



**LIFE PROJECT – ECODEFATTING
LIFE13 ENV/IT/00470**

“Environmentally friendly natural products instead of chemical products in the degreasing phase of the tanning cycle”

**DELIVERABLE - ACTION D.3
ECODEFATTING technical manual**



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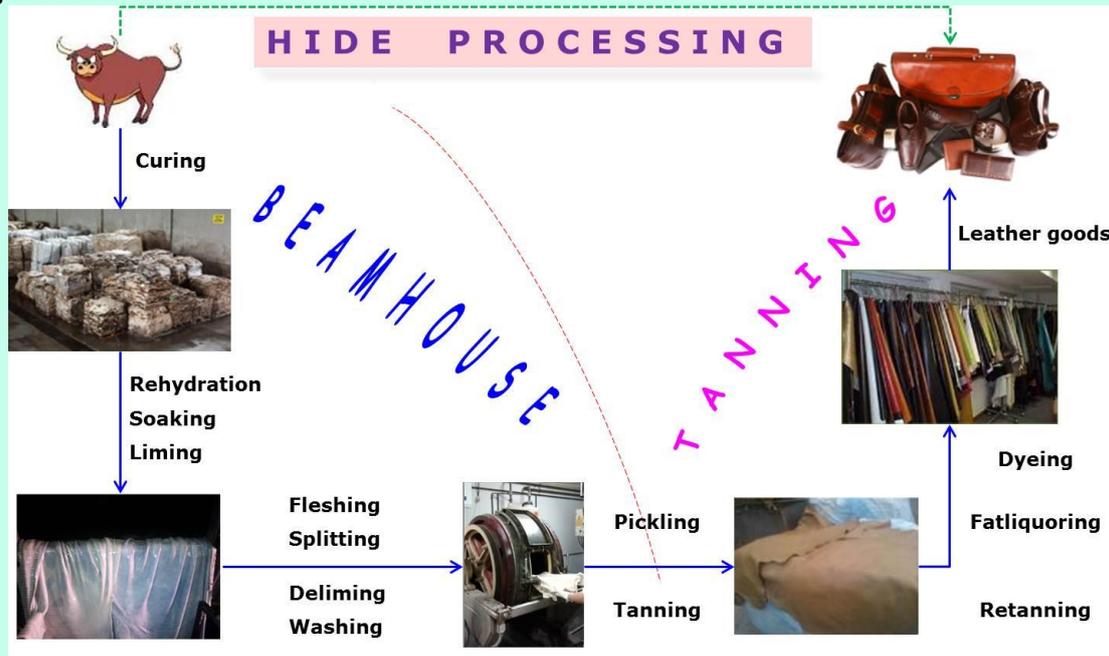
2. List of abbreviations, acronyms and symbols

°Be	Baumè degree	min.	minutes
°C	Celsius degree	NaCl	sodium chloride
>	higher than	NaHCO ₃	sodium bicarbonate
pH	hydrogenionic concentration	NaHS	sodium hydrosulfide
Ca(OH) ₂	calcium hydroxide	NaHSO ₃	sodium bisulfite
Cr	chrome	NaOH	sodium hydroxide
<i>e.g.</i>	<i>exemplii gratia</i> (for example)	Na ₂ CO ₃	sodium carbonate
h	hour	Na ₂ S	sodium sulfide
H ₂ SO ₄	sulphuric acid	Na ₂ SO ₄	sodium sulphate
<i>i.e.</i>	<i>id est</i> (that is)	NH ₄ Cl	ammonium chloride
MgO	magnesium oxide	w/w	weight to weight ratio

3. Overview of tannery operations

Leather is a general name to describe materials of added value, obtained from the elaboration of different type of hides or skins (the waste of slaughterhouses) from: bovines, horses, sheep and lambs, goats and kids, pigs, kangaroos, reptiles, stingrays and sharks. The entire sequence from raw hides to the finished leather can be divided in two big groups: the beamhouse and the tanning operations (**Figure 3.1**).

Figure 3.1



The first ones act primarily on raw hides, whereas the second ones deal with the job of turning animal hides into leather, including some additional actions such as dyeing, specific fatliquoring, polishing and other refining activities. The sequence of the beamhouse operations can start either from dry, salt wet or fresh hides, depending on how far away tanneries are from the location of hide supplying. Specifically:

- **curing** is necessary when hides have to travel long distances, before they reach the tanneries. Fresh hides after flaying are dehydrated with common salt, to preserve them from putrefaction. If curing is quite extreme, hides become stiff and dry. On the other hand, the hides may contain 40-50% (w/w) of water.
- **rehydration** is carried out on dry cured hides. It can either be carried out as a separate operation or be combined with soaking. Cured hides are given back the lost water as excess salt is removed, to allow the subsequent elaborations. Hides become soft, possibly with a certain degree of swollenness and they are ready for the hides-turning-leather processing.
- **soaking** aims at removing all foreign matter from the hides, allowing them to acquire back their original condition just after flaying. Fresh hides do not require soaking. All salt is removed and the hides are washed out from any residual blood, dirt and dung, using surfactants (to aid the penetration of water into the hides), alkalis (e.g., Na_2CO_3 , NaOH to

- soften the collagen structure), bactericides (to prevent bacterial growth) and proteolytic enzymes to accelerate the soaking (if required).
- **Liming** is carried out with $\text{NaHS}/\text{Na}_2\text{S}/\text{Ca}(\text{OH})_2$ at pH 12. The sulfide salts are strong reducing agents, capable to break the molecular structure of hair, constituted mainly by keratin. Hair is weakened and lost, since its interaction with the collagen structure of hides becomes loose. Concomitantly, defatting agents are added during the liming, to free the hides from excess fat. Usually, the amount of defatting agents is calculated on the weight of raw hides and it represents a percentage ranging from 0.2 to 0.5%. The combination of the sulfide salt action with that of the defatting agents makes the hides soft and malleable. According to the type of leather, different commercial preparation of proteolytic enzymes may also be added into the drum. These enzymes do the job of the ancient hide bating carried out with dung as a separate stage, solubilizing the most lipophilic proteins. This has the effect to make the internal structure of collagen even more loose, giving an even softer touch to the hides. The degree of swollenness may be controlled by the insertion of salt into the liming bath.
 - **fleshing and splitting** are carried out mechanically, to make the surface even and smooth. According to the type of customer request, hides may even be split in two portions, obtaining the so called crust hide and split grain hide. This latter operation may even be carried out on pretanned hides.
 - **deliming and washing** is necessary to remove excess lime and sulphide salts from the hides. The isoelectric pH of the hides is lowered to 7.5-8.5 with organic or inorganic acids, combinations of them, including inorganic salts (e.g. NH_4Cl). The swollenness of hides is reduced and proteolytic enzymes are added to continue the bating activity, already started during the liming. According to the type of hides, defatting agents are also added in this phase: either as a single shot or in two aliquots.
 - **pickling** can be considered the end of the deliming/washing stage, since the enzymatic activity stops. The hides are treated with acids that lower the pH to 3-3.5, removing any residual alkali. Salts (e.g., NaCl , Na_2SO_4) are generally added to the pickling bath before adding acid, to prevent the swelling of the collagen. During this operation, expert tanners may also add pretanning agents, to confer long term stability to the hides, that are half way to become leather. The main reason behind the pickling is to avoid the contact of subsequent tanning agents with hides at high pH, since tanning agents tend to modify their structure, becoming less active (i.e., they do not penetrate deeply into the hides) and precipitating on the surface of hides giving out stains.
 - **tanning** is the definite stabilization of the hides, that become leather (i.e. rot-proof). Tanning can be carried out with metal based salts (the most used is chrome bisulphate) or with tannins extracted from particular trees (Argentinian Quebracho, European chestnut, Peruvian Tara, Acacia). According to these two general methods, the resulting leather specimens have different organoleptic properties, mechanical resistance and aspect, that will determine their final destination down to the manufacturing line of leather goods. Tannins tend to confer a natural look to leather, whereas salt based tanned leather is more appropriate

for furniture design. Other tanning methods involve the use of organic compound based agents such as, aldehydes, quinones, triazines and specific resins.

The tanning stage formally ends the beamhouse operations. The subsequent retanning, fatliquoring, dyeing and refining phases are usually carried out in different premises and/or by specialized companies, that purchase the leather already produced by other tanners: either in the wet blue form (when tanned with chrome) as crust or split grain or in the vegetable tanned form (when tanned with natural tannins). Ecodefatting demonstrates the use of a novel defatting agent during the **rehydration/soaking, liming and deliming/washing** stages. The new product is a combination of known substances to tanners (i.e., ethoxylated alcohols) and unprecedented compounds derived from natural sources. This combination achieves several objectives: the sustainability of the production process for the new formulation, the reduction of the chemical emissions associated to the production of the raw ingredients, the good performance of defatting and the generation of effluents compatible with wastewater plant schemes.

4. General procedures for processing hides with Ecodefatting product EDF-20

Hide processing is an empirical practice, which is customarily updated according to tanners' experience. From time to time tanners do use commercial products for specific applications, defining work recipes that are used from day to day to carry out production campaigns. Some of the most used trade mark products are:

- Ledermol 51: a sulfonated C₁₄-C₁₇-sec-alkane;
- Basic 14 and Biokal RM: sequestering and chelating agents;
- Prolime RBE, Prolime NX, Rinazim and Depilzim: mixtures of proteolytic enzymes;
- Linedeg ARG: a solution of diethanolamine;
- Prokal 700 and Prokimid: a mixture of NH₄Cl, adipic, succinic and glutaric acid;
- Prokal T: a mixture of NH₄Cl, formic acid H₂SO₄;
- Ledermerc 1: a mixture of NH₄Cl and proteolytic enzymes;
- Ecovit 90: a solid preparation containing Na₂CO₃;
- Biokal STR: a solution of NaOH and dimethylamine;
- Biosint CR: a solution of NaOH;
- Biokal SH: a buffer solution of thioglycolic acid and its sodium salt.

The amount of all chemical and enzymatic products as well as that of water are expressed in terms of percentage by weight (w/w) taking the weight of the lot of hides as reference. In some cases it is necessary to control the pH of the beamhouse baths as well as their density according to the Baumé scale (°Bé). In this case, NaCl is added to the baths according to the weight of hides into the drum.

4.1. Bovine hides.

The following steps have to be carried out one after the other on raw hides, as follows:

- Desalination/rehydration: charge the lot of hides into a drum and add water (100%) at 30°C. Add Na₂S (0.1%) and keep the drum under rotation for 60 min.. Drain the liquid content, add water at 26-27°C and keep rotation for 5 min.. Drain the liquid.

- **Soaking:** add water (80%) at 27°C, followed by Ledermol 51 (0.15%), **EDF20** (0.2%), Basic 14 (0.2%), Prolime RBE (0.35%) and Na₂CO₃ (0.8%). Keep the rotation for 3 h and add Linedeg ARG (0.5%). Keep rotating for further 2 h and drain the liquid content.
- **Liming:** add water (100%) followed by Linedeg ARG (0.3%), NaHS (1.5%), Ca(OH)₂ (2.0%) and rotate the drum for 30 min.. Add Basic 14 (0.2%) followed by Na₂S (2.5%), Ca(OH)₂ (3.5%) and rotate the drum for 1 h. Add Prolime NX (0.25%) followed by **EDF20** (0.2%) and water (20%). Rotate the drum for 1 h and then keep rotating it for 5 min. at time clockwise and anticlockwise over a period of 14 h. Drain the liquid content, add cold water (100%) and rotate for further 3 h. Drain the liquid and collect the hides.
- **Fleshing:** use an appropriate cutting machine, to bring the hides up to the desired thickness.
- **Deliming:** charged the fleshed hides into the drum and add warm water (100%) at 35°C, followed by **EDF20** (0.1%) and Prokal 700 (0.3%). Rotate the drum for 20 min., add water (30%) at 30°C, Prokal 700 (1%) and **EDF20** (0.2%). Rotate for 10 min. and add Prokal T (1.2%). Rotate for 15 min. and add further Prokal T (1.3%). Rotate for 40 min. and add Ledermac 1 (0.03%). Rotate for 15 min. and drain the liquid content.
- **Pickling:** add water (30%) and NaCl (5%) and rotate the drum for 10 min.. Add formic acid (1%) and rotate for 20 min.. Add H₂SO₄ (1.3%) and rotate for 3 h. Drain the acidic liquid and collect the pickled hides.

At this stage the hides are ready either for a preliminary pretanning stage or for tanning according to one of the methods mentioned earlier. The above procedure of hide processing is normally reported in a schematic fashion, within a table structure as follows (**Table 4.1.1**):

Table 4.1.1 Procedure to process bovine hides

Stage	%	Product	T (°C)	t (min)	Rotation	Action
Desalination	100	H ₂ O	30			
	0.1	Na ₂ S		60	<input checked="" type="checkbox"/>	drain
	200	H ₂ O	26-27	5	<input checked="" type="checkbox"/>	drain
Soaking	80	H ₂ O	27			
	0.15	Ledermol 51				
	0.2	EDF20				
	0.2	Basic 14				
	0.35	Prolime RBE				
	0.8	Na ₂ CO ₃		180	<input checked="" type="checkbox"/>	
	0.5	Linedeg ARG		120	<input checked="" type="checkbox"/>	drain
Liming	100	H ₂ O				
	0.3	Linedeg ARG				
	1.5	NaHS				
	2.0	Ca(OH) ₂		30	<input checked="" type="checkbox"/>	
	0.2	Basic 14				
	2.5	Na ₂ S				
	3.5	Ca(OH) ₂		60	<input checked="" type="checkbox"/>	
	0.25	Prolime NX				
	0.2	EDF20				
	20	H ₂ O		60 (5/h) 840	<input checked="" type="checkbox"/>	
	100	H ₂ O		3	<input checked="" type="checkbox"/>	drain
Fleshing and splitting						
Deliming	100	H ₂ O	35			
	0.1	EDF20				
	0.3	Prokal 700		20	<input checked="" type="checkbox"/>	drain
	30	H ₂ O	30			
	1	Prokal 700				
	0.2	EDF20		10	<input checked="" type="checkbox"/>	
	1.2	Prokal T		15	<input checked="" type="checkbox"/>	
	1.3	Prokal T		40	<input checked="" type="checkbox"/>	
	0.03	Ledermac 1		15	<input checked="" type="checkbox"/>	drain
Pickling	30	H ₂ O				
	5	NaCl		10	<input checked="" type="checkbox"/>	
	1	HCO ₂ H		20	<input checked="" type="checkbox"/>	
	1.3	H ₂ SO ₄		180	<input checked="" type="checkbox"/>	drain
Tanning						

4.2. Equine hides.

The following steps have to be carried out one after the other on raw hides, as follows:

- **Soaking:** charge the lot of hides into a drum and add water at 27°C (200%) followed by Na₂S (0.1%) and EDF-20 (0.2%). Rotate the drum for 90 min. and drain the liquid. Add water at 27°C (100%) and rotate the drum for 30 min.. Drain the liquid and add water at 27°C (80%) followed by Ecovit 90 (0.8%), Biokal STR (0.5%), Biosin CR (0.6%), EDF-20 (0.3%) and Na₂CO₃ (0.3%). Rotate the drum for 3 h and add Biokal RM (0.5%). Rotate the drum for 2 h and add Rinazim (0.01%). Rotate the drum for 14 h at 26°C, checking the pH which has to stay between 9 and 9.5. Drain the liquid.
- **Liming:** add water (100%) followed by Biokal SH (1.0%) and Ca(OH)₂ (1.0%). Rotate the drum for 30 min. and add Na₂S (1.0%) followed by NaHS (1.0%). Rotate the drum for 30 min. and then, keep the drum steady for further 30 min.. Add Ca(OH)₂ (5%) followed by

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Na₂S (2.5%), Biokal STR (0.5%) EDF-20 (0.2%) and Depilzim (0.1%). Rotate the drum for 1 h and drain the liquid. Add water (150%) at 25°C, rotate the drum for 5 min., drain and collect the hides.

- *Fleshing*: use an appropriate cutting machine, to bring the hides up to the desired thickness.
- *Deliming*: charged the fleshed hides into the drum and add warm water (100%) at 35°C, followed by Prokimic (0.4%) and **EDF20** (0.1%). Rotate the drum for 20 min. and drain. Add water (60%) at 30°C and Prokimic in two aliquots (1 and 2%) rotating the drum 30 min. at time. Add NaHSO₃ (0.5%) and NaCl (0.5%) and rotate the drum for 1 h. Add Ledermac 1 (0.06%) and **EDF20** (0.2%), rotate the drum for 45 min. and drain the liquid. Add water (300%) and Prokimic (0.3%), rotate the drum for 5 min. and drain the liquid.
- *Pickling*: add water (40%) and NaCl (5%) and rotate the drum for 10 min.. Add formic acid (0.8%) and rotate for 30 min.. Add H₂SO₄ (1.1%) and rotate for 2 h. Drain the acidic liquid and collect the pickled hides.

At this stage the hides are ready either for a preliminary pretanning stage or for tanning according to one of the methods mentioned earlier. The above procedure of hide processing is normally reported in a schematic fashion, within a table structure as follows (**Table 4.1.2**):

Table 4.2.1 Procedure to process equine hides

Stage	%	Product	T (°C)	t (min)	Rotation	Action
Soaking	200	H ₂ O	27			
	0.1	Na ₂ S				
	0.2	EDEF20		90	<input checked="" type="checkbox"/>	drain
	100	H ₂ O	27	30	<input checked="" type="checkbox"/>	drain
	80	H ₂ O	27			
	0.8	Ecovit 90				
	0.5	Biokal STR				
	0.6	Biosint CR				
	0.3	EDEF20				
	0.3	Na ₂ CO ₃		180	<input checked="" type="checkbox"/>	
	0.5	Biokal RM		120	<input checked="" type="checkbox"/>	
	0.01	Rinazim	26	840	<input checked="" type="checkbox"/>	pH 9-9.5 drain
Liming	100	H ₂ O				
	1.0	Biokal SH				
	1.0	Ca(OH) ₂		30	<input checked="" type="checkbox"/>	
	1.0	Na ₂ S				
	1.0	NaHS		30	<input checked="" type="checkbox"/>	
				30	no	
	5	Ca(OH) ₂				
	2.5	Na ₂ S				
	0.5	Biokal STR				
	0.2	EDEF20				
0.1	Depilzim		60	<input checked="" type="checkbox"/>	drain	
150	H ₂ O	25	5	<input checked="" type="checkbox"/>	drain	
Fleshing and splitting						
Deliming	100	H ₂ O	35			
	0.4	Prokimic				
	0.1	EDEF20		20	<input checked="" type="checkbox"/>	drain
	60	H ₂ O	30			
	1+2	Prokimic		30	<input checked="" type="checkbox"/>	
	0.5	NaHSO ₃				
	0.5	NaCl		60	<input checked="" type="checkbox"/>	
	0.06	Ledermac 1				
	0.2	EDEF20		45	<input checked="" type="checkbox"/>	drain
	300	H ₂ O				
0.3	Prokimic		5	<input checked="" type="checkbox"/>	drain	
Pickling	40	H ₂ O				
	5	NaCl		10	<input checked="" type="checkbox"/>	
	0.8	HCO ₂ H		30	<input checked="" type="checkbox"/>	
	1.1	H ₂ SO ₄		120	<input checked="" type="checkbox"/>	drain
Tanning						

4.3. Sheep and pig skins

Generally, sheep and pig skins are purchased by tanners in the pickled form directly from the supplier, who has already carried out an approximate treatment of the skin following similar recipes described for the elaboration of bovine and equine hides. The subsequent defatting prior to tanning serves, to rectify the precedent defatting operations and make the skins uniform. The following steps have to be carried out one after the other from pickled skins, as follows (**Table 4.3.1**):

- **Depickling:** charge the lot of skins into the drum and add water at 20°C (100%) followed by NaCl (10%) to obtain 8°Bé. Rotate the drum for 30 min.. Add NaHCO₃ (3%) and keep the rotation for 3 h until pH is higher than 6. Drain the liquid.
- **Defatting:** Add water (100%) at 35°C and NaCl (10%) to obtain 8°Bé. Rotate the drum for 15 min. and drain the liquid. Add water (100%) at 35°C, followed by NaCl (10%) to obtain 8°Bé and rotate the drum for 10 min.. Add EDF-20 (4.0%) and keep the rotation for 1 h. Drain the liquid. Add water (100%) at 35°C, NaCl (10%) to obtain 8°Bé, rotate the drum for 15 min. and drain the liquid. Repeat this latter operation for two more times, having care to add water at 30°C the second time and at 25°C the third time.
- **Pickling and tanning:** add water (60%) at 20°C and NaCl (8%) to obtain 6-7°Bé. Rotate the drum for 10 min.. Then, add 90% solution of H₂SO₄ (10:1) (0.8%) and rotate the drum for 30 min.. Add a 16% solution of formic acid (1:5) (0.8%) and rotate the drum for 10 min. to reach pH 2.8-3.0. Add chrome salts (6%) to the bath and keep rotating the drum for 1 h. Add MgO (1.2%) and rotate for 14 h to reach pH 4. Finally, add a fungicide (0.1%) to the bath and rotate the drum for 20 min.. Drain the liquid, collect the leather lot and dry it in air.

At this stage the hides have become leather and they are ready for further tannery operations such as retanning, fatliquoring and dyeing. The above procedure of hide processing is normally reported in a schematic fashion, within a table structure as follows (**Table 4.1.3**):

Table 4.3.1 Procedure to process sheep and pig skins.

Stage	%	Product	T (°C)	t (min)	Rotation	Action
Depickling	100	H ₂ O	20			
	10	NaCl		30	<input checked="" type="checkbox"/>	8°Bé
	3	NaHCO ₃		180	<input checked="" type="checkbox"/>	pH > 6 drain
Defatting	100	H ₂ O	35			
	10	NaCl		15	<input checked="" type="checkbox"/>	8° Bé drain
	100	H ₂ O	35			
	10	NaCl		10	<input checked="" type="checkbox"/>	8° Bé
	4.0	EDF20		60	<input checked="" type="checkbox"/>	drain
	100	H ₂ O	35			
	10	NaCl		15	<input checked="" type="checkbox"/>	8° Bé drain
Pickling Tanning	100	H ₂ O	30			
	10	NaCl		15	<input checked="" type="checkbox"/>	8° Bé drain
	100	H ₂ O	25			
	10	NaCl		15	<input checked="" type="checkbox"/>	8° Bé drain
	60	H ₂ O	20			
8	NaCl		10	<input checked="" type="checkbox"/>	6-7° Bé	
0.8	H ₂ SO ₄ (10:1)		30	<input checked="" type="checkbox"/>	pH 2.8-3.0	
0.8	formic acid (1:5)		10	<input checked="" type="checkbox"/>		
6	Cr salts		60	<input checked="" type="checkbox"/>		
1.2	MgO		840	<input checked="" type="checkbox"/>	pH 4	
0.1	fungicide		20	<input checked="" type="checkbox"/>	drain	