INESCOP

ENVIRONMENTAL DEMONSTRATION OF NATURAL PRODUCTS AT LABORATORY LEVEL

ACTION 4

DELIVERABLE 1

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LIFE ECOFATTING PROJECT
LIFE10 ENV/IT/000364

ENVIRONMENTALLY FRIENDLY NATURAL PRODUCTS INSTEAD OF CLOROPARAFFINS IN THE FATTING PHASE OF THE TANNING CYCLE

Prepared by INESCOP

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1. INTRODUCTION

This report presents the results of the environmental demonstration of the natural products at laboratory level. For this, different types of hides have been fat-liquored employing products developed by SERICHIM by carrying out trials at laboratory level.

In previous test developed by SERICHIM and COLORTEX, the best results were obtained using Cl-Palmlernel oil (as substitute of CPs) and SCl-Palmkernel oil (as substitute of SCP).

Once these products were selected by COLORTEX and SERICHIM, and after the characterisation of the 10 reference fatliquoring product families, the laboratory tests were conducted on the natural-origin products developed in the project.

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, always maintaining the quality of leather.

2. LABORATORY SCALE TRIALS

2.1. Description of laboratory scale trials.

The laboratory-scale leather fat-liquoring trials were conducted at INESCOP-U.T Vall d'Uixó facilities using the selected products. The trials were carried out in rotating stainless steel tanning drums measuring 300 mm in diameter and 150 mm in width respectively, featuring systems for automation, control and dosage of water and reactants.

Figure 1. Laboratory-scale rotating drums at INESCOP-UT Vall d'Uixó facilities.

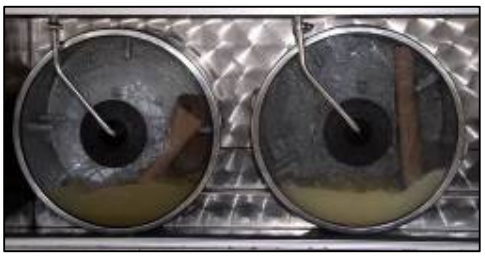


Figure 2. Detail of laboratory-scale trials at INESCOP-UT Vall d'Uixó facilities.

In each test with the calf hides, 1 sq. foot pieces of wet-blue shaved hides with a thickness of 1.5 mm were processed. These pieces of wet-blue cattle hides had been prepared for the fat-liquoring operation by means of a standard process of neutralisation, retanning and dyeing. In the same way, in tests with sheepskin, 1 sq. foot pieces of wet-blue shaved hides with a thickness of 1.2 mm were processed.

The formulations used in these tests are shown in Table 1 where it is indicated, for the different operations, the product used, the percentage by weight with respect to the wet-blue leather introduced into the tanning drum, temperature, rotating time and checks to be performed.

PROCESS/PRODUCTS	% by wet-blue weight	Tª (ºC)	Time (min.)	pH	Remarks
RETANNNG					
Rinse with water	200	40			
Acetic Acid	0'2				
Degreasing surfactant	0'2		20'		
Drain and wash					
Water	100	40			
Synthetic Chromium	5		30'		
Sodium Formiate	1			4'1	Check pH
Drain					
NEUTRALISATION					
Water	200	40			
Synthetic buffered solution	2				
Sodium Formiate	1		40'	4'5	Check pH
Sodium bicarbonate	1		15'		
Acrylic Resin	5		60'		
Drain and wash					
DYEING					
Water	50	25			
Synthetic Phenol	5		20'		
Filler	5				
Dispersing Agent	1				
Powdered dye	1		45'	4'6	Check through section
Water	200	60			
Formic Acid	0'5		30'	3'8	Check pH
Drain and wash					

Table 1. Description of the retanning, neautralisation, and dyeing processes.

Once the hides had been retanned, neutralised and dyed, the fat-liquoring stage was performed, according to the process described in Table 2:

PROCESS/PRODUCTS	% by wet-blue weight	Tª (ºC)	Time (min.)	pH	Remarks
FAT-LIQUORING					
Water	5000	45-50			
Fat-liquoring product	8 [1]		90’		
Formic acid (1:10 dilution)	3		20’		Check pH
Wash, drain drum, take bath sample and remove leather					
Air dry					

Table 2. Description of the leather fat-liquoring process.

Once this operation was completed, a sample of the waste fat-liquoring bath and a sample of each one of the obtained leathers were taken for their characterization.

2.2. Definition of parameters to be analysed

INESCOP has defined the parameters to be analysed, as much in fat-liquoring products and the wastewater produced in the fat-liquoring stage as in the leather obtained. Table 3 shows the parameters analysed for assessing the environmental impact of fat-liquoring products:

Tests on fat-liquoring products (heavy metals)
As (mg/l)
Cd (mg/l)
Pb (mg/l)

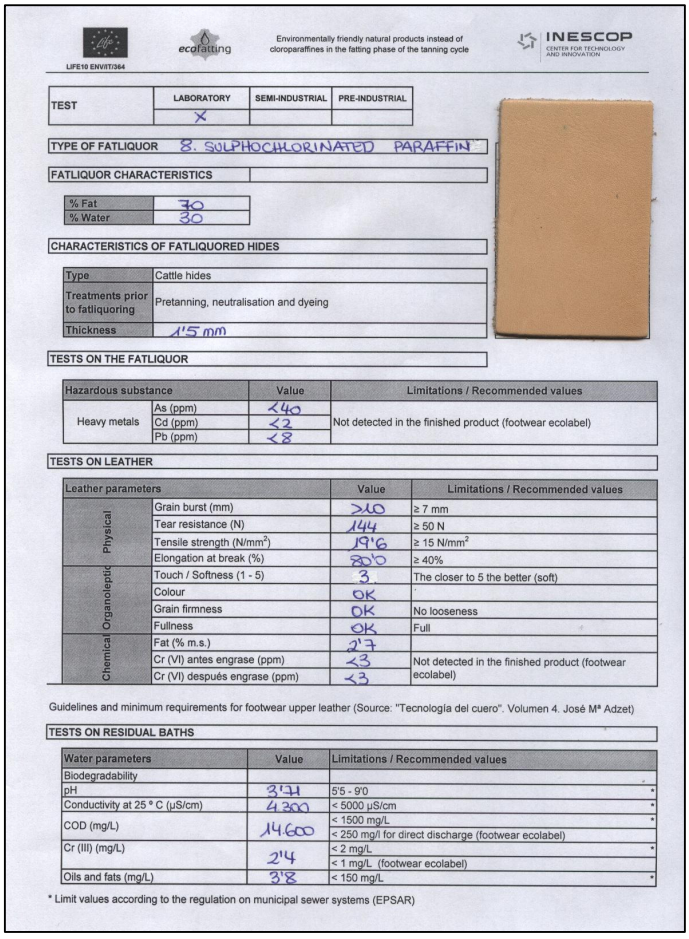
Wastewater parameters
pH
Conductivity at 25 º C (µS/cm)
BOD_5 (mg O_2/l)
COD (mg O_2/l)
Biodegradability (BOD/COD)
Cr (III) (mg/l)
Oils and fats (mg/l)

[1] 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 fat-liquoring product so as to ensure the addition of the same amount of grease to all leathers.

Leather parameters	
Organoleptic	Touch / Softness
	Colour
	Grain firmness
	Fullness
Physical	Shrinkage temperature (ºC)
	Tear resistance (N)
	Tensile strength (N/mm^2)
	Elongation at break (%)
Chemical	Extractable substance by using CH_2Cl_2 (% m.s.)
	Cr (VI)

Table 3. Assessment of the environmental impact of fat-liquoring products; parameters to be analysed.

The tests were monitored by means of control sheets for tests & results, which contain information about test type, type of fat-liquoring product and characteristics, type of skin and treatment, fat-liquoring products analysis, leather analysis: physical tests - chemical tests and organoleptic properties and wastewater analysis.



LIFE10 ENV/IT/364 — ecofatting — Environmentally friendly natural products instead of cloroparaffines in the fatting phase of the tanning cycle — INESCOP CENTER FOR TECHNOLOGY AND INNOVATION

TEST	LABORATORY	SEMI-INDUSTRIAL	PRE-INDUSTRIAL
	X		

TYPE OF FATLIQUOR: 8. SULPHOCHLORINATED PARAFFIN

FATLIQUOR CHARACTERISTICS

% Fat	70
% Water	30

CHARACTERISTICS OF FATLIQUORED HIDES

Type	Cattle hides
Treatments prior to fatliquoring	Pretanning, neutralisation and dyeing
Thickness	1'5 mm

TESTS ON THE FATLIQUOR

Hazardous substance		Value	Limitations / Recommended values
Heavy metals	As (ppm)	<40	Not detected in the finished product (footwear ecolabel)
	Cd (ppm)	<3	
	Pb (ppm)	<8	

TESTS ON LEATHER

Leather parameters		Value	Limitations / Recommended values
Physical	Grain burst (mm)	>10	≥ 7 mm
	Tear resistance (N)	144	≥ 50 N
	Tensile strength (N/mm^2)	19'6	≥ 15 N/mm^2
	Elongation at break (%)	80'0	≥ 40%
Organoleptic	Touch / Softness (1 - 5)	3	The closer to 5 the better (soft)
	Colour	OK	
	Grain firmness	OK	No looseness
	Fullness	OK	Full
Chemical	Fat (% m.s.)	2'7	
	Cr (VI) antes engrase (ppm)	<3	Not detected in the finished product (footwear ecolabel)
	Cr (VI) después engrase (ppm)	<3	

Guidelines and minimum requirements for footwear upper leather (Source: "Tecnología del cuero". Volumen 4. José Mª Adzet)

TESTS ON RESIDUAL BATHS

Water parameters	Value	Limitations / Recommended values
Biodegradability		
pH	3'71	5'5 - 9'0 *
Conductivity at 25 ° C (µS/cm)	4300	< 5000 µS/cm *
COD (mg/L)	14600	< 1500 mg/L *
		< 250 mg/l for direct discharge (footwear ecolabel)
Cr (III) (mg/L)	2'4	< 2 mg/L *
		< 1 mg/L (footwear ecolabel)
Oils and fats (mg/L)	3'8	< 150 mg/L *

* Limit values according to the regulation on municipal sewer systems (EPSAR)

Figure 3. Control sheets for tests & results.

In Annex 1, there are images of the trials being carried out in laboratory conditions and the physical test on obtained leathers.

3. ENVIRONMENTAL IMPACT OF NATURAL FAT-LIQUORING AGENTS

In all trials carried out, the obtained leathers have good physical strength and adequate smoothness, softness, fullness and flexibility, and no significant difference between the different fatliquoring agents has been detected.

The environmental evaluation of the results of the carried out tests is done through:

- the analysis of natural fat-liquoring products
- the characterization of natural fat-liquoring residual baths
- the analysis of leathers: physical tests, chemical tests and organoleptic properties

3.1. Analysis of fat-liquoring products

The evaluation of the characteristics possessed by the natural fatliquoring products chosen to be used in the tests was carried out by determining the levels of arsenic, cadmium, and lead contained in the products, in order to prevent these substances from being present in leather in accordance with the criteria of the European Eco-label for footwear (Decision 2009/563/EC).

The determination of the chemical parameters of the natural fatliquoring products showed its conformity to the limits established in the European Eco-label for footwear, since the findings of the analysis showed results that were less than the aforementioned limit for all of the products:

Arsenic: < 60 ppm *
Cadmium: < 6 ppm *
Lead: < 8 ppm*

* Limit of detection of the analysis technique employed

3.2. Characterisation of natural fat-liquoring residual baths

The evaluation of the impact of the natural fat-liquoring on wastewater was achieved by the characterisation of the fat-liquoring waste-baths obtained in the different tests carried out, determining the most significant parameters in accordance with international standards. The table 4 below shows the selected control parameters and the testing standards used:

PARAMETER	STANDARD
pH	---
Conductivity	UNE-EN 27888:1994. Determination of electrical conductivity. (ISO 7888:1985).
COD	UNE 77004:2002. Determination of the chemical oxygen demand (COD).
BOD_5	UNE-EN 1899-1:1998 Determination of biochemical oxygen demand after *n* days (BODn).
Total Cr	UNE 77061:2002 Chromium determination.
Oils & Fats	Standard Methods for the Examination of Water and Wastewater_SM 5520 B

Table 4. Standards used in the characterization of tanning wastewater.

Table 5 shows the results obtained in the laboratory scale tests with bovine leather, using the natural fatliquoring products selected as optimum for the fatliquoring stage.

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	6,290	0.41
CLP	Chlorinated paraffin (44 % Cl)	3.3	6,500	12,600	5,540	0.44
FAME	Chlorinated vegetable fatty acid methyl ester (48.6 % Cl)	3.2	5,100	12,800	7,170	0.56
CLP_S	Sulpho-chlorinated paraffin (44 % Cl)	2.4	12,100	10,300	4,225	0.41
FAME_S	Sulpho-chlorinated vegetable fatty acid methyl ester (38 % Cl- 8.6 % S)	2.4	10,200	5,440	2,990	0.55

Table 5. Characterisation of bovine leather fatliquoring baths
(Ecofatting fatliquoring products/ laboratory scale tests)

The tests carried out show that the biodegradability of the FAME fatliquoring bath samples (based of fatty acid methyl esters) improves by 34 - 36% with respect to the average value of the assessed fatliquoring products (1-10 product families).

Table 6 shows the results obtained in the laboratory scale tests with sheep hides, using the natural fatliquoring products selected as optimum for the fatliquoring stage.

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	6,290	0.41
CLP	Chlorinated paraffin (44 % Cl)	3.7	8,350	1,800	968	0.54
FAME	Chlorinated vegetable fatty acid methyl ester (48.6 % Cl)	3.6	7,670	1,681	723	0.43
CLP_S	Sulpho-chlorinated paraffin (44 % Cl)	3.4	10,300	1,345	403	0.30
FAME_S	Sulpho-chlorinated vegetable fatty acid methyl ester (38 % Cl- 8.6 % S)	3.4	9,700	940	435	0.46

Table 6. Characterisation of sheep hides fatliquoring baths
(Ecofatting fatliquoring products/ laboratory scale tests)

The tests completed show that the biodegradability of the FAME fatliquoring bath samples (based of fatty acid methyl esters) improves by 4.9 – 12.2 % with respect to the average value of the assessed fatliquoring products (1-10 product families).

3.3. Characterisation of fat-liquoring leathers

The characterisation of fatliquored leather was conducted from three points of consideration:

- Organoleptic tests.
- Physical resistance tests.
- Chemical tests.

3.3.1. Organoleptic tests

The parameters considered in the organoleptic tests were: touch, colour, and firmness factors.

Regarding the *touch* of the leathers tested, this was graded on the level of softness obtained, assigning a value of 1 for the lowest level of softness and 5 for the highest. In table 7 the results of this test are displayed, observing an adequate level of leather softness in all leather hides.

Reference		Calf hides Touch (1-5)	Sheep skins Touch (1-5)
1-10 Fatliquoring product families' average		4	4
CLP	Chlorinated paraffin (44 % Cl)	5	5
FAME	Chlorinated vegetable fatty acid methyl ester (48.6 % Cl)	5	5
CLP_S	Sulpho-chlorinated paraffin (44 % Cl)	5	5
FAME_S	Sulpho-chlorinated vegetable fatty acid methyl ester (38 % Cl- 8.6 % S)	5	5

Table 7. Touch test on fatliquored leather hides.

In reference to the *firmness* of the leather, continuous flexing of the leather was carried out to test the degree of adhesion of the grain. With all of the natural fatliquors that were tested, none produced leather with loose grain characteristics; all of the resulting leather possessed adequate levels of firmness.

Finally, regarding *colour*, differences in final leather colour tone were observed upon the use of the various natural fatliquors, but no significant differences were present.

3.3.2. Physical resistance tests

The quality assessment on the production of fatliquoring hides is done through physical validations in accordance with accepted standards (EN, ISO, etc.). The table below shows the selected control parameters and the testing standards used:

PARAMETER	STANDARD
Thickness (mm)	ISO 2589:2002 (IULTCS/IUP 4) Determination of thickness
Tear strength (N)	ISO 3377-2:2002 (IULTCS/IUP 8) Determination of tear load -- Part 2: Double edge tear
Tensile strength (N/mm^2)	ISO 3376:2002 (IULTCS/IUP 6) Determination of tensile strength and percentage extension
Elongation at break (%)	ISO 3376:2002 (IULTCS/IUP 6) Determination of tensile strength and percentage extension
Grain burst (mm)	ISO 3379:1976 (IULTCS/IUP 9) Determination of distension and strength of grain -- Ball burst test

Table 8. Standards used in the physical validations of fatliquoring hides.

The cattle hide leather samples obtained during the tests on a laboratory 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 9 shows the results of the physical characterisation of the bovine hides.

Reference		Tear strength (N)	Tensile strength (N/mm^2)	Elongation at break (%)
1-10 Average		156	17	72
CLP	Chlorinated paraffin (44 % Cl)	85	10.7	49.3
FAME	Chlorinated vegetable fatty acid methyl ester (48.6 % Cl)	119	20.3	66
CLP_S	Sulpho-chlorinated paraffin (44 % Cl)	331	25.4	85.3
FAME_S	Sulpho-chlorinated vegetable fatty acid methyl ester (38 % Cl- 8.6 % S)	214	21.4	78.9
Recommended values		>150	>15	>40

Table 9. Physical characterisation of bovine leather (laboratory scale tests)

The sheep skins samples obtained during the tests on a laboratory 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 sheep skins.

Reference		Tear strength (N)	Tensile strength (N/mm^2)	Elongation at break (%)
1-10 Average		156	17	72
CLP	Chlorinated paraffin (44 % Cl)	63	10.7	58.1
FAME	Chlorinated vegetable fatty acid methyl ester (48.6 % Cl)	89	20.3	77.6
CLP_S	Sulpho-chlorinated paraffin (44 % Cl)	123	16.2	69.2
FAME_S	Sulpho-chlorinated vegetable fatty acid methyl ester (38 % Cl- 8.6 % S)	119	17.6	65.6
Recommended values		>50	>15	>40

Table10. Physical characterisation of bovine leather (laboratory scale tests)

5.3.3. Chemical tests on leather

The quality assessment on the production of fatliquoring hides is done through chemical validations in accordance with accepted standards (EN, ISO, etc.). The table below shows the selected control parameters and the testing standards used:

PARAMETER	STANDARD
Matter soluble in dichloromethane (%)	ISO 4048:2008 Leather - Chemical tests - Determination of matter soluble in dichloromethane
Chromium(VI) (mg/kg)	ISO 17075:2007 Leather - Chemical tests - Determination of chromium(VI) content

Table 11. Standards used in the chemical validations of fatliquoring hides.

The cattle hide leather samples obtained during the tests on a laboratory scale were subjected to different chemical analysis according to international standards (EN-ISO) to test their suitability to be used in the manufacture of footwear components. Table 12 shows the results of the chemical characterisation of the bovine hides.

Reference		Matter soluble in Cl_2CH_2 (% m.s.)	Chromium(VI) (mg/kg)
1-10 Average		4.4	14.3
CLP	Chlorinated paraffin (44 % Cl)	8.6	2.6
FAME	Chlorinated vegetable fatty acid methyl ester (48.6 % Cl)	7.7	2
CLP_S	Sulpho-chlorinated paraffin (44 % Cl)	10.1	2.3
FAME_S	Sulpho-chlorinated vegetable fatty acid methyl ester (38 % Cl- 8.6 % S)	10.1	1.8
Recommended values		<3	< 3

Table 12. Chemical characterisation of bovine leather (laboratory scale tests)

The sheep skins samples obtained during the tests on a laboratory scale were subjected to different chemical analysis according to international standards (EN-ISO) to test their suitability to be used in the manufacture of footwear components. Table 13 shows the results of the chemical characterisation of the sheep skins.

Reference		Matter soluble in Cl_2CH_2 (% m.s.)	Chromium(VI) (mg/kg)
1-10 Average		4.4	14.3
CLP	Chlorinated paraffin (44 % Cl)	6.3	<3
FAME	Chlorinated vegetable fatty acid methyl ester (48.6 % Cl)	7.5	<3
CLP_S	Sulpho-chlorinated paraffin (44 % Cl)	4.1	<3
FAME_S	Sulpho-chlorinated vegetable fatty acid methyl ester (38 % Cl- 8.6 % S)	3.7	<3
Recommended values		<3	< 3

Table 13. Chemical characterisation of sheep skins (laboratory scale tests)

4. CONCLUSIONS

In all trials, leathers were obtained with an acceptable appearance, full and firm, with a soft and pleasant feel and no significant differences were observed in the addition of the different fatliquoring tested.

The determination of the chemical parameters of the natural fatliquoring products showed its conformity to the limits established in the European Eco-label for footwear, since the findings of the analysis showed results that were less than the Arsenic, Cadmium and Lead limit for all of the natural products.

The evaluation of the impact of the natural fat-liquoring on wastewater was achieved by the characterisation of the fat-liquoring waste-baths obtained. The tests show that the biodegradability of the FAME fatliquoring bath samples (based of fatty acid methyl esters) improves by 5 - 36% with respect to the average value of the assessed fatliquoring products (1-10 product families).

Regarding the *touch* of the leathers tested, this was graded on the level of softness obtained, assigning a value of 1 for the lowest level of softness and 5 for the highest. In table 7 the results of this test are displayed, observing an adequate level of leather softness in all leather hides (3-5), except those subjected to the fatliquoring process using sulphited fish oil, which demonstrated a lower level of softness (2).

In reference to the *firmness* of the leather, continuous flexing of the leather was carried out to test the degree of adhesion of the grain. Loose grain is an undesirable effect in leather, since during use as part of finished products (e.g. shoes, leather garments, etc.), wrinkles begin to form in areas where flexing movements take place. With all of the natural fatliquors that were tested, none produced leather with loose grain characteristics; all of the resulting leather possessed adequate levels of firmness.

Regarding *colour*, differences in final leather colour tone were observed upon the use of the various natural fatliquors, but no significant differences were present.

Finally, the determinations of physical and chemical parameters of the leathers have shown to be compliant with the limits required for footwear manufacture.

5. PHOTO GALLERY

The images that have been collected show the laboratory tests conducted during the different stages of the natural fatliquoring process at laboratoruio level.