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Best Available Techniques in Leather Tanning

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Abstract

In the last few decades, the decreasing level of natural resources together with greater environmental awareness has led to a redirection of industrial aims in many companies to make their production processes more sustainable. Nevertheless, despite the increasing environmental awareness, the tanning industry is still producing different environmental impacts throughout its industrial processes, in terms of resource consumption (hides and skins, water, chemicals, energy, etc) and in terms of generation of wastewater, solid waste and atmospheric emissions. As a consequence, the knowledge and implementation of alternative methods that reduce the environmental impact of the production processes need to be promoted even more.

In this context, the project "Promotion of best available techniques in the European footwear and tanning sectors (ShoeBAT)" was launched. This project is coordinated by INESCOP and supported by the European Commission under the LIFE programme. As its main activity, the project has created an electronic platform exclusive for the footwear and tanning industries. This platform offers easy and understandable access to the necessary information about the uses of more than 70 environmentally friendly techniques.

Apart from the clear benefit in general environmental terms that can be obtained from the implementation of such techniques, other non-environmental advantages can be achieved by using such information, such as the potential reduction in costs, but also the improvement in the corporate image.

This paper shows the results obtained in the project so far.

Keywords: environment, sustainability, information, techniques, technologies, leather, tanning.

1. Introduction.

The leather sector produces different environmental impacts throughout its industrial processes, in terms of resource consumption (hides and skins, water, chemicals, energy, etc) and in terms of generation of wastewater, solid waste and atmospheric emissions. The main environmental impacts come from solid waste and wastewater. For example, in a European tannery, in order to obtain one ton of leather, an average of 450 kg of chemical products are used, producing around 35-50 m3 of wastewater and 700 kg of different solid waste.

Considering that more than 180,000,000 m2 of leather were produced in Europe (Cotance Statistics 2012), the following environmental impacts may have happened:

-Wastewater: 50 million m3/year
-Solid waste: 740,000 tons/year
-Atmospheric emissions: 10,000 tons of VOC/year

In this context, the project "Promotion of best available techniques in the European footwear and tanning sectors (ShoeBAT)" was launched, its main goal being an electronic platform for retrieving the necessary information about the uses of more than 70 environmentally friendly techniques. The ShoeBAT project is coordinated by INESCOP with the collaboration of IPS (Instytut Przemyslu Skórzanago, Oddzial w Krakowie) in Poland and CGS (C.G.S. di Coluccia Michelle & C. sas.) in Italy, and supported by the European Commission under the LIFE programme.

Although during this project Best Available Techniques for footwear have also been identified, this paper will focus on BATs for tanneries.

2. Materials and methods.

As a preparatory action, various techniques that are more respectful towards the environment and could have several applications in the tanning industries have been identified and studied in depth. Especially in regard to the tanning industry, we have conducted an exhaustive study of the European Commission's document "Best Available Techniques reference document for the tanning of hides and skins" (Joint Research Centre 2013).

Other techniques, not included in the above mentioned document, have been studied and compiled; for example, the use of titanium or oxazolidine in the tanning process.

As a result, one study about the Best Available Technologies (BATs) has been realized. More than 70 techniques related to the tanning industry have been identified.

For compiling data, first of all a database was created, enabling the management of information in fields and indexing by key words. In this way it has been possible to manage the translation of the content of the e-platform into the four languages of the partnership (English, Spanish, Italian and Polish). It is worth mentioning that for indexing by keywords the General Multilingual Environmental Thesaurus has been used (European Environment Agency 2004).

Figure 1: ShoeBAT database.

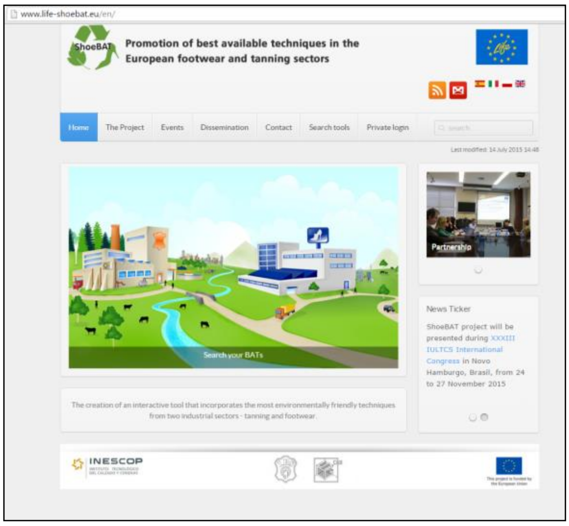

Figure 2: www.life-shoebat.eu

Updated information about the degree of implementation of BATs in the tanning industry has also been collected. With this objective, surveys were distributed by the partners among European tanning industries. These surveys have been also useful for checking the environmental awareness of the companies.

The core of the project consisted in the creation of an e-platform. This e-platform is actually capable of facilitating the knowledge and implementation of the best available technologies in the footwear and leather tanning industries.

Using the web application front-end, it is possible to access the information through a logic search engine, retrieving by key words or terms included in relevant fields of each BAT. It is important to note that the companies can make personalised queries about which of the various BATs would work best for a possible application in their industrial processes. It is also possible to retrieve the information in a printable format.

Apart from the search engine, the graphic image or recreational area of the platform has been developed. Different stages of the production processes of leather have been designed for this purpose. The user is able to obtain basic information of the BATs from the graphic image moving the cursor over the images. Once the user views the pop-up texts, it is possible to get more detailed information by clicking “Read More”.

Figure 5: Image of the e-platform and pop-up text

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A system for compiling contact data of suppliers has also been implemented in the platform. It contents data of equipment and chemical compounds suppliers for footwear companies and tanneries. A help desk is also available.

3. Results and discussion.

As a result of the analysis of the BATs included in the platform, below there is a summary of the Best Available Techniques for the tanning sector. Most of them are classified into the main production stage where they may be mainly applied.

3.1. Storage

One of the BATs at this stage is that the time of storage of the raw hides be as reduced as possible, using freshly flayed hides or skins. This way it will not be necessary to use salt preservation, pesticides or long cooling storage, with the consequent savings in energy, and water consumption in the beamhouse. Furthermore, the company will have the great advantage of avoiding the legal and sanitary consequences that the tannery may suffer from their final products being contaminated with forbidden pesticides or biocides. This means that proximity to the slaughterhouse is a guarantee for sustainability.

The removal of salt by mechanical shaking is also a relevant BAT to reduce the salinity of the wastewater of the whole process.

3.2. Beamhouse

The fact that the skins arrive to the tannery, not only in a short period of time after the animal is slaughtered but also as clean as possible, is highly relevant. As less manure is attached to the hides and skins less environmental impact will be reflected, as for example less solid waste, less wastewater and BOD (Biological Oxygen Demand) in wastewater to be treated in the water treatment plant.

With the implementation of green fleshing, which is a method of scrapping the flesh side before any processing or immediately after soaking instead of after liming, the company will use less chemical products. The surface of the hides and skins to be treated will be reduced and the fleshings will be free of chemical products. This way they can be used to get other by-products, for example tallow.

In order to reduce the concentration of hair waste in tannery effluents due to the degradation activity of sulphides in the unhairing process, sodium hydroxide can be used. It makes sulphide links found in hair and in the upper layer of the skin turn far more resistant, but this effect of increased resistance does not affect hair roots; therefore, the subsequent unhairing treatment using sulphides will act much more efficiently at hair roots, thus removing them from the skin, but preserving the structure of hair.

In order to reduce sulphide discharge into wastewater and due to the possible emission of hydrogen sulphide at the workplace, it is advisable to reduce the use of inorganic sulphides in the unhairing stage, for example using unhairing enzymes.

The effluents from the unhairing and liming processes may contain high concentrations of sulphur compounds. When the pH of these effluents falls below 9.5, hydrogen sulphide gas appears. A measure for avoiding this risk is oxidizing the effluents by biological means or by adding chemicals (SO4Mn2) before being mixed with other acid effluent or being discharged to the general mixing tank.

With respect to the mechanical operations in the stage, lime splitting is a relevant technique. The splitting of limed hides may be considered more environmentally friendly than splitting after tanning (blue splitting), since it saves chromium and yields a by-product that can be used for food casings or for the production of gelatine.

The use of ammonium compounds in deliming can be replaced partially or completely with the injection of carbon dioxide gas, thus reducing the nitrogen discharges into the atmosphere and wastewater. Besides, ammonium salts used in deliming may be partially or completely replaced with weak organic acids. The advantage of substituting ammonium salts is that ammonia levels in the wastewater are reduced.

3.3. Tanning

Waste chrome is contained in liquid waste, sludge and tanned solid waste. In general, chrome uptake under typical technological conditions is around 60 - 80% of the offer; therefore, chrome is a component that has to be strictly monitored because chrome discharge from tanneries is subject to strict regulations throughout the world. In practice, three principal measures to **maximize chrome utilization in tanning processes** should be implemented in tanneries:

Measures to be taken in previous process steps:

- Thorough liming produces more groups where the chromium complex can be bound.
- Splitting after liming facilitates chromium penetration and reduces chemical input.

Measures for ensuring high efficiency in the process:

- The chromium input should be optimized during conventional chrome tanning to reduce the possible waste (lowest possible quantity of chromium should be used).
- Use of short floats for reducing the chromium input, combining a low chromium input with a high chromium concentration.

Processing parameters (pH and temperature):

- Tanning cannot start at a temperature higher than 30 °C.
- Increasing float temperature progressively.
- Enough time must be allowed for penetration and reaction of chromium.

Salt-free systems, based on **non-swelling polymeric sulphonic acids** are available. This BAT reduces the discharge of chloride and sulphate salt and enhances the exhaustion in the tanning step.

Exhausted tanning floats may be reused at either the pickling or tanning steps. There are two options for the recycling of exhausted tanning liquors**:** Recycling the tanning liquors to the pickling process and recycling the tanning liquors to the tanning process.

Chromium recovery from tanning baths through precipitation and separation is also a BAT. Chromium precipitated by sulphuric acid is used for getting a new solution that can be used as a partial substitute for fresh chromium salts. This technique is used for the treatment of effluents from the chromium-tanning process including washing floats and liquid from sammying.

The development **of wet white pretanning systems using aldehydes** was undertaken for the reduction of chromium in effluents and solid waste. These systems have become more and more used for the production of chromium-free leather for specific applications. In particular, installations producing leather for the automotive industry.

Use of **pretanning agents to aid tannin penetration** and of **short floats** in drum tanning is also a good technique. These systems have a pretanning step in common with, for example, polyphosphates and/or syntans (synthetic tannins). The addition of syntans will make the vegetable tannins penetrate the hides quicker and hence reduce the tanning time.

3.4 Post tanning

In the same way as in the tanning process, some measures for optimizing parameters in retanning are **to control the levels of chemical input, the reaction time, pH and temperature**. These processing parameters should be controlled for minimizing chemical wastage and environmental pollution and maximizing the uptake of retanning chemicals.

The **exhaustion of the dyestuffs** is quite desirable. A very important factor for obtaining a high degree of fixation of dyes is to end the operation at a relatively low pH value.

Several process changes can be implemented to reduce metal discharges for example, using **high-exhaustion tanning, or ageing of chrome-tanned leather**. This way it will be possible to reduce leaching of the chromium during post-tanning. The slight increase in the metal content caused by this stage can be avoided if acid **dyes without metals** are used.

Optimized fatliquoring in order to ensure the maximum uptake of fatliquors can be relevant for reducing wastewater contamination, especially in the production of soft leathers, which require large amounts of fatliquor. Improvements can be achieved by higher exhaustion. The **addition of amphoteric polymers** improves the exhaustion of fatliquors.

The improvement of drying techniques to reduce energy use may be also implemented in the process. Some techniques can be: low temperature, drying machines with reduced energy consumption, careful control of temperature, humidity and time, elimination of the greatest amount possible of water in sammying, keeping the amount of exhaust air as low as possible.

The amino resins used in the post tanning stage to give the leather fullness and as penetrators of dyes may be substituted by **vegetable or proteinic agents**. So the presence of nitrogen in wastewater and formaldehyde in leather will be avoided. Besides, if the presence of ammonia is reduced traces of hexavalent chromium will disappear.

3.5. Finishing

Reduced amounts of waste and solvent emissions into the air are the main environmental benefits of implementing **curtain and roller coating**. The avoidance of the mist and solid particulate emissions associated with spraying is also beneficial in both techniques and, in the case of roller coating, wastage rates of 3-5% are reported as opposed to 40% for conventional spraying.

3.6 Wastewater treatment

The mechanical and physicochemical treatments have the main goal of getting a sludge that contains the pollutants from the effluents. The environmental benefits brought about by these techniques are relevant. Some of them are detailed below:

- Up to 30-40% of gross suspended solids in the raw waste stream can be removed by properly designed screens.
- Only with the mechanical treatment and by means of a preliminary settling operation, it is possible to remove up to 30% COD, thus saving flocculating chemicals in the next stage and reducing the overall quantity of the sludge generated.
- With the subsequent physico-chemical treatment, it is possible to achieve a reduction by up to 55-75% in the COD.
- A significant reduction in the concentration of substances in the wastewater, particularly chromium (up to 95%) and sulphides (up to 95%) can also be achieved.
- Preparation of wastewater for biological treatment.

Effluent from tanneries after mechanical and physico-chemical treatment may go through an additional **biological treatment**. Most biological treatment plants use the activated sludge (bio-aeration) method. This uses the metabolic activity of microorganisms in suspension. They convert the dissolved, biologically convertible contents into carbon dioxide and activated sludge.

The ammonium compounds in the wastewater are originated mainly from the use of chemicals containing ammonium compounds in deliming and dyeing and from proteins released in the beamhouse. These compounds can be removed by **biological nitrogen elimination** which is a process performed in two main steps: nitrification and denitrification.

In order to remove suspended solids after wastewater treatment, **sedimentation tanks or flotation** are used. The separation of the activated sludge from the purified overflow is normally carried out by continuous sedimentation in a post-purification tank. With sedimentation, the sludge is separated from the liquid phase by gravity settlement. Sludge can also be dewatered by means of **filter presses, belt presses, centrifuges and thermal treatment**.

3.7 Air emissions

Because of the limited applicability and effects of air abatement techniques, the best option to control VOC emissions is the **use of water-based chemicals for coating.** Without the implementation of solvent-free finishing, a large tannery could be evaporating 250 kg solvent per hour, half from the spraying machines and half from the driers. Final lacquers may contain 90 to 150 g solvent per m2 leather. Proposed legislation to control the emission of volatile organic compounds has stimulated the development of water-based alternatives to solvent-based finishes, mainly top coat lacquers.

Airborne particulate matter can arise in the handling of powdery process chemicals. For the most effective **control of dust** and to prevent fugitive emissions, the following considerations should be taken into account: dust should be controlled at source, for example using soluble packaging, operations and machines producing dust should be grouped in the same area to facilitate dust collection, and fans need to be purpose-designed for low power consumption and noise levels.

3.8 Waste minimization

Some measures to minimize the production of wastes in the effluent treatment plant are detailed below:

- Reduction of the input of process agents in order to decrease the effluent.
- Concentration and generation of sludge.
- Optimization of the type and the amount of precipitation agents applied.
- Separation of specific fractions of residues and different wastewater streams for efficient treatment and production of lower amounts of sludge.

The **reduction of waste production in the facilities** is also essential for an optimized waste treatment system. Organic materials are separated from the main product stream at various process stages. Hair residues can be compacted to reduce volume before further treatment or disposal, and can be used, for example, as a fertilizer. Also sheep wool can be used by the textile industry, e.g. in carpet manufacture. Wool can also be composted together with other wastes.

3.9 Substitution of substances

Possibilities exist for replacing halogenated organic compounds in degreasing either by using **non-halogenated solvents** or by changing over to **an aqueous degreasing system**. Linear alkyl polyglycol ethers, carboxylates, alkyl ether sulphates and alkyl sulphate can be used instead of halogenated solvents. Prevention measures such as closed systems, solvent recycling, emission abatement techniques and soil protection can also reduce the emissions.

It is possible to use fatliquors which do not contain halogenated compounds and do not require stabilization by organic solvents and perform with improved exhaustion. For example, methacrylates, silicone oils or modified silicone oils. The use of preparations containing more than 1% of chlorinated alkanes of chain length C10 to C13 is banned in the EU for the fatliquoring of leather (European Commission REACH 2006).

It is possible to use water-repellent agents, oil-repellent agents, and soil-repellent agents,

which do not contain halogenated organic compounds. For some types of leather products, both anti-soiling and water repellent properties are required at the same time, then a complete substitution is not possible. For leather requiring only a water-repellent finish, halogen-free water-repellent agents with a different chemical basis are used depending on the specified finish requirements.

Alternatives to halogenated flame-retardants exist for the leather industry. Flame resistance is possible by applying **appropriate syntans** and the addition of **melamine resins** in the retanning process. Also inorganic phosphorus compounds (such as ammonium polyphosphate) and silicon polymer products could be considered as an alternative to achieve fire resistance.

The use of nonylphenol (NPE) in leather processing is now restricted under the REACH Regulation. The main alternatives in the degreasing of sheepskins are linear alcohol ethoxylates with different chain lengths and ethoxylation degrees. These compounds show much lower toxicity than NPE and can be degraded to non-toxic.

3.10 Other processes.

Good practice to control the **emissions of noise and vibration** may use several techniques as the ones listed below:

- Preventative maintenance and replacement of old equipment can considerably reduce the noise levels generated
- Change of operating speeds so as to avoid creating resonances.
- Keeping as much distance as possible between the noise source and those likely to be affected by it.
- Use of resilient machine mountings and drives to prevent the transmission of vibration.
- Using a building designed to contain the noise or a noise barrier.
- Silencing of exhaust outlets.

It is good practice for **rainwater** falling on the roofs of the buildings and on the paved yard areas, which cannot be contaminated, to be collected separately from the process effluent so as to reduce the volume of water requiring treatment. With respect to these yard areas, they can be protected from contamination by permanent physical barriers.

4 Conclusion.

Environmental protection is a key factor for the future of the footwear and leather sectors. European environmental regulations are becoming stricter and companies must limit their emissions and discharges to even lower limits than those established in other production areas outside Europe, therefore they need to adapt their production facilities through the implementation of technologically advanced processes that bring about sustainable solutions. In this sense, **the Life ShoeBAT project will help footwear and tanning companies get to know and implement the techniques able to improve their environmental situation,** in terms of waste minimisation, reduction of water and energy consumption, among others. These savings in energy, water or waste are very likely to have a positive impact on the companies' economy in the medium or long term by reducing their costs.

1. Acknowledgements.

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