90min[3]
Tannage	2.5	Chrome powder (33 basicity)	Run 30min
	2.0	Chrome powder (33 basicity)	Run 30min
pH adjust	0.5	Sodium formate	Run 30min
Basification	0.2	Basifying agent[4]	Run 30min
	0.1	Basifying agent	Run 60min
Tannage	100	Recovered used chrome float at 60°C[5]	
	0.15	ELIPO-D[6]	Run 240min
Drain only DO NOT WASH Discharge hides		Collect float from drum, screen and collect together with all drainings from unloading, handling and stacking the wet-blue hides for recycling.	

[1] The float level is the minimum required to disperse chemicals before the combined main pickle and chrome pre-tannage.
[2] Temperature may be adjusted according to prevailing temperature requirements.
[3] Time depended upon hide category, lime split or full substance.
[4] Conventional powder basifying agent.
[5] Temperature may be adjusted according to prevailing temperature requirements.
[6] BIOSK fungicide product.

3.3 Technical advantages

The technology offers 100% use and uptake of active chemicals and a reduction in the neutral salt offer. Moreover, the conditions required in the chemical processing do not need to become extreme to achieve a high uptake.

The pH at the end of tanning does not need to be unusually high, the floats very low, neither are specialised products and controls needed to achieve a chromium uptake that might be classed as good, but always less than 100%. In this study the final floats at the end of tannage are higher than found in many processes, and in one example it is said to be as great as 150%. But, because of the full containment and recycling of the active chemicals within the two self-contained loops, a lower efficiency in each individual cycle is quite acceptable. More moderate conditions that may better suit wet-blue manufacture can thus prevail as all unused chemicals remain for recycling.

It is noted that the leathers produced are clean and show no remaining hair or residues. They are relaxed and well extended, and there is also an absence of chrome staining that is difficult to manage in direct chrome recycling systems. However, in this situation the novel technique used for simultaneous acid pickling and pre-chroming provides an advantage. These leathers have high commercial value as indicated by the volume of production and the acceptance of this technology in the three major tanneries which form the base for this paper.

TABLE IV
Reductions in offers of chemicals and water (spread of values from three tanneries)

Water/chemicals	Reduction in chemical offer % (on wet-salted weight)
Sodium sulfide + sodium hydrosulfide	0.4–1.5
Lime	1.0–3.5
Common salt	3.0–4.0
Chromium tanning agent	1.0–2.5
Water savings	200–300 litres/hide

TABLE V
Reductions in chemicals and water based on previous (conventional) processing (spread of values from three tanneries)

Water/chemicals	Reduction in chemical offer % (on wet-salted weight)
Sodium sulfide + sodium hydrosulfide	18 – 50
Lime	17 - 43
Common salt	57 - 71
Chromium tanning agent	More than 29
Water savings	Up to 50% (excluding saving made by any re-use of used soak floats)

Each tannery has adjusted the technology to meet their own individual needs, and inevitably processes are changed over long time periods, so there are no absolute values to judge any advantage. However, savings in chemical use and water have been given, and can be expressed as a spread of values across the three tanneries a shown in Table IV.

Similarly, the chemical savings as a percentage of the original chemical offers have also been given and are shown in Table V.

4. CONCLUSIONS

A radically different approach to the manufacture of chromium-based tannages has been developed. This technology centres on self-contained systems for unhairing/liming and pickle/tanning that ensure that the uptake of processing chemicals in these manufacturing stages is complete.

This approach reduces the offers of active chemicals that are required for processing, eliminates the chemical waste from these process stages, reduces water use, and avoids the treatment of sulfides and chromium from wet-blue manufacture. This has not been previously achieved.

The technology requires only the most basic chemicals and equipment although auxiliary products can be included. In manufacture, the focus can remain on making a high quality product and side-step the many technical problems associated with high uptake systems that may be sensitive to control and never 100% efficient.

The technology provides very significant environmental advantages, although these cannot be accurately quantified. This is because each of the tanneries not only manufactures wet-blue hides, but continues to process to the finished state. Some of the wet-blues are also sold to other tanners or are part of contract tanning. Moreover, process changes have been made since the introduction of this technology to retanning/fatliquoring processes to meet changing customer demands. There were also changes in water consumed to take into account, and although the waste waters from each tannery came from different departments, these wastewaters were mixed together for effluent treatment.

However, sulfides are no longer an issue for treatment, and this has resulted in an absence of odour across the effluent treatment plants. There are no chromium-based compounds in the wastewater from wet-blue manufacture, thus avoiding the route of separation, collection, precipitation and possible regeneration.

The biological load is reduced, there is less nitrogen from hair breakdown, and the sodium chloride and TDS content is reduced. The volume of settled solids is significantly reduced, and the management associated with these sludges and their disposal as waste. The hair that is recovered is very intact, low in moisture and volume, and uncontaminated by products from subsequent processing.