1. Background.

In the last decades, the evolution of the industry has been coupled with a growing awareness of the protection of the environment, also promoted by the enforcement of new regulations, which are increasingly restrictive, relative to the control of waste and waste disposal. On the other hand, the current technological development requires the availability on the market of new environmentally friendly production systems, without losing competitiveness, which implies the implementation of the Best Available Technologies in the industrial processes, in the framework of the European Directive 96/61/EC relative to the Integrated Prevention and Pollution Control (IPPC).

In this context, the leather industries must look for production alternatives minimising the environmental impacts derived from their industrial activities, mainly in the stages which have the greatest effect on the environment, as is the case of the tanning stage.

Tanning is a process in which by means of the addition of a tanning agent (chromium salts, aluminium, zirconium, etc. or vegetable extracts of mimosa or quebracho tree, etc.) it is possible to stabilise the skin structure by forming transversal bonds among its fibres. The tanning agent blocks carboxylic groups, in the case of mineral tanning agents, or the amine groups, in the case of vegetable tanning agents, and joins the proteinic colloid thus increasing the crosslinking of collagen fibres. This way, the leather is turned into a durable material in respect of physical and biological degradation. The complete tanning process, including finishing treatments, lends the leather the characteristics of resistance, smoothness, softness, colour, etc. required for its industrial application.

Currently, chrome tanning is the most widely used technique for leather tanning, as it offers a product with the best performance at a reasonable price. By this technique, around 8% of the leather weight is added as chromium salt. However, a significant share of the pollution resulting from tannery wastewater comes from this stage, due to the chrome that is not fixed to leather amounting 15% of the total chrome added to the tanning bath. Tannery wastewater is usually homogenised with the rest of industrial effluents and chrome precipitates as chromium hydroxide, thus being retained in the sludge of the water treatment plants.

Another environmental impact, which cannot be easily corrected in tannery wastewater, is salinity, reaching conductivity values on the order of 10,000-12,000 µs/cm. The main contribution to the effluent salinity is derived from the salt used for the preservation of the skins after flaying, followed by the high salinity of the pickling baths (preparation of skins with salts and acids prior to the addition of the tanning agent) and the tanning stage. Therefore, 30% of the chlorides contained in the effluent come from the pickling bath, and 60% of the sulphates come from the tanning bath.

For these reasons, both from an environmental and financial point of view, it is necessary to put forward new alternatives for the reduction of chrome content in effluents and their salinity, as well as for the reduction of water and raw material consumption.

The possible alternatives that may be adopted in the pickling process for the reduction of salinity are:
- **Avoiding pickling.** This option can only be considered in the case of thin leather and requires strict controls in order to obtain reproducible results.

- **Salt-free pickling or pickling using a small amount of organic acids (phenol or naphtalen-sulphonic).** However, the products available on the market enjoyed little success and their use may cause the appearance of undesirable phenolic compounds in wastewater or process residues.

- **Pickling bath recycling.** This solution is the simplest one from the operational and financial point of view, as it is not necessary to use different products from the common ones. The process basically consists of storing the pickling bath in order to subsequently filter it and to increase the amount of acid and salt, thus being possible to reach a reduction in salt consumption by up to 95%.

In the case of chrome tanning, the following actions can reduce salinity and chrome content:

- **Using tanning processes with high exhaustion** (short baths and significantly masked with a high mechanical effect) thus avoiding the presence of chrome in effluents and reducing the amount of sludge produced. However, the exhaustion of the tanning bath shows some drawbacks, given that contractions and creases can appear on the leather.

- **Using liquid tanning agents with a low content in salts,** thus reducing the salinity of the wastewater. The main drawback of these products is that they can be more expensive than the conventional tanning agents.

- **Tanning bath recycling.** This alternative leads to the effluent with the lowest salinity as well as to savings on the order of 25% of chrome used.

With regards to tanning bath recycling, there are two alternatives depending on the fact that a different bath is used for tanning or the same pickling bath is reused for tanning. In the first case, two basins must be provided in order to introduce pickling and tanning baths after being filtered or clarified. Subsequently, it will be necessary to adjust the ionic force of the pickling bath prior to the addition of acids as well as to know the chrome content of the exhausted baths in order to be adjusted.

In the latter case, tanning wastewater is reused as pickling bath for the next batch. The wastewater is reconstituted by adding the acid required to finish the operation and a small amount of salt, if necessary. After the time needed to finish the operation, the required amount of salt is added, which is normally 75% of the usual amount as the residual chrome in the bath should be taken into account.

In previous studies carried out at Mare Nostrum and INESCOP, the feasibility of recycling tanning-pickling baths was verified by checking that after seven cycles the bath was stabilised and the concentrations of the analysed parameters (chlorides, sulphates, chrome, conductivity and density) were kept constant being only necessary to add a small amount of reagents to obtain the desired concentration. Under these conditions, it was observed that the appearance of the leathers after tanning was normal, with no differences in colour or general appearance, and the physical and chemical properties were similar to those obtained by means of a conventional tannage.

Likewise, through pickling-tanning bath recycling tests at laboratory, it was checked that apart from carrying out a filtering and clarifying treatment for the elimination of solids, it was also necessary to eliminate bath fats as their accumulation in the wastewater was detrimental for the process.
2. Project approach.

The study of the problems above, the existing alternatives and the results obtained in previous tests led us to consider as the most feasible solution the recycling of the pickling-tanning bath, both due to the simple equipment necessary for the treatment of the bath to be recycled and for the easy controls to be carried out.

In this context the project "Tannery Wastewater Recycling in Leather Industries (TARELI)" was launched, which was selected by the European Commission within the LIFE-Environment Programme and developed by the Technological Institute for Footwear and Related Industries, INESCOP, in collaboration with the tannery CURTIDOS MARE NOSTRUM, S.L.

The TARELI project consisted of designing, building and setting up a Demonstration Plant for the treatment and recycling of pickling-tanning baths, with a treatment capacity of 25 m$^3$/day.

The main objective of the project is to demonstrate the feasibility of recycling pickling-tanning baths, ensuring the quality of the final product at all times and achieving, on the one hand, the reduction of saline pollution caused by pickling and tanning baths and, on the other hand, the reduction of chromium salt in tanning wastewater.

3. Project development.

The project began in October 2001 and from September 2002 the Demonstration Plant is installed at CURTIDOS MARE NOSTRUM, allowing the execution of real tests on pickling-tanning bath recycling to validate the proposed technology.

Thanks to the tests carried out at the Demonstration Plant it was possible to optimise the conditions under which the pickling-tanning bath should be recycled, mainly focusing on the treatment between cycles and the number of effective cycles without draining the bath. Subsequently quality control tests were conducted on the obtained leathers at INESCOP’s laboratories.

Finally, and given the characteristics of LIFE projects, during 2003 several activities for the dissemination of project results were carried out mainly consisting of fair exhibitions, publication of papers in specialised journals and at INESCOP’s web site, a report on project results and demonstration workshops in the Demonstration Plant at CURTIDOS MARE NOSTRUM.
3.1. **Demonstration Plant.**

The treatment and conditioning plant for pickling-tanning wastewater to be reused in the industrial process is equipped with the following systems:

- Wastewater channelling.
- Wastewater pre-treatment and pumping to the homogenisation basin.
- Treatment of the pickling-tanning bath to be reused by means of a flotation system for the elimination of fat and a clarifier to settle all the suspended leather particles.
- Storage, conditioning and control of the characteristics of the bath to be reused.

The functioning and the systems comprising the Demonstration Plant are shown in the layout in Figure 1.
Wastewater channelling.

Traditionally, the baths from the different process stages were drained by opening the drum valves and leaving the bath to drain to the ground to be subsequently gathered in collection boxes were the different wastewaters were mixed, thus making their reuse impossible. In order to avoid this drawback, the drain systems of the tanning drums have been modified by installing some curved channels equipped with a flexible outlet in order to separate the wastewater of the tanning drums (Figure 2). The new channels are equipped with a flexible hose to be connected to different outlets, according to the destination of the wastewater of the tanning drum (to be recycled or to be sent to the treatment plant for industrial wastewater).

Likewise, the way to discharge the pickling-tanning bath has been optimised for its total treatment and reuse, ensuring that all the bath is drained and avoiding, as much as possible, sweeping suspended matter. In this sense, emphasis was put on the definition of the drum rotating speed during draining, the valve opening and the type of channelling for bath collection.

Finally, the tanning wastewater is led to a channel where the system where fine leather particles sediment is located.

Figure 2. Channelling system (in blue colour) of pickling-tanning baths.

Pre-treatment

The channels collect the wastewater and lead it to the plant inflow channel, where the pre-treatment system is located (self-cleaning sieve) which separates all the solids bigger than 1 mm. The solids separated from the bath are pumped to an hydraulic press where they are crushed and introduced in a container for their subsequent disposal.

Pumping-homogenising basin

Once pre-treated, wastewater flows by gravity to the pumping basin equipped with a stirring system to keep the bath homogenised. Likewise, a level detector controls the system so that there is always an average level in the basin and preventing it from going below the safety minimum level to avoid problems in the pump and the stirring rod.

Flotation tank
From the pumping basin and by means of a pneumatic pump, the wastewater is led to the flotation tank, controlling the flow in order to ensure the operating parameters set for the system dimensions.

The flotation tank, which has a rectangular ground plan, is equipped with an air microbubble diffuser at the bottom. The microbubbles generated have a two-fold effect: the formation of foam and the desemulsification of fat that, together with small particles, floats with foam in the tank surface. A surface sweeper takes the foam to the flotation tank outlet, where it is separated and channelled to the sewer system of the company.
**Sedimentation**

The pre-treated wastewater flows by gravity to a truncoconical-shaped clarifier comprised of a stilling hood, a bottom sweeper, a perimetral outlet and a pneumatic valve for solids drain. The laminar flow within the clarifier is very low in such a way that the upward speed is lower than 0.4 m/h, which ensures that all the leather particles in suspension are settled. The bottom sweeper, equipped with a motor and a reducer rotating 360° every 30 minutes, leads the particles to the centre of the cone and the clarifier is drained after certain periods of time by means of a pneumatic valve with a timer so as to be able to modify draining times.

**Storage and recirculation**

The clarified water, free from fats and suspended solids, flows by gravity to the storage tanks (6 units with a capacity of 6 m³ each) which are interconnected in their bottom parts and where activated carbon air purification systems have been installed in the vent holes.

Besides, the system is equipped with level probes and a pH controller as well as a continuous conductometer in order to control the quality of the recovered liquor.

Finally, a manually operated pumping station takes the chromium liquor from the storage tanks to the drums inlet. The recovered liquor does not directly go into the drums, but it firstly goes into an intermediate tank serving as “lung” where some products are added in order to readjust the bath conditions.

Figure 3 shows the flotation, sedimentation and automatic control systems of the Demonstration Plant.

![Figure 3. Demonstration plant: flotation, sedimentation and control.](image)
3.2. Cyclic leather tanning tests. Technology validation.

After the setting up of the Demonstration Plant, cyclic pickling-tanning tests were carried out for technology validation, using the wastewater of a batch for the next one after being treated in the Demonstration Plant.

The cyclic tests have been carried out on leather with a homogenous origin preserved in a cold-storage chamber at Curtidos Mare Nostrum. No differences in colour or appearance of the tanned leathers were noticed in the tests.

With regards to the analytical parameters of the bath, the results show that the parameters analysed (pH, conductivity, density, chlorides, sulphates, chrome, solids in suspension and fats) are stabilised and the values obtained do not imply interferences in the pickling-tanning process. Figures 4, 5 and 6 show the stabilisation of these parameters from the third cycle.

**Figure 4.** Cyclic tanning tests. Evolution of sulphates, chlorides and chrome.

**Figure 5.** Cyclic tanning tests. Evolution of conductivity.
In parallel to the execution of these analyses, physical and chemical tests for quality control of the leathers were carried out, both on wet-blue and crust leathers. The results showed that there were no significant differences in the leathers obtained with recycled baths (samples with the reference “R”) in respect of the leathers obtained by the conventional process (samples with the reference “NR”). Therefore, both physical and chemical tests are within the limits established by the standard UNE 59-900.99, Footwear. Men’s footwear. Specifications and Test Methods.

As an example, Tables 1 and 2 show the results of the physical and chemical tests, respectively, on “crust” leathers obtained in the test no. 5, without recirculation (NR) and with recirculation (R) of the pickling-tanning bath.

<table>
<thead>
<tr>
<th>Test</th>
<th>Sample reference</th>
<th>TEST 5</th>
<th>Recommended value</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Sample reference</td>
<td>423025</td>
<td>423025</td>
</tr>
<tr>
<td></td>
<td>NR</td>
<td>R</td>
<td>NR</td>
</tr>
<tr>
<td>Thickness (mm)</td>
<td>2.0</td>
<td>2.1</td>
<td>2.0</td>
</tr>
<tr>
<td>Tensile strength (N/mm²)</td>
<td>Average</td>
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<td>25.0</td>
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<tr>
<td>Elongation at break (%)</td>
<td>Average</td>
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<td>70</td>
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<tr>
<td>Tear resistance (N)</td>
<td>Average</td>
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<td>167</td>
</tr>
<tr>
<td>Ball burst (mm)</td>
<td>&gt;10</td>
<td>&gt;10</td>
<td>&gt;10</td>
</tr>
</tbody>
</table>

Table 1. Physical tests on “crust” leathers obtained in the test no. 5, without recirculation (NR) and with recirculation (R) of the pickling-tanning bath.
<table>
<thead>
<tr>
<th>Test</th>
<th>TEST 5</th>
<th>Recommended value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample reference</td>
<td>423025</td>
<td>423025</td>
</tr>
<tr>
<td>Moisture content (%)</td>
<td>NR</td>
<td>NR</td>
</tr>
<tr>
<td>13.9</td>
<td>13.8</td>
<td>13.3</td>
</tr>
<tr>
<td>Chrome content (%Cr₂O₃)</td>
<td>NR</td>
<td>R</td>
</tr>
<tr>
<td>3.5</td>
<td>3.4</td>
<td>3.3</td>
</tr>
<tr>
<td>Acidity, pH value.</td>
<td>NR</td>
<td>R</td>
</tr>
<tr>
<td>4.1</td>
<td>4.2</td>
<td>4.1</td>
</tr>
<tr>
<td>Difference index</td>
<td>NR</td>
<td>R</td>
</tr>
<tr>
<td>0.5</td>
<td>0.4</td>
<td>0.4</td>
</tr>
<tr>
<td>Fat content (%)</td>
<td>NR</td>
<td>R</td>
</tr>
<tr>
<td>2.8</td>
<td>3.1</td>
<td>3.5</td>
</tr>
<tr>
<td>Colour</td>
<td>NR</td>
<td>R</td>
</tr>
<tr>
<td>Clean, intense</td>
<td>Normal</td>
<td>Normal</td>
</tr>
<tr>
<td>Feel</td>
<td>NR</td>
<td>R</td>
</tr>
<tr>
<td>Normal</td>
<td>Normal</td>
<td>Normal</td>
</tr>
</tbody>
</table>

Table 2. Chemical tests on “crust” leathers obtained in test no. 5, without recirculation (NR) and with recirculation (R) of the pickling-tanning bath.

4. Obtained results.

The project “Tannery wastewater recycling in Leather Industries” has successfully achieved the foreseen objectives. The scientific and technical results have been quantified and verified in the technology validation stage, obtaining the following results:

- Savings in consumption in the pickling-tanning bath:
  - 97% of water
  - 55% of salt
  - 21% of acids
  - 14% of chrome
  - 17% of basifiers

- Reductions achieved in the effluents:
  - 18% of conductivity upon entry into the Treatment Plant for Industrial Wastewater (TPIW)
  - 32% of chrome upon entry into the TPIW
  - 27% of chrome in purification sludge

- Quality maintenance in leathers
To summarise, the implementation of pickling-tanning bath recycling technology in the leather industries will involve the following benefits:

- Significant reduction of the environmental impact of the industrial activity due to a reduction in water consumption and effluent disposal,

- Improvement of competitiveness due to a reduction of costs derived from a lower raw material consumption,

- Possibility to create new jobs, both at the company for the installation maintenance and at auxiliary service companies, such as engineering offices, workshops, etc,

- Greater respect for the environment of the European tanneries.

Likewise, the development of the project can enhance the application of the proposed technology in other leather industries and in other countries by adjusting the operational parameters and the installation size to the needs of the companies, given that the recycling of pickling-tanning baths is a clean technology that can be extended to the largest number of leather industries. In addition, the development of this system can enhance the recycling of other tannery wastewaters such as liming and deliming baths.