

Reduction of the Salt Freight in Tannery Effluent

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Introduction

In our modern, industrialised society responsibility for active environmental protection is already one of the most important aspects. Not surprisingly environmental awareness has grown immensely in leather production as it has elsewhere too. Tough official regulations governing effluents, waste air and solid waste disposal provide the legislative background to this increased environmental sensitivity. To meet the specified limit values products and application methods must measure up to stringent requirements. Optimum exhaustion of products, environmental compatibility of the by-products formed and avoidance of waste are very important. Compliance with stricter effluent legislation and landfill regulations are difficult challenges to both the leather industry and the industry supplying it with chemicals. In a modern, look-ahead tannery, environmental protection is therefore every bit as important as leather quality, productivity and profitability.

Salt in the effluent is the most difficult form of pollution to be dealt with in the leather industry. COD and BOD can be dealt with in the beamhouse process and in the water treatment plant. In addition to its polluting effects, chloride corrodes metal and sulphate damages concrete. To dispose of salt containing waste water or to remove salt from wastewater only elaborate methods are available all having their pros and their cons (**Figure 1**). In addition to their polluting properties, chloride salts corrode metal and sulphate salts damage concrete.

applied methods to reduce the salts (concentration) disposed
<p>solar-pan-evaporation (India) + recycling the salt residue</p> <ul style="list-style-type: none"> ▪ low efficiency, slow to evaporate, often large areas of land needed ▪ low start-up cost, overall cost high ▪ salt residues often contaminated
<p>spray irrigation</p> <p>Australia successfully sprays up to 10'000 mg/l TDS* containing wastewater on farmland.</p> <ul style="list-style-type: none"> ▪ low start-up cost ▪ salt residues often contaminated ▪ build-up of salt in the soil
<p>ultra filtration + recycling a large portion of the water</p> <p>concentration of the salts</p> <ul style="list-style-type: none"> ▪ expensive technology to start up ▪ disposal of the saline concentrate unsolved
<p>discharge directly into the sea</p> <ul style="list-style-type: none"> ▪ only feasible in some areas close to the sea ▪ rivers can dry up because no water is put back in them
<p>dilution with domestic wastewater prior to discharge to rivers or sea</p> <p>is used in UK</p> <ul style="list-style-type: none"> ▪ possible in some areas but often difficult to arrange and control
<p>biological conversion to reduce sulphate to elemental sulphur</p> <ul style="list-style-type: none"> ▪ only for sulphate containing wastewater, requires sophisticated bioreactors
<p>* TDS = Total Dissolved Solids</p>

Figure 1

Methods to reduce salt offer

If salt in the wastewater is to be reduced it has to be looked at from where the salt freight originates. The basic rule of a tannery is what you put in also comes out.

Salt enters the beamhouse process in various ways. It comes in as common salt used for the conservation of raw hides, the carrier or standardising salt used to formulate powder products and the salts used in the beamhouse processes. For a tannery processing salted hides the biggest salt component in the waste water is chloride (**Figure 2**). The chloride found in the waste water is mainly brought in by the conservation salt, some by the pickle salt and a very small part by the carrier salt (**Figure 3**). To give an idea of the dimensions; the daily output of common salt of the Montebello, Italy, water treatment plant in the year 2000 was 120 ton!

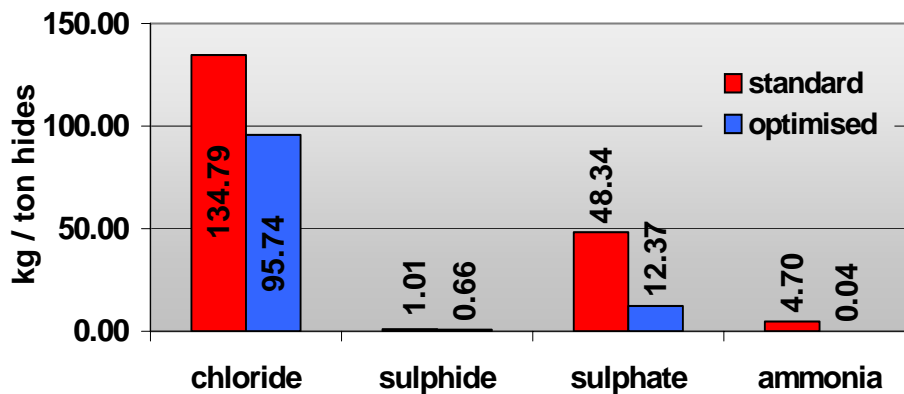


Figure 2, Salts in Beamhouse Waste Water

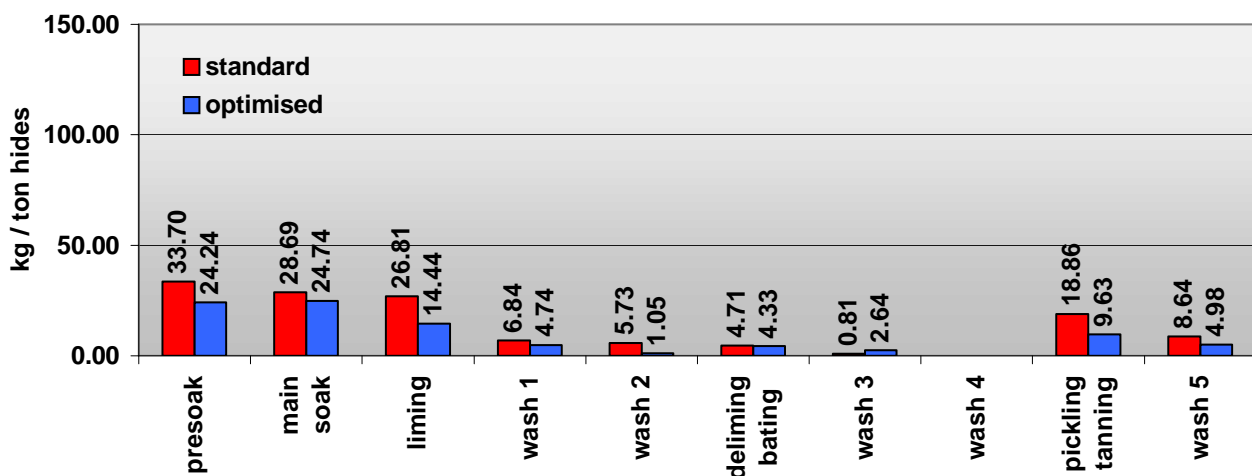


Figure 3, Chloride Comparison in Beamhouse Waste Water

There are various methods to reduce the common salt freight in the waste water. Looking at the total salt freight the procedure having the biggest impact is to use fresh or dried hides. When this is not possible mechanically removing the conservation salt** (**Figure 4**) if carried out efficiently will have a big effect as well. Low salt pickling and with much less impact, the use of salt-free products can be considered as well.



Figure 4, Desalting Drum

Conservation salt

Since the conservation salt is the major contributor to the total salt freight in the waste water, it pays to have a closer look at it.

For each ton of raw hides about 400 kg salt are used to preserve them. About half of this salt enters into the tannery waste water. So simply eliminating the conservation salt means that about 67% of the total salt freight of the waste water is dealt with (**Figure 5**). It has to be mentioned, that in addition to creating problems in the waste water the salt, is contributing to the solid waste as well (**Figure 6**). The other half of the 400 kg salt used per ton of raw hides ends up as solid waste, of this about 100 kg actually of this enters the tannery area and has to be disposed off there as well.

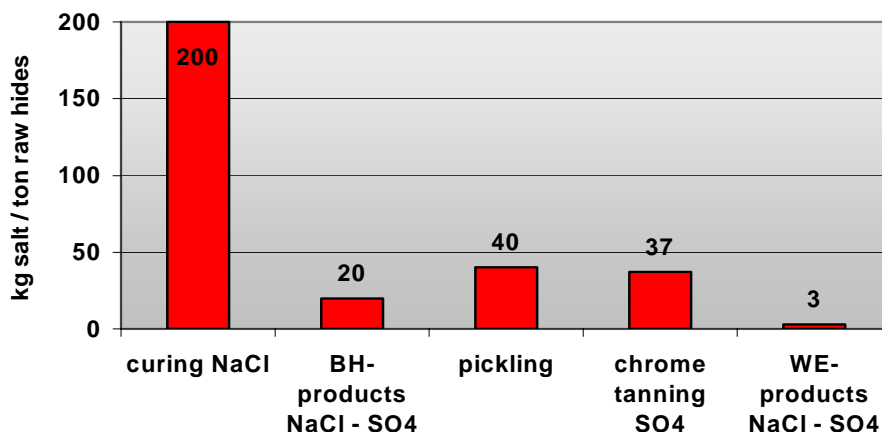


Figure 5, Sources of Salt in Waste Water

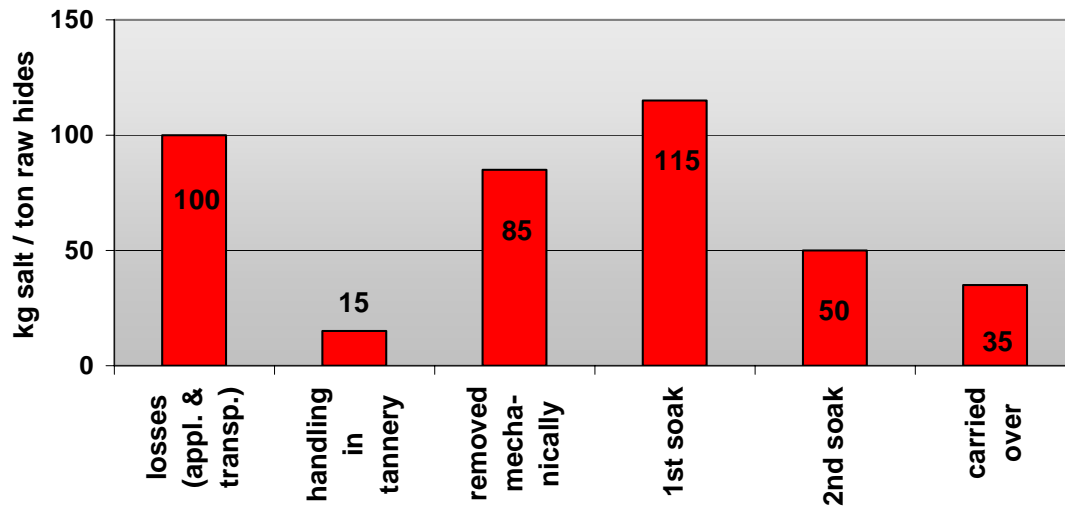


Figure 6, Mass Balance of Salt applied in Curing

Conservation salt functions

The conservation effect of salt is well-known. Basically the salt dehydrates the hide from 60 – 70% water to a level of about 14% where micro-organisms have difficulties to grow. The direct bacteriostatic effect of the salt on most bacteria can be ignored.

An effect of the conservation salt to be mentioned here is the hydrotropic effect. During conservation the salt is denaturising interfibrillar protein, which later on in soaking and liming is easier released, if the salt is not dosed in sufficient quantity (if less than 20% with as worst concentration 4%) it can even attack the collagen.

Systems and products allowing elimination of salt for conservation

Very common is the direct processing of hides in the cases where the slaughterhouse is close to the tannery and logistics are well organised. As an intermediate solution hides coming from a bit further away are treated with a bactericide (1). In this condition they can be transported for up to one day to the tannery.



Figure 7, Cooling Hides

Another commonly practised way of working is either chilling the hides by chipped ice, or by cooling in a refrigerated container (**Figure 7**) or by using ice-cold water. The effect can be improved by using a bactericide (1) in the water to produce the ice.

Drying the hides is practised as well but it is not advisable as an alternative way to preserve them.

Pickle salt

This salt is the second biggest contributor of the total salt freight in the wastewater (**Figure 3**). Common salt in the pickle float is the source for chlorides. Sulphuric acid is the major source for sulphates with sulphate masked chrome as the second source. Unfixed chromium sulphate is contributing to the salt in the wastewater as well.

Functions of pickle salt

The main function of salt in the pickle is to avoid the pelts from swelling in the acid condition. The pickle acid shifts the equilibrium in favour of the positive charges in the lateral amino sites. If there would be no salt in the pickle this would generate repulsive forces within the structure, which would shift the polypeptide chains away from each other. This would then create empty spaces in which water would penetrate rapidly. The very strong osmotic pressure would then destroy the pelt from within. However, salt avoids swelling in the pickle by reversing the osmotic pressure. In a good pickle these two forces are balanced out.

Pickle salt has a hydrotropic effect on the pelt that is increased substantially at a pH under the iso-electric point of 5.5. This effect makes the leather softer.

Systems and products allowing reduction or elimination of salt for pickling

Dynamic Tanning

In this process a modified polysulphonic acid (2) (**Figure 8**) replaces almost all mineral acid and allows substantial reduction of the common salt used in the pickle. In addition it reduces chrome in the wastewater by improving uptake and fixation (**Figure 9**). As a further effect it makes a substantial reduction of the pickle process time possible (**Figure 10**).

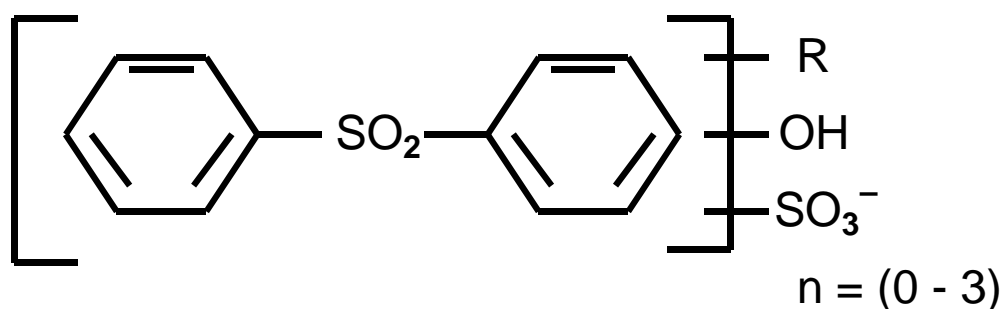
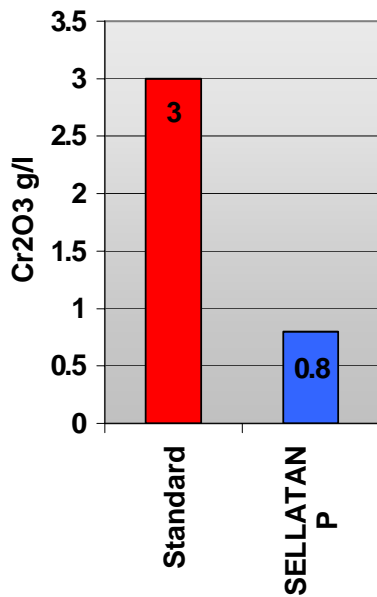


Figure 8,
Simplified Structure of SELLATAN® P



Figure, 9 Chrome Uptake

Pickle	50% water 20°C		
	3% salt	run 10'	Bé 3 – 4
	0.5% formic acid 85% (1:5)	run 30'	
	1.5% SELLATAN® P (1:3)	run 30'	pH 3.2 – 3.4
Tanning	5% chrome salt 26/33		
	0.1% ARACIT® 4A	run 60'	pH 2.9
	0.35% CROMENO® FB	run 8 h	
drain	pH 3.8 – 4.2; T 42 – 45°C		pass boil test
Wash	100% water 20°C		
	0.05% ARACIT® 4A drop	run 20'	

Figure 10, Recipe Shoe Upper on Lime Split ,
 Material 3.5 mm, Dynamic Tanning

Open Chrome Recycling

This system (part of the BMBF* project ‘Integrated Environmental Protection in the Leather Industry’) allows drastic reduction of the chlorides, sulphates and chrome in the discharged float (Figure 11). Basically it is a recycling system that works using a counter-stream principle (Figure 12). An investment in one or two storage tanks has to be made. The modified polysulphonic acid (2) plays a major role in this system as well (Figure 13). This system has the advantage over a closed pickle and a closed chrome float recycling system in that no accumulation of any component has to be dealt with.

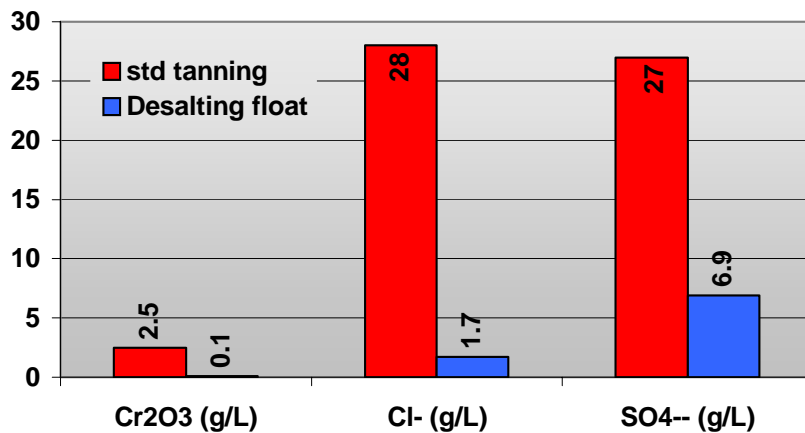


Figure 11, Open Chrome Recycling System – Values in Discharged Float

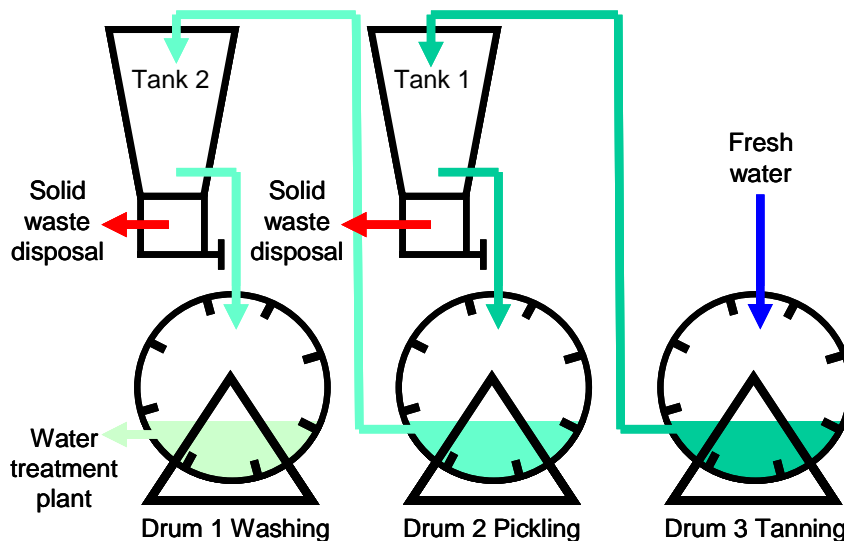


Figure 12, Open Chrome Recycling System – Set-up

BATING as usual, end-pH between 7 and 7.5

WASH 2 X as usual

DESALTING	120	Exhausted pickle bath (tank 2)	45'	pH 5.5-6
drain in water treatment plant				
PICKLING	0.5	Na-Formate		
	0.5	CORIPOL PL		
	0.2	BORRON T	20'	
+	20	Exhausted tanning bath (tank 1)		
	2	SELLATAN P		
	0.4	Sulphuric Acid		add in 30'
	0.5	CROMENO M	15'	
+	40	Exhausted tanning bath (tank 1)		
	0.6	Formic Acid	3 h	add in 30'
drain in tank 2				
		pH~3.5; cut 100%; Bé~4; T°C 25-28		
TANNING	5	Chrome salt (33°, 26%)	90'	
+	60	Water 60°C		
	0.1	ARACIT 4A	30'	
+	0.5	CROMENO MFN/1		
	0.05	CROMENO M	o/n	
drain in tank 1				
		pH 4; T°C 40-42		
WASH	50	Water 20°C		
	0.05	Formic Acid	15'	
drain in tank 1				
		drop		

Figure13, Open Chrome Recycling - Recipe Upholstery Leather

Modified Ester (3) **

This acid-free product allows a substantial reduction of common salt, the elimination of sulphuric acid and the optimisation of chrome fixation (**Figure 14, 15 and 16**). The product is especially useful for application on thinner pelts.

Depickled and degreased as usual

Washed with cold water

TANNING	50	Water 20°C		
	0.5	CORIPOL DX 1202	20'	pH ~ 4.3
+	1.0	CROMENO XT	1 h	
+	8	Chrome salt (33°, 26%)	30'	check Ø
+	0.1	ARACIT 4A	8 h	pH ~ 2.6
+	1.2	Sodium Formate	1 h	pH ~ 3.4
+	0.5	SELLASOL NG gran.	1 h	pH ~ 3.8
+	100	Water 40°C	1 h	
drain				
WASHING	100	Water 25°C		
	0.05	ARACIT 4A	45'	
drop				

Figure 14, CROMENO XT – Sheep Nappa on NZ pickled pelts

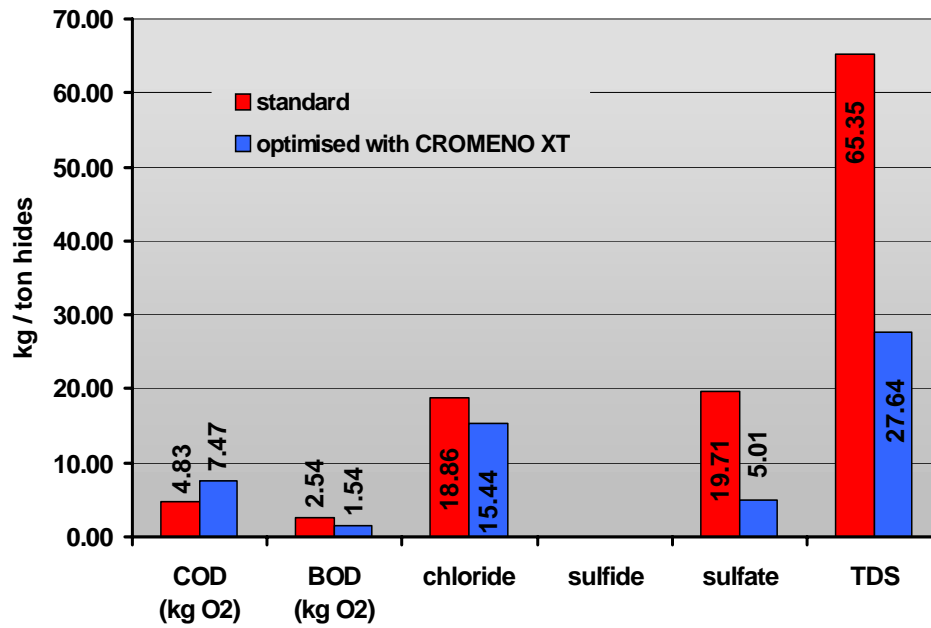


Figure 15, CROMENO XT - Pickle Effluent Values

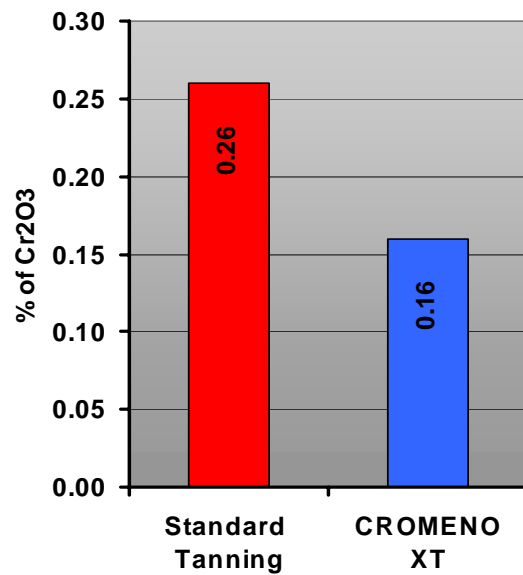


Figure 16, Chrome Uptake

Acidified Modified Ester (4)

This product is an acidic version of the Modified Ester (3). It allows the use on thicker pelts (Figure 17).

DELIMING	100	Water 27°C			
	0.1	BORRON N 90	30'		
+	1.5	Ammonium Sulphate	30'		
		drain			
BATING	10	Water 27°C			
	3.5	Ammonium Sulphate			
	1.3	DERMASCAL F	2.5 h	pH ~ 8	
	20	Water 27°C			
	0.05	BORRON N 90			
	1.0	OROPON OR	1 h		
		drain			
WASH 2X	100	Water 27°C	10'		
		drain			
PICKLING	20	Water 27°C			
	0.5	CORIPOL GA			
	4	Salt	10'	Bé ~ 8	
+	1.0	Formic Acid 85% (1 : 5)	30'		
+	1.5	CROMENO XP	2 h	pH ~ 3.7	
TANNING	+	6	Chrome powder 33°, 26%	4 h	
	+	0.1	ARACIT 4A	1 h	Cut Ø
	+	0.3	Sodium Formate	1 h	pH ~ 3.8
	+	60	Water 45°C	4 h	pH ~ 3.8
			drain		T >40°C
WASHING	100	Water 27°C			
	0.05	ARACIT 4A	30'		
		drain			

Figure 17, CROMENO XP – Wet-Blue on Brazilian Bovine full substance

Pickle float recycling

When the pickle float is able to be retained separately it can be recycled. This can save up to 80% of salt and 20 – 25% of the normal addition of formic and sulphuric acids. To ensure a consistent result it is essential to drain the washing float very well before pickling. It has to be noted that in the subsequent chrome tanning bath, up to 2% salt might be needed to adjust the Baumé value. Accumulation of natural grease has to be avoided by skimming-off the grease. An investment in a storage tank and skimmer has to be made. It has to be noted that this system is not often practiced.

Deliming and bating

Ammonium salts and sodium bisulphite are salts used in deliming and bating.

Reduction or elimination of ammonium salts in deliming and bating

Ammonium salts can be eliminated completely by using CO₂ deliming and ammonium-free bating agents. On thicker pelts CO₂ deliming does not work properly because of slow penetration. In many cases though, even on thinner pelts CO₂ deliming does not always work in a consistent way.

Modified Dicarboxylic Acid Mix (5)

This product represents a group of products free of ammonium salts and based on dicarboxylic acids. In addition to these products, blends of dicarboxylic acids with ammonium salt are also available. Depending on the amount of ammonium salts in these products they can contribute to the reduction of ammonium salts in the waste-water.

Modified Functional Ester (6) **

This product is based on esters and is completely salt free. All types of pelts can be delimed without ammonium salts and without problems. The product does not allow the pH to drop below 8.5. This product ideally is combined with a liquid salt free bating agent (7).

Salt-free products

To formulate powder products often sodium chloride or sodium sulphate are being used as a carrier or standardising agents. Since they increase the chloride and sulphate freight in the waste water, the use of products without these salts can be considered. One way is to use liquid, salt-free formulations and the other is to use concentrates. In most cases concentrates are ruled out because of the significantly larger influence a weighing error has and because they often do not allow proper distribution in the system. Bating enzymes are an example where lower concentrations are advisable for these reasons.

Conclusion

A major reduction of salts in the wastewater of a beamhouse is easy to achieve by simple means. The best solution from the environmental point of view is to process fresh or chilled hides. These hides might have a short-term, salt-free preservation with bactericides – proximity to the slaughterhouse has to be a given.

Whenever salted hides have to be processed mechanical removal of the curing salt** is the cheapest and easiest solution.

Of the leather production processes the pickle offers the best opportunity to reduce salt in the waste water. With the Open Chrome Recycling Process a system is available to achieve the best results. In the deliming process ammonium-free chemicals have to be considered to further reduce the salt freight. A hair save liming process**, allowing substantial reduction of sulphates in the waste water is advisable as well.

The use of salt-free products has very little impact on the total salt freight but increase the cost substantially.

Products mentioned

1. ARACIT[®] KL new
2. SELLATAN[®] P liq.
3. CROMENO[®] XT
4. CROMENO[®] XP
5. DERMASCAL[®] DGS new
6. DERMASCAL[®] CD
7. OROPON[®] ANZ.

Footnotes

* BMBF = German Ministry of Education and Research

** In the figures comparing standard values with optimised values these measurements were taken to optimise the salt freight.

Acknowledgements

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