ECO-FRIENDLY ALTERNATIVES TO BATING AND FATLIQUORING PROCESSES

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Abstract

Over recent decades, environmental and health protection factors have been completely implemented as an industrial management tool, thus meeting consumer demand for cleaner products and environmentally friendly companies.

The development of such products is highly dependant on the tanning technologies employed, which have significantly evolved in recent years. These improvements have been partly brought about by the development of numerous R&D projects promoted by European research centres and financially supported by the European Commission through various programmes. Among these programmes, LIFE+ contributes to the improvement of the environmental impact through the development of demonstration projects on innovative techniques and the dissemination of the results obtained from them.

The Center for Technology and Innovation, INESCOP, in collaboration with European tanneries, research centres and universities, is developing several projects aiming to improve the environmental impact of tanneries. INESCOP is currently involved in two EU projects related to the leather sector:

- LIFE PODEBA Project "Use of poultry dejection for the bating phase in the tanning cycle ".

- LIFE ECOFATTING Project "Environmentally friendly natural products instead of chloroparaffins in the fatting phase of the tanning cycle ".

This paper presents the main results obtained so far in the framework of the above-mentioned projects in which INESCOP is currently participating.

Keywords: enzymes, poultry dejection, bating, fatliquoring, chloroparaffins

1. Introduction

The tanning process is carried out over multiple stages in which tanners seek to optimise the quality and performance of the leather at the same time as attempting to reduce the costs of production and the environmental impact of the process. The adequate development of the first stages of the process (soaking, dehairing, deliming/bating stages) is fundamental in guaranteeing the quality of the finished leather, avoiding problems with wrinkling, grain looseness, low physical resistance, etc.

In the case of the bating stage, the use of enzymes is also inherent, in that only via the use of proteolytic enzymes it is possible to produce a loosening of the collagen structure of the skin, the principle aim of this stage. Furthermore, the enzymes used for bating reduce the alkaline swelling of the skin produced in the dehairing/liming stage, and also enable the elimination of fats, non-fibrous proteins, hair remains etc.

The intensity of the bating depends on the desired type of leather to be obtained as the final product, making it necessary to adequately control the process variables such as the enzyme activity of the product employed, the duration, temperature and pH of the operation, and the mechanical action. If the bating is insufficient due to it not being carried out in optimal conditions, the resulting leather could end up being hard, rough, with loose grain, and with hair-root and epidermis remains. On the contrary, excessive bating could provoke an intense weakening of the fibrous texture and an excessive elasticity and sponginess in the leather, with no fullness and low physical resistance.

The advances in biotechnology have led to the industrial production of enzymes by means of microbial fermentation in aerobic cultures on bacteria and fungi strains [1]. However, for years the presence of proteolytic enzymes in animal dejections has been a natural source of the enzymatic products used in leather bating-

In this context, the LIFE PODEBA project, “Use of poultry dejection for the bating stage in the tanning cycle,” has set the demonstration of recycling of poultry waste as its main objective, which, after having been treated, can be reused in the bating stage of the leather tanning process due to its enzymatic capacity. Technically the project has been developed in four stages:

- The conditioning of poultry dejection and the determination of its enzymatic activity.
- The use of poultry dejection in the bating stage of the tanning process.
- Obtaining leather of quality adequate for the manufacture of footwear and clothing.
- An evaluation comparing the environmental impact of the use of poultry dejection with that of commercial products.

On the other hand, the fatliquoring stage gives leather its original flexibility back, which is lost throughout the different process stages. This operation implies the addition of various fatliquoring products that keep fibres apart from each other and lubricated, so that they can better slide on each other. The greater or less degree of leather flexibility depends on the quantity and type of fats used, in such a way that by changing the percentages and combinations of fatliquoring products employed, it is possible to obtain different types of leather suitable for the manufacture of different articles.

The raw materials used for the production of fatliquoring products can be either of natural (fatty acid triesters of glycerol of animal or vegetable origin) or synthetic (paraffins, chlorinated paraffins and mineral oils) origin [2]. Such products are insoluble in water; therefore, they have to be subjected to a chemical transformation process (sulphation, sulphitation, phosphatisation, chlorination, sulphonation, etc.) through which polar groups are added to enable their emulsion in water [3].

Chloroparaffins (of petrochemical origin) have been widely used in the leather fatliquoring process, mainly because of their chemical stability, low cost and good application performances; however, they raise increasing concern due to their high chlorine content and low biodegradability. For this reason, the main objective of the LIFE ECOFATTING Project – “Environmentally friendly natural products instead of chloroparaffins in the fatting phase of the tanning cycle " – is to develop an innovative technology for leather fatliquoring based on more biodegradable, natural products. This project addresses the following actions:

- Development of more environmentally friendly, natural fatliquoring products.
- Comparative assessment of the environmental impact of various conventional fatliquoring products and that of the natural products developed in the project.
- Production of leather, the quality of which is suitable for the production of footwear and leather articles.

This paper describes the tests and analyses carried out, as well as the results obtained so far in both projects.

Experimental: materials and methods

Bearing in mind the different nature of the projects presented in this paper, the experimental procedures followed in each project are also different. Space constraints prevent a detailed description of the experimental procedures carried out; therefore, these have been summarised below.

The LIFE PODEBA Project

The poultry dejections (PD) were obtained from a laying hen intensive livestock farming facility located in Mordano, Emilia-Romagna (Italy). Poultry dejections were collected by manure belts and dried by Manure Drying System (MDS), one of the most efficient drying systems [4].

Poultry manure has a thick, gluey appearance, with humidity of around 70%, along with an unpleasant smell, because of which it is necessary to carry out previous conditioning of the samples so that their use and handling may be similar to that of commercial products usually applied, reducing the smell factor whilst maintaining its enzyme activity. This process consists of maturing and stabilizing biomasses under reduction of smelling emissions, according to a patented process (EP1314710; AMEK, CTI, 2002) [5].

The effectiveness of the conditioning treatment was evaluated via the measurement of VOC, NH3, CO2 , sulphur, and mercaptan emissions [6], as shown in Table 1; along with the enzyme activity of poultry manure, both before and after conditioning.

Parameter	Analysis method
VOCs	Gas chromatography Mass Spectrometry
Amonio (NH_3)	Spectrophotometry
Carbon dioxide (CO_2)	Gas chromatography
Dimethylsulphide $(CH_3)_2S$ Dimethyldisulphide $(CH_3)_2S_2$	Gas chromatography Mass Spectrometry
Methylmercaptan (CH_3SH)	Gas chromatography

Regarding the determination of the enzyme activity of poultry manure, owing to the granular form of the samples, a procedure was established to prepare the samples for their analysis. This procedure is based upon the standard for waste leaching for its characterisation, and it consists of the grinding of the samples (particle sizes of 4 mm maximum), the leaching of the waste in water being stirred for 24 hours at 50 rpm, and the subsequent vacuum filtration.

The determination of the enzyme activity of poultry manure permits the evaluation of the possibilities of the use of this waste in the bating stage. The characterisation of the enzyme activity of the samples can be carried out by using different methods according to the substrate used as a reference (casein, haemoglobin, etc.), and the method of detection (titration, spectrophotometry, etc.). In this case, the determination of the enzyme activity was carried out by means of the Lohlein-Volhard method [7]. This method is based on the digestion of a casein substrate by means of the proteolytic activity of enzyme products contained in the sample being tested. Through this method, enzyme activity is measured in Lohlein-Volhard Units per gram (LVU/g), defined as that amount of enzyme which digests 1.725 mg of casein.

The testing on the utilisation of the conditioned poultry manure in the bating stage of leather tanning was conducted at INESCOP's tanning pilot plants (Figure 1). In the tests carried out, pelt cattle hides, with a thickness of 2.5 mm, and split into sides (half of a hide) were processed. These hides were subjected to a conventional deliming process through the use of ammonium sulphate, and, following this, the bating process was completed using different poultry manure samples.

Figure 1. Tanning drum used for bating tests using poultry manure

By way of comparative reference, the bating was carried out using 1% of a commercial standard product with an enzyme activity of 900 LVU/g; consequently, depending on the enzyme activity of each manure sample, the percentage of the sample to be added to the pelt-split hide was recalculated, maintaining the consistency of the operation conditions: i.e. pH value, temperature, rotation speed and duration. Progress in the bating stage is evaluated by marking a fingerprint on the hide at 15 minute intervals, as is shown in Figure 2.

Figure 2. Verifying progress during the leather bating process.

After the bating stage, pickling was done, and, after that, tanning was carried out using basic trivalent Chromium salts. After tanning, the leather hides were sammied and skived to 1.5 mm to proceed with the neutralisation, retanning, dying, and fatliquoring, all using standard procedures.

The formulations used in these tests are shown in Table 2, where, for each of the operations, the table also indicates the product used, the percentage in weight, the temperature, and operation times, as well as the checks conducted (pH, salinity of the bath etc.)

Tabla 2. Testing formula.

Process	%	Product	°C	Rotation time	pH	Remarks
Deliming	200	Water	30	20’		
		Drain bath				Rinse twice
	100	Water	35	20’		
	1.0	Ammonium sulphate		15’		pH
	1.0	Ammonium sulphate		15’		pH
		Rotate		30’ - 45’	< 8	Check cross-section with colourless phenolphtalein
	0.5	Degreasing surfactant		20’		
Bating	200	Water	38			
	X	Poultry manure (*)		45’ - 60’		
		Drain bath				Bath sample
	200	Water	20	5’		Rinse twice
		Drain				

(*)*Recalculated for each poultry manure sample according to its enzyme activity, so that it is equivalent to 1% (over pelt split weight) of a commercial product of 900 LVU/g*.

The LIFE ECOFATTING Project

During the fist stage of the LIFE ECOFATTING project, the fatliquoring product families that are most widely used by European tanneries were assessed from the point of view of their environmental performance, setting the parameters to be analysed, as much in fatliquoring products and the wastewater produced in the fatliquoring stage, as in the leather obtained (physical, chemical and organoleptic parameters).

The results obtained will be used as a standard against which the improvement of the environmental impact of the natural fats developed will be compared. For this, the fatliquoring product families to be assessed were firstly selected, as shown in Table 3.

Table 3. Fatliquoring product families evaluated

1	Sulphated olein	6	Sulphated ester
2	Sulphonated olein	7	Phosphoric ester
3	Sulphited olein	8	Sulphochlorinated paraffin
4	Sulphited fish oil	9	Synthetic oils
5	Sulphated lecithin	10	Fatliquoring polymer

Then, the laboratory-scale and semi-industrial scale leather fatliquoring tests were conducted at INESCOP facilities using the selected products. These tests were carried out on wet-blue cattle hides and sheepskins that had been prepared for the fatliquoring operation by means of a standard process of neutralisation, retanning and dyeing. The laboratory-scale tests were carried out in pilot drums (Figure 3) using 1 sq. foot pieces of leather prepared for fatliquoring. Subsequently, semi-industrial scale tests (Figure 4) were conducted on whole leathers.

Figures 3 and 4. Laboratory scale and semi-industrial scale fatliquoring tests.

INESCOP facilities

In both cases the fatliquoring process performed on neutralised, retanned and dyed leather is shown in Table 4:

Table 4. Working procedure for leather fatliquoring

PRODUCT/PROCESS	% by wet-blue weight
Water (45-50 ºC)	500 %
Fatliquoring product	8 % (*)
Rotate for 90 min	
Formic acid (1:10 dilution)	3%
Rotate for 20 min	
Wash, drain drum, take bath sample and remove leather Air dry	

(*) In commercial products, greases are mixed with water or emulsifiers with an active ingredient concentration of 65-80%. For this reason, the percentage of the commercial product added is recalculated for each fatliquoring product so as to ensure the addition of the same amount of grease to all leathers

Once this operation was completed, a sample of the waste fatliquoring bath and a sample of one of the obtained leathers were taken for the determination of the selected physical parameters.

After the characterisation of the 10 reference fatliquoring product families, the same tests were conducted on the natural-origin products developed in the project. These products are based on C12-C18 chain fatty acid methyl esters of palm oil, subjected to a chlorination process to reach a chlorine content similar to that of commercial products (44%). The results obtained in these tests were compared with the reference values so as to be able to assess the improvement of the environmental impact of the products developed.

Concerning the appearance of the leather samples obtained, in all cases the assessed fatliquoring products conferred adequate softness, fullness and flexibility on the leather. Some differences in shade were observed, which were not considered significant.

Results and Discussion

A brief summary of the main results achieved to date in each project is given below.

The LIFE PODEBA Project

The results of the characterisation of the aqueous extract of the different poultry manure samples tested are shown in Table 5.

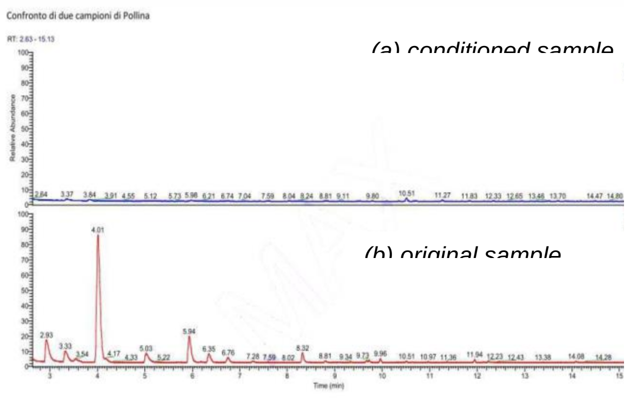
Table 5. Results of the analysis of the enzyme activity of poultry manure.

SAMPLE	Humidity (%)	LVU/g (sample weight)	LVU/g (dry sample weight)
FRESH	69	423	1.364
DRY	20	295	354
AMEK MDS	33	328	438
AMEK V	42	267	456
AMEK G	8	298	323
AMEK PO	20	378	472
C1	16	519	621
C2 (P70)	16	427	511
P120	18	350	489
C4	18	445	575

The results were validated through the testing of a commercial product, the enzyme activity of which was known, obtaining a deviation of between 8 and 15%, coinciding with the error established in the analysis procedure. The original sample possessed an enzyme activity of 1,364 LVU/g over dry weight, similar to the commercial bating products (1,000-2,000 LVU/g) which, after conditioning treatment, stabilised at around 500 LVU/g.

On the other hand, there was evidence that, through the use of the process conducted, there was a reduction in the level of VOC emissions, in accordance to what can be seen in Figure 5, in which the upper line graph corresponds to the conditioned sample, whilst the lower line graph corresponds to the sample that was not subjected to conditioning.

Figure 5. Determination of VOCs in poultry manure samples:
(a) conditioned sample, (b) original sample.



The absence of peaks in the conditioned sample (top image) in comparison to the original sample (lower image) shows the deodorisation of the poultry manure samples, which simplifies the use of these products in the bating stage of the tanning process.

The evaluation of the environmental impact of the use of poultry manure in the bating stage, in substitution of commercial enzyme products, was conducted via the characterisation of residual baths from the deliming/bating phases, which resulted from the tests conducted. In this regard, the most significant parameters, in accordance to international standards, were determined; the results obtained are shown in Table 6.

Table 6. Characterisation of the residual baths of the deliming/bating process.

Sample	pH	Conductivity (µs/cm)	Suspended solids (mg/l)	COD (g O2/l)	BOD_5 (g O2/l)	TKN (mg/l)	NH_4^+ (mg/l)	$S^=$ (mg/l)
Commercial product	8.1	8,870	516	9.8	4.8	1,424	1,090	0.5
AMEK V	7.9	6,842	1,433	14.1	8.4	1,431	1,120	4.1
AMEK G	8.0	5,508	1,829	10.6	6.0	927	725	2.4
AMEK PO	8.2	6,420	1,128	4.9	3.6	819	685	0.1
C2 (P70)	8.1	5,242	1,540	5.4	3.8	740	580	0.1

The characterisation of the residual baths resulting from the deliming/bating process showed a significant reduction in the environmental impacts of those baths where poultry manure was being used, which, in the case of the nitrogen content in the wastewater, measured as TKN/NH4+, was reduced by more than 50%. On the contrary, the content of solids suspended in the residual baths was higher owing to the very nature of the poultry manure samples.

The cattle hide leather samples obtained during the tests on a semi-industrial scale were subjected to different quality control processes according to international standards (EN-ISO) to test their suitability to be used in the manufacture of footwear components. Table 7 shows the results of the physical characterisation of the hides.

Table 7. Physical characterisation of leather (poultry manure bating enzymes).

PARAMETER	MINIMUM	MAXIMUM	AVERAGE	RECOMMENDED VALUES
Thickness (mm)	2.2	2.4	2.3	> 1.1
Tear strength (N)	242	257	246.5	> 150
Tensile strength (N/mm^2)	28.2	29.1	28.7	> 15
Elongation at break (%)	70.2	97.2	83.0	> 40
Grain burst (mm)	>10	>10	>10	> 8

The determination of the physical parameters of leather demonstrated that, in all cases, the recommended values for the manufacture of footwear were fulfilled.

Finally, the chemical validation of the leather obtained during the tests, on a semi-industrial scale, was carried out via the chemical characterisation of the leather according to accepted standards (EN. ISO. etc.), as well as the verification of the compliance with the criteria of the European Eco-label for footwear (Decision 2009/563/EC):

- Cr (VI) content in leather: not detected
- As, Cd and Pb content in leather: not detected
- Formaldehyde content in leather ≤ 150ppm
- Pentachlorophenol (PCP) content in leather: not detected
- Tetrachlorophenol (TCP) content in leather: not detected
- Azo-dye content in leather: < 30 ppm

The determination of the chemical parameters of the leather showed its conformity to the limits established in the European Eco-label for footwear.

The LIFE ECOFATTING Project

The environmental impact of the wastewater of the different fatliquoring product families assessed was carried out through the characterisation of the waste fatliquoring baths. The most significant parameters were assessed in accordance with international standards. Table 8 shows the results obtained for the different fatliquoring product families studied in semi-industrial scale tests, as well as the average reference values to facilitate the comparison of results:

Table 8. Characterisation of leather fatliquoring baths (reference fatliquoring baths / semi-industrial scale tests)

Reference		pH	Conductivity (µs/cm)	COD (mg O_2/l)	BOD_5 (mg O_2/l)	Biodegradability (BOD_5 / COD)
1	Sulphated olein	3.9	3,000	13,800	5,106	0.37
2	Sulphonated olein	3.9	3,000	15,000	8,850	0.59
3	Sulphited olein	3.7	1,900	17,800	8,366	0.47
4	Sulphited fish oil	3.8	2,100	18,300	8,052	0.44
5	Sulphated lecithin	3.8	2,200	17,400	6,960	0.40
6	Sulphated ester	3.5	2,500	15,900	7,632	0.48
7	Phosphoric ester	3.6	2,100	14,700	3,087	0.21
8	Sulphochlorinated paraffin	3.9	5,000	12,700	4,858	0.36
9	Synthetic oils	3.7	2,900	12,900	5,418	0.42
10	Fatliquoring polymer	3.8	2,800	15,100	2,567	0.17
Average reference values		*3.8*	*2,750*	*15,360*	*6,089.6*	*0.39*

Table 9 shows the results obtained in the tests using the natural fatliquoring products assessed to date for the fatliquoring stage (semi-industrial scale tests):

Table 9. Characterisation of leather fatliquoring baths (Ecofatting fatliquoring products/ semi-industrial scale tests)

Reference		pH	Conductivity (µs/cm)	COD (mg O_2/l)	BOD_5 (mg O_2/l)	Biodegradability (BOD_5 / COD)
1-10 Fatliquoring product families' average		*3.8*	*2,750*	*15,360*	*6,089.6*	*0.39*
CLP	Chlorinated paraffin (44 % Cl)	3.7	5,520	12,800	5,120	0.40
FAME	Chlorinated vegetable fatty acid methyl ester (44 % Cl)	3.6	3,960	13,100	6,812	0.52
CLP_S	Sulpho-chlorinated paraffin (44 % Cl)	3.6	6,150	13,600	4,800	0.36
FAME_S	Sulpho-chlorinated vegetable fatty acid methyl ester (44 % Cl)	3.7	5,100	10,400	5,340	0.51

The tests completed so far show that the biodegradability of the FAME fatliquoring bath samples (based of fatty acid methyl esters) improves by 30-33% with respect to the average value of the assessed fatliquoring products (1-10 product families).

Furthermore, the cattle hide leather samples obtained during the tests on a semi-industrial scale were subjected to different quality control processes according to international standards (EN-ISO) to test their suitability to be used in the manufacture of footwear components. Table 10 shows the results of the physical characterisation of the hides.

Table 10. Physical characterisation of leather

Reference	Thickness (mm)	Tear strength (N)	Tensile strength (N/mm^2)	Elongation at break (%)	Grain burst (mm)
1-10 Average	*1.5*	*212*	*17.4*	*84.2*	*> 10*
CLP	1.6	136	20.6	59.1	> 10
FAME	2.2	142	16.6	72.10	> 10
CLP_S	2.3	240	17.2	66.2	9.7
FAME_S	2.2	160	18.2	45.3	8.6
Recommended values	*>1.1*	*>150*	*>15*	*>40*	*>8*

The determination of the physical parameters of leather demonstrated that the recommended values for the manufacture of footwear were fulfilled.

Conclusions

With regard to the LIFE PODEBA project, the findings show that the use of poultry manure in the bating phase of leather production results in leather with a pleasant appearance and good resistance, along with adequate softness, flexibility, grain firmness, and fullness, without witnessing any differences with the results obtained from the use of commercial enzyme products.

In relation to the conditioning of the samples, the drying and deodorising treatment used considerably simplifies the use of these waste products, and, after having optimised it, it does not interfere in the enzyme activity of the poultry manure, which has been established at around 500 LVU/g. This entails a slight increase of the usual dosage by 1%, or prolonging the operation time a little bit.

In relation to the environmental impact, the values obtained in the characterisation of the deliming/bating baths in the different tests conducted show that in all of them, there is a significant reduction in the impact on the environment, mainly regarding the nitrogen content of the wastewater, measured as TKN/NH4+, and COD, observing an increase in the quantity of the suspended solids, owing to the granular nature of the poultry manure samples.

The determination of the physical parameters of the leathers bated with the conditioned poultry manure has demonstrated the fulfilment of the limits established for the manufacture of footwear articles. As regards the chemical characterisation of this leather, the results show the compliance with the limits set by the criteria of the European Eco-label for footwear.

In short, conducting the leather bating process using conditioned poultry manure of proven enzyme activity implies a considerable reduction in the environmental impact of this stage in the process, whilst maintaining the quality of tanned leather.

With regard to the LIFE ECOFATTING project, in all cases the fatliquoring products assessed through laboratory scale and semi-industrial scale tests proved to confer adequate softness, fullness and flexibility on the leather. Some differences in shade were observed, which were not considered significant.

In the characterisation of the wastewater of the assessed product families, it was observed that the polluting load of all baths was quite similar, so none of them stood out for its low environmental impact.

The tests completed so far on alternative fatliquoring products show a higher degree of biodegradability for the products based on vegetable-origin fatty acid methyl esters, thus obtaining leather with suitable appearance and touch, which also meets the recommended values for footwear manufacture.

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