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Liming, deliming and bating: a natural and enzymatic approach by eco agents

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Summary

Beamhouse process in tanneries is a very pollutant process. Although some of the pollution is intrinsic of the hide, part of the pollution is added by the chemicals used in the process. This study used natural and eco products to reduce the pollution and its toxicity added by the treatment. Molasses, a protease and an amylase were used in liming instead amine products, citric acid and acetic acid were used in deliming instead ammonium sulphate and a natural enzyme, extracted from the peel of the pineapple, was used in bating. These alternative natural and eco agents were used against a normal process. The results obtained compared to a normal process were very good indicating a better opening up of the hide and a sulphide reduction in liming, an important reduction of ammonium in deliming and a promissory possibility in bating. Physico-mechanical tests show the same behaviour of the crust obtained and similar organoleptic properties. The extract from the peel of the pineapple showed a good ULV activity but needs some work more in order to stabilize the enzyme. The pineapple pulp extract was studied too showing a better ULV activity but a strong bating effect that needs to be optimized.

1. Introduction

Leather industry transforms raw skins into leather using mechanical and chemical operations. Some chemicals normally used have a large contribution for the pollution load.
In normal liming and deliming, the use of chemicals as amines, sodium sulphide and ammonium sulphate has a great contribution to the added pollution of leather industry.
In recent years, the progress of the biotechnology, in particular of the enzymatic technology, gave us new knowledge about enzymes and provided us with new enzymatic biocatalysts, highly selective and stabile[1]. This progress increased the field of enzyme application. Enzymes have been used in leathermaking for many years, mostly in bating, by the use of bacterial and pancreatic proteases. Recently, the range of enzymes application in the tanning industry has been enlarged to other process areas as: soaking, unhairing, degreasing and post-tanning[2,3,4,5,6].
The majority of tanneries still use deliming products based on ammonia, despite the environmental pressure for a reduction in nitrogen concentration in the effluent[7].
In this study natural products are used to reduce and eliminate some of those chemicals, in particular molasses and enzymes and natural deliming agents. A natural enzyme, extracted from the pineapple peel and pulp, was used in bating.

2. Materials and Methods

Bovine hides were obtained from a lot of domestic salted hides of 20-30 kg from Curtumes Aveneda (a Portuguese leather company from Ovar). The domestic sheep skins were obtained from Curtumes J. B. Salgueiro (a Portuguese leather company from Alcanena).
For the unhairing, the eco products introduced were a natural cane molasses and three enzymes: a lipase, Defat 50 (Cromogenia-Units, Spain); a protease, Mystozyme ECO-S (Catomance, England) and an amylase, Mazyme SDL (Aquitex, Portugal). For deliming, natural organic acids were used: citric and acetic acid. The peel of pineapples from Brazil was used to obtain a natural enzyme for bating.

Liming trials

Liming trials with bovine hides were done at a bench scale according to the process presented in Figure 1.

Process Stage	%	Chemical	T / ºC	Time	Control
Washing	300	Water	20		
	0,2	Bactericide		2 h - Run 30 minutes / h	
Drain					
Soaking	300	Water	25		
	0,2	Wetting / Degreasing agent			
	0,1	Bactericide			
	0,1	Sodium carbonate		2 h - Run 10 minutes / h	pH = 9,0 - 9,5
+	0,1	Sodium carbonate			
	0,5	Degreasing agent		Over night - 10 minutes / h	pH = 8,5 - 9,0
Drain					
Liming	100	Water	25		
	0,1	Wetting / Degreasing agent			
	A	Calcium hydroxide			
	B	Sodium sulphide			
	C	Mystozyme ECO-S (Protease)			
	D	Defat 50 (Lipase)			
	E	Mazyme SDL (amylase)		Run 2 h	
+	F	Sodium sulphide			
	G	Calcium hydroxide		Run 2 h	
				Run 2 h	
Drain					
Washing	200	Water	20	Run 15 minutes	
Drain					

Figure 1 – Liming process for bovine hides

Different quantities of lime, sodium sulphide and enzymes were used for each trial according Table 1. A normal process uses 3% of lime and 2,5% of sodium sulphide.

Table 1 – Quantities of lime, sodium sulphide and enzymes used

Trial	Dosage / % (weight of product / weight of hide)				
	Calcium hydroxide (A+G)	Sodium sulphide (B+F)	Mystozyme ECO-S (C)	Defat 50 (D)	Mazyme SDL (E)
BovRib1	0	2	0,3	0	0
BovRib2	0	1,5	0,3	0	0
BovRib3	0	1,5	0,3	0	0,3
BovRib4	0	1,5	0,3	0,3	0,3
BovRib5	0,75	1,5	0,3	0,3	0,3
BovRib6	1,5	1,5	0,3	0,3	0,3
BovRib7	1,5	1,25	0,3	0,3	0,3
BovRib8	1,5	1	0,3	0,3	0,3

The evaluation of the unhairing efficiency was done by a scale between 1 (the more difficult to unhair) and 5 (the best unhairing result).

Liming trials with sheep skins were done in order to evaluate the anti-wrinkle performance of cane molasses against an amine liming assistant normally used. The process used is shown in Figure 2.

Process Stage	%	Chemical	T / ºC	Time	Control
Washing	600	Water	20		
	0,1	Sodium carbonate		3 h - Run 30 min / h	
Drain					
Soaking	600	Water	25		
	0,3	Wetting / Degreasing agent			
	0,3	Bactericide			
	0,2	Sodium carbonate		Over night - Run 10 min / h	pH = 8,0 - 8,5
+	0,3	Sodium carbonate			
	0,2	Lipase			
	0,3	Protease			
	1	Degreasing agent		Run 4 h	pH = 8,5 - 9,0
Drain					
Liming	400	Water	25		
	0,3	Wetting / Degreasing agent			
	1	Anti-wrinkle			
	1,5	Calcium hydroxide			
	3	Sodium sulphide		Run 2 h	
+	1	Anti-wrinkle			
	2,5	Calcium hydroxide			
	3	Sodium sulphide		Run over night	
Drain					
Washing	600	Water	20		
	0,8	Sodium polyphosphate		Run 30 min	
Drain					

Figure 2 – Liming process for sheep skins

The anti-wrinkle effect was evaluated comparing the salted skin weight with the skin weight after liming, calculating a ΔP(%) by the next expression:

$$\Delta P(\%) = (\text{skin weight after liming} - \text{salted skin weight})/\text{salted skin weight}$$

Deliming trials

Deliming trials were done with bovine hides at a bench scale according the process presented in Figure 3, where the work conditions are shown in Table 2.

Process Stage	%	Chemical	T / ºC	Time	Control
Washing	200	Water	30	Run 15 min	
Drain					
Deliming	150	Water	35		
	A	Deliming agent			
	0,5	Sodium bisulfite		Run B	pH = C / cross section = colourless
+ (Bating)	0,6	Protease		Run 45 min	
Drain					
Washing	200	Water	20	Run 15 min	
Drain					
Pickling	100	Water	20		
	10	Sodium chloride		Run 15 min	ºBé = 6,5 - 7,5
+	0,5	Formic acid (1:10)		Run 15 min	
+	D	Sulfuric acid (1:10)		Run over night	pH = 2,7 - 3,0 / cross section = yellow
+ (Tanning)	7	Chrome salt (26% Cr_2O_3; 33% Bas.)			
	0,2	Fungicide		Run 3 h	
+	0,7	Basifying agent		Run over night	pH = 3,7 - 3,9
Drain					
Washing	300	Water	20	Run 30 min	
Drain					

Figure 3 – Deliming process for bovine hides

Table 2 – Work conditions for deliming

Trial	Deliming agent	A / %	B / hours	C / pH	D / %
BovCurt1	Desencalante E-93	2	2	8,0	1,1
BovCurt2	Ammonium sulfate	2	2	8,8	1,3
BovCurt3	Citric acid	1	20	7,9	0,9
BovCurt4	Acetic acid	1	20	6,7	0,9

Pollution load from these trials wastewaters was measured and evaluated according to the Standard Methods[8].

Natural enzyme

The enzyme extraction from the pineapple peel was done by grinding and pressing, obtaining an extract with enzymatic activity. The same process was used with pineapple pulp. The enzymatic activity was determined by the Löhlein-Volhard method: a LVU activity unit is the necessary enzyme quantity to digest 1.725 mg of casein in this method conditions. The enzymatic extracts were tested as bating agents against a normal bating agent (Oropon OR from TFL) using bovine hides. The bated

hides were tanned and passed to crust state, submitted to physical tests: tear strength and grain cracking and evaluated for tightness and softness.

3. Results and Discussion

Liming results

As mentioned before the evaluation of the unhairing efficiency was done by a scale between 1 (the more difficult to unhair) and 5 (the best unhairing result). This evaluation is completely qualitative, based in ocular observation. Therefore, we present the results in Table 3 but also some images which allows a better understanding of the trials differences regarding unhairing efficiency.

Table 3 – Results for bovine hide unhairing

Trial	Result
BovRib1	3
BovRib2	2
BovRib3	3
BovRib4	4
BovRib5	3
BovRib6	5
BovRib7	4
BovRib8	1

Figure 4 – BovRib8

Figure 5 – BovRib2

Figure 6 – BovRib4

Figure 7 – BovRib7

Figure 8 – BovRib6

Through these results, we observed a clear synergy between the three tested enzymes - protease, lipase and amylase – in order to increase the efficiency of hair removal. We could easily conclude that is possible to use only 1,5% of lime and 1,5% of sodium sulphide when these three enzymes are used, resulting in a good unhairing. This means a reduction of about 40% of sodium sulphide and 50% of lime, when compared with a traditional process.

The test of natural anti-wrinkle agents was performed according to the process presented in Figure 2. The obtained results as well as the anti-wrinkle tested are mentioned in Table 4.

Table 4 – Anti-wrinkle trials and results

Trial	Anti-wrinkle agent	Results		
		ΔP / %	COD / ppm	N total / ppm
MestRib1	None	102	24000	1500
MestRib2	Ehravit MB (TFL)	57	11000	1200
MestRib3	Cane molasses	86	21000	1100
MestRib4	Beet molasses	130	45000	2800

As could be seen in the previous table, comparing the performance of the two different tested molasses, the one that more closely approaches the performance of Ehravit MB (commercial amine based liming agent from TFL) was cane molasses. As a matter of fact, beet molasses didn't show a slight potential for this application. In order to prove the potential of cane molasses, we have made a new trial, according to the same process, but doubling the quantity of cane molasses. The result for ΔP was 31%, clearly proving the effectiveness of the product.

Deliming results

In order to evaluate the performance of organic acids as deliming agents we have made several trials as mentioned in the previous chapter. To make the proper evaluation of the benefits associated to these products we have measured the environmental impact – NH_4 content and N_{total} content in deliming wastewaters and Cr_2O_3 content in tanning wastewaters – and the impact in tanning efficiency – shrinkage temperature. The results are presented in Table 5.

As shown by the table above, there are clear advantages, from the environmental point of view and also for the increase of tanning efficiency, when using the tested natural organic acids instead of the traditional deliming agents. The main disadvantage of deliming with only acetic acid or citric acid is the excessive processing time, which difficult the application of this technology at industrial scale. However, we figure feasible at industrial scale a considerable reduction of the traditional ammonium sulphate dosage, with the use of a small quantity of natural organic acids, reducing the environmental impact and increasing tanning efficiency.

Table 5 – Results for deliming trials

Trial	Deliming wastewater - NH_4 / ppm	Deliming wastewater - Ntotal / ppm	Tanned leather - Shrinkage temperature / ºC	Tanning wastewater - Cr_2O_3 / ppm
BovCurt1	2500	2100	90,5	6600
BovCurt2	3200	2600	91,0	6300
BovCurt3	1100	1200	96,5	4200
BovCurt4	890	1200	97,0	4300

Natural enzyme results

The average extraction yield (percentage of extract obtained from a given quantity of pulp used) for three extractions from the pineapple pulp was equal to 60%. Solids in the extract were about 9% on average. The enzyimatic activity, evaluated by the Lohlein-Volhard method, gave an average value of 3000 LVU/g of extract.

The average extraction yield (percentage of extract obtained from a given quantity of peel used) for three extractions from the pineapple peel was equal to 65%. Solids in the extract were about 9% on average. The enzyimatic activity, evaluated by the Lohlein-Volhard method, gave an average value of 1050 LVU/g of extract.

These enzymatic extracts were tested in bating against a commercial enzyme (Oropon OR from TFL) at a bench scale with bovine hides and sheep skins with good results. To validate these results three trials were done at a pilot scale with sheep skins (four skins in each trial) according Table 6.

Table 6 – Work conditions for the pilot trials

Trial	Work conditions			
	time / min.	pH	T / ºC	Enzyme quantity
Standard	30	7,8	32	0,8% Oropon OR
Pulp	30	7,8	32	0,25% Pulp extract
Peel	30	7,8	32	1,0% Peel extract

The normal fingerprint test for bating was done with good results for the three trials showing a stronger bating effect for the pulp extract. The bated skins were tanned and passed to crust state by a normal process, submitted to physical tests: tear strength and grain cracking, and evaluated for tightness and softness. The skins from the standard and peel extract trials had a good softness and tightness; the skin from the pulp extract trial had a good softness but presented some grain looseness. The results of physical tests are shown in Table 7.

Table 7 – Results of physical tests

Trial	Grain cracking distension (mm)	Tear strenght Load (N)
Standard	9,0	56,3
Pulp	9,2	52,1
Peel	8,6	58,0

As shown by the table above, the results are good for a sheep skin and similar, indicating a good potential for this natural enzyme.
The enzymatic activity of the extracts was evaluated over time. It was verified a reduction of the enzymatic activity which shows the need to study a way to improve the enzyme stabilization.

4. Conclusions

This work showed the potential of enzymes and cane molasses in liming allowing to a reduction in chemical pollutants as sodium sulphide and amine based products. Natural organic acids applied in deliming have a good potential to improve a significant reduction of ammonium salts.
A natural enzyme extracted from pineapple waste, the pineapple peel, has a good potential for a bating agent but needs more research work in order to obtain a stable and reliable product.

5. References

1. Alexander, K. (1989), "Enzymes in the tannery: catalysts for progress?", World Leather, August/September, 38–39.
2. TFL (1998), "Beamhouse: ecology meets economy: Oropon", TFL leaflet.
3. Sorensen, N. (1991), "Novo Nordisk enzymes for the leather industry", Denmark, NOVO leaflet.
4. Fiegel, T. (1998), "Use of enzymes in the beamhouse – possibilities and limitations", World Leather, May, 55 to 59.
5. Crispim, A., Mota, M.(2003), "Unhairing with enzymes", JSLTC, Journal of the Society of Leather Technologists and Chemists, Vol. 87, p. 198-202, November.
6. Thanikakaivelan, P., Chandrasekaran, B., Bharath,C.K., Saravanabhavan, S., Anandhi, C., Rao, J. R., Nair, B.U.(2006), "Single setp hair removal and fiber opening process: simultaneous and successive addition of protease and α – amylase, JALCA, Vol.101, p.388- 398.
7. Patrice Monteiro de Aquim, Mariliz Guterres and Jorge Trierweiler (2010), "Assesment of Water Management in Tanneries", JSLTC - Journal of the Society of Leather Technologists and Chemists, Vol. 94, p. 253-258, November-December.
8. Standard Methods for the Examination of Water and Waste Water, 17th ed, Washington, 1989.

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