LIFE14 ENV/IT/000443 - LIFETAN PROJECT

Lifetan

Eco friendly tanning cycle

Manual of an innovative technology for leather tanning with natural products

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Italian National Agency for New Technologies, Energy and Sustainable Economic Development
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DELIVERABLE ACTION D.2

Manual of an innovative technology for leather tanning with natural products

TABLE OF CONTENTS

Lifetan

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1. INTRODUCTION

Leather tanning involves a number of sequential operations, from cleaning and preparation through collagen stabilisation by reaction with a tanning agent, to the final improvement of physical and aesthetic properties.

This process implies the use of a significant amount of chemicals dissolved in water that penetrate into leather and react to confer different properties. In most of the operations the substances that are not fixed end up in wastewater, with the resulting environmental impact. Furthermore, in recent years, there has been a dramatic increase in restrictions on the content in certain chemicals, either imposed by legislation or by famous brands.

In the last years, these technological challenges have been addressed through various projects related to the development of products intended for the environmental improvement of the tanning process and the suitable composition of leather. Such projects, which were executed with the financial support of the European Union through the LIFE Programme, focused on the demonstration of more sustainable products free from restricted substances for the bating, defatting, tanning, dyeing and fatliquoring stages of the tanning process, namely:

- Recycling deodorised poultry manure into the bating stage as an alternative to the use of commercial enzymatic preparations, thus notably reducing the nitrogen content in wastewater (LIFE PODEBA, www.podeba.eu).

- Using defatting products based on waste sugars from the food industry that are more biodegradable and free from restricted substances, such as nonylphenol and nonylphenol ethoxylates (LIFE EcoDefatting, www.life-ecodefatting.com).

- Using oxazolidine as an alternative tanning agent to the use of trivalent chromium salts, allowing the production of high-quality, more biodegradable leather free from metals that avoids the possible oxidation to hexavalent chromium (LIFE OXATAN, www.oxatan.eu).

- Using more natural, highly soluble dyes free from auxiliary chemicals, thus improving the impact on wastewater conductivity (LIFE BioNaD, www.lifebionad.com).

- Using natural oil derivatives for leather fatliquoring, as an alternative to the use of short-chain chloroparaffins, which are currently restricted (LIFE ECOFATTING, www.pi.iccom.cnr.it/ecofatting/).

Every of these projects individually assessed the technical feasibility of these alternative processes by means of pilot-scale tests on leather, leather quality control and the analysis of their impact on wastewater.

In these context, the main objective of the European project LIFETAN, ‘Eco friendly tanning cycle’, is to comprehensively demonstrate the viability of the technologies developed in the above-mentioned projects jointly in the whole tanning process, by replacing restricted chemicals with other more biodegradable and less polluting substances while ensuring the quality of leather.

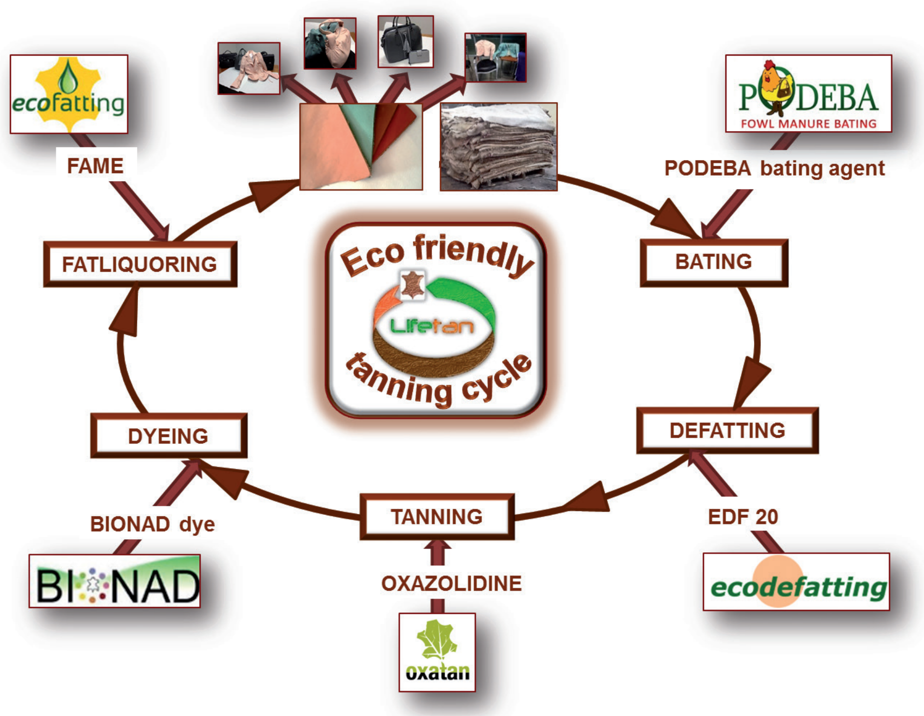


Figure 1- Integration in the LIFETAN project of various sustainable technologies in the tanning process.

The LIFETAN project has been partially funded by the European Union through the LIFE Programme, and is coordinated by the Italian National Agency for New Technologies, Energy and Sustainable Economic Development (ENEA). Partners to this project are INESCOP (Spain), the Institute of Chemistry of Organometallic Compounds of the National Research Council (ICCOM-CNR, Italy), the tannery Tradelda (Spain) and the tannery Newport (Italy).

The project objectives have been validated through pilot-scale tests and the process feasibility was assessed through:

- the study of the interactions of products with the collagen fibrils of leather by means of Attenuated Total Reflectance – Fourier Transform Infrared Spectroscopy (ATR-FTIR), Thermogravimetric Analysis (TGA) and Scanning Electron Microscopy (SEM);
- the characterisation of residual baths from each stage;
- the quality control of leather by means of physical and chemical tests according to standard test methods;
- the production of footwear and leather goods;
- the lifecycle analysis (LCA) of the developed process.

This project is an important breakthrough in environmental protection and sustainable development in the European leather and footwear industries, where the tanning process combines alternative products that allow the production of high-quality, ecofriendly leather, free from restricted substances.

This Manual explains in detail the know-how of the new leather natural techniques utilizing the LIFETAN innovative technology and will serve as a formative-informative tool of the LIFETAN project.

The manual is addressed to tanners, traders, technicians, end users and people involved in the tanning industry sector, including specialized decision makers at all levels; therefore it contains the protocols, procedures and characteristics of the LIFETAN process, including qualitative and quantitative data, detailed process information and an assessment of the technical and environmental advantages of the integrated system.

2. THE TANNING PROCESS

Tanning is one of the oldest trades of humanity, with references on the use of leather in cave paintings and archaeological sites worldwide that prove this. Tanning had an accidental nature in its prehistoric origins, slowly evolving until turning in the Middle Ages into a craft. At the end of the nineteenth century, the first scientific studies were started which, with the industrial revolution and the development of the relevant machinery, led to the current leather production technology.

The tanning process consists in turning a putrescible organic product, fresh animal skin, into a resistant, durable and very nice-looking material that can be used for the manufacture of footwear, leather goods, upholstery, garments, etc.

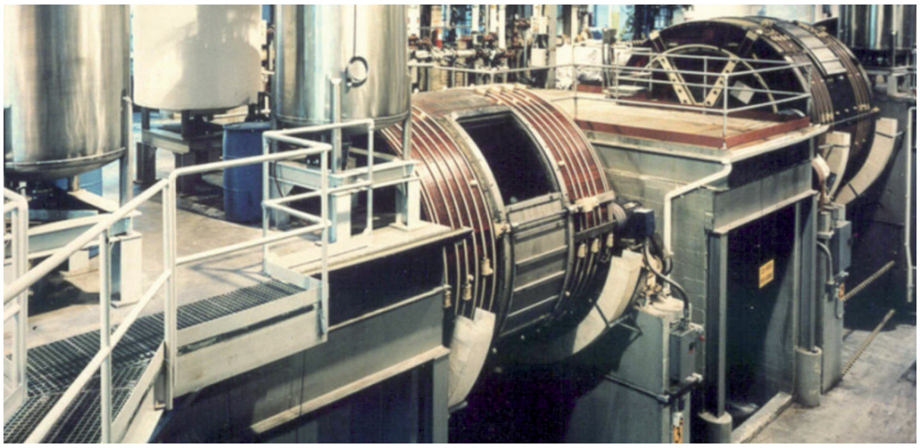
The hides and skins used are mainly from cattle, sheep, goat, pig and, in a lesser amount, reptiles, birds and fish. Leather processing can start little after slaughtering the animal, but in many cases the hides and skins are stored for a long time, a preservation treatment being necessary to prevent the growing of microorganisms and the associated putrefaction.

The curing process is carried out in collection centres, inside or outside abattoirs, to avoid the putrefaction and loss of quality of the raw material, which requires the time between collection and preparation to be as brief as possible. For this, when the material cannot be processed immediately, it must be cured by one of the available methods: refrigeration (chilling) for short periods, drying (by air or in chamber), salting, dry salting and use of biocides or products to prevent bacterial attack.

Hides and skins are usually cured in abattoirs and sometimes the gatherers/ wholesalers re-preserve them, putting hides and skins in pallets, leaving them in cold areas of the warehouse or refrigerated. The degree of curing of the skin varies, although currently all the skins are prepared to be transported everywhere in the world, and involves a curing treatment preventing deterioration over long periods of time and allowing very aggressive transport conditions. If the skins have to be stored for a long time in the tannery, they are kept in refrigerated conditions to avoid deterioration and quality loss.

In the industrial process several chemical and mechanical operations are carried out, using different technologies and chemical products depending on the type of skin to be processed and the final use, based on the specific tannery needs.

The tanneries of the beginning of the twentieth century were big factories where the treatment of hides and skins, with all its complexity, was slowly carried out, manually and with very few mechanical means. Nowadays, the work conditions have been radically transformed with the incorporation of the instrumentation that engineering, electronics and computing provide, so that a spectacular optimization could be achieved both from the output of the process and the final quality of the leathers, trying also, to minimize the impact of this activity on the environment by developing clean and innovative technologies.



Figures 2-3. Manual tanning works in tanneries in Igualada, Barcelona (Spain) at the end of the nineteenth century and appearance of a current tannery.

The process to obtain finished leather from fresh hides or skins can be divided into multiple steps, which in turn can include four stages: Beamhouse operations, Tanning, Post-tanning and Finishing.

The Beamhouse operations for a conventional process are the following: soaking, dehairing, liming, fleshing and splitting. The objective of this stage of the process is to clean the skin, remove the adipose tissue and the hair and adapt the thickness of the skin to the desired value. Usually deliming, bating are considered in beamhouse (BREF TAN, 2013).

The Tanning steps for a conventional process are: deliming, bating, degreasing, pickling and tanning. The objective of this stage of the process is to partially degrade the structure of the skin to facilitate the penetration and the subsequent fixing of chemicals, to adjust the pH to the adequate value for tanning, and to stabilise the structure of the collagen by adding tanning agents (the most common ones are chromium salts or vegetable extracts). Also, for sheepskin there is usually a degreasing step after pickling. After the tanning step the skins are now stable and in this state they are called 'wet-blue', if tanned with chromium, or 'wet-white', if another tanning agent was used.

The Post-tanning steps for a conventional process are the following: shaving, neutralisation, retanning, dyeing, fatliquoring, sammying and drying. The objective of this stage of the process is to adjust the desired thickness for the skin, achieving the characteristics of fullness and colour, and to bring the skin to a suitable moisture content. In this stage the skin is called 'crust'.

Finally, the Finishing stage for a conventional process consists in diverse mechanical operations and/or the application of various products on the surface to give the leather the final texture and appearance desired.

Figure 4. Leather finishing by roller coating

According to the type of starting hide or skin, or the final product to be obtained, these stages can be carried out in a different way and, consequently, many variations to the conventional process can be found. The stages of the tanning process are listed in Table 1.

RAW HIDES OR SKINS	
BEAMHOUSE	Sorting - Trimming Soaking - Liming Fleshing – Pelt splitting
TANNING	Deliming - Bating Degreasing Pickling Tanning Sammying
POST-TANNING	Splitting Shaving Retanning Neutralisation Dyeing Fatliquoring Sammying Drying Staking
FINISHING	Finishing Mechanical operations Sorting - Packing - Dispatching
FINISHED LEATHER	

Table1. Stages of the tanning process

After all this laborious production process comprising numerous chemical processes and mechanical operations, tanned hides and skins are obtained, which are suitable for use in the manufacture of different articles. Also, as in every industrial activity, the process has a significant impact on the environment, which is summarised in Figure 5.

On the other hand, according to the mass balance, the European leather industry releases a high polluting wastewater, being this one of the major environmental concerns in this sector.

The IPPC (integrated pollution prevention and control) policies promoted by the EU and the new clean production technologies, which are increasingly known and implemented, can reduce this environmental impact at source, in both the consumption of natural resources and in the generation of contaminated effluents and waste, being these the objectives of the LIFETAN project.

INPUTS	
Salted raw hide	1000 kg
Water	20 - 40 m^3
Chemicals	400 – 600 kg
Energy	9 – 42 GJ

OUTPUTS		
Leather	200 - 250 kg	
Wastewater	20 - 40 m^3	
COD		230 kg
BOD		100 kg
SS		150 kg
Chrome (III)		5 - 6 kg
Sulphides		10 kg
Solid waste	450 – 730 kg	
Untanned trimmings		120 kg
Untanned fleshings		170 – 350 kg
Untanned scraps		225 kg
Finishing dust		2 kg
Finishing trimmings		30 kg
Wastewater sludge		500 kg
Air - Organic solvents	40 kg	

Figure 5. Mass balance of the tanning process for a conventional (Chrome tanning) process for bovine salted hides (adapted from BREF TAN, 2013)

3. THE LIFETAN TANNING PROCESS WITH NATURAL PRODUCTS

3.1. Environmental impact of stages involved in LIFETAN project

The LIFETAN project involves five principal stages (in green bold letter in Table 1). Below are briefly technically described these stages and its main environmental impacts, the way to reduce the waste water pollution and its contain in restricted substances.

Deliming and Bating

Deliming is the process that removes lime and alkaline products from the inside of the skin. This way the swelling of the limed skin is achieved. The lime dissolved in interfibrillary liquids and the one deposited on the fibres can be easily removed using some washes prior to liming. The rest of the lime is removed by adding buffered solutions of ammonium or organic salts, or carbon dioxide. These agents, combined with the alkaline products of the limed skin, provide readily water-soluble products that can be removed by a simple wash. When adding theses acids, the pH has to be equal to or greater than 7.5, otherwise the skin would undergo undesired acidic swelling.

The objective of bating is to achieve, using proteolytic enzymes, the de-swelling and relaxation of the skin, while cleaning up any remaining epidermis, globulins, elastins, hair and fat, as a secondary effect, making the grain finer and softer grain. Some interesting bates are:

- Pancreatic enzymes-based bates.
- Fungal and bacteria proteases-based bates, their activity being lower than that of the pancreatic trypsin.

Deliming and bating wastewater usually contains a high concentration of nitrogen, which is difficult to remove due to its high solubility. The presence of nitrogen is a major problem in many countries due to it causes the eutrophication of watercourses and the pollution by nitrification of the groundwater, a source for drinking water. The nitrogenous compounds can be broken down by combining intensive aerobic and anoxic biological treatment. The oxygen demand is very high, thus leading to correspondingly high operational and energy costs (calculations show that with typical tannery effluent, some 40% of the oxygen requirements are spent on removing the nitrogen component).

Several components in tannery effluent contain nitrogen as part of their chemical structure. The most common chemicals are ammonia (from deliming/bating materials) and the nitrogen contained in proteinaceous materials (from liming/unhairing operations). The use of ammonium salts in the process is a main source of ammonia nitrogen in tannery effluents (up to 40 percent). Other sources of ammonia nitrogen are dyeing and animal proteins generated from beamhouse operations.

The majority of total nitrogen matter (measured as Total Kjeldahl Nitrogen, TKN) is discharged from the deliming/bating process in the beamhouse operations, which, as a whole, account for approximately 85 percent of TKN load from a tanning facility.

Prevention and control measures that reduce the nitrogen load in effluents include the use of ammonium-free deliming agents as, for instance, the PODEBA bating agent, based on deodorised poultry manure (DPM) proposed in the LIFETAN project.

Defatting

At this stage the natural fat of the skin is removed to facilitate the penetration of reagents and to avoid undesired reactions and stains on the skin. This operation is carried out by direct emulsion of fat in an aqueous medium using surfactants or solvents. When degreasing using surfactants, the process can be improved using lipolytic enzymes that degrade the skin's fat, which facilitates fat emulsion and solubility to reduce its molecule size.

The leather production process could be disturbed by a high content of natural fat on hides, especially in sheep and lamb skins, some kinds of goat skins, pig skins and many cattle hides, which could cause eruptions and staining of the leather. Therefore most of the natural fat has to be removed or, with a lower fat content, be distributed over the cross-section of the skin. This is the objective of the defatting process. An inadequate degreasing process may cause significant defects in finished leather, among which are:

Fatty spew	Fine white, crystalline coating or light film occurring on dried or finished leathers, mainly on chrome-tanned leathers, after a short or prolonged period of storage. In most cases distributed over the entire leather surface, sometimes occurring only in parts. Encouraged by alternate cold and warm storage, high humidity, on leathers that have not been neutralized completely and by the action of bacteria and mould fungi. Contact with and open flame will melt this coating and it can thus be distinguished from efflorescence of salts.

Fat stains	Formation of oily dark-coloured irregular fat stains may occur in the renal region, on the neck and back part of sheep and lamb skins, some kinds of goat skins, pig skins and cattle hides, in particular if the rawstock comes from fattened animals. In most cases they are due to the excretion of liquid fatty substances. These unpleasant fat stains can no longer be removed if they form insoluble soaps with lime, chrome or aluminium salts.
Fat grooves	Found in fine-wooled and some coarse-wooled sheep skins, mainly in the neck or shoulder region. They occur as raised parallel strips running from the back towards the flanks and containing increased deposits of fat. Furthermore these sections are often loose-grained and result in callouses on the grain in the leather due to an inadequate penetration of tannin.
Fat soaps	High contents of natural fat react with cationic metallic salt such as chrome, aluminium, zirconium tanning agents to form insoluble soaps and result in heavy staining.

The defatting process is often executed after bating by a treatment with surface-active substances, mostly by adding fat-dissolving organic degreasing agents. Degreasing of pickled pelts is more efficient, especially for sheep and lamb skins.

One part of the defatting molecule is water soluble (hydrophilic part) and the other one is water-insoluble and fat-soluble (lipophilic part). The relationship between these two parts is expressed by the numerical value of HLB (Hydrophilic Lipophilic Balance) which have values from 1 to 60. A high HLP value indicates that the surfactant is soluble in water and therefore has a good wet ability. A medium HLP value indicates that the detergent has surfactant capacity (first removes the dirt and then emulsified). Finally, a low HLP value indicates good emulsifying power.

In the degreasing of skins generally are used products with low HLB value (about 10-15) for their ability to emulsify the animal natural fat accumulated in the interfibrillar spaces, which can be easily removed by washing. In general, the effectiveness of degreasing products increases if the process is performed using relatively short baths and warm water (about 28-30 °C).

Surfactants are used in many different processes in the tannery, such as soaking, liming, degreasing of sheepskins, tanning and dyeing. Therefore, these products must be stable over a wide range of pH values and should also be stable to electrolytes, particularly if are used in degreasing of pickled sheep-skins.

Nonylphenol ethoxylate (NPE) surfactants were used in the leather industry in the past but these products can be degraded to smaller chain NPEs and nonylphenol, both of which are toxic. The European Union carried out an extensive risk assessment of nonylphenol which concluded that nonylphenol displays an endocrine-disrupting activity and the use of NPE in leather processing is now restricted under the REACH regulation (Regulation EC No 1907/2006 of the European Parliament and of the Council of 18 December 2006 concerning the Registration, Evaluation, Authorisation and Restriction of Chemicals).

Table below shows the restrictions of Alkylphenol and Alkylphenol ethoxilates (NF, NFES, OF, OFES) in the EU.

COUNTRY	LIMIT	OBSERVATIONS	LEGAL REFERENCES
ALKYLPHENOL AND ALKYLPHENOL ETHOXILATES (NF, NFEs, OF, OFEs)			
European Union	1 000 mg/kg	Nonylphenol (NF) and Nonylphenol Ethoxilates (NFEs). Shall not be placed on the market, or used, as substances or in mixtures in concentrations equal to or greater than 0.1% by weight (1 000mg/kg) textiles and leather processing, except processing with no release into waste water, systems with special treatment where the process water is pre-treated to remove the organic fraction completely prior to biological waste water treatment (degreasing of sheepskin).	Regulation (EC) 552/2009 (Modification Annex XVII REACH)
Switzerland	1 000 mg/kg	It is prohibited to place textile and leather processing agents on the market if their content of octylphenol (OF), nonylphenol (NF) or their ethoxylates is 0.1% or more by mass (1 000 mg/kg), except when: (1) processing does not result in the release of octylphenol ethoxylates (OFEs) or nonylphenol ethoxylates (NFEs) into wastewater, or (2) in installations for special treatment, such as sheepskin degreasing, where process water is pre-treated to remove the organic fraction completely prior to biological wastewater treatment.	Ordinance on Chemical Risk Reduction, ORRChem of 18 May 2005

Table 2. Legal limitations on hazardous chemical substances employed in the defatting stage

The main alternatives in the degreasing of sheepskins are linear alcohol ethoxylates with different chain lengths and ethoxylation degrees. These compounds show a much lower toxicity than NPE and can be degraded to non-toxic. The efficacy of C10 linear alcohol ethoxylate as a degreasing agent is comparable to that of NPE. Each one of the aliphatic ethoxylated alcohols has distinct properties, so that the process design differs depending on the material chosen, for instance, the natural defatting products proposed in the LIFETAN project, developed previously in the LIFE ECODEFATTING project.

Tanning

The skin, once adequately prepared in previous processes, is subjected to the tanning process in which it turns into leather, namely, the skin becomes rot-proof, stabilizing its protein structure by crosslinking collagen chains with the tanning agent by means of chemical bonds. Due to the wide variety of hides and skins, it is easy to assume that there are many different types of tannages. All these tannage types can be grouped into:

- Tanning with inorganic products or mineral tanning, using chromium salts, aluminium, iron, titanium, etc.
- Vegetable tanning, using natural vegetable extracts.
- Tanning with organic products like syntans, aldehydes and quinones, sulphochlorinated paraffins and multiple resins.

The traditional tanning process, used in more than 90% of leather tanned worldwide, consists in the application of trivalent chromium salts, which interact with the skin's collagen, acting this way as a tanning agent. This process confers leather excellent physical, mechanical and chemical properties and a high stability to manufacturing processes and the passage of time, with shrinkage temperatures over 100 °C. However, in some cases, chromium allergies may arise or even, under certain conditions, trivalent chromium can oxidize to hexavalent chromium, which is a carcinogenic compound that can be present in tannery wastewater and solid waste with a considerable impact on the environment and human health.

There is also recent environmental pressure on tanning industries and a tendency to stricter environmental requirements for leather, which has led to the implementation of improvements in the tanning processes to reduce pollution, and the search for innovative tanning technologies alternative to chromium, thus avoiding at source the problems derived from its use. Therefore, there is the need to develop a new tanning technology that provides, using processes with less environmental impact, quality leathers that comply with the market's requirements in terms of quality and content in restricted substances. In this sense, the LIFE OXATAN project proved that the use of oxazolidine as a tanning agent, combined with other agents (vegetable or synthetic) allow quality leathers to be obtained, which can be employed by footwear, upholstery and leathergoods industries.

The main advantage of oxazolidine tanning is that it allows high performance leather to be obtained, while managing to avoid the presence of metals both in liquid and solid waste derived from the tanning process. This way, it is possible to considerably reduce the environmental impact generated during the tanning process and also at the end of the leather lifecycle, either in the form of leather trimmings when different goods are manufactured or when they are disposed of after use.

The environmental impact of chrome (Cr) discharged from tanneries has been a subject of extensive scientific and technical dispute. Cr (VI) compounds are responsible for the majority of the health problems associated with all chromium compounds. Normally, during the tanning process only Cr (III) salts are used. Nevertheless, under certain conditions the Cr (III) can be transformed into Cr (VI).

However, many studies report that the effluents from tanning industry are often adversely affecting human life, agriculture and livestock. The residents, especially the tannery workers have been the victims of this pollution, which has led to severe ailments such as eye diseases, skin irritations, kidney failure and gastrointestinal problems. Table below shows the restrictions of hexavalent Chromium in the EU.

Although the legislative limits on the disposal of solid chrome-containing waste have been relaxed in some countries, liquid emissions remain strictly regulated throughout the world. Limits on total chrome discharge in effluent vary widely between 0.05 and 10 mg/l for direct discharges into water bodies and 1- 50 mg/l on indirect discharges into sewage systems.

COUNTRY	LIMIT	OBSERVATIONS	LEGAL REFERENCES
		CHROMIUM VI	
European Union	3 mg/kg	Shall not be detected in professional footwear.	Directive 1989/686/EC Standard ISO 20347
Spain			RD 1407/1992
European Union	3 mg/kg	Leather articles, or leather parts of articles, coming into contact with the skin, shall not be placed on the market if they contain chromium (VI) in concentrations equal to or higher than 3 mg/kg chromium VI of the total dry weight of the leather.	Regulation (EU) 301/2014 (amending Annex XVII to the REACH Regulation)
Spain	3 mg/kg	The Cr VI content in footwear shall not exceed 3 mg/kg (limit value established in the standard UNE EN ISO 20347:2013)*. *This is the limit required by the Official Service of Surveillance, Certification and Technical Assistance for Foreign Trade (SOIVRE) and the National Institute for Consumer Protection (INC), under RD 1801/2003 relative to general product safety, which provides that when there is no compulsory safety limit established by the legislation in force, those limits established in other documents such as Spanish Standards (UNE), European (CEN) Standards or best practice codes on product safety shall apply.	RD 1801/2003 + Standard UNE EN ISO 20347:2013
Germany	< 3 mg/kg	Leather products in direct contact with the skin.	Consumer Products Regulation (BedGgstVÄndV, annex 4, section 2)

Table 3. Legal limitations on hazardous chemical substances employed in the tanning stage

Dyeing

Leather dyeing includes a group of operations aiming to confer certain coloration to the tanned skin, be it superficial, partial or total.

From a chemical point of view, dyes are classified as natural and synthetic; the same way there are vegetable and synthetic tanning agents. The commercial series of dyes gather dyes of very different chemical composition, but of similar dyeing behaviour with regard to fastness, penetration power, matching capability, degree of opacity, method of use, etc. According to these characteristics dyes are classified as: acid dyes, direct dyes, basic dyes, metal-complex dyes and reactive dyes.

The objective of post-tanning operations is to adjust the desired thickness for the skin, achieving the characteristics of fullness and colour, and to bring the skin to a suitable moisture content. The post-tanning steps for a conventional process are the following: shaving, neutralisation, retanning, dyeing, fatliquoring, sammying and drying.

Leather dyeing includes a group of operations aiming to confer certain coloration on the tanned skin, be it superficial, partial or total. Nowadays, the dyeing process is carried out inside drums using a dye or a mixture of dyes which transfer certain specific colour and properties to leather. Before leather dyeing, it is necessary to adjust leather pH (6 - 6.5) to activate the linking points of dyes with the leather's collagen fibres. It is also important to adequately select the retanning and fatliquoring products to be used, since these can affect dye penetration and colour depth. Finally, adding anionic dispersing agents enhances dye penetration and colour evenness on the surface.

Regarding to their environmental impact, post-tanning processes contribute to neutral salts, mainly sulphate, COD and heavy metal pollution. These apart, non-fixed dyes, biocides and some heavy metal add to non-biodegradable pollution load of wastewater streams. The contributions to BOD, suspended solids, chloride loads in wastewater are significantly lower from the post tanning operations in comparison to the total discharge. But the contribution of Chromium (50-300 mg/l), TDS (3,000-5,000 mg/l), sulphate (1,500-2,500 mg/l) and insoluble COD are significant due to the presence of non-biodegradable matter. It is therefore necessary to carry out treatability studies on the proprietary formulations of dyes so that non-degradable substances may be avoided, improving the biodegradability of the wastewater, as naturalised dyes developed in the LIFE BioNaD project which were used in the LIFETAN project.

On the other hand, there are some legal limitations on hazardous chemical substances employed in the dye formulations (table 4).

<table>
<tr><th>COUNTRY</th><th>LIMIT</th><th>OBSERVATIONS</th><th>LEGAL REFERENCES</th></tr>
<tr><td colspan="4">AZOCOLOURANTS AND AZODYES</td></tr>
<tr><td rowspan="2">European Union</td><td>List of 22 amines not detected (30 mg/kg)</td><td>Azodyes that may release one or more of the 22 aromatic amines listed below shall not be placed on the market, or used, in textile and leather articles which may come into direct and prolonged contact with the human skin or oral cavity.
<table>
<tr><th></th><th>NAME</th><th>CAS No.</th><th></th><th>NAME</th><th>CAS No.</th></tr>
<tr><td>1</td><td>Biphenyl-4-ilamine</td><td>92-67-1</td><td>12</td><td>3,3'-Dimethylbenzidine</td><td>119-93-7</td></tr>
<tr><td>2</td><td>Benzidine</td><td>92-87-5</td><td>13</td><td>4,4'-Methylenedi-o-toluidine</td><td>838-88-0</td></tr>
<tr><td>3</td><td>4-Chloro-o-toluidine</td><td>95-69-2</td><td>14</td><td>6-Methoxy-m-toluidine</td><td>120-71-8</td></tr>
<tr><td>4</td><td>2-Naphthylamine</td><td>91-59-8</td><td>15</td><td>4,4'-Methylene-bis-(2-chloroaniline)</td><td>101-14-4</td></tr>
<tr><td>5</td><td>o-amino azotoluene</td><td>97-56-3</td><td>16</td><td>4,4'-Oxydianiline</td><td>101-80-4</td></tr>
<tr><td>6</td><td>5-Nitro-o-toluidine</td><td>99-55-8</td><td>17</td><td>4,4'-Thiodianiline</td><td>139-65-1</td></tr>
<tr><td>7</td><td>4-Chloroaniline</td><td>106-47-8</td><td>18</td><td>o-Toluidine</td><td>95-53-4</td></tr>
<tr><td>8</td><td>4-Methyl-m-phenylenediamine</td><td>615-05-4</td><td>19</td><td>4-Methoxy-m-phenylenediamine</td><td>95-80-7</td></tr>
<tr><td>9</td><td>4,4'-Methilenedianiline</td><td>101-77-9</td><td>20</td><td>2,4,5-Trimethylaniline</td><td>137-17-7</td></tr>
<tr><td>10</td><td>3,3'-Dichlorobenzidine</td><td>91-94-1</td><td>21</td><td>o-Anisidine</td><td>90-04-0</td></tr>
<tr><td>11</td><td>3,3'-Dimethoxybenzidine</td><td>119-90-4</td><td>22</td><td>4-Aminoazobenzene</td><td>60-09-3</td></tr>
</table></td><td rowspan="2">Regulation (EC) 552/2009 (Modification Annex XVII REACH)</td></tr>
<tr><td>1 000 mg/kg (Blue dye)</td><td>“Blue dye”: CAS No. (118685-33-9): shall not be placed on the market, or used, as a substance, or in mixtures in concentrations greater than 0.1 % by weight (1 000 mg/kg), where the substance or the mixture is intended for colouring textile and leather articles.</td></tr>
<tr><td>Switzerland</td><td>1 000 mg/kg (Blue dye)</td><td>“Blue dye”: shall not be placed on the market, or used, as a substance, or in mixtures in concentrations greater than 0.1 % by weight (1 000 mg/kg), where the substance or the mixture is intended for colouring textile and leather articles.</td><td>Ordinance on Chemical Risk Reduction, ORRChem of 18 May 2005</td></tr>
<tr><td>Turkey</td><td>30 mg/kg</td><td>The limitations in place in the European Unión also apply in Turkey for the same 22 amines in footwear and leather products.</td><td>Notification No. 29236. Official Gazette of the Republic of Turkey</td></tr>
<tr><td>China</td><td>30 mg/kg</td><td>It is not permitted to manufacture, place on the market or import footwear and fur containing any of the 23 following amines:
<table>
<tr><th></th><th>NAME</th><th>CAS No.</th><th></th><th>NAME</th><th>CAS No.</th></tr>
<tr><td>1</td><td>Biphenyl-4-ilamine</td><td>92-67-1</td><td>13</td><td>3,3'- Dimethylbenzidine</td><td>119-93-7</td></tr>
<tr><td>2</td><td>Benzidine</td><td>92-87-5</td><td>14</td><td>p-Cresidine</td><td>120-71-8</td></tr>
<tr><td>3</td><td>4-Chloro-o-toluidine</td><td>95-69-2</td><td>15</td><td>2,4-Diaminotoluene</td><td>95-80-7</td></tr>
<tr><td>4</td><td>2-Naphthylamine</td><td>91-59-8</td><td>16</td><td>2,4-Xilidine</td><td>95-68-1</td></tr>
<tr><td>5</td><td>2-Amino azotoluene</td><td>97-56-3</td><td>17</td><td>4,4'- Methylene-bis-(2-chloroaniline)</td><td>101-14-4</td></tr>
<tr><td>6</td><td>2-Amino-4-nitrotoluene</td><td>99-55-8</td><td>18</td><td>4,4'-Oxydianiline</td><td>101-80-4</td></tr>
<tr><td>7</td><td>p- Chloroaniline</td><td>106-47-8</td><td>19</td><td>4,4'-Thiodianiline</td><td>139-65-1</td></tr>
<tr><td>8</td><td>2,4-Diaminoanisole</td><td>615-05-4</td><td>20</td><td>2-Toluidine</td><td>95-53-4</td></tr>
<tr><td>9</td><td>4,4-Diaminodiphenylmethane</td><td>101-77-9</td><td>21</td><td>2,6-xilidine</td><td>87-62-7</td></tr>
<tr><td>10</td><td>3,3-Dimethyl-4,4diaminodiphenylmethane</td><td>838-88-0</td><td>22</td><td>2,4,5-Trimethylaniline</td><td>137-17-7</td></tr>
<tr><td>11</td><td>3,3'- Dichlorobenzidine</td><td>91-94-1</td><td>23</td><td>2-Anisidine</td><td>90-04-0</td></tr>
<tr><td>12</td><td>3,3'-Dimethoxybenzidine</td><td>119-90-4</td><td></td><td></td><td></td></tr>
</table></td><td>GB 20400-2006</td></tr>
</table>

Table 4. Legal limitations on hazardous chemical substances employed in the dyeing stage

Fatliquoring

The fibres of the wet leather move easily since it is a very flexible material; but when the leather dries it can become hard due to the fact that the fibres have dehydrated and have grouped forming a compact substance.

The fatliquoring operation is carried out with the aim to obtain flexible and soft-feeling leather, which is achieved by the incorporation of water soluble or insoluble fats. These maintain the fibres separated and lubricate them so that they can glide off each other.

The greater or lesser degree of flexibility of leather depends on the quantity and type of fat used, which conditions the product that needs to be obtained so that by varying the fat percentages and the combinations of fatliquoring agents different products are obtained.

Traditionally, the process of fat-liquoring tanned leathers is carried out by either coating the hide with crude oil or by mixing this with soaps during the natural drying phase. Later, with the emergence of surfactants and the ability to produce fat emulsions, fat-liquoring began to be conducted by bathing the materials inside drums or paddle vats.

Fat-liquoring products are formulated from a variety of different raw materials, such as vegetable oil trioleins, alcohol and fatty acids, fish oil, paraffins, lanolin, lecithin, etc. Then, different polar groups are added by sulphation, sulphonation, phosphatisation, chlorination, etc. in order to make them emulsifiable in water and to enable them to properly penetrate leather. Thus, this makes it possible to synthesise a large variety of fat-liquoring products.

The most commonly of the fat-liquoring product families used in EU tanneries selection are:

- Sulphated olein
- Sulphated ester
- Sulphonated olein
- Phosphoric ester
- Sulphited olein
- Sulphochlorinated and chlorinated paraffines
- Sulphited fish oil
- Synthetic oils
- Sulphated lecithin
- Fat-liquoring polymer

being the short chain chlorinated paraffins the one's of the most used due to its high efficiency and low cost.

Chloro-alkanes (C10-13), also called short chain chlorinated paraffins (SCCP) are a complex mixture of closely related chemicals namely hydrocarbons having 10 to 13 carbon atoms arranged in chains and containing 50-70% by weight of chlorine. Short chain length chlorinated paraffins are reported to be used in the leather industry as fat liquoring agents. They show better adhesion to the animal skin than natural oils, with similar fattening and softening properties. They also impart better washability to the leather than natural oils. They are usually applied to the moist dressed leather in the form of a 10-30% emulsion or are added to sulphated or sulphonated oil or synthetic emulsifying agents.

However, it was also stated that as a result of concerns over the release of adsorbable organic halogens it is possible that chlorinated fat liquoring products will be replaced by other products, for instance, the fatliquoring products developed in the LIFE ECOFATTING project.

Excessive exposure to chloro-alkanes (C10-13) may affect the kidney, liver and thyroid gland, and there is some evidence that the substances may cause cancer. Chloro-alkanes (C10-13) are not easily biodegradable and are bioaccumulative. They have been detected in marine and fresh water animals and in sediments in industrial areas and have also been found in remote locations. The substances are very toxic to aquatic life. The persistence, tendency to bioaccumulate, toxicity and occurrence of chloro-alkanes (C10-13) in remote locations gives rise to concerns of possible harmful effects on a global scale.

All chlorinated paraffins have the potential to form toxic products if heated in a fire. Chloro-alkanes (C10-13) are listed as priority hazardous substances in the Water Framework Directive, and as priority substances (along with medium chain (C14-17) Chloro-alkanes) under Regulation 793/93.

Table below shows the restrictions of short chain chlorinated paraffins the EU.

COUNTRY	LIMIT	OBSERVATIONS	LEGAL REFERENCES
CHLOROALKANES C10-C13			
European Union	10 000 mg/kg	The production, placing on the market and use of substances or preparations containing chloroalkanes in concentrations lower than 1% (10.000 mg/kg) by weight shall be allowed.	Regulation (EU) 519/2012 (Modification Annex I Regulation 850/2004)
	1 500 mg/kg	It is prohibited the production, place on the market and use of substances or preparations containing chloroalkanes in concentrations higher than 0.15% (1 500 mg/kg).	Regulation (EU) 2030/2015 (Modification Annex I Regulation 850/2004)
Switzerland	10 000 mg/kg	It is prohibited to place on the market plastics and rubbers, sealants, textiles or leather processing agents if they contain more than 1% short-chain chlorinated paraffins by mass (10 000 mg/kg).	Ordinance on Chemical Risk Reduction, ORRChem of 18 May 2005
Canada	Prohibited	It is prohibited to manufacture, use, sell, or import these substances or products containing them.	SOR/2012-285

Table 5. Legal limitations on hazardous chemical substances employed in the fat-liquoring stage

In summary, the main environmental impact and hazardous substances in the tanning process at the bating, defatting, tanning, fatting and dyeing stages are:

TANNING STAGE	TRADITIONAL PRODUCT	ENVIRONMENTAL IMPACT
Bating	Enzymatical products	Presence of ammonium in wastewater
Defatting	Alkylphenol and alkylphenol ethoxilates	Restricted substances (EU regulations)
Tanning	Chromium salts	Restricted substances (EU regulations)
Dyeing	Azocolorants and azodyes Acid dyes mixed with surfactants, dispersing agents, paraffin, inorganic salts, etc.	Restricted substances (EU regulations) Increase of conductivity and non-biodegradable organic load in wastewater
Fatting	Chlorinated paraffins short chain (C10-C13)	Restricted substances (EU regulations)

Table 6. Summary of toxical products in the tanning process at the bating, defatting, tanning, fatting and dyeing stages

3.2. The leather tanning technology with natural products

This section describes the developed methodology based on the use of natural products in the whole tanning process, specifically process at the defatting, bating, tanning, fatting and dyeing stages.

Once the beamhouse operations are finished, the leather tanning process with natural products starts. This process is based on a group of chemical and mechanical operations intended to prepare hides for the tanning process by means of the defatting and bating stages, to achieve stabilization of the protein structure of the skin by means of the reaction of collagen proteins with oxazolidine at the tanning stage and to improve their physical and chemical properties at the dyeing and fatliquoring operations, replacing commercial products by natural products with lower impact on the environment and the human health in the five stages.

Hide processing is often an artisan practice, which is customarily updated according to tanners' experience. The amount of chemical and natural 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). The tanning process with natural products is described with detail below. For more details on single stages (bating, degreasing, tanning, dyeing and fatliquoring), also check the specific manuals available on single project website (see page 3). Also the use of natural products with standard Chromium tanning have been successful applied.

De-liming/Defatting process with natural product (EDF-20)

De-liming is the process that removes lime and alkaline products from the skin. This way the swelling of the limed skin is achieved. The lime dissolved in interfibrillary liquids and the one deposited on the fibers (it's only light soluble) can be easily removed using some washes prior to liming. The rest of the lime is removed by adding buffered solutions of ammonium or organic salts, or carbon dioxide. These agents, combined with the alkaline products of the limed skin, provide readily water-soluble products that can be removed by a simple wash. When adding theses acids, the pH has to be equal to or greater than 7.5, otherwise the skin would undergo undesired acidic swelling.

At this stage the natural fat of the skin is removed to facilitate the penetration of reagents and to avoid undesired reactions and stains on the skin. This operation is carried out by direct emulsion of fat in an aqueous medium using the natural defatting product (EDF20). Below is shown a typical recipe of defatting with EDF20. We report a range, for each stage, because dosage depends on the type of leather and its final use and also tannery practice. The dosage is 0.7 % for bovine hides prepared for shoes and bag manufacturing.

PROCESS/PRODUCTS	% pelt weight	T (ºC)	Time (min)	Remarks
DELIMING				
Water	100	30	20'	
Drain bath - Rinse twice				
Water	100	35	20'	
Ammonium sulphate	1.0		15'	
Ammonium sulphate	1.0		15'	pH<8.0
Check cross-section with colourless phenolphthalein				
Defatting natural product (EDF20)	0.7÷2		20'	
Rinse twice				
Drain				

Bating with natural products (PODEBA DPM)

The objective of bating is to achieve, using proteolytic enzymes, the de-swelling and relaxation of the skin, while cleaning up any remaining epidermis, globulins, elastin, hair and fat, as a secondary effect, making the grain finer and softer grain.

Traditionally, animal dung, mainly dog and chicken dung would have been used as the source of the enzymes. The digestive tracts of these animals are a rich source of therelevant enzymes. In more recent times the enzyme was extracted from pancreas of cattle. This gland produces a series of active substances able to decompose the proteins and fats.

Bating with such extracts, being unhygienic and hard to control, it has been displaced by artificial bates that simplify the exact dosage and correct control of the operation. From here the significance of our project. We have solved the problem of hygiene of the poultry dejections and made an interesting bates agent easy and ecological with no purpose problems.

By contrast, pancreatic enzymes-based bates are formulated with a large percent of excipients that have a strong ecological impact.

The poultry manure has relaxation properties on the hides and skins in the bating phase because contains the same enzymes present in the conventional products. Passed through a patented biological process, the manure is deodorized, his bacterial content downed and activity maintained (PODEBA deodorized poultry manure, PODEBA DPM).

The skins/hides outgoing of the deliming phase, at pH 8-8,5, went undergo to the bating. At first clear water is added at room temperature, 150% on the weight of skins.

Next PODEBA DPM is added and it reacts during 30-40 minutes. The outcome of the relaxation of the skins is hand tested and this time is eventually extended. The DPM show an enzymatic activity of the same order of size (500-800 LVU) of the commercial product and we use it in the same mode. The difference spotted in the process are due to physical condition of the PODEBA DPM: it need more time to imbibe with water and set the enzyme free. In the next table a typical recipe of bating with PODEBA DPM.

The formulations used in these tests are shown in table below, 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.). The dosage and timing have to be tailored on own process for the different kind of hides. For example, the tested dosage is 0.7 % for bovine hides prepared for shoes and bag manufacturing.

PROCESS/PRODUCTS	% pelt weight	T (ºC)	Time (min)
BATING			
Water	200	38	
PODEBA DPM	0.7÷2		45’-60’
Drain bath			
Water	200	20	5’
Rinse twice			
Drain			

Pickling

This stage can be considered as a complement of deliming and definitive interruption of the enzymatic effect of the bating process. Also, after pickling the skin is prepared for the tanning operation.

The pickling operation is more important with respect to the subsequent tanning operation, since, if unpickled, the pH of the skin would be high and the salts of the mineral tanning agent would gain higher basicity. In these pH conditions, over-tanning would affect the outer layers, which would make it difficult for the tanning agent to diffuse into the internal layers, thus shrinking the grain layer and precipitating the hydrolyzed mineral agent on it.

In the pickling operation, the skin is treated with acid products that add an important quantity of acids to the skin and at the same time manage to lower its pH to 3-3.5 removing totally the skin’s alkali.

The acids that are used are sulphuric acid, formic acid and acetic acid, according to this recipe:

PROCESS/PRODUCTS	% pelt weight	T (ºC)	Time (min)	pH	Remarks
PICKLING					
Water	50	20			
Salt	8		10’		Check 6-7ºBe
Sulphuric acid 1:10	1		30’		
Formic acid 1:5	1		180’	3.5	Check pH 3.5 in bath and cross-section with bromocresol green

Oxazolidine tanning

The oxazolidine tanning procedure is carried out on the pickled bath. Firstly, a pre-fatliquoring is done to lubricate the fibres, facilitate the penetration of the products and improve the feel of the skins. This process is carried out adding 5% (by pelt weight) of a commercial product combination of phosphoric esters and synthetic fats, leaving them to rotate in the drum for 30 min at a slow speed (4-6 rpm).

After the pre-fatliquoring, a tanning agent is added, in this case 3%-5% (by pelt weight) of oxazolidine, and the skins are left to rotate for 90 min at a speed of 6-8 rpm and for the whole night with the drum working automatically (5 minutes in motion, with the previous speed and 55 minutes stopped).

Once the reaction of oxazolidine with the skin collagen has finished, the pH of the leather is checked, which must have a value of 4.5-5.0, and the penetration of oxazolidine is also checked by cutting a small sample and applying the indicator (bromcresol green) to the cross section.

If the oxazolidine has penetrated through the whole cross section of the skin, the cross section will show a homogeneous greenish coloration, while if it has not penetrated the whole cross section there will be a lighter shade at the centre of the cross section.

In this case, the rotation of the drum will be extended for 60 min and the penetration will be checked again, repeating this operation as much as needed.

PROCESS/PRODUCTS	% pelt weight	Time (min)	Remarks
TANNING			
Pre-fatliquoring			
Pre-fatliquoring agent	5	30’	
Tanning			
Oxazolidine (100%)	3÷5	90’	
Automatic over night			Check pH (4.5-5.0) and cross section

Retanning

At this stage, according to the type of re-tannage selected (synthetic or vegetable), the following products are added to the same oxazolidine tanning bath:

- 15% (by pelt weight) of substitution synthetic retanning agent: sulphone condensation product and aromatic sulphonic acid or
- 15% (by pelt weight) of vegetable retanning agent: mix of tara, quebracho and mimosa
- 5% (by pelt weight) of Chromium salts.

The addition is carried out in three successive doses of 5% (by pelt weight), separated by a 60 min interval, with the drum rotating at a speed of 8-10 rpm.

Once the reaction of synthetic and vegetable retanning agents with oxazolidine and with the skin collagen has finished, the pH of the leather is checked, which must have a value in the range of 5.0-5.5 and the penetration of the retanning products is also checked by cutting a small leather sample and applying the indicator (bromcresol green) to the cross section.

If the retanning agents have penetrated through the whole cross section of the leather, the cross section will show a homogeneous green-bluish coloration, while if it has not penetrated the whole cross section, the centre of the cross section will have a lighter shade.

In this case, the rotation of the drum will be extended for 60 min and the penetration will be checked again, repeating this operation as much as needed.

Finally, the bath is drained and the drum unloaded, leaving the leathers to rest on a horse for 12 hours to stabilize the tanning bonds formed.

The mechanical operations required for the article to be processed are then carried out, which mainly consist of sammying and shaving the leathers to give them the desired thickness.

PROCESS/PRODUCTS	% pelt weight	Time (min)	Remarks
RETANNING			
Synthetic/vegetable tanning	5	60’	
Synthetic/vegetable tanning	5	60’	
Synthetic/vegetable tanning	5	60’	Check pH(*)
Check pH (5.0 – 5.5) and cross section			
Drain and remove leathers			
Leathers are left to rest for 12 hours			
Sammying and shaving			

(*) If the pH>3, successive doses of 0.20% formic acid are added (although it is not usually necessary)

Neutralisation

The leathers shaved to the desired thickness are loaded in the drum for neutralisation. The alkaline nature of oxazolidine simplifies the neutralisation stage, reaching the final tanning pH with a lower addition of basifying agent. In these conditions, the bath is formulated with 200% water at 30 °C, 1% sodium formiate and 0.5% sodium bicarbonate (by shaved leather weight), and the drum is rotated at 10 rpm.

After 40 min, the pH of the leather is checked, which must have a value in the range of 5.5-6.0 and the penetration of the neutralising products is also checked by cutting a small leather sample and applying the indicator (bromcresol green) to the cross section.

If the neutralizing agents have penetrated through the whole cross section of the leather, the cross section will show a homogeneous bluish coloration, while if it has not penetrated the whole cross section; the centre of the cross section will have a lighter shade.

In this case, successive additions of 0.2% sodium chloride will be made to reach this pH value, extending drum rotation for 30 min and repeating this operation as much as needed.

Once the desired pH has been reached, the leathers are gently washed to remove the excess neutralising reagents and the bath is drained.

PROCESS/PRODUCTS	% shaved weight	T (ºC)	Time (min)	Remarks
NEUTRALISATION				
Water	200	30		
Sodium formiate	1.0			
Sodium bicarbonate	0.5		40’	Check pH
Check pH (5.5 – 6.0) and cross section				
Drain bath and wash leathers				

Dyeing and fat with naturalised dyes and fatliquorings

Once the leathers have been neutralized, washed and the bath has been drained, the dyeing operation is carried out, if desired. For this, the desired natural dyestuff is added on the wet leathers (dry dyeing, without water, to improve the dyestuff penetration crossing through the whole section of the leather) on a ratio (by shaved leather weight) of 3% for sheep and pigskin and 5% for cow hide (for its greater thickness), and the drum is rotated for 30 min at 10 rpm so that the colour can penetrate.

Next, the colour penetration is checked by cutting a small leather sample. If the dyestuff has penetrated through the whole cross section of the leather, the cross section will show a homogeneous coloration, while if it has not penetrated the whole cross section; the centre of the cross section will show a lighter shade.

In this case, successive additions of 0.5% dyestuff are made in order for the dyestuff to penetrate the leather, extending the rotation of the drum for 20 min and repeating this operation as much as needed. In general, leather neutralization is achieved with an initial dose of formiate and bicarbonate so it is not necessary to extend the neutralization stage.

Next, a similar bath is prepared; it is added to the drum and left to rotate at 12-15 rpm for 30 min.

After this time, in which the natural fatliquoring has penetrated the leather lubricating the fibres, 5% re-tanning agent (by shaved leather weight) is added to the bath to improve the appearance and properties of the leather, such as its fullness, feel, compactness, physical resistance, improvement on the retention capacity of the print, of the buffing, etc.

The type of final re-tanning agent used will depend on the appearance and intended use for which each leather is processed, but it must have a low formaldehyde content. The re-tanning agent is left to act for 30 min with the drum rotating at 12-15 rpm.

Finally, 2% formic acid (dilution 1:10) is added (by shaved leather weight and on two consecutive doses separated by 15 minutes), which causes a decrease in the leather pH (<3) and a change in the polarity of the leather that favours the fixation of the naturalised dyestuff and fatliquoring products.

The formic acid is left to act for 20-30 min, with the drum rotating at 12-15 rpm.

Once the dyestuff and fatliquoring are fixed, the drum is drained and the leathers are washed to remove the excess unfixed reagents, using 200% water (by shaved leather weight), in a closed-door drum for 5 min and then the bath is drained.

PROCESS/PRODUCTS	% shaved weight	T (ºC)	Time (min)	pH	Remarks
DYEING/FATLIQUORING					
Dyeing					
Dyestuff	3÷5		30’		
Check cross section					
Fatliquoring					
Water	100	40			
Natural fatliquoring	5		30’		
Drain					
Water	100	40			
Natural fatliquoring	4		30’		
Syntetic retanning product	5		60’		
Drain					
Formic acid (1:10 v/v)	1		15’		
Formic acid (1:10 v/v)	1		15’	<3	Check pH and Tg
Check pH <3					
Drain bath and wash leathers					

Final conditioning

The conditioning treatment of the drained and washed leathers is carried out to remove the free formaldehyde. For this, the formaldehyde sequestering bath is added, which is formulated with 100% water at 35 °C and 2% hydroxylamine sulphate (by shaved leather weight), leaving it to act for 60 min.

Finally, the bath is drained and the leathers are unloaded, leaving them to rest for their subsequent sammying, drying, mechanical operations and finishing in accordance with their desired final appearance.

PROCESS/PRODUCTS	% shaved weight	T (ºC)	Time (min)	pH	Remarks
FINAL CONDITIONING					
Water	100	45			
Sequestering agent	2		60’		Check Tg
Drain and remove leathers					
Rest					
Sammying, drying and mechanical operations					
Finishing operations					

3.3. Assessment of the technical and environmental advantages of the LIFETAN tanning technology

The results derived from the development of the LIFETAN tanning technology with natural products showed that the obtained leather had good physical strength and adequate appearance and feel for the manufacture of different articles and no significant differences respect to leathers processed with commercial products are observed.

The tanning degree of leather was assessed through the determination of the Shrinkage Temperature (Tg), giving values between 75 and 82 °C, which were acceptable for the production of most products (footwear, handbags, jackets, etc.).

The technical validation of LIFETAN tanning technology was first assessed according to standardised quality control tests to check the compliance with recommended values and the suitability of leather for footwear manufacturing.

Likewise, some footwear styles and upholstery, leather goods and apparel? products were manufactured and no differences were observed in leather processing or in the final appearance of the articles produced.

Furthermore, oxazolidine-tanned leather meets the requirements relative to the limit content in hazardous substances according to the criteria of the European Ecolabel for footwear set forth in the Commission Decision 2002/231/EC:

PARAMETERS	STANDARD	MEASURED VALUES (*)
Chromium (VI)	ISO 17075:2007	≤ 10 ppm
Formaldehyde	ISO 17226-1:2008	≤ 150 ppm
Pentachlorophenol	ISO 17070:2006	Not detected
Lead	ISO 17072-2:2011	Not detected
Cadmium	ISO 17072-2:2011	Not detected
Arsenic	ISO 17072-2:2011	Not detected
Aromatic amines (derived from azo-colorants)	ISO 17234-1:2010	Not detected

(*)Not detected means below the detection limit

Regarding the environmental impact of this technology, the characterisation of the effluents from LIFETAN tanning processes showed similar values to those obtained in chrome tanning. However, oxazolidine tanning effluents are chrome-free and consequently the oxidation of trivalent chromium to its hexavalent state is avoided and the metal-free sludge derived from wastewater treatment is more likely to be reused, e.g. for agriculture. This way, it is possible to dramatically reduce the environmental impact generated during the tanning process and also at the end of the leather lifecycle, either in the form of leather trimmings when different goods are manufactured or when they are disposed of after use.

Furthermore, LIFETAN waste waters are more biodegradables than the ones used in the traditional processes, which reduces the environmental impact of the process and a priori implies a higher feasibility of the biological treatment of waste waters.

In conclusion, the main benefits of the LIFETAN technology for tanning with natural products are summarized below:

Defatting/Bating stage:	Traditional process:	TKN: 1.650 mg/l
	Naturalised process:	TKN: 650-790 mg/l
	Reduction obtained:	**↓ +50%**
	Expected results:	*↓ 30%*
Pickling/tanning stage:	Traditional process:	Chromium: 380-545 mg/l
	Naturalised process:	Chromium: not detected
	Reduction obtained:	**↓ 100%**
	Expected results:	*↓ 100%*
Post-tanning stages:	Traditional process:	Chromium: 48-62 mg/l
	Naturalised process:	Chromium: not detected
	Reduction obtained:	**↓ 100%**
	Expected results:	*↓ 100%*
All naturalised process:	Free of ammonium sulfhate salts in the bating phase	
	Free of chlorine and sulphochlorinated paraffins (100% reduction)	
	Free from synthetic chemical dyes (100% reduction)	
	Free from Alkylphenol and Alkylphenol ethoxilates (100% reduction)	
	Higher biodegradability: > 30% (easier biological wastewater treatment)	
	Chrome-free leather and leather wastes	
	Chrome-free sludges from wastewater treatment	

LIFETAN Eco friendly tanning cycle
LIFE14 ENV/IT/000443

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