journal of ageic Vol:63 N4 2012

# Chrome-free leather, tanned with oxazolidine

M. Roig1, V. Segarra1, M. Bertazzo1, M. A. Martínez1, J. Ferrer1, C. Raspi2

1 Footwear Technological Institute (INESCOP). Polígono Industrial Campo Alto - 03600 Elda (Spain).
e-mail: medioambiente@inescop.es
2 CGS s.a.s. (CGS) Borgo Stretto 10, Pisa (Italy)

**Abstract:** At present, chrome tanning is the most widely used technique for leather tannage, accounting for more than 90% of leathers tanned worldwide. However, chrome tannage involves serious environmental risks resulting from the possible oxidation of chromium to a hexavalent state, although tanners are aware of the carcinogenic effect, in accordance with the International Agency for Research on Cancer (IARC). For this reason, the market has shown a growing demand for "ecological" products, especially regarding the development of tanning processes using alternative tanning agents different from chromium.

Alternative tanning technologies include the use of oxazolidine in combination with other retannig agents of vegetal or synthetic origin, which allow for obtaining quality leathers that may be used by footwear and upholstery industries.

Within this context, the European project "Environmentally Friendly Oxazolidine-Tanned Leather (OXATAN)" emerged, aimed at the demonstration, promotion and dissemination of oxazolidine tanning techniques, with the support of the European Commission within the framework of the LIFE+ Programme. This report includes the results obtained so far from different trials carried out at semi-industrial and industrial scale concerning leather tanning using oxazolidine, as well as the corresponding validation of environmental improvement achieved.

Therefore, leathers obtained from the first tests meet the requirements of the European Ecolabel for Footwear. In addition, the improved biodegradability of tanning residual effluents was verified and the absence of chromium in solid waste and wastewater treatment sludge was demonstrated.

## 1 Introduction

The transformation of an animal's skin into tanned leather involves carrying out a series of chemical processes and mechanical operations where a putrescible material, consisting especially of proteins, becomes a stable and resistant material that can be used in the manufacture of footwear, leather goods, upholstery, clothing, etc.

The traditional tanning process, used in more than 90% of the leathers tanned in the world, is the application of trivalent chromium salts, which interact by chemical bonding with the carboxylic groups of collagen in the skin, giving to the leather its strength and stability properties (Figure1).

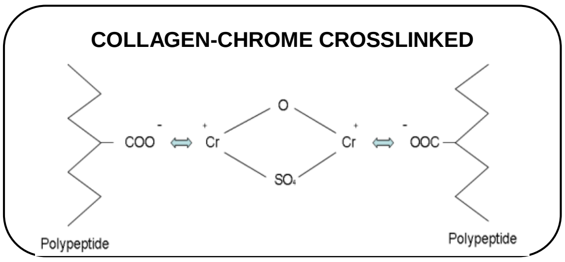


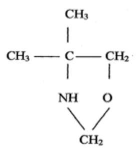
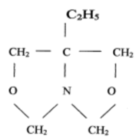
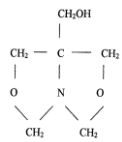

Figure 1. Collagen-chrome crosslinked

This process gives the leathers excellent physical properties and high stability for the footwear manufacturing processes. However, in some cases, may pose allergy to chromium or even, trivalent chromium can be partially oxidized to hexavalent chromium, a carcinogenic compound that may be present in wastewater and solid waste from tanneries, with considerable impact on the environment and human health.

Furthermore, the crisis that the leather sector is experiencing and the competition of third countries with low labour costs, leads to the need for new market strategies. Within this context, eco-design is presented as an innovative instrument contributing to the development of more environmentally friendly and competitive products, which in addition to providing added value, are useful products for the development of a new company approach, allowing for the identification of new business opportunities. This way, in Europe, more and more leather companies commit to eco-design as a competitive factor. That is why it is very important to implement new chrome-free tanning techniques thus avoiding the problem at the point of origin. In this sense, previous research studies demonstrated that using oxazolidine tanning agent combined with other (vegetable or synthetic agents) allows for the obtaining of quality leathers that can be used by footwear and upholstery industries.

Oxazolidines are saturated heterocyclic compounds prepared by reacting primary amino alcohols with formaldehyde. Monocyclic or bicyclic oxazolidine ring structures are formed depending on the choice of starting chemicals, it is therefore possible to synthesize a variety of oxazolidines from different amino alcohols. Oxazolidines are highly useful chemicals for a wide variety of applications: corrosion inhibitors, emulsifiers, diluents or tanning agents. The oxazolidine marketed for use as tanning agents [1] (Table 1) are water soluble compounds, compatible with most chemicals normally used in tanning operations and can be introduced at several points in the tanning process.

Table 1. Properties of the oxazolidines used as tanning agents

| Type | Oxazolidine A | Oxazolidine E | Oxazolidine T |
|---|---|---|---|
| Name | 4,4-Dimethyl-1-oxa-3-azacyclopentane | 5-Ethyl-1-aza-3,7-dioxabicyclo [3,3,0] octane | 5-Hydroxymethyl-1-aza-3,7-dioxabicyclo [3,3,0] octane |
| Molecular structure |  |  |  |
| CAS Registry No. | 51200-87-4 | 7747-35-5 | 6542-37-6 |
| Molecular weight (g/mol) | 101.17 | 143.18 | 145.18 |
| pH | 11.0 | 11.2 | 9 |
| Aspect | Yellow liquid | Yellow liquid | White powder |

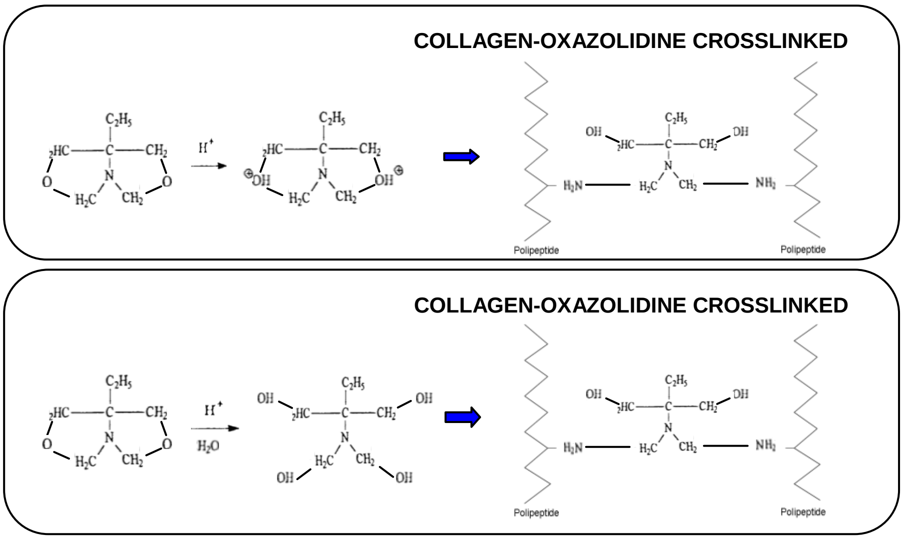
The reviewed literature [2, 3] and preliminary tests conducted by INESCOP under a laboratory scale show the oxazolidine E as an effective alternative for use as tanning agent. Tests results presented in this document were carried out using this product in different proportions (3% and 5% in weight). As a tanning agent, Oxazolidine E will undergo an irreversible reaction with the hide substrate over a wide pH range (best success is attained when the pH is 4.0 or higher) and at a rate which is readily controlled by operating conditions (dosage, time of introduction, etc.).

The capacity of the Oxazolidine E for tanning leather is based on the formation of a reaction intermediate due to:

- the protonation of oxygen of each ring in acid medium, which weakens the C-O bond or,
- the oxazolidine rings opening caused by hydrolysis in an acid medium to provide an intermediate with two N-(hydroxymethyl) groups,

and the subsequent nucleophilic attack of the collagen amino groups to this intermediate specie (Figure 2).

Figure 2. Collagen-oxazolidine crosslinked




Leathers tanned with chromium salts have a high stability, determined by a shrinkage temperature (Tg) over 100° C, while the leathers tanned with oxazolidine alone reach shrinkage temperatures of below 75º C. It is therefore necessary to carry out the oxazolidine tanning in combination with synthetic or vegetable tanning agents to achieve higher shrinkage temperatures and obtain leather of comparable quality to the chrome tanned leather.

This paper presents the results obtained to date, coming from different tanning tests on calf and sheep leathers, at a semi-industrial scale, using oxazolidine in combination with synthetic or vegetable re-tanning agents as an alternative to traditional chrome tanning. In it, it is presented the procedures followed, physical and chemical characterization of the obtained leathers, as well as the impact of this technology on waste water and solid waste generated.

## 2. Experimental procedure: materials and methods

Tests for oxazolidine tanning in combination with synthetic or vegetable re-tanning were done in INESCOP pilot tanning plants (Figure 3) and the operating conditions were determined in previous trials at a laboratory scale.

The tanning tests with oxazolidine were carried out on rotating tanning drums of 900 and 1,200 mm diameter respectively and 400 mm width, made of bolondo wood and featuring systems for automation, control and dosage of water and reactants.

Figure 3. Tanning drum used in tanning tests on a semi-industrial scale

In each test with the calf hides, whole pickled hides with a thickness of 2.5 mm divided into sides (half hide) were processed. After the tanning process, the calf leathers were shaved to 1.5 mm for the dyeing and fat-liquoring processes. In the same way, in tests with sheepskin, whole pickled and degreased skins were used, with a thickness of 1.2 mm, so no shaving process operation was needed.

In the tests carried out, skins were tanned using 3% or 5% oxazolidine combined with:

- synthetic re-tanning agent: condensation product of sulphone and aromatic sulphonic acids with low phenol and formaldehyde contents.
- vegetable re-tanning agent: mixture of extracts of tara, quebracho and mimosa

and performing a subsequent re-tanning, dyeing and fat-liquoring process common to all of them.

Likewise, the same combinations were carried out using basic chromium salts as a tanning agent in order to use these leathers as a comparative reference. The formulations used in these tests are shown in Table 2 where it is indicated, for the different operations, the product used, the percentage by weight with respect to the pickled leather introduced into the tanning drum, temperature, rotating time and checks to be performed (pH, bath salinity, etc..).

Table 2. Steps of the oxazolidine tanning process

| PROCESS/PRODUCTS | % pickled weight | Tª (ºC) | Time (min.) | pH | Remarks |
|---|---|---|---|---|---|
| **TANNING** | | | | | |
| Water | 70 | 25 | | | |
| NaCl | 7 | | 10’ | | Check 8º Be |
| Add the hides | | | | | |
| Pre-fatliquoring | 5 | | 30’ | | |
| Oxazolidine E (100%) | 3 / 5 | | 60’ | | Check through section |
| Automatic over night | | | | | |
| Synthetic/vegetable tanning | 5 | | 60’ | | |
| Synthetic/vegetable tanning | 5 | | 60’ | | |
| Synthetic/vegetable tanning | 5 | | 60’ | | Check pH |
| Draining, waste-bath sampling and wash | | | | | |
| **NEUTRALIZATION (*)** | | | | | |
| Water | 200 | 30 | | | |
| Sodium formiate | 1.5 | | | | |
| Sodium bicarbonate | 1 | | 40’ | 5.5-6.0 | Check pH |
| Drain | | | | | |
| **DYEING / FAT-LIQUORING** | | | | | |
| Dye | 1-2 | | 30’ | | |
| Water | 100 | 40 | | | |
| Fatliquoring (sulphonated triolein) | 2 | | | | |
| Waterproof Fatliquoring | 4 | | 30’ | | |
| Water | 100 | 40 | | | |
| Fatliquoring (sulphonated triolein) | 2 | | | | |
| Waterproof Fatliquoring | 4 | | 30’ | | |
| Synthetic tanning | 5 | | 30’ | | |
| Formic acid (1:10 v/v) | 2 | | 20’ | | |
| Drain and wash | | | | | |
| Water | 100 | 45 | | | |
| Sequestering agent | 2 | | 60’ | | Check Tg |
| Drain | | | | | |

(*)Calf skins are shaved to 1.5 mm and the formula goes on using the shaved weight.

The obtained leathers have an acceptable appearance and adequate smoothness, softness, fullness and flexibility. The evaluation of the results of the carried out tests is done through the characterization of obtained leathers and effluents in accordance with accepted standards.

## 3. Results and discussion

### 3.1. Physical characterization of obtained leathers

Calf and sheep leather samples obtained in the tests at semi-industrial scale undergo various quality tests according to international standards (EN-ISO) to check their applicability to the manufacture of footwear and upholstery articles. The determinations of physical parameters of the leathers have shown to be compliant with the limits required for footwear and upholstery articles manufacture. Table 3 contains the results of the physical characterisation of the obtained leathers (average values).

Table 3. Physical tests on calf leathers and sheepskins tanned with oxazolidine

| PARAMETER | CALF LEATHER | SHEEP LEATHER | RECOMMENDED VALUES |
|---|---|---|---|
| Thickness (mm) | 1.9 | 1.5 | > 1.1 |
| Tear strength (N) | 187 | 69 | > 50 |
| Tensile strength (N/mm2) | 20 | 16 | > 15 |
| Elongation at break (%) | 103.5 | 76 | > 40 |
| Grain burst (mm) | 9.3 | 9.9 | > 8 |
| Shrinkage temperature (ºC) | 80 | 77 | > 70 |
| Shrinkage temperature (ºC) | 80 | 77 | > 70 |

The degree of tanning of leathers was checked through the determination of the Shrinkage Temperature (Tg), presenting values between 76 and 82 ºC for all leathers tanned with oxazolidine, which were acceptable for footwear and upholstery products manufacture. Furthermore, no significant differences were observed in the addition of a greater proportion of oxazolidine, therefore it is considered that 3% is the optimum dose for tanning using this technology.

Finally, the ability of this oxazolidine leather has been checked through the manufacturing of different models of shoes and upholstery, leather goods and garments products (Figures 4, 5 and 6). The manufacturing process is carried out as usual and no differences are observed in the processes or in the final appearance of the models produced.

Likewise, some tests on vulcanised footwear manufacture were also carried out and, although the heat setting temperature is around 140 ºC, this leather also proved to be suitable for this kind of footwear.

Figure 4. Children’s footwear (DECHICS), men’s penny loafers (MOSEIPE) and occupational footwear - clogs (DIAN) manufactured from oxazolidine tanned hides.

Figure 5. Women’s footwear (TPSP), casual and vulcanised footwear (CALZADOS CANÓS GARCÍA, S.L.) manufactured from oxazolidine tanned hides.


Figure 6. Upholstery, leather goods and garments products manufactured from oxazolidine tanned hides

### 3.2. Chemical characterization of obtained leathers

The chemical validations of oxazolidine tanned leathers to manufacture footwear and upholstery products are done through the chemical characterization of leathers in accordance with accepted standards (EN, ISO, etc.) and by checking the compliance with the criteria of the European Eco-label for footwear (Decision 2002/231/EC):

- Cr (VI) in leather ≤ 10 ppm
- As, Cd and Pb in leather: undetected
- Formaldehyde in leather ≤ 150 ppm
- Pentachlorophenol (PCP) in leather: abscence
- Tetrachlorophenol (TCP) in leather: abscence
- Azoic colourings in leather: abscence

The determinations of chemical parameters of the leathers have shown to be compliant with the limits required for the European Eco-label for footwear, except for formaldehyde content in leather that exceeded the limit (150 ppm).

In order to solve this problem, it was necessary to study and optimise reduction alternatives by means of the addition of products able to react with free formaldehyde present in leather, thus transforming it in a soluble product that can be removed by rinsing with water, without compromising leather quality.

The test results showed that the optimum solution was adding a 2% ratio of a sequestering chemical during the final rinsing, thus obtaining leather with a formaldehyde content lower than 50 ppm, which is far below the limit established in the proposal (<150 ppm). Furthermore, using 4% of this product allows a greater reduction of formaldehyde content in leather, thus obtaining values below 15 ppm, although this implies an increase in production costs that should be considered by the user.

Likewise, it was checked that adding this product did not produce leather detanning, since the shrinkage temperature and the physical properties of the leather were maintained.

### 3.3. Characterization of the tanning waste-bath

The evaluation of the impact of the oxazolidine tanning process on the waste water was achieved by the characterization of the tanning waste-baths obtained in the different tests carried out, determining the most significant parameters in accordance with international standards. Table 4 shows the

results obtained (average values), compared with typical values of a conventional chrome tanning, both for tests with calf leather as well as with sheep leather.

Table 4. Characterization of effluent from calf leather and sheepskin oxazolidine tanning.

| PARAMETER | CALF LEATHER | SHEEP LEATHER | CHROME TANNING RANGE |
|---|---|---|---|
| pH | 5.7 | 4.7 | 3.8 – 4.0 |
| Conductivity (mS/cm) | 110 | 90 | 70 - 80 |
| COD (g O2/l) | 123 | 92 | 40 - 100 |
| BOD (g O2/l) | 45 | 32 | 15 - 40 |
| TKN (mg/l) | 4,275 | 152 | 500 – 3,000 |
| Cl- (g/l) | 41 | 112 | 20 - 60 |
| Total Cr (g/l) | ND | ND | 3 – 6 |
| Toxicity (U.T.) | 4,100 | 2,343 | 2,000 – 4,000 |

ND: NOT DETECTED

Regarding the characterization of the wastewater, the values of the parameters set by the tanning with oxazolidine, although slightly higher, are comparable in order of magnitude to those obtained using chromium salts.

Also, oxazolidine tanning effluents are chrome-free; therefore, the possible trivalent chromium oxidation into hexavalent chromium, which is a carcinogenic substance harmful to health and the environment, is prevented and the sludge derived from wastewater treatment is more likely to be reused, eg. for agriculture.

### 3.4. Toxicity tests on tanning waste-bath.

On the other hand, given the organic nature of oxazolidine, toxicity tests were conducted on activated sludge in order to compare waste.

To corroborate these results, a 24 h toxicity test was done, where the activated sludge gets in contact with the wastewater (dilution 1:100 tanning waste-bath) over a period of 24 h, comparing the respiration rate of microorganisms with a standard sample nontoxic. This test showed that the respiration inhibition rate of activated sludge due to the action of chromium waste bath was 40% higher than that of oxazolidine waste bath.

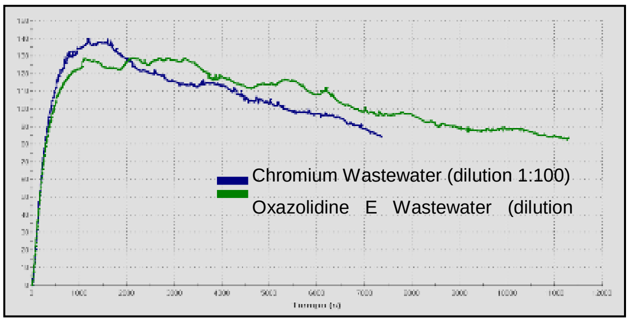



Figure 7. Cumulative toxicity tests on oxazolidine and chromium waste baths (1:100 dilution)

baths from oxazolidine and chrome tanning. This way, the feasibility of the biological treatment of effluents can be assessed. These tests were performed using advanced respirometric reactor using a biological laboratory in which are added, progressively, aliquots of 10 ml of the sample to an initial volume of 1,000 ml of sludge. A 1:100 dilution of both baths (oxazolidine and chrome) was done, simulating the real contribution of these baths in total wastewater from a tannery.

The toxic effect of the added samples was proven by the sharp decrease in the sludge respiration curve, which was experimentally determined by the curve slope. In this test, see Figure 7, the decrease in microorganism respiration was more marked in chromium waste bath, which proved a higher toxic effect of chromium waste bath than that of oxazolidine waste bath.

This proves a higher biodegradability of oxazolidine effluents, thus their biological treatment a priori seems to be more feasible.

### 3.5. Biodegradability tests on obtained leathers

Through these tests, an estimate of the degree of biodegradability of leathers according to the tanning technology employed (chromium or oxazolidine) is obtained, which allows to compare between the two technologies regarding their waste environmental impact.

Since there is currently no method or specific standard for determining the biodegradability of tanned leather, it has been employed a method designed and optimized by INESCOP and the Universidad Miguel

Hernandez (Elche-Spain) [4]. This method is based on a standard for assessing the aerobic biodegradation of polymers in the presence of municipal wastewater (ASTM D5209-92) using collagen as the reference standard substance and tannery wastewater as inoculum for measuring biodegradability.

The tests were carried out on a equipment (Figure 8) in which the sample of leather dust gets in contact with the inoculum on bacteria material culture, while maintaining constant agitation and temperature for a period of one month.

The biodegradation of the samples is evaluated by indirect measurement of the CO2 generated in function of time and the degree of biodegradability is calculated based on the relationship between the theoretical maximum production and actual production of CO2, based on the content of soluble organic carbon content in each leather sample.

Figure 8. Leather biodegradability test equipment.

In the test carried out, the biodegradation of chromium calf leathers, oxazolidine E and a pure collagen pattern has been compared. As expected, pure collagen, used as test pattern, presented a biodegradation rate of 85% in 700 hours, while chromium leather shown a 12% and oxazolidine leather a 55% (Figure 9).

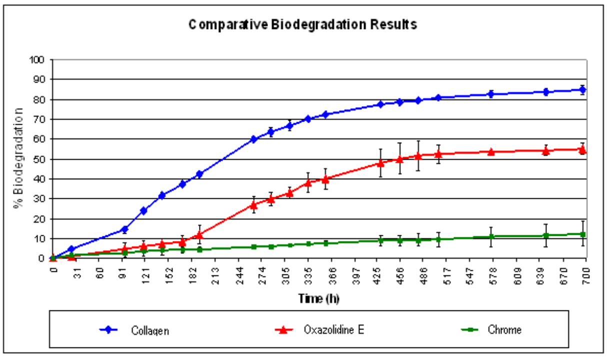



Figure 9. Biodegradability results on Collagen, Oxazolidine and Chromium leather

Biodegradability tests on leather showed that oxazolidine-tanned leather waste is 43% more biodegradable than chrome-tanned leather waste. These results show a significant improvement in the biodegradation of waste coming from oxazolidine leather with respect to chromium and support the use of tanning oxazolidine as an alternative to chromium salts in leather tanning process, since the waste generated are biodegradable and therefore more easily to be treated.

## 4. Conclusions

The results show that by tanning with oxazolidine, in combination with synthetic or vegetable re-tanning, the obtained leathers have good physical strength and adequate smoothness, softness, fullness and flexibility, and no significant difference between the two combinations has been detected.

Regarding the proportion of oxazolidine used (3 or 5%), no differences were found in the leathers, either in appearance or in their physical properties, therefore it is considered that 3% is the optimum dose for tanning using this new technology. Also, the selection of a synthetic or vegetable re-tanning will depend on each individual case, selecting the synthetic re-tanning for clear colours and high light-fastness, while the vegetable re-tanning can be used for darker colours.

The determinations of physical parameters of the leathers have shown to be compliant with the limits required for footwear and upholstery articles manufacture and the ability of this oxazolidine leather has been checked through the manufacturing of different models of shoes and upholstery products. The manufacturing process is carried out as usual and no differences are observed in the processes or in the final appearance of the produced articles.

About the chemical validations of oxazolidine tanned leathers, the results show to be compliant with the limits the limits required for the European Eco-label for footwear criteria.

Regarding the environmental impact, the values for oxazolidine tanning parameters, although slightly higher, can be compared to those obtained in chrome tanning but test show a higher biodegradability of oxazolidine effluents, thus their biological treatment a priori seems to be more feasible. Also, oxazolidine tanning effluents are chrome-free and the sludge derived from wastewater treatment is more likely to be reused, e.g. for agriculture. On the other hand. biodegradability tests on leather showed that oxazolidine-tanned leather is more biodegradable than chrome-tanned leather waste.

In short, oxazolidine tanning implies a significant benefit in that it is possible to considerably reduce the environmental impact produced during the tanning process and at the end of the lifecycle of products manufactured using this kind of leather.

Finally, it should be highlighted that there is a growing interest on the metal-free leather market, both inside and outside the European Union, as proven by the interest shown by the footwear, upholstery, garments and leather goods products manufacturers collaborating in this project in assessing the performance of oxazolidine-tanned leather.

## 5. References


[1] Angus Chemie GmbH. *Oxazolidines Technical Data Sheet*.

[2] Kitty Qu, Jeff Yang, et al. *"Oxazolidines: the versatile leather tanning agents"*. Leather March 2008, p 38-40.

[3] D'Aquino A., Barbani N., D'Elia G., et al. *"Combined organic tanning based on mimosa and oxazolidine: development of a semi-industrial scale process for high-quality bovine upper leather"*. Journal of the Society of Leather Technologists and Chemists. Vol. 88, p 47-55.

[4] De la Casa Lillo M.A., Díaz Tahoces A., Mazón Canales P., De Aza Moya P.N., Segarra Orero V., Martínez Sanchez M.A., Bertazzo M. *"Biodegradation of leather: establishment of a valuation method using aerobic microorganisms from tannery wastewater"*. XI National Congress of Materials. Zaragoza. June 2010.


## 6. Acknowledgments


To the European Commission, LIFE-Environment Program, for the support to the LIFE Project "Environmentally friendly oxazolidine-tanned leather (OXATAN)", with reference number LIFE08 ENV/E/000140.