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Agenda item 7: Draft Guide towards a more sustainable tannery sector in the Mediterranean

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Chapter 1. Introduction

1.1 Introduction

This technical guide has been prepared under the Medpartnership project. The Strategic Partnership for the Mediterranean Sea Large Marine Ecosystem (MedPartnership) is a collective effort of leading organizations (regional, international, nongovernmental, etc.) and countries sharing the Mediterranean Sea towards the protection of the marine and coastal environment of the Mediterranean. The MedPartnership is being led by United Nations Environment Programme (UNEP) Mediterranean Action Plan (MAP) and the World Bank and is financially supported by the Global Environment Facility (GEF), and other donors, including the European Union (EU) and all participating countries.

This guide has been developed by UNEP-MAP with the support of the Regional Activity Center for Sustainable Consumption and Production (SCPRAC) on the framework of the project Sub-component 2.1 which aims at facilitating policy and legislation reforms for pollution prevention and control. This Sub-component seeks to develop and improve the legislative and institutional framework in the region and to implement National Action Plan (NAP) priority actions that will protect and reduce the inputs of contaminants to the Mediterranean marine environment from land based activities.

This document is also an update or extension work of the study developed by the SCPRAC in the year 2000 called "Pollution prevention opportunities in the Tanning sector industry within the Mediterranean region".

The present document, compared to the first version, is focused on providing updated pollution prevention options and specifically priority or immediate actions in the tanning industry in Mediterranean countries, although it can be applied worldwide. Due to the diversity of Mediterranean countries, this guide should be adapted to countries conditions. The final objective of this guide is to provide information to Mediterranean countries to establish a minimum set of pollution prevention actions, called in the text as "the 10 most immediate pollution prevention options" in the tanning sector that can lower the environmental and human health impact of the industry at a cost-effective level for the private sector.

1.2 Contents of the guide

This technical guide has been structured to show a minimum set of pollution prevention actions for the tanning sector that are crucial to lower the environmental and human health impact, easily implemented and at an affordable cost in any Mediterranean country.

Chapter 1 provides background information, the scope of the document and information on alternatives to leather that can prevent the environmental and human health impact while promoting local employment and sustainable economic opportunities.

Chapter 2 provides a summary of the associated environmental problems caused by the tanning sector in the air, water and soil vectors and main generated pollutants.

Chapter 3 describes a summary of some available tools to implement a sustainability policy in the tanning sector companies.

Chapter 4 provides first a summary of most pollution prevention opportunities in the tanning sector. Then the chapter describes the 10 most cost-effective pollution prevention actions needed to increase the sector efficiency and lower the environmental and human health impact of the tanning sector, especially in developing countries of the Mediterranean region.

Chapter 5 shows several case studies on pollution prevention opportunities, more sustainable companies and other cases in the tanning sector.

1.3 Prevention of pollution: Alternatives to leather

There are plenty of alternatives to leather that clearly consume less resources, water, energy and dangerous chemicals for its production per ton of leather or alternative product along its life cycle, including a reduction in its CO2 footprint.

Alternatives to leather might include plant-based textiles and leather products and petroleum-based textiles and leather.

Plant-based textiles and leather are renewable, biodegradable and non-toxic and are also an appealing opportunity for green entrepreneurship, especially in the increasingly demanding European market for green products. Local renewable resources might be used as materials to produce green alternatives to leather to lower costs, generate local employment, social benefits, sustainable economic activity and prevent pollution and human health problems. In this regard, please check the case study on Ecozap shoes in the case studies section of this document.

These bio-based materials used as a substitute of leather might be made of cotton, cork, kelp (ocean leather), hemp, jute, palm, palm-tree, seeds, organic cotton, natural latex, fiber of coconut, rind of rice, wood, sap of tree, bamboo, pure 100 % un-bleached and un-dyed natural wool, pineapple fibers, etc.

On the other hand, Petroleum-based textiles and leather might be less interesting from the sustainability point, since these products are not coming from renewable sources and cannot be considered as environmentally friendly. Petroleum-based textiles and leather might also be considered of high impact since they are non-renewable and produced with harmful substances such as polyvinyl chloride (PVC) and others. Some examples of petroleum-based leather might include poromeric imitation leathers (polyurethane plus polyester), corfam, leatherette, koskin, etc.

Chapter 2. Tanneries and the environment

2.1 Introduction

The environmental impact of tanneries might vary depending on the quality and quantity of generated pollution and the proximity of contaminant effluents to "receptors" (humans, plants, animals or ecosystems exposed to pollutants). Sensitive receptors include, for example, hospitals, schools, daycare facilities, elderly housing and convalescent facilities as well as ecosystems. These are areas more susceptible to the adverse effects of exposure to toxic chemicals, pesticides, and other pollutants.

When auditing an industrial site or tannery, it is important first to know the quality and quantity of pollutants being released into the environment and second, the type and proximity of receptors, in order to established a pollution prevention strategy to lower or eliminate the impact on them.

2.2 Water consumption

Water is a limited resource worldwide. The already existing water shortage in the Mediterranean is expected to grow in the future as water demand increases and climate change affects the availability of water. In addition, water pollution is also threatening the accessibility to good quality water due to poor waste water treatment, disposal and other pollution sources.

Managing water resources in a sustainable manner is crucial for the future of the Mediterranean basin. There is an urgent need to manage scarce water resources sustainably. Accurate water accountability is needed to know sources and uses of water, water flows, water stocks and services, for wise decision making to solve the problem.

Within the industrial sector, the tanning sector is considered a large consumer of water and heavy polluting industry. Water used may come from rivers, groundwater, municipal supply or from private-owned sources. High consumption of water and increased levels of environmental pollution deteriorate water quality, thus decreasing the amounts available for human consumption and other uses. This improper management of water resources is causing in some places scarcity of clean water and high human risk for local population and ecosystems.

Water consumption in the tanning sector includes process water, and also technical water which is needed for cleaning, energy use, waste water treatment, and sanitary purposes. Process water consumption varies greatly from tannery to tannery, depending on used technology, processes involved, raw material used, and manufactured products, but accounts for about 80% of the total water consumption. Technical water accounts about for the other 20% of total water consumption.

Water consumption significantly varies between tanneries and type of hides, but on average, is usually between 25 to 80 m3 per ton of hides. Minimum water use including process and technical water might be as low as 12 to 25 m3 per ton of hides, so there is an important room for improvement in the global tanning sector.

2.3 Impact on surface and groundwater

The composition of water effluents greatly varies between tanneries. Nevertheless, all untreated water effluents coming from tanneries might cause significant environmental impact.

Untreated wastewater discharged into close rivers or water canals eventually reaching the sea, will deteriorate rapidly the physical, chemical, and biological properties of the receiving water bodies. Untreated wastewater contains three main types of matter and chemicals that cause great damage:

- Suspended solids;
- Organic matter and;

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- Chemicals and toxic residues.

First, suspended solids are mainly generated in the effluents of the liming process. Suspended solids such as lime or insoluble salts will cause turbidity on the water and by settlement damage on the bottom of the receiving water body destroying habitats, microorganisms and other living life.

Second, organic matter decomposes in the water at a high pace depleting the dissolved oxygen necessary for this process and also causing noxious odors. Due to the fact oxygen is vital for aquatic life, dissolved oxygen would highly affect water biodiversity.

Third, chemicals and toxic residues might vary depending on the final product and chosen processes but chemical such as sodium sulphide, calcium hydroxide, acids, carbonates, sulphites, sulphates, chromium, ammonia, solvents, etc. are usually generated in the tanning processes. The discharge of these chemicals makes the water unsafe for any domestic usage or recreational activity.

Groundwater is another important source of water supply. When wastewater from ponds, pipes, drains or direct discharge on land and chemicals from inadequate storage and spills, percolate into the soil, dangerous tanning pollutants can reach the groundwater. The above mentioned tanning pollutants can reach the groundwater causing contamination of the water supply for local communities and a serious threat to human health. In addition, less groundwater is available for water supply, causing even more stress on water resources or water shortage.

2.4 Impact on land

Inadequate environmental management at tanneries and especially on the management of wastewater, chemicals and hazardous waste can importantly damage the underlying soil. This soil impact can occur on pits and ponds, storage areas of chemicals and hazardous waste, waste dump areas, etc.

Discharging untreated or highly polluted wastewater, chemicals or hazardous waste on land might greatly disrupt any future use of the land such as for agriculture, recreation or urbanization. Contaminated soil might be unsuitable for agriculture production, recreation purposes and urbanization for a long period of time unless expensive decontamination measures are taken.

In regards to chemicals and hazardous waste, poor storage and management might cause great impact on land. If chemicals or hazardous wastes are dumped on land, this will cause damage on soil and eventually on groundwater as pollutants will slowly percolate until reaching aquifers and then moving into pumping wells that might be used for water supply or agriculture purposes, causing the introduction of pollutants in the food chain.

2.5 Impact on air

The impact on the air from the tanning activity might come from the production of different gaseous emissions such as:

- Odors
- Hydrogen sulphide, ammonia and sulphur dioxide
- Volatile Organic Compounds (VOCs)
- Dusts and other particulates
- Gases coming from energy source

Odors. Odors might occur from decaying biological material of poorly managed waste, improperly stored and cured hides, poorly maintained waste water treatment plant, beamhouse processes and some toxic substances such as hydrogen sulphide, ammonia, etc.

Hydrogen sulphide, ammonia and sulphur dioxide. Sulphide emissions are coming from dehairing and waste treatment while ammonia emissions come from un-hairing and de-liming liquors and the decomposition processes. Sulphur dioxide emission comes from post-tanning operations.

Volatile Organic Compounds (VOCs). VOCs coming from the consumption of organic solvents in the degreasing of sheepskins and finishing operations might be emitted on posing a workplace health problem. These emissions can be avoided if the applied technology and controls at the plant are efficient.

Dusts and other particulates. Leather dust and other particulates might arise from mechanical operations such as dry shaving, milling drums, buffing and staking and during the handling of powdery chemicals. Leather dust and other particulates are considered as a potential carcinogen for exposed workers.

Gases coming from energy source. These gases are usually emitted from boilers and energy generators, including typical air pollution contaminants such as CO, CO2, NOx, and SOx.

In order to protect the environment, workforce health and the surrounding area of the plant from odors and harmful emissions, special attention should be devoted at least to the emission values of ammonia, hydrogen sulphide, volatile organic compounds (VOCs), total particulate matter, carbon monoxide and nitrogen oxides.

2.6 Impact on waste management systems

By-products and waste generated during leather production might include trimmings from raw hides, lime fleshing, lime split and pelt trimmings, chromium shavings, chromium split, chromium leather trimmings, buffing dust, finishing chemicals, sludge from waste water treatment, packaging, salt, organic solvents, residues of process chemicals and auxiliaries, fats from degreasing, finishing sludge, residues from air abatement other than buffing dust, such as activated carbon filters and sludge from wet scrubbers, and residues from waste treatment.

In order to avoid these by-products and wastes to be disposed in landfills and create harmful odors, severe soil and groundwater contamination and adverse health effects on local population, an environmentally sound management and recycling of each by-product and waste should be developed at local level. Tanneries produce some by-products that can be used by other actors. For wastes that cannot be used or recycle, a final disposal option must be found and might vary depending on local conditions and infrastructure.

In addition, if untreated wastewater is discharged in the municipal wastewater system, this might cause encrustation in sewers, solid deposition, corrosiveness of wastewater pipes and malfunctioning of wastewater treatment plant biological processes from chemicals discharge.

If waste is finally sent to landfills, special linings and leachate treatment systems should be installed to control the percolation of chemicals and sludge into the soil and groundwater, and eventually reaching the water supply and surrounding ecosystems.

2.7 Minimum recommendations for proper environmental management

In order to improve the environmental management of tanneries and lower environmental and human health impacts, the following minimum environmental management measures (not technological) are recommended to implement in any tannery:

1. Chemicals and hazardous waste. All chemicals, hazardous waste and fossil fuels should be stored on a covered and paved area with secondary spill containment with at least equal capacity to the stored quantity, in order to prevent soil and groundwater contamination.

Hazardous waste should be stored to a maximum of 6 months and then properly manage for final elimination or recycling (and complying with local legislation).

- 2. Chemicals, by-products and waste. No chemicals, hazardous waste, non-hazardous waste and by-products should be dumped, burned or buried anywhere. These hazardous materials should be sent to authorized landfills or handed to authorized waste management companies.
- 3. Wastewater. Before discharging any wastewater into the municipal sewer system or any other location, a previous characterization of the wastewater stream and continuous monitoring must be implemented to comply with local environmental legislation.
- 4. Wastewater. No untreated or highly contaminated wastewater should be discharged in close rivers, water canals, groundwater and land, to avoid high environmental, economic and social impact.
- 5. By-products and waste. All potentially hazardous waste must be characterized (analyzed) in order to know if the waste can be classified as hazardous or non-hazardous, and implement appropriate management and recycling for each type of waste.
- 6. By-products and waste. An environmentally sound management and recycling plan of every generated by-product and waste should be developed collaborating with the local public administration.
- 7. Odors. In order to prevent odors, it is necessary the correct management of accumulated wastes, cured and stored hides, beamhouse processes and the wastewater treatment plant.
- 8. Emissions. All air emissions should be characterized (analyzed) setting limited emission values according to local environmental legislation and health and safety standards.
- 9. Emissions. If possible, the use of renewable energy should be implemented to avoid greenhouse and other harmful emissions while lowering costs and providing local employment opportunities (renewable energy is locally produced).

Chapter 3. Tools for a more sustainable tannery

3.1 Introduction

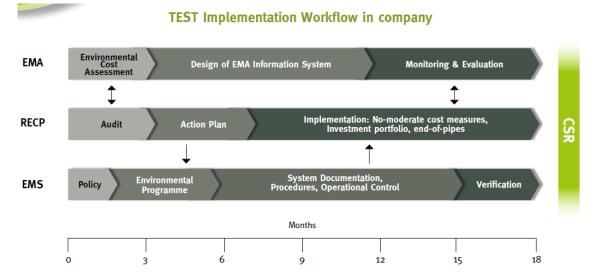
This chapter describes a summary of some available tools for tanning sector companies that can be useful to improve its efficiency, company value and profitability, improve the environmental management, meet international environmental standards for export, improve companies' image and reputation and advance on the sustainability and responsibility path.

3.2 Transfer of Environmentally Sound Technology (TEST)

The Environmentally Sound Technology methodology was developed by United Nations Industrial Development Organization (UNIDO) in 2000 and is aimed at improving environmental management and competitiveness of companies in developing countries and with transition economies.

The Transfer of Environmentally Sound Technology (TEST) methodology consists of five management tools at company level with the aim of changing management practices in a holistic manner in order to ensure the sustainable introduction of green practices.

TEST combines the essential elements of tools like Resource Efficiency & Cleaner Production (RECP), Environmental Management Systems (EMS) and Environmental Management Accounting (EMA) as part of Corporate Social Responsibility (CSR), applied on the basis of a comprehensive diagnosis of enterprise needs (Initial Review). As a result of the customized integration and implementation of these tools and their elements, the key output is the adoption of best practices, new skills and management culture, enabling the company to carry on the improvement journey towards sustainable entrepreneurship. TEST is building on management of change and addresses not only the operational level of a business, but also the managerial and strategic levels.



For more information, please visit the website: <u>www.unido.org/en/what-we-do/environment/resource-</u>efficient-and-low-carbon-industrial-production/watermanagement/test.html

3.3 Best Available Techniques (BAT) Reference Document for the tanning of hides and skins

The BAT reference document for the Tanning of Hides and Skins forms part of a series presenting the results of an exchange of information between European Union (EU) Member States, the industries concerned, non-governmental organizations promoting environmental protection and the Commission, to draw up, review, and where necessary, update BAT reference documents as required by Article

13(1) of the Directive 2010/75/EU of the European Parliament and the Council on industrial emissions (integrated pollution prevention and control).

The BAT reference document (BREF) on Tanning of Hides and Skins was adopted by the European Commission in 2013. This document is the result of a review of that BREF. The review commenced in April 2007.

Chapters 1 and 2 provide general information on the tanning of hides and skins and on the industrial processes and techniques used within this sector. Chapter 3 provides data and information concerning the environmental performance of installations within the sector, and in operation at the time of writing, in terms of current emissions, consumptions and nature of raw materials, water consumption, use of energy, and the generation of waste. Chapter 4 describes in more detail the techniques to prevent or, where this is not practicable, to reduce the environmental impact of installations in this sector that were considered in determining the BAT. This information includes, where relevant, the environmental performance levels (e.g. emission and consumption levels) which can be achieved by using the techniques, the associated monitoring and the costs and the cross-media issues associated with the techniques. Chapter 5 presents the BAT conclusions as defined in Article 3(12) of the Directive. Chapter 6 presents information on 'emerging techniques' as defined in Article 3(14) of the Directive. Concluding remarks and recommendations for future work are presented in Chapter 7.

For more information, please download the document: <u>https://ec.europa.eu/jrc/en/publication/reference-reports/best-available-techniques-bat-reference-</u> <u>document-tanning-hides-and-skins-industrial-emissions</u>

3.4 The Leather Working Group

The Leather Working Group (LWG) was formed in April 2005 to promote sustainable and appropriate environmental stewardship practices within the leather industry. As part of this the LWG created a protocol to accurately assess the compliance and environmental stewardship practices of leather manufacturers. The group endeavors to promote improvement in the tanning industry by creating alignment on environmental priorities by bringing visibility to best practices and providing guidelines for continual improvement. It is the group's objective to work transparently, involving tanners, brands, retailers and other relevant supply chain representation with input from leading centers of excellence within the leather industry and the utilization of peer reviews from non-governmental organization (NGO) bodies, academic institutions and other stakeholder organizations.

The environmental auditing protocol and reporting mechanism have been developed and refined during each phase of the project in conjunction with the brand, tanner and supplier members. The protocol is seen as a dynamic improvement tool and is regularly reviewed by the members of the LWG to ensure that it is both challenging but realistic and achievable. It aims to tackle important topical issues, and reflect improvements or changes of technology within the sector.

For more information, please visit the website: <u>www.leatherworkinggroup.com</u>

3.5 European ecolabel: footwear

The EU Ecolabel helps consumers identify products and services that have a reduced environmental impact throughout their life cycle, from the extraction of raw material through to production, use and disposal. Recognized throughout Europe, EU Ecolabel is a voluntary label promoting environmental excellence which can be trusted.

One of the European ecolabels is on footwear products. The ecological criteria for footwear (Decision 2009/563/EC) are in some cases process related (i.e. emissions from the production of material, use of Volatile Organic Compounds during final assembly). In other cases they are related to the use of certain materials or substances and in other cases they are related to the final product.

These criteria aim in particular at limiting the levels of toxic residues and the emissions of volatile organic compounds, and at promoting a more durable product. Appropriate test ensure that the product is conform to fitness for use.

The EU Ecolabel logo on footwear tells consumers the following about footwear products: Limited water pollution during production, reduction of emissions of volatile organic compounds during production, exclusion of substances harmful for the environment and health, limited residues of metals and formaldehyde in the final product, use of recycled packaging and careful control of different aspects of durability.

In addition, the product also complies by excluding or limiting the use of substances such as exclusion of certain azo dyes, exclusion of PVC (except recycled PVC for outsoles), no arsenic, cadmium and lead in the final product, limited use of formaldehyde and hexavalent chromium, etc.

For more information, please visit the website: http://ec.europa.eu/environment/ecolabel/products-groups-and-criteria.html

3.6 Corporate Responsibility

Corporate Responsibility (CR) is a business strategy and approach that creates long-term shareholder value by generating opportunities and managing risks deriving from economic, environmental and social developments in an increasingly resource-constrained world. Leading corporate responsibility companies create long-term shareholder value by gearing their strategies and management to harness the market's potential for sustainability products and services while at the same time successfully reducing and avoiding sustainability costs and risks that competitive companies must address.

CR is also the commitment of business to contribute to sustainable economic development, working with employees, their families, the local community and society at large to improve their quality of life while preserving the environment.

Corporate Responsibility strategy for companies includes measuring and performing not only at economic-financial level but also at social and environmental levels, what we called the triple bottom line.

The benefits are quite notorious. Economic benefits include augmenting the value of the company, improving the company transparency and accountability, improving good governance, improving risk management and license to operate, reducing risk and fines, applying a code of business ethics, etc.

Environmental benefits might include reducing energy, water and materials costs, improving waste management and recycling and re-use of materials, lowering wastewater streams, reduce chemicals and associated risks and costs, reducing air emissions and noise, increasing the use of renewable energy, etc.

Social benefits include improving employee benefits, labor conditions and productivity while retaining intellectual capital and talent, improving health and safety and workplace conditions, improve employee training and education, avoid children workforce, provide equal opportunities for all, respect human rights, etc. Other benefits include improving corporate reputation and image, improving stakeholder dialogue and partnership, implementing responsible marketing, etc.

Some of the key issues to advance on corporate responsibility include business innovation, ecoefficiency, establishing a stakeholder dialogue and partnership, establishing ethical values, and improving company image and reputation.

Chapter 4. Pollution prevention options

This chapter is focused on providing updated pollution prevention options for the tanning industry in the Mediterranean. The first section of this chapter is specifically devoted to present priority or immediate actions that could be taken in the tanning industry in Mediterranean countries, although it can be applied worldwide. The called below "10 most immediate pollution prevention options" are establishing a minimum set of pollution prevention actions in the Mediterranean tanning sector which are considered by the authors as most cost-effective to lower the environmental and human health impact of the tanning activity.

The second part of this chapter includes a summary of Best Available Techniques (BAT) considered adequate for achieving a high level of environmental protection in the leather tanning industry.

4.1 The 10 most immediate pollution prevention options

The 10 proposed most immediate pollution prevention options for the Mediterranean tanning industry are the following:

Fiche 1 (Storage): Removal of salt

Fiche 2 (Beamhouse): Enzymatic unhairing

Fiche 3 (Tanyard): Increasing the efficiency of chromium tanning.

Fiche 4 (Post tanning): Substitution of nitrogenous compounds in post-tanning.

Fiche 5 (Finishing): Curtain or roller coating (non-spraying)

Fiche 6 (Wastewater treatment): Mechanical and physico-chemical treatment.

Fiche 7 (Air emissions): Water-based chemicals for coating.

Fiche 8 (Waste minimization): Organic waste fractions and by-products

Fiche 9 (Substitution of substances): Substitution of octylphenol and nonylphenol ethoxylates in the aqueous degreasing of sheepskins.

Fiche 10 (Other): Process water management.

Fiche 1 (storage): removal of salt

BAT No. 1

STAGE: STORAGE

BAT: REMOVAL OF SALT

The reduction of salts present on cured hides or skins would be necessary to reduce salinity of the wastewater generated during the soaking stage at the beginning of the tanning process.

Technical description

Wet salting is one of the most commonly used hide and skin curing practices in the world. Salt is generally cheap and widely available: it has good dehydrating properties. Curing salt is removed during soaking and discharged into waste soak streams. The salt discharged into the soak liquor increases the total dissolved solids content of ground water. Of late, the negative environmental implications of saline effluent from tanneries have been the object of increased attention, particularly those aspects related to high total dissolved solids (TDS) and chlorides.

Dry salted hides are opened out for processing in such a way that they are shaken or tumbled, so that loose salt crystals fall off and are not taken into the soaking process, avoiding that this salt pollutes the wastewater. This operation can be carried out mechanically by using industrial automatic equipment or by manual means. It is estimated that around 6-8% of the original salt content of the hide is eliminated, corresponding to about 5% of the total salt discharge from the tannery.

To test the efficacy of the technique, the treated batch of hides/skins may be shaken again and the loss in weight must not exceed 1%.

Environmental benefits & Driving forces

- Desalting of raw stock reduces TDS level in the composite tannery wastewater by about 15%. Practically, it has been seen that TDS in the composite effluent of a tannery processing salted raw hides/skins to semi-finished leather is reduced from 12,000-18,000 mg/l to 10,500-15,700 mg/l (corresponding to about 5% of the total salt discharge from the tannery) on account of desalting of raw stock, collection and proper disposal of the dusted salt,
- No commercially viable technology for removing salts from the tannery has been developed to date.

Cross media effects

- Mechanically shaking off the salt can influence the quality of the hides. The salt crystals can produce abrasion of the grain during drumming.
- The recovered salts might be disposed of at appropriated landfills.
- The reuse of salt is not easy since it might be too dirty to be used in the pickle liquors without sterilization with heat.

Economics

- Mechanical desalting of raw hides requires an investment in equipment for de-salting. The cost of an industrial desalting drum of 7.70 x 2.70 x 3.90 m (length x width x height) is about EUR 47,000.
- In the case of small skins (lamb, goat, etc.) and/or small batches, it is also possible to reduce salt content in raw skins using simple manual equipment that does not require high investments, although it is more labour intensive and less efficient than mechanical equipment.
- An option to save costs may be centralized removal and collection systems.
- Though desalting may not directly result in considerable financial benefit, indirect benefits include more efficient soaking, reduction in the volume of soak liquor discharged and in total

dissolved solids (TDS) and chlorides contained on it, which prevents salt entering the groundwater and soil.

Equipment

- Mechanical desalting: Mechanical desalting drum or a brush type desalting machine.
- Manual desalting: Dome type wooden frame.

- EC, BREF on Tanning of Hides and Skins. Joint Research Centre. 2013.
- Pollution Prevention Opportunities in the Tanning Sector Industry within the Mediterranean Region. Regional Activity Centre for Cleaner Production (RAC/CP)
- Desalting of Raw Hides/Skins and Reuse of Dusted Salt in Pickling Operation. UNIDO, 2001: http://leatherpanel.org/content/desalting-raw-hidesskins-and-reuse-dusted-salt-pickling-operation

Fiche 2 (beamhouse): enzymatic unhairing

BAT No. 2

STAGE: BEAMHOUSE

BAT: ENZYMATIC UNHAIRING

Separation of the hair from the epidermis by the addition of enzymatic products, avoiding the use of sulphide.

Technical description

By means of unhairing and liming, the hair is removed from the skin and the epidermis and collagen fibers are loosened. This process is usually carried out by adding lime and sulphides, as well as small quantities of amines and surfactants. Recently, some improvements have been implemented in this process, for instance hair-save unhairing and the reduction of sulphide dosage or replacement with lower environmental impact products, such as unhairing enzymes.

In this case, the sulphide-free unhairing process is realized by the addition of enzyme products (protease and keratinease) in alkaline medium (pH 11-12), without sulphide salts. Then, the hair is loosened and the mechanical effect separates it from the epidermis. In addition, the enzymes cause the swelling of the skin, preparing it for the later stages. It is recommended to remove continuously the hair from the float using a recirculation and a filter system.

The amount of products used in tanneries, whether these are of chemical or any other nature, should be adjusted to the optimal formulations for each process and type of leather. Over-dosing can result in higher production costs and greater environmental impacts, since the excess product becomes waste. However, under-dosing can be detrimental to the final product quality and also has financial repercussions, in addition to the environmental risk that may be caused by final products that cannot be commercialised and end up as waste. Therefore, a good and simple practice consists in weighing the products to be used and adjusting the dosage to each process and type of leather. This not only improves the environmental impact but also brings about savings in production costs.

Environmental benefits & Driving forces

- Lower environmental impact in the wastewater given that sulphides are not used.
- Hair is removed in solid form so the level of wastewater pollution (COD) is reduced.
- Reduction of the consumption of water (less washes than using sulphide).
- The treatment of wastewater needs less stages and reagents (because the sulphide oxidation is not necessary) and produces less sludge.
- The toxicity of wastewater is reduced since the enzymes are not persistent and they are easily inactivated and biodegradable.
- Enzymes allows smooth removal of hide hairs, imparts cleaner grain surface improving softness and area-yield.

Cross media effects

- Monitoring, well prepared staff and constant analytical controls to maintain optimum operating conditions and to avoid problems of quality in leathers (grain looseness).

Economics

The cost in chemicals (sulphide-substituting enzymes) can even double, and the costs of maintenance and control of the new process are higher. However, this increase in cost can be balanced out through a decrease in the cost of wastewater treatment because in the water treatment plant the stage of oxidation of sulphides disappears, which implies a significant reduction in investment and exploitation costs (mainly due to the high energy consumption of aeration systems).

- Decrease in sludge volume and therefore in the costs of its disposal.

Equipment

The process is carried out in the same premises without the need to make modifications since it is just a change of reagents.

- Buckman. Enzymatic soaking and liming: advances on the search for sustainability. Technical workshop of the AAQTIC. Buenos Aires, Nov. 2013
- Pollution Prevention Opportunities in the Tanning Sector Industry within the Mediterranean Region. Regional Activity Centre for Cleaner Production (RAC/CP)

Fiche 3 (tanyard): increasing the efficiency of chromium tanning

BAT No. 3

STAGE: TANYARD

BAT: INCREASING THE EFFICIENCY OF CHROMIUM TANNING

It is relevant to optimize the parameters of the process to increase the proportion of the conventional chrome-tanning agent taken up by the hides or skins.

Technical description

Chrome tanning is the most common type of tannage in the world. Chrome tanned leathers are characterized by top handling quality, high hydro-thermal stability, user-specific properties and versatile applicability. Waste chrome from leather manufacturing, however, poses a significant disposal problem. Waste chrome is contained in liquid waste (spent floats from tanning and re-tanning, as well as waste from sammying and draining), sludge (dewatered slurry resulting from sedimentation of suspended solids during physico-chemical effluent treatment) and tanned solid waste (split, shavings, buffing dust as well as crust and finished leather trimmings).

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 maximizing 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 must 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.
- End values of above 50 °C and pH 4 are recommended if they are compatible with good leather properties.
- Enough time must be allowed for penetration and reaction of the chromium.

It is possible achieving up to 90% chromium uptake by respecting both physical (pH, temperature) and chemical parameters (float levels, chromium input).

The amount of products used in tanneries, whether these are of chemical or any other nature, should be adjusted to the optimal formulations for each process and type of leather. Over-dosing can result in higher production costs and greater environmental impacts, since the excess product becomes waste. However, under-dosing can be detrimental to the final product quality and also has financial repercussions, in addition to the environmental risk that may be caused by final products that cannot be commercialised and end up as waste. Therefore, a good and simple practice consists in weighing the products to be used and adjusting the dosage to each process and type of leather. This not only improves the environmental impact but also brings about savings in production costs.

Environmental benefits & Driving forces

The advantages are:

- lower consumption of water and tanning agents
- lower volume of wastewater
- lower amount of chromium contained in waste and effluents
- lower amount of chromium in the sludge generated during wastewater treatment

In general, leather manufacture produces a chrome discharge of 3-7 kg Cr/t hides, which corresponds to a concentration of 60-140 mg Cr/l in mixed wastewater streams with a water consumption of 50 m3/t hides. Increasing the efficiency of the tanning process, the chrome concentration ranges between 10 and 14 mg Cr/l, with a standard effluent production of 30 m3/t hides. After precipitation, a concentration of about 1 mg Cr/l should be attained, below the legislative requirements most frequently stipulated (1-4 mg Cr/l).

Cross media effects

None

Economics

Some figures of implementation of short floats:

- Savings in chromium salts (28%) and water (40%).
- Saving in wastewater treatment as 30% reduction of chrome in effluents (before treatment).

Equipment

- The technique can be applied more easily when new installations are built or when new drums are installed.
- Tanneries equipped with steam sources can have drums featuring automatic tanning bath heating systems using steam injection (indirectly to avoid hide damage by means of internal distributors), with an added cost of 3,500 €:
- Where steam is not available, drums are equipped with an external tanning bath recirculation system which is heated by a heat exchanger. The costs of this system are more variable and depend on the drum size, type of exchanger fluid (water/oil), etc. By way of example, for a large drum (up to 4.50 m wide) the system requires a thermal oil heat exchanger, which increases the cost by 18,000 €. For smaller drums, this cost is reduced because a hot water exchanger is enough.
- Extensive adaptation is required to use existing drums for heated processing because a heating system and automatic process control equipment are required. However, not all existing drums are suitable for such adaptations.

- EC, BREF on Tanning of Hides and Skins. Joint Research Centre. 2013.
- Chrome Management in the Tanyard. UNIDO, 2000: http://leatherpanel.org/content/chrome management in the tanyard
- www.olcinagroup.com

Fiche 4 (post tanning): substitution of nitrogenous compounds in post-tanning

BAT No. 4

STAGE: POST TANNING

BAT: SUBSTITUTION OF NITROGENOUS COMPOUNDS IN POST TANNING

Substitution of amino resins in the retaining stage (urea-formaldehyde and melamine-formaldehyde) and ammonia, used as a dye penetrator.

Technical description

In the post-tanning operations some nitrogen compounds are used to give the leather fullness (by means of amino resins as urea formaldehyde or melamine formaldehyde resins) and as a 'penetrator' for dyes (by means of ammonia), which causes the presence of nitrogeneous species in the process wastewater.

The amino resins should be replaced with other filling agents (for instance, vegetable or proteinic retanning agents) to avoid the presence of nitrogen in wastewater as well as the presence of free formaldehyde in leather.

Furthermore, ammonia can be substituted as a penetrator of the dyestuff because it could also cause the formation of traces of hexavalent chromium in leather. Alternatively the penetration of the dyestuff through the substrate can be aided by thorough neutralization using neutralizing syntans and natural or synthetic anionic retanning agents prior to dyeing.

Additionally, ammonia-free dyeing can be improved by using short and cold dyeing bath, better pH control of the leather cross-section prior to dyeing and, if necessary, by increasing the penetration time.

The amount of products used in tanneries, whether these are of chemical or any other nature, should be adjusted to the optimal formulations for each process and type of leather. Over-dosing can result in higher production costs and greater environmental impacts, since the excess product becomes waste. However, under-dosing can be detrimental to the final product quality and also has financial repercussions, in addition to the environmental risk that may be caused by final products that cannot be commercialised and end up as waste. Therefore, a good and simple practice consists in weighing the products to be used and adjusting the dosage to each process and type of leather. This not only improves the environmental impact but also brings about savings in production costs.

Environmental benefits & Driving forces

- Discharges of nitrogen can be avoided if the proposed techniques are used.
- The substitution of amino resins with other filling agents for improving the leather fullness avoids the possibility that traces of free formaldehyde may appear in leather.
- The substitution of ammonia as a penetrating agent avoids the possibility that traces of hexavalent chromium may be formed in leather.

Cross media effects

None

Economics

- The costs of vegetable or proteinic retaining agents are slightly higher than the cost of amino resins (around 2-2.5 €/kg compared with 1,8-2 €/kg). Likewise, the cost of a penetrator of the dyestuff is much higher than the cost of ammonia (around 1.5 €/kg compared with 0.5 €/kg).
- This technique imply a slightly increase in process costs, which is balanced out through a decrease in the cost of wastewater treatment because in the water treatment plant the stage of

nitrification/de-nitrification disappears, which implies a significant reduction in investment and exploitation costs (mainly due to the high energy consumption of aeration systems).

- By replacing these products, formaldehyde presence in leather is avoided, as well as the possible formation of hexavalent chrome, which can avoid severe financial losses due to returns/retention of non-compliant goods, fines, etc.

Equipment

The process is carried out in the same premises without the need to make modifications, since it is just a change of reagents.

- EC, BREF on Tanning of Hides and Skins. Joint Research Centre. 2013.
- Ludvik J., The scope for decreasing pollution load in leather processing, 2000.
- Suppliers, 'Information from various suppliers to the tanning industry (suppliers of chemicals and machines)', Personal Communication, 2008.

Fiche 5 (finishing): non-spraying curtain or roller coating

BAT No. 5

STAGE: FINISHING

BAT: CURTAIN OR ROLLER COATING (NON-SPRAYING)

The leather to be finished is fed into the machine through a curtain of liquid or by impregnated rollers.

Technical description

Curtain coating:

The leather is fed through a curtain of liquid, which is deposited onto the leather surface. The technique is used for the application of heavy finish layers. The technique requires the use of specific equipment.

Roller coating:

The finish is applied by grit rollers to the surface of the leather, similar to the process used in printing. Differences exist concerning the grit size of the roller, the direction of application and the speed of the conveyor and the rollers. The operation needs careful adjustment with respect to speed, viscosity and cleaning of rollers to produce the desired quality. It might not be applicable to very thin leathers. This process is used especially, but not exclusively, to treat large pieces of leather.

Environmental benefits & Driving forces

- Reduced amounts of waste and solvent emissions to air are the main environmental benefits.
- The avoidance of the mist and solid particulate emissions associated with spraying is also beneficial.
- Roller coating wastage rates of 3-5% are reported as opposed to 40% for conventional spraying.

Cross media effects

The roller coating technique is not as flexible as spraying and can be applied only for the production of leathers with a coated grain, not for aniline, aniline-type or semi-aniline leathers.

Economics

The cost of a curtain machine is around EUR 75,000. The cost of a reversed roller coating machine (3000 mm) equipped with a feeder and three rolls is approximately EUR 175,000.

Equipment

The technique can be applied to both new and existing plants, but involves the purchase of new equipment as curtain machines or roller coating machines. In case of implementation of a roller coating machine, the same drying unit as for the spraying booth can be used.

- EC, BREF on Tanning of Hides and Skins. Joint Research Centre. 2013.
- Pearson et al., BLC Information Document -No 200- Best Available Technologies, 1999.
- A. Bacardit y Ll. Ollé. Maquinaria de curtidos. Escola Universitària d'Enginyeria Técnica de Igualada.

Fiche 6 (wastewater treatment): mechanical and physico-chemical treatment

BAT No. 6

STAGE: WASTEWATER TREATMENT

BAT: MECHANICAL AND PHYSICO-CHEMICAL TREATMENT

These operations include several operations as screening of gross solids, skimming of fats, oils, and greases and removal of solids by sedimentation, sulphide oxidation and suspended solids, chromium and COD removal by coagulation/ flocculation and precipitation. Pollutants contained in effluents are converted into sludge which is easier to dispose of.

Technical description

Mechanical treatment:

- Reduction of the solid and organic content in the wastewater through primary sludge separation.
- Pre-treatment includes screening to remove coarse material.
- Skimming of fats, greases and oils.
- Gravity settling (sedimentation).

Physico-chemical treatment:

- Sulphide oxidation from beamhouse effluents (by aeration in the presence of manganese salts or hydrogen peroxide to avoid odor production).
- Chromium precipitation is more efficient if it is carried out in separated effluents after screening. It is suggested to increase the pH to above 8 using an alkali.
- Flow equalization, physico-chemical treatment for COD removal and balancing.
 - The balancing tanks need to be able to hold at least one day's effluent.
 - Combining effluents can often lead to co-precipitation of pollutants, thus improving the efficiency of COD removal.
 - In order to optimize the removal of suspended solids and COD, the pH of the effluent needs to be controlled.
 - If no chromium precipitation has been carried out yet, chromium hydroxide will be formed at this stage and removed.
 - Flotation may be used, by employing fine air or gas bubbles to lift the suspended solids to the surface.

In the different treatment stages, it is important to determine the adequate reagents, dosage and operating conditions by means of on-site testing in order to achieve optimal performance. Over-dosing can result in higher treatment costs and greater sludge volume which can sometimes lead to poor performance, even though a higher amount of reagents has been used. However, under-dosing can be detrimental to the final effluent quality and also has financial and legal repercussions, such as the increase in discharge taxes and the refusal of discharge authorisation.

Environmental benefits & Driving forces

- 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 of up to 55-75% in the COD.
- A significant reduction of 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.
- The environmental regulations in the different countries lay down discharge limits.

Cross media effects

- Pollutants contained in effluents are converted into sludge therefore a disposal route for the separated solid waste has to be found.
- It is important to adequately select the reagents and coagulant and flocculant dosage to prevent the formation of excess sludge.

Economics

Capital and running costs are significant.

Equipment

The design of a tannery effluent treatment plant (ETP) must always be tailored to the requirements of each company, mainly to the industrial process carried out, its location and its limitations for discharge of wastewater. The costs of ETPs will depend on the design and degree of automation of the facility.

By way of example, for a small European tannery with a discharge volume smaller than 5 m³/day operating per batches and with a very low degree of automation, the investment in a physico-chemical treatment plant can range between 120,000 and 150,000€, with a treatment cost of 2.5-3 €/m^3 . In the case of a medium tannery with a discharge volume of 5-10 m³/h, the investment in an automated physico-chemical treatment plant in continuous mode can be estimated between 210,000 and 280,000 €, with a treatment cost of 2-2.5 €/m^3 .

- EC, BREF on Tanning of Hides and Skins. Joint Research Centre. 2013.
- Pearson et al., BLC Information Document -No 200- Best Available Technologies, 1999.
- Introduction to treatment of tannery effluents, UNIDO, 2011
- EC, BREF on Common Waste Water and Waste Gas Treatment/Management Systems in the Chemical Sector (CWW), 2003.

Fiche 7 (air emissions): water-based chemicals for coating

BAT No. 7

STAGE: AIR EMISSIONS

BAT: WATER-BASED CHEMICALS FOR COATING

Use of finishing products which are dispersed in water rather than in solvent.

Technical description

Conventional chemicals used for coating comprise all or a selection of the following:

- color spray: applying color to undyed leather or adjusting the dyed color of leather using dye dissolved in solvent;
- grain impregnation with a polymeric dispersion diluted in solvent to penetrate and improve the firmness and smoothness of the surface acrylates are most commonly used;
- base coat, consisting of a polyacrylate, polybutadiene or polyurethane binder with pigments and auxiliaries to ensure good surface color and adhesion;
- effect color is sprayed (if the leather is semi-aniline) and
- top coat, consisting of a nitrocellulose or polyurethane lacquer.

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 which have mainly been the top coat lacquers. There is also a need to eliminate hazardous crosslinking agents used to improve abrasion and rub resistances in acrylic and polyurethane dispersions.

Environmental benefits & Driving forces

In the finishing operations, emissions from solvents impose a workplace health problem. It would be quite feasible for tanneries to apply aqueous finishes for base and middle finish coats and to apply aqueous nitrocellulose with polyurethane or polyacrylate top coats. Environmental friendly crosslinking agents or self-crosslinking reactive polymers could also be incorporated.

Benefits are felt from the reduction of VOCs in the workplace. If efficient technology and controlled operations are used, these emissions would be avoided.

Cross media effects

The use of organic solvents in top-coats and special effects finishes is still common in tanneries. However, the range of organic solvent-free (aqueous-based) and low-solvent finishes is increasing continuously. Whereas several solvent-free finishes are now available from a wide range of chemical suppliers, developments are continuing to improve the technical performance of these finishes. Acrylates and polyurethanes have been identified as being particularly suitable to create organic solvent-free finishes.

Economics

The disadvantages are higher chemical costs (around 3.5 ϵ /kg for aqueous-based top-coats compared with 3 ϵ /kg for solvent-based top-coats) and changes in the physical properties of finishes, which can be compensated by the reformulation of finishes. New materials are under development at more competitive prices.

Equipment

The process is carried out in the same premises without the need to make modifications since it is just a change of reagents. There are a number of tanneries in Europe using these techniques.

S	Sources								
_	EG DDEE	-	C T T' 1	1.01.1	I. D	1.0.	0010		

- EC, BREF on Tanning of Hides and Skins. Joint Research Centre. 2013.
- Pollution Prevention Opportunities in the Tanning Sector Industry within the Mediterranean Region. Regional Activity Centre for Cleaner Production (RAC/CP)
- http://leatherpanel.org

Fiche 8 (waste minimization): organic waste fractions and by-products

BAT No. 8

STAGE: WASTE MINIMISATION

BAT: ORGANIC WASTE FRACTIONS AND BY PRODUCTS

The reduction of waste production inside installations is essential for an optimized waste treatment system.

Technical description

The reduction of waste production inside installations is essential for an optimized waste treatment system. Large amount of waste consists of organic materials such as hair or wool, trimmings, fleshings, splits, shavings, fats and grease, which can be reused. As long as these fractions are not contaminated or hardly contaminated with chemicals, recovery options can be considered that offer economic as well as environmental advantages.

Organic materials are separated from the main product stream at various process stages. Some of these materials are by-products for which there are established uses, while others are wastes for which a disposal route must be found. Waste and by-product streams may be subjected to rendering or other treatment:

- The hair residues from the unhairing step using hair-saving techniques are partially destroyed. After washing, hair residues can be compacted to reduce volume before further treatment or disposal. Hair can be used as a fertilizer because of the nitrogen content, as a filling material, as a protein hydrolysate, for generation of biogas by anaerobic digestion or be landfilled after composting.
- Sheep wool can be used by the textile industry, e.g. in carpet manufacture. Wool can also be composted together with other wastes.
- Collagen can be obtained from limed trimmings and splits. Collagen has various uses as meat and bakery product additives, in the manufacture of sausage casings, pharmaceuticals, cosmetics and as additives to rubber products. Food grade gelatine can also be produced.
- Technical gelatine and glue can be produced from untanned materials.
- Tallow recovery from limed trimmings, fleshings and splits can be performed in rendering plants or on site. They may need pre-treatment with acids before conversion. In some cases, tallow can be separated and recovered after a thermal pre-treatment and may be used as a substitute fuel.
- Recovery of protein hydrolysate, chromium-containing sludge and fat from chrome tanning splits and shavings, for use as retanning products or conversion into fertilizer. Laboratory analysis should be implemented to assure sludge is suitable to use it as fertilizer, while complying with environmental legislation.

Further treatment options for organic waste and sludge from wastewater treatment dependent on the composition are composting, recycling in agriculture, generation of biogas by anaerobic digestion and thermal treatment. Treatment to reduce the water content may be applied.

Environmental benefits & Driving forces

The reduction of wastes sent for disposal is the main reason for using these techniques, as well as obtaining useful by-products and the production of energy.

Cross media effects

Some treatments can be annoying due to a potential production of foul odors.

Economics

This good practice involves savings in disposal costs.

Additionally, there may be some return from the sale of by-products.

Energy recovery may be economically beneficial.

Equipment

Each treatment for organic waste reuse requires specific facilities in separate plants. Sometimes plants can be used by a number of tanners or on site on a small scale. The optimum arrangement has to be found depending on the local environment and the local options available.

- EC, BREF on Tanning of Hides and Skins. Joint Research Centre. 2013.
- Spain, Aplicaciones del Manual Media a Sectores Industriales Sector de Curtidos de Pieles Animales, 1997.

<u>Fiche 9 (substitution of substances): substitution of octylphenol and nonylphenol</u> <u>ethoxylates in the aqueous degreasing of sheepskins</u>

BAT No. 9

STAGE: SUBSTITUTION OF SUBSTANCES **BAT:** SUBSTITUTION OF OCTYLPHENOL AND NONYLPHENOL ETHOXYLATES IN THE AQUEOUS DEGREASING OF SHEEPSKINS

Use of linear alcohol ethoxylates instead of alkylphenol ethoxylates in the aqueous degreasing of sheepskins.

Technical description

Surfactants are used in many different processes in the tannery, such as soaking, liming, degreasing of sheepskins, tanning and dyeing. 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.

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. Possible differences in their effectiveness have to be taken into account in the case of the need for a change in the quantity used. Each one of the aliphatic ethoxylated alcohols has distinct properties, so that the process design differs depending on the material chosen.

Environmental benefits & Driving forces

- Lower toxicity in water and easier biological degradation.
- No toxic bioaccumulable degradation products.
- The need for pre-treatment to remove the organic fraction completely prior to biological wastewater treatment is avoided.
- Legislation restricting the use of NPEs, now incorporated into REACH.

Cross media effects

None observed so far.

Economics

The products are commercially available from a number of chemical suppliers. The operational data will depend on the type of production.

The costs of linear alcohol ethoxylates can be compared to those of alkylphenol ethoxylates. Higher costs are possible if the substitution requires higher concentrations of the surfactant to achieve the same effect.

Equipment

The process is carried out in the same premises without the need to make modifications since it is just a change of reagents.

- EC, BREF on Tanning of Hides and Skins. Joint Research Centre. 2013.
- AIICA, aqueous degreasing of fatty sheepskins through the replacement of ethoxylated nonylphenol by biodegradable ethoxylated alcohols and further recycling, 2005.

Fiche 10 (other): process water management

BAT No. 10

STAGE: OTHER

BAT: PROCESS WATER MANAGEMENT

A good process water management reduces the global environmental impact of tanneries.

Technical description

The first step to efficient process water management involves optimization of water consumption and lowering the consumption of chemicals used in the process and in the wastewater treatment. This will reduce both the necessary size of the wastewater treatment plant and the energy consumption.

Process efficiency is achieved by the optimization of the mechanical movement, good distribution of chemicals and control of the chemical dosage, pH, and temperature, which are essential parameters for both quality and effective use of the plant. The efficiency of water use can be enhanced in the tanning process by:

- **Increased volume control of processing water**: some measures must be taken against inefficient use of water as a serious worker-training programme, a clearly communicated code of practice for operators and the installation of basic technical equipment for water control.
- 'Batch' versus 'running water' washes: running water washes are one of the major sources of water wastage because the control with regards to flow rate and time necessary is minimal. Batch washes often yield savings of over 50% of total water and a great uniformity of the end-product is also attained.
- **Modifying existing equipment to use short floats**: the short float technique yields a reduction in water consumption and processing time, savings in chemical input because of a higher effective concentration and increased mechanical action. By modifying the equipment to utilize short floats, 40-80% floats instead of 100-250% are achieved for certain process steps.
- Using modern equipment for short floats; the installation of modern tannery machines can reduce water consumption by 50% in addition to chemical savings. Depending on the cost of water, the high cost of the machines can often be justified by the water and chemical conservation and reduction of chemical input they make possible.
- An effective preventive/corrective maintenance programme; leaks in pipes and process vessels can account for considerable losses of water. Preventive maintenance programmes can prevent losses while corrective maintenance can only minimize the loss.

Environmental benefits & Driving forces

If the tannery implements efficient technical control and good housekeeping, a water consumption of approximately 12-25 m3/t (for bovine hides) can be achieved, versus 40 m3/t commonly employed. The economic feasibility of a change in consumption to this level depends greatly on the cost of water consumption.

Economizing in the use of water does not in itself reduce the pollution load, but it nevertheless has a number of beneficial effects:

- the saving of energy as a consequence of saving hot water;
- an improved uptake of chemicals and consequently savings of chemicals result from the use of shorter floats:
- the use of batch washing makes better control possible.

Additionally and importantly, the lower effluent volume makes it possible to construct a wastewater treatment plant with smaller capacity in the physico-chemical stages, or to increase the efficacy of physico-chemical treatment in an existing treatment plant.

Cross media effects

None

Economics

An efficient control of water consumption will require the investment in an automated dosage system for water. The investment cost will be around EUR 10,000 for an automatic water dosing system controlling the water dosage to 5-8 drums.

Equipment

These techniques to reduce water consumption can be implemented by both new and existing installations. The use of short floats requires either new equipment or modification of existing equipment.

- EC, BREF on Tanning of Hides and Skins. Joint Research Centre. 2013.
- UNEP, Tanneries and the Environment (Technical Guide), 1991.

4.2 Summary of the Best Available Techniques for the tanning sector

In the last few decades, the decreasing level of natural resources together with a greater environmental awareness has led to a redirection of industrial aims in many companies to try and make their production processes more sustainable. In this sense, the different industrial sectors are becoming more and more aware of the environmental impacts of their processes and are beginning to adopt more environmentally friendly techniques. In the tanning industries, the knowledge and use of alternative methods that reduce the environmental impact of their production processes need to be promoted, since the tanning production sectors play a fundamental role in the economies of many countries, especially in the Mediterranean area.

The leather sector produces different environmental impacts throughout their industrial process, 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 around 50 m³ of wastewater and 700 kg of different solid waste are produced. Roughly speaking, for the processing of 1 ton of salted cattle hide by means of a conventional tanning process, the environmental balance would be as detailed in table below.

Raw hides	1 tonne	Leather	200-2	50 Kg	
				COD	230-250 K
		Waste		BOD	~ 100 K
			15-50 m3	ss	~ 150 K
		water		Chromium (III)	5-6 K
Water	15-50 m3			Sulphides	~ 10 K
Mater	13-30 1110			Untanned trimmings	~ 120 K
				Untanned fleshings	~ 70-350 K
				Tanned splits and	
		Solid		shavings	~ 225 K
Chemicals	~ 500 Kg		~ 450-730 Kg		22010
enenieure		Waste		Finished leather dust	~ 2 K
				Finished trimmings	~ 30 K
				i moneu u migo	
				Sludge treatment	
				e	

Table 1. Environmental balance in an average European tannery.

Considering that more than 44,000 tons of leather were produced in Europe in 2011, during that year the following figures of environmental impact may have happened:

- Wastewater:15 million tons m³/year
- Solid waste: 210,000 tons/year
- Atmospheric emissions: 7,000 tons of VOC/year

This document will describe the Best Available Techniques (BAT) considered adequate for achieving a high level of environmental protection in the leather tanning industry. However other techniques may exist, or may be developed for an individual installation in order to get a more sustainable production in the tanning industry.

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These techniques will be classified in the following process stage or scope: storage, beamhouse, tanyard, post-tanning, finishing wastewater treatment, air emissions, waste minimization, substitution of substances and others. Chapter 4.1 describes more in detail a BAT example selected from each process stage.

The main source of information to elaborate this chapter has been the Best Available Techniques (BAT) reference document for the tanning of hides and skins, 2013. (BREF). This BREF document was produced by the European Integrated Pollution Prevention and Control Bureau (EIPPCB) at the European Commission's Joint Research Centre – Institute for Prospective Technological Studies (IPTS) and was drawn up in the framework of the implementation of the Industrial Emissions Directive (2010/75/EU) and is the result of the exchange of information provided for in Article 13 of the Directive for the Tanning of Hides and Skins.

4.2.1 Storage

Reduction of the time of the storage of raw hides by cooling

With regard to this stage of the process the best recommendation is that the **time of storage of the raw hides be as reduced as possible**, using freshly flayed hides or skins, in this way it will be not necessary to use salt conservation, pesticides neither long cooling storage with the consequent saving 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 have for their final products being contaminated by not allowed pesticides or biocides. That it is to say that the nearby of the slaughterhouse is a guarantee for the sustainability.

Reduction of the time of the storage of raw hides by cooling				
Main advantages	 Reduction of salt in effluents. Reduction of water for processing fresh hides compared with the water needed for processing salted hides. 			

If the tannery uses salted hides, there are some techniques that may be applied as **shaking salt** hides in a mechanical way. This technique will be described in more detail in chapter 4.2.

4.2.2 Beamhouse

Cleanliness of the hides and skins

The **cleanliness of the hides and skins**, that it is to say, that the skins arrive to the tannery, not only in a short period of time after the animal be 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.

Cleanliness of the hides and skins				
Main advantages	 Improving the quality of final leather Reduction of water consumption Reduction of BOD in wastewater 			

Green fleshing

If the fleshing process is realized in an early process of the stage it is called **green fleshing**. With the implementation of this process the company will use less chemical products during the process due

that the surface of the hides and skins to be treated will be reduced and the fleshing will be free of chemical products and then they can be used as disposal for getting other products, for example tallow

Green fleshing	
Main advantages	 More rapid and uniform penetration of chemicals into the hide in next stages. The wastewater volume in the unhairing and liming step is reduced. Fleshings can be processed into tallow since they are free from chemical products

Alkali pretreatment in unhairing

In order to **reduce the concentration of hair waste** in tannery effluents due to the degradation activity of sulphides in the unhairing process, a technique can be used, which consists of taking advantage of the different chemical behavior in the presence of alkalis of the keratin that is found in the hair and in the upper layers of the skin, and the collagen or immature keratin that is found in hair roots. For example, the **treatment with sodium hydroxide** 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 root, thus removing it from the skin, but preserving the structure of hair. This way the degradation of hair is avoided, thus preventing the creation of solid waste in wastewater, which is much more difficult to manage than full hair in dissolution. The early use of a physical filter for the effluents containing hair makes it possible to reduce COD (Chemical Oxygen Demand).

Alkali pretreatment in unhairing	
Main advantages	 Reduction of organic load in wastewater Saving on chemicals in wastewater treatment. Lower volume of sludge.

Use of inorganic sulfides in unhairing

In order to **reduce sulphide discharge into wastewater** and due to the possible emission of hydrogen sulphide at the work place, it is advisable to reduce the use of inorganic sulphides in the unhairing stage. In practice it is not possible to eliminate completely the use of these compounds, although it is possible to reduce the risks by combining the **use of organic sulphides** with inorganic ones and **enzymes**.

Use of inorganic sulfides in unhairing	
Main advantages	Reduction of sulphide discharges in wastewaterReduction of the risk of hydrogen sulphide at work place

Another Best Available Technique is the use of enzymes in unhairing. This technique will be described in more detail in chapter 4.1.

pH control for prevention of H₂S emissions

As it was commented before it is a reality that the effluents from the unhairing and liming processes may contain high concentrations of sulphur compounds. In the case 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 before being mixed with other acid effluent or being discharged to the general mixing tank which generally has a pH of 8.5 - 9.0.

If sulphide-bearing effluents are to be mixed with other acidic or neutral effluents before full oxidation of the sulphide is achieved, then the mixing must be carried out in an isolated tank, with an adequate extraction system.

pH control for prevention of H ₂ S emissions	
Main advantages	 Avoid gas concentration in the tannery Prevent emissions to the air Reduce odor disturbances

Lime splitting

With respect to the mechanical operations in the beamhouse, the **lime splitting** is a relevant technique. This operation consists on dividing the hide horizontally into an outer grain and a flesh layer. The splitting can be done also after chromium tanning, in the wet blue condition, but 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.

Lime splitting	
Main advantages	 Chemical consumption and processing time in subsequent processes is reduced Water consumption in the subsequent process is reduced. Reduction in the amount of solid waste containing chromium is achieved.

Use of CO₂ in deliming

The use of ammonium compounds in deliming can be replaced partially or completely by the **injection of carbon dioxide gas**, reducing **the nitrogen discharges** to the atmosphere and wastewater.

Use of CO ₂ in deliming	
Main advantages	 Little process control is necessary and the gas is easily injected into process vessels. Reduction of the discharge of ammoniacal nitrogen in the effluent. Reduction of the emission of ammonia gas in work place

Use of weak organic acids in deliming

Ammonium salts used in deliming may be partially or completely replaced by **weak organic acids**. Magnesium lactate, organic acids such as lactic acid, formic acid and acetic acids, or esters of organic acids can be used to substitute ammonium compounds in the deliming process. The advantage of substituting ammonium salts is that **ammonia levels in the wastewater are reduced.**

Use of weak organic acids in deliming	
Main advantages	 Reduction of the discharge of ammoniacal nitrogen in the effluents Reduction of the emission of ammonia gas in work place.

4.2.3 Tanning

Use of polymeric sulphonic acids instead of NaCl

Pickling using **alternatives to salt (NaCl)** in the float. Salt-free systems, based on **non-swelling polymeric sulphonic acids** are available. The technique is implemented in several companies where there are restrictions to disposal of salt due to local conditions.

Use of polymeric sulphonic acids instead of NaCl	
Main advantages	The discharge of chloride and sulphate salts is reduced.The exhaustion in the subsequent tanning step is enhanced.

Recovery of degreasing solvents by distillation

The dry **degreasing process** of wool-on skins is usually carried out in closed machines with abatement measures for air and wastewater releases and the used **solvent** is automatically distilled and **reused**.

Recovery of degreasing solvents by distillation	
Main advantages	 Reduction of toxicity, flammability and explosion prevention. Safety at the workplace. Preventing the VOC emissions. Residues can be collected for further processing. For example, the production of tallow or fatliquors.

Another Best Available Technique is to increase the efficiency of chromium tanning. This technique will be described in more detail in chapter 4.1.

Recycling and reuse of chromium solutions

Exhausted tanning floats are 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.

If the company recycles the tanning liquors to the pickling process the exhausted tanning bath can only partly be recycled into the next batch of pickle liquor. For recycling into the pickling float the liquor is passed through a nylon screen and, after 24 hours, passed to a tank where it is mixed with the pickle acid. The hides are drummed in a brine solution, and then the pickle/chrome liquor is added. After the standard pickling time, the fresh chromium input is added. If the company **recycles the tanning liquors to the tanning process,** then hides are taken out of the drums at the end of the process, allowing about 60% of the float to be recovered.

Recycling and reuse of chromium solutions	
Main advantages	 Recycling to the pickling process: On average, 50% of the tanning float can be recycled, which is equivalent to up to 20% of the fresh chromium input. Salt carried over in the spent tanning liquor allows for a reduction of 40% in the salt added to the brine solution. Chromium discharge can be reduced by 50% . Recycling to the tanning process: The fresh chromium input can be reduced by 25% for bovine hides and up to 50% for sheepskins. Chromium discharge in the effluents can be reduced by 60%.

Chromium recovery through precipitation and separation

The **chromium recovery through precipitation and separation** consists on the separation of chromium salts from the aqueous effluent stream by precipitation, with dewatering of the precipitate. The chromium precipitated by sulphuric acid is used for getting a new solution that can be used as a partial substitute for fresh chromium salts. The technique is used for the treatment of effluents from the chromium-tanning process including washing floats and liquid from sammying.

Chromium recovery through precipitation and separation	
Main advantages	 From the chemical point of view, chromium (III) recovery is a simple process with excellent environmental results. Efficiencies above 95% of chromium precipitation are reported. The recovered chromium sulphate solution can be recycled into the tanning process by replacing up to 35% of the fresh added chrome tanning salt. Reduction of chromium in wastewater and sewage sludge. Recovery common installations can be constructed in tannery conglomerations in order to benefit from economies of scale

Pretanning using aldehydes, producing chromium-free leather

The development of **wet white pretanning systems** using for example **aldehydes** was undertaken to address environmental matters, in particular the reduction of chromium in effluent and solid waste. These systems have become more and more used for the production of chromium-free leather for specific applications. Several tanneries in Europe use the technique. In particular, installations producing leather for the automotive industry.

Pretanning using aldehydes, producing chromium-free leather

Main advantages	 Reduction of the chromium emissions to the effluents (no chromium discharge) and less solid waste containing chromium. Glutaraldehyde is a widely used chemical. Extensive measures have been taken to monitor any negative effect in the urban sewage treatment plant, and no negative effects have been noticed. The possibilities for a disposal of waste tanned with chromium may become more difficult and expensive in the future.
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Pretanning followed by vegetable tanning with high uptake of tanning agents

Use of **pretanning agents to aid tannin penetration** and of short floats in drum tanning is also a good technique used in several tanneries in Europe. These systems have in common a pretanning step 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. It can be applied in pits or in drums or in a combination of both.

Pretanning followed by vegetable tanning with high uptake of tanning agents		
Main advantages	 Increase in the uptake of vegetable tannins into the leather. Reduction in the discharge of COD. Reduction in the process time for vegetable tanning. Drum processes for sole leathers are designed to be closed systems, so that very little waste liquor is discharged. 	

4.2.4 Post tanning

Process changes to reduce metal discharges

Several **process changes can be implemented to reduce metal discharges**, for example, using highexhaustion tanning, or ageing of chrome-tanned leather to reduce leaching of the chromium during post-tanning. Filtration of loose chrome-tanned leather fibers is also part of this process. In relation with metal complex dyestuffs for leather, the coordinating metal atom is iron, chromium, copper or cobalt. The slight increase in the metal content, due to this stage can be avoided if acid dyes without metals are used, provided that the same final properties can be obtained.

Process changes to reduce metal discharges		
Main advantages	 The quantity of metals (in particular chromium) in the wastewater will be reduced. The quantity of metals (in particular chromium) in the leather waste will be reduced. A reduction of the leaching of chromium during the post-tanning processes can be obtained either using high-exhaustion chrome-tanning systems or allowing the necessary time for the tanned leather to age prior to the post-tanning processes. 	

Optimizing process parameters in retanning

Some measures for **optimizing process parameters in retanning** in order to ensure the maximum uptake of retanning chemicals may be 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. The parameters data will depend on the properties of the final product.

Optimizing process parameters in retanning	
Main advantages	- Reduced discharge of retanning agents to the wastewater.

Optimization of process parameters to ensure the maximum uptake of dyes

It is very desirable that for achieving an **optimized dyeing** the exhaustion of the dyestuffs be as high as possible and that the dyes be firmly bound to the leather at the end of the process. A very important factor for obtaining a high degree of fixation of dyes is to end the operation at a relatively low pH value. Chemicals applied in the dyeing process that have not been retained can color the effluents and some substances have a high potential environmental impact.

Optimization of process parameters to ensure the maximum uptake of dyes	
Main advantages	- Aesthetic and economy reasons as discolored wastewater are avoided. The consumption of expensive dyes is reduced.

Optimized fatliquoring

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.

Optimized fatliquoring	
Main advantages	 The COD in the wastewater from the post-tanning operations may be reduced significantly. An exhaustion of fatliquor equivalent to 90% of the original offer can be considered achievable.

Another Best Available Technique is the substitution of nitrogenous compounds in post-tanning. This technique will be described in more detail in chapter 4.1.

Use of liquid and low dust dyes

The option of using **liquid dyes and de-dusted powdered dyes** makes it possible to achieve a reduction or the elimination of suspended particulate matter in the air exhausted from dye-handling areas. Liquid dyes and dyes generating low levels of particulate matter were developed to prevent health impacts by dust emissions on the workforce while handling the products.

Use of liquid and low dust dyes

Main advantages	- Increasing workplace safety due to the reduction or elimination of suspended particulate matter in the air exhausted from dye-handling areas.
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Improved drying techniques

The improvement of **drying techniques** to reduce energy use may be 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 greatest possible amount of water in sammying, keeping an amount of exhaust air at the necessary minimum.

Improved drying techniques	
Main advantages	- Reduced energy use may be achieved.

4.2.5 Finishing

Improved techniques for spray coating

There are fundamental differences between curtain coating, roller coating, and spraying of leather. Due to the relevance of the **curtain and roller coating**, this treatment is described in more detail in chapter 4.1.

Nevertheless, there are some details that may be relevant to be explained **about improved techniques for spray coating**. These techniques can be high-volume-low-pressure (HVLP), mainly used for upholstery leather, airless spray guns and computer aided spraying.

Improved techniques for spray coating	
Main advantages	 Reduced wastage of coating materials. HPLV and airless spraying improve spraying efficiency up to 75%, compared to spraying efficiency as low as 30% for conventional spraying operations. The bounce-back in HPLV technique is considerably reduced compared with conventional spraying. Computer-aided spraying can prevent 75% of the finish being lost as overspray. The emissions of spray mists are reduced, and because coating efficiency is improved, solvent emissions are reduced too.

4.2.6 Wastewater treatment

Wastewater treatment consists of a combination of several processes as the mechanical treatment, physic-chemical treatment, biological and biological nitrogen elimination.

The mechanical and physico-chemical treatments are described in more detail in chapter 4.1.

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. Other substances, such as metals are absorbed by the sludge.

Biological treatment	
Main advantages	 Meeting with legal discharge limits. The technique can achieve a reduction of oxygen demand, to a level where it can either be safely discharged to a water body or meet the specification of an organization providing off-site treatment.

Biological nitrogen elimination

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 a preliminary stage of the process nitrogen in proteins is converted to ammoniacal nitrogen, and this technically precedes nitrification. In the nitrification stage, the ammoniacal nitrogen is oxidized into nitrate.

This process takes place under aerobic conditions. In the denitrification stage, the nitrate is biologically reduced to gaseous nitrogen, most of which escapes into the surrounding atmosphere. A further part of the nitrogen is bound in the biomass. Denitrification takes place under anoxic conditions.

Biological nitrogen elimination		
Main advantages	 Further reduction of wastewater pollution (compared with just a physico-chemical treatment). Reduction of emissions of nitrogen compounds to aquatic environment, by closing the natural nitrogen circle. Reduction of leakages of sulphur compounds to air and related odors emissions. 	

Removing suspended solids after the wastewater treatment

In order to **remove suspended solids after the 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. Dewatering is often practiced to reduce the volume of the sludge for disposal. Sludge can be dewatered by means of filter presses, belt presses, centrifuges and thermal treatment. In most cases, flocculation agents have to be added.

Removing suspended solids after the wastewater treatment	
Main advantages	 Reduction in suspended solids in the wastewater and reduced water content in the sludge. Production of a clearer effluent and reduced water content in the sludge. Increased range of possibilities for sludge disposal. Reduced transport costs for sludge disposal

4.2.7 Air emissions

Because of the limited applicability and effects of air abatement techniques, the best option to control the VOC emissions is the use of water-based chemicals for coating. This technique has been described in more detail in chapter 4.1.

Abatement of ammonia and hydrogen sulphide

Despite the fact that primary measures for **ammonia and hydrogen sulphide reduction** had been implemented and that these substances have been removed by extraction ventilation systems, it is possible that the concentration of these emissions be still perceptible in the work place and outside the premises. In this case, exhaust air treatment will be required. The techniques to apply may be biofilters and/or wet scrubbers. These last one will use an acidic solution for abating ammonia and an alkaline solution for abating sulphide.

Abatement of ammonia and hydrogen sulphide	
Main advantages	 Abatement performance increase. Reduction of odor nuisance at work place and outside premises. Reduction in disposal costs.

Control of the emission of dusts and other particulate matter to the air

Airborne particulate matter can arise during handling of powdery process chemicals. For the most effective **control of dust** and to prevent fugitive emissions the following considerations should have been 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 the fans need to be purpose designed for low power consumption and noise levels. Besides ducts need to be designed for the desired suction pressure at the machine hood and smooth airflow.

Control of the emission of dusts and other particulate matter to the air			
Main advantages	The reduction of particulate matter emissions to the air.Enhanced safety at the workplace		

4.2.8 Waste minimization

Disposal of effluent plant wastes

Waste treatment at the end of the production process is still necessary for materials which cannot be reused. Since the implementation of the EU Directive on the landfill of waste (1999/31/EC), the landfill of untreated organic waste has become more difficult and in some Member States, effectively banned.

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.

At the end of the process of the effluent treatment plant, the waste materials from effluent treatment consist of a small amount of course material and a large quantity of sludge of various kinds.

Disposal of effluent plant wastes			
Main advantages	Some reduction of wastes sent for disposal is possibleMeeting with legal landfill legislations		

Another Best Available Technique is the separation of organic waste fractions and utilization of byproducts. This technique will be described in more detail in chapter 4.1.

4.2.9 Substitution of substances

Responsible management by the tanner requires awareness of substances and their fate during and after the process. Information available from suppliers in product data sheets should cover any environmental risk. The European Regulation on the Registration, Evaluation, Authorization and Restriction of Chemicals (REACH) introduces a requirement that suppliers shall provide information on environmental risks.

Another Best Available Technique is the substitution of octylphenol and nonylphenol ethoxylates. This technique will be described in more detail in chapter 4.1.

Substitution of halogenated organic compounds in degreasing

Possibilities exist for **replacing halogenated organic compounds in degreasing** either by using nonhalogenated 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 reduce the emissions.

Substitution of halogenated organic compounds in degreasing			
Main advantages	- The substitution of halogenated organic solvents in the degreasing step by surfactants clearly shifts the contamination risk away from air emissions, waste and soil to the watercourse.		

Substitution of halogenated organic compounds in fatliquors

It is also possible to use fatliquors which do not contain halogenated compounds and that do not require stabilization by organic solvents (and therefore do not contribute to the AOX (absorbable organic halogen (X)) 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 fatliquoring of leather (REACH Annex XVII point 42).

Substitution of halogenated organic compounds in fatliquors

Main advantages	 The substitution of halogenated organic solvents in the degreasing step by surfactants clearly shifts the contamination risk away from air emissions, waste and soil to the watercourse. Safety at the workplace is increased.
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Substitution or optimization of halogenated organic compounds in water-, soil- and oil-repellent agents

It is possible using 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 (paraffin formulations, polysiloxanes, modified melamine resins or polyurethanes). For combined water-, soil-and oil-repellent finishing of leather, in most cases fluorocarbon compounds (long or short chain poly-and perfluoroalkil substances, PFASs) are still used, but the toxicity of these substances specially to workers health and to the environment makes sensible to avoid them.

Substitution or optimization of halogenated organic compounds in water-, soil- and oil- repellent agents				
Main advantages	 Elimination of emissions of PFASs into the environment. Decrease of the COD and the elimination of halogenated compounds from the effluent. Elimination of the emission of organo-halogenated contaminants. Short-chain fluorinated alkanes are less bioaccumulative than the long-chain ones, but are still toxic and as persistent as the long-chain ones, and larger quantities are needed to provide the same performance, so its use is not advised. As added value, the product can be marketed as Poly- and Perfluoroalkyl substances (PFASs) free. 			

Substitution of halogenated organic compounds in flame retardants

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 retaining process. Also inorganic phosphorus compounds (such as ammonium polyphosphate) and silicon polymer products used in finishing could be considered as an alternative to achieve fire resistance.

Substitution of halogenated organic compounds in flame retardants			
Main advantages	 Reduction of the concentration of halogenated compounds in the effluents. As added value, the product can be marketed as halogenated flame retardants free 		

<u>4.2.10 Other processes: Monitoring, decommissioning, noise and vibration control, reduction of water consumption.</u>

Monitoring

Monitoring of the environmental outputs and emissions from an industrial activity is essential to their effective control. Generally speaking, the monitor activities in the tannery could consist on the following:

- Wastewater:

Standardized analysis and measurement methods exist for wastewater effluent parameters such as COD, BOD, SS (suspended solids), TKN (total Kjeldahl nitrogen), ammonia, total chromium, sulphides, chloride, AOX, conductivity, pH and temperature.

- Emissions of hydrogen sulphide, ammonia or volatile organic compounds: It is relevant to carry out maintenance of the abatement equipment and recording indicators such as the pH potential of the liquid at the outlet from a wet scrubber. At sites where annoyance due to odors is likely to be caused, monitoring of hydrogen sulphide, ammonia and other substances at the downwind boundary of the site may be required.

- Organic solvent:

Keeping an inventory is advisable to establish the total solvent emissions per m2 of leather produced.

- Waste fractions:

Keeping an inventory according to type, amount, hazard and recycling or disposal route is also advisable.

- Chemical products:

A chemical inventory is essential as part of good housekeeping techniques and it is also essential in good environmental management of emissions and in accident preparedness programmes. The use of a simple **balance** to weigh chemicals is essential to ensure adequate dosage, thus reducing unnecessary costs and preventing chemicals from turning into waste or contaminating wastewater.

- Energy:

The consumption of water, electricity, heat and compressed air, should be recorded. A total of all energy use at the installation should be calculated.

- Noise:

Where there are residences or other noise-sensitive locations near to the tannery, sound levels should be measured outside the tannery buildings on appropriate parts of the site.

	Monitoring
Main advantages	 Optimization of the general process of the tannery, proving beneficial both economically and in terms of production. Minimization of the potential hazards at the workplace. Minimization of the environmental impact.

Decommissioning

When decommissioning a tannery, the aim should be preventing the impact on the environment in general and in particular on the immediate surroundings, leaving the area in such a way that it could be reused. This includes activities from the shutdown of a plant itself, the removal of buildings, equipment, residues from the site, and contamination of surface waters, groundwater, air or soil.

The legal framework for the decommissioning of installations varies greatly between countries, and any provisions and duties laid down in a permit will depend strongly on the local environment and on the legislation to be applied.

The decommissioning operations include:

- Clean-up, dismantling of installations and demolition of buildings.
- Recovery, treatment and disposal of material derived from general clean-up, plant demolitions, demolition of buildings, and dismantling of environmental units.

- Survey of possible contamination.
- Traffic due to transport and demolition activities.

Decommissioning		
Main advantages	 Meeting with legislations of the country. Enhancing the value of the land. Preventing potential environmental impacts. 	

Noise and vibration control

Good practice to control the emission 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.
- Placing 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.

Noise and vibration control		
Main advantages	Safety at the workplace is increased.Noise emission reduction.	

Reduction in water consumption: rain water management

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.

Rainwater from paved yard areas in which spills of process liquids or chemicals are likely to occur is collected as a process effluent. It is good practice that this affected yard area be as small as possible, so as to minimize the amount of rainwater collected.

Rain water management			
Main advantages	 Reduction of the volume of water to be dealt with as process effluent. Reduction of the risk of overwhelming effluent treatment equipment in periods of heavy rain. Effluent treatment costs can be reduced. 		

Another Best Available Technique is **process water management**. This technique will be described in more detail in chapter 4.2.

Reduction of water consumption: reuse of floats in soaking and liming process

For reuse, the water from tanning and dyeing is treated in a sedimentator and utilized for soaking in the liming drum and as rinse water after liming. The acidic wastewater from tanning, retanning, dyeing

and fatliquoring is treated mechanically and is subsequently alkalized and sedimented with the addition of polyelectrolytes and metal salts. The water thus treated is used in soaking. The rinse water from before deliming is reused for the first rinse stage after liming. The second rinse water after liming is stored, sedimented and temperature-controlled in a tank and is used the next day as the first rinse. Due to high organic and sulphide loading, the first rinse has to be treated and cannot be reused in the process.

Reuse of treated wastewater in soaking and liming processes			
Main advantages	 Reducing water consumption for economic and environmental purposes. A saving of approximately 20% of total water consumption can be achieved. Through this measure it is possible to reduce freshwater consumption in soaking and liming by 60%. 		

Chapter 5. Pollution prevention case studies

5.1 Case Study 1. INESCOP (Spanish Footwear Technology Institute), Elda, Alicante (Spain)

INESCOP, the Spanish Footwear Technology Institute, is an independent service organisation. INESCOP began its activities in 1971 and works as a private non-profit making organisation.



Figure 1. INESCOP's Headquarters in Spain

INESCOP provides specialised services for the tanneries, and the activities span the wide range of scientific and technical needs of national and international companies such as the testing and assurance of quality, the organisation of the productive processes, the development of new materials and advanced technologies, sustainability and environmental improvement, specialised training of human resources and technology transfer, and applied research in general.

INESCOP carries out activities in 58 countries and works as a support tool to companies of the leather sector, and is provided with the most modern and technological equipment, which is necessary in order to guarantee services of the highest quality and in line with the most advanced of their kind, at a worldwide level. The human resources at INESCOP are made up of more than 100 professionals.

Services for the leather sector

The main services offered by INESCOP to the leather sector are:

- Quality and environmental testing (physical, chemical and biological tests).
- Environmental audits.
- Support for the development and implementation of sustainable technologies.
- Updates about legislation and hazardous substances regulations.
- Wastewater analysis and advice on wastewater treatment and recycling.
- Updates about sectoral technical **information** and specialised **training** courses on: leather analysis and characterisation, environmental management, chromium free tanning, wastewater treatment, etc.
- Participation in **leather standardisation** activities.
- Preparation and development of **R&D** projects, from **prototype/demonstration** stage to **commercialisation**.

Beyond those services, INESCOP is also experienced in **Centre Model Transfer Projects** since, in many cases, requests have been made by a regional or national government, or a development agency to support the establishment of technology centres similar to INESCOP in other countries.

Successful Project Examples

1) EU Project: "**Tanning Wastewater Recycling in Leather Industries** (Ref. LIFE00 ENV/E/000498 – TARELI): the main objective of this project was to demonstrate, on an industrial scale, the technical and financial feasibility of the recycling of pickling-tanning residual baths. The main results achieved were as follows:

- Reduction in water consumption by 97% in the pickling-tanning process.
- Reduction in reagent consumption (55% sodium chloride, 21% acids, 14% chromium salt, and 17% basifiers)
- Reduction in effluent salinity by 18%.
- Reduction in chrome content in wastewater treatment sludge by 27%.

2) EU Project: **Environmentally Friendly Oxazolidine-Tanned Leather** (Ref. LIFE08 ENV/E/000140 - OXATAN): the purpose of this project was to demonstrate the feasibility and financial viability of leather tanning with oxazolidine, which avoids the environmental impacts associated with chrome tanning. The main results were:

- Chrome-free leather
- Oxazolidine-tanned leather waste is more biodegradable.
- Oxazolidine leather meets the EU Ecolabel criteria for footwear
- No significant changes to the traditional chrome-tanning process
- Comparable performance to that of chrome-tanned leather
- Verified the viability to manufacture quality footwear



Figure 2. Footwear samples manufactured with oxazolidine leather

3) EU Project "**Demonstration of clean technologies in tanning processes in Egypt** (LIFE04 TCY/ET/000045 - ECOTAN)" aiming to boost the environmental Egyptian capacities for the tanning sector. The main results were:

- An environmental laboratory was created to carry out different environmental tests and measurements such as emissions, noise and water.

- A pilot tanning plant for the demonstration of new and clean processes
- A physical-chemical wastewater treatment pilot plant

The success of this project brought about, among other achievements, the creation in Egypt of the LTTC (Leather Tanning Technology Center).

5.2 Case Study 2. Ecozap shoes (Spain)



Company overview

At the beginning of 2007, Ecozap journey starts as a Spanish ecological shoe maker company in Madrid. Ecozap philosophy is to use ecological materials in all shoe models manufacturing. Ecozap shoes are made from noble materials, without toxic substances both on its nature extraction and on its processing, avoiding the generation of pollution. Some models are made of recycled materials giving to not biodegradable materials, a second life.

Almost all models are made in Spain or Portugal in order to reduce emissions caused by its transport to the main consumers market. If they come from abroad, they are manufactured by Fair Trade.

Ecozap offers its products worldwide. Nevertheless, Ecozap recommends clients to buy shoe models produced as close as possible to their place of residence in order to reduce CO2 emissions.

The Ecozap technology and materials used for shoe making are the following:

- Organic products from nature, with no leather: Hemp, jute, palm, palm-tree, seeds, organic cotton, natural latex, fiber of coconut, rind of rice, cork, wood, sap of tree, pure 100 % unbleached and un-dyed natural wool.
- Vegetable tanned leather: organically tanned leather with vegetable extracts from the bark of Mimosa and Quebracho trees, oak, blockhead, tare and valonea. No chemicals, metals, chrome and lead are used in the tanning processes. Shoe inks don't have any benzidines either azo compounds.
- Re-used and recycling materials: Some used materials are tires, bottle caps, etc.
- Suitable for allergic people: Ideal for allergic people to chrome, lead, glues, potassium dichromate, thiuram, etc.

Ecozap shoes insoles are made of cork and latex while soles from rubber or leather. The building materials at the local shop are also ecological. Company's CO2 emissions are compensated yearly. Transportation through the company uses sustainable means of transport as cycling in order to reduce CO2 emissions.

All Ecozap products are ecologically evaluated according to their environmental and social impacts based on its CO2 emissions, raw materials and social commitment of each product. For more information, please visit the website here: <u>http://ecozap.es/en/ecozap-valuation-legend</u>

Benefits and saving opportunities

Some of the environmental, economic and social benefits generated by the company include the following:

- Most materials used for shoe making are natural, biodegradable, renewable, non-toxic and some recycled.
- If leather is used on the shoe making, the company only uses vegetable tanned leather;
- Vegetable tanned leather might be more expensive than using conventional leather for shoe making, but the responsible client is willing to pay more for a more sustainable product or a "luxury" product;

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- Costs are reduced due to minor use of chemicals, petroleum-based products and substitution of chemicals by natural products causing less environmental impact;
- The process is more ecological due the substitution of chrome by vegetable products for leather tanning;
- The generation of wastewater is less harmful causing less environmental impact and lowering costs;
- Hazardous waste generation is minimum;
- The generation of air emissions (ammonia, VOCs (solvents), leather dust, chemicals dust, SO2, H2S, etc.) is minor.

Sources/related links

For more information, please visit the website: www.ecozap.es

5.3 Case Study 3. MED TEST. Société Moderne des Cuirs et Peaux (SMCP) (Tunisia)

Company overview

SMCP is a leather company founded in Sfax in 1965. The tannery's production is distributed in ovine skins (57%, 525 tons/year), goat skins (10%, 90 tons/year) and bovine skins (33%, 300 tons/year). It produces for both local and international market.

The company joined the MED TEST project in order to identify opportunities for improvement regarding the pollution linked to its activity and to improve its environmental performance, which will in turn help it to conform to regulations and facilitate access of its goods to the international market.

While the company is already in the process of implementing an ISO 9001 standard, its adhesion to MED TEST represents an opportunity to integrate in the near future an Environmental Management System (EMS) in line with ISO 14001 standards.

Benefits

The MED TEST project has identified an opportunity for \$US 97,200 of annual savings in electricity, water and chemicals, against a \$US 287,000 investment with a three-year payback period. The identified cleaner production measures are under implementation.

The gains resulting from the minimization of chemicals use are mainly as a result of substantial reductions in the volume of chrome (up to 77%) as well as of auxiliary products (e.g. salt), which are estimated at 15%.

Water consumption has been reduced by 22% through the installation of new systems for dosing and control water in the drums, hide splitting and recycling of pickle liquors.

Insulating steam and hot water pipes has reduced energy costs. The tannery plans to cut down its thermal energy consumption by 10% in the coming years, when the tannery's industrial area will be connected to the public natural gas network.

As for environmental improvements, the company has focused on a reduction of its wastewater loads and an improvement of the existing water treatment plant, to achieve 80% reduction in COD, corresponding to annual financial gains of \$US 14,000. Taking into account all the

measures adopted by the company, substantial environmental gains have been achieved, corresponding to approximately 40% reduction of chlorides discharges.

Parallel to the identification of minimization opportunities, the company has outlined its own environmental policy and begun to look for further areas of potential improvements.

Saving opportunities

Measure	Economic key figures			Resource savings per year	
	Savings [USD/yr]	Investment [USD]	PBP [yr]	Water, Chemicals	Energy [MWh]
Hide splitting	26000	72000	2.5	1,850 m³ water	-
Water savings, dosing and control in the drums	17 000	35000	2	5,500 m ³ water	68
Hot water/steam pipes insulation	1700	5 000	3	-	31
Drumming and salt reduction	17 000	43 000	2.5	72 tons of Cl	-
Reuse of recovered chromium	24000	107 000	5	24 tons of Cr	-
Recycling of pickle liquors	11500	25000	3	2,250 m ³ water	-
TOTAL	97 200	287 000	3		99

Hide splitting: This option limits the consumption of chemicals (15 tons/year of chrome) and water (1,850 m3/year, i.e. 4% of the global process water), thus minimizing the environmental impact of the site.

Water savings – dosing and water control in the drums: In addition to using drums with low water consumption, already installed some years ago, the tannery has proceeded to install an on line metering system for water flow and bath temperature in the drums, which has led to savings in water (10%) and thermal energy (7%).

Insulation of hot water and steam pipes: Heat dispersion through the hot water and steam pipes causes a significant loss in thermal energy. Their insulation allows for a reduction of thermal energy consumption (3%), as well as of CO2 (10 tons).

Reduced use of salt in skin and leather drumming before soaking: The tannery's equipment, with a perforated shaking drum, facilitates the elimination of salt from the salted hides before the soaking stage, which results in the elimination of 120 tons/year of salt, in a 40% reduction of chlorides in wastewater, and in lowering COD and BOD5 loads.

Reuse of recovered chromium: The chromium sulphate recovered after precipitation and filtering can replace 46% of the new chromium with no impact on the quality of finished leather. This technique allows for the reuse 24 tons/year of recovered chromium otherwise discharged as sludge, and for \$US 24,000/year savings, taking into account the additional electricity costs.

Recycling of pickle liquors: Pickle liquors can be recycled in the pickling process or reused in the tanning process, allowing for a reduction of the quantities of salt and effluents discharged into the sewer. As a result, the lower demand for chemicals entails a reduction of 45 tons/year of salt; of 5% of the annual water consumption within the production process; and of wastewater pollution loads, especially in sulphur acids, formic acids and COD.

5.4 Case Study 4. MED TEST. Tanneries Mégisseries du Maghreb (TMM) (Tunisia)

Company overview

TMM, founded in 1976, is part of a Tunisian holding company. Heavily export-reliant, it operates in the leather sector and annually produces about 20 million square feet of ovine and bovine leather.

The company joined MED TEST in order to identify opportunities for improvement, reduce pollution and integrate Best Technologies Available (BTA) and Good Environmental Practices (GEP) into the production process.

The company was already certified ISO 9001 at project's start. Taking advantage of its participation in MED TEST, it has initiated an Environmental Management System (EMS) in conformity with ISO 14001 and plans to implement Corporate Social Responsibility (CSR) in the near future, following ISO 26000 standards.

Benefits

The MED TEST project has identified an opportunity for \$US 446,800 of annual savings in electricity, gas, water and chemical products against an investment estimated at \$US 523,000. The return on investment is expected within a little more than one year. The identified cleaner production measures are under implementation.

Energy costs have been reduced by 15% through fuel switch to natural gas, insulation of steam and hot water distribution systems, installation of an economizer at the boiler, recovery of compressors heat losses into the dryer section, as well as the adjustment of the power factor.

The financial gains resulting from the reduced use of chemical products (e.g. chrome) and auxiliary products such as salt in the production process are estimated at 10%.

Water costs have been reduced by 14% thanks to the optimization of water consumption in the drums and according to the hourly tariffs, the reuse of vacuum dryer condensates as well as the retrieval of process bathwaters (soaking baths) and their reuse.

Other environmental improvements have been achieved in terms of reduction of wastewater pollution loads, corresponding to approximately: 50% of chlorides through the use of punched drums and the installation of a refrigerated chamber for fresh hides storage, 39% of BOD5

and 25% of COD in comparison to the annual loads, resulting mainly from the separation and retrieval of hairs before the process, the processing of sulphide and chrome baths, and the softening of process water (dyeing).

These measures have cut operating costs of the wastewater treatment plant and improved its efficiency through annual reductions of 100 tons COD and 35 tons of nitrogen.

Parallel to the identification of minimization opportunities, the company has charted its own environmental policy and is implementing an EMS in conformity with ISO 14001 standards, thanks to the identification of further areas of improvement.

Saving opportunities

Measure	Eco	nomic key figures		Resource saving	s per year
	Savings	Investment	PBP	Water,	Energy
	[USD/yr]	[USD]	[yr]	Chemicals	[MWh]
Reduced use of salt through drumming and cold conservation of skins	75000	92000	1.2	965 tons salt	-
Water savings	47 000	150000	3.2	Water 46000 m ³	-
Steam system and compressors	222800	46000	0.2	-	1705
Valorization of splits	55000	110000	2	1 500 tons waste	-
Reuse of retrieved chrome	30000	100000	3.3	150 tons chrome	-
Hair retrieval	17 000	25000	1.5	-	9
TOTAL	446800	523000	1.2		1714

Reduced use of salt, drumming and cold conservation of skins: The installation of a cold chamber for fresh hides storage helps minimize or even completely eliminate salt as a conservation agent. This option provides for net savings of \$US 50,000/ year, taking into account additional electricity costs. Moreover, the company acquired a punched drum facilitating the elimination of all conservation salt stuck on the skins before the soaking process. It allows for a 50% reduction of salt in all liquid effluents, and therefore of chloride, COD and BOD5 loads.

Water savings: The tannery has implemented several measures to cut down water consumption, which include the optimization of water consumption in the drums, the recycling of soaking and rinsing baths from tanning and post-tanning processes and their reuse in similar processes. The installation of submeters at each process enables an increased consumption control as well as the easy detection of possible overconsumption.

Steam system and compressors: The tannery has focused its efforts to cut down energy consumption through: the installation of a boiler economizer, the insulation of steam and hot water pipes, the recovery of heat losses from the compressor into the dryer, and the fuel switch to natural gas.

Valorization of splits waste: The tannery has put in place an equipment to process splits resulting from the fleshing processes valorizing 1,500 tons/year of this kind of waste. The splits are ground then heated up to 75°C. The obtained liquid is separated in 2 phases: one proteinaceous

phase valorized as fertilizer and retanning agent, and one fat phase valorized in the soap industry and as leather nourishment product.

Reuse of retrieved chrome: This technique allows replacing 30% of the new chrome with no effect on quality, thus saving 150 tons/year of chrome otherwise disposed of with the sludge.

Hair retrieval: The retrieval of intact hair from the drum through the installation of a filtering and recirculation system of the liming baths permits to reduce wastewater pollution loads by

approximately 40% of TSS, 30% of BOD5, 25% of COD and 50% of sulphides. This allows for electricity savings within the sewage treatment plant of about \$US 8,000/year, corresponding to 48 tons of CO2 per year and a 300 tons/year reduction of TSS.



5.5 Case Study 5. MED TEST. Tannerie du Nord Utique (TNU) (Tunisia)

Company overview

Based in the Utique industrial zone, TNU is a Tunisian company operating in the leather sector and producing for both local and international markets. Its total production amounts to 1.385 tons/year, segmented into different kinds of skins: bovine (58%), ovine (27%) and goat (15%).

The company joined the MED TEST project in order to identify opportunities for improvement regarding pollution linked to its activity and introduce Best Available Technologies (BATs) and Best Environmental Practices (BEPs).

Taking advantage of its adhesion to MED TEST, TNU has become familiar with EMS in line with the ISO 14001 standard and plans to implement it in the company.

Benefits

MED TEST has identified an opportunity for \$US 126,585 of annual savings in electricity, water and chemicals against an investment of \$US 186,150 with a payback period of less than two years. The identified cleaner production measures are under implementation.

Energy costs are expected to be reduced by 70% by switching boiler fuel to gas once the industrial area is connected to the public natural gas network, installing a boiler economizer, an insulating steam and hot water pipes, and demineralizing well water used for boiler feed.

The financial gains resulting from the reduction of chemicals are estimated at 5% for finishing products, 30% for chrome and 10% for auxiliary products such as salt.

Water costs have been cut down by 8% through the installation of a high volume/low pressure pistol in the finishing process; the use of a trial drum for testing purposes to improve quality and splitting of bovine hides.

Further environmental benefits, especially through drumming before soaking, have been achieved in terms of reduction of wastewater pollution loads, corresponding to about 10% of chlorides and 5% of annual COD flux.

These measures have minimized the operating costs of the water treatment plant and allowed for annual reductions of 130,000 kg of COD and 65,000 kg of BOD5.

In parallel with the identification of cost minimization opportunities, the company is in the process of elaborating its own environmental policy so as to undertake the implementation of EMS in conformity with the ISO 14001 standard.

Measure	Eco	nomic key figures		Resource savings per year	
	Savings [USD/yr]	Investment [USD]	PBP [yr]	Water, Chemicals	Energy [MWh]
Using a test drum to improve quality	10715	21150	2	1,500 m ³ water	
Drumming before soaking and salt reduction	8 5 7 0	25000	3	170 tons salt	-
Hot water/steam generation and distribution system	63 000	64000	1	-	1,197
Installation of high volume/ low pressure pistol for finishing	2150	2 500	1	5% finishing chemicals 300 m³ water	-
Hide splitting	42150	73 500	1.7	28 tons Cr 2,100 m³ water	-
TOTAL	126 585	186150	1.5		1,197

Saving opportunities

Using a test drum to improve quality: The use of the tannery's equipment with a test drum will make it possible to diversify production without squandering raw materials and auxiliary products and renew it by following fashion trends. It will also reduce COD (3%), as well as total water consumption, and most of all facilitate substantial gains in hides.

Hot water/steam generation and distribution system: Insulating hot water and steam pipes allows for a reduction of thermal energy consumption by 4%. Installing a boiler economiser, a softener for boiler water and switching fuel to natural gas will bring forth very substantial financial and environmental benefits, adding up to 70% of total annual thermal energy consumption.

Drumming before soaking and salt reduction: The installation of a punched drum enables the elimination of salt from the salted hides before the soaking stage, which results in the elimination of 170 tons/year of salt, a 10% reduction of wastewater chlorides and lower COD and BOD5 loads.

Hide splitting: This option limits consumption of chemicals (28 tons/year of chrome) and water (1,800 m3/year, i.e. 4% of the global process water), thus minimizing the end-of-pipe environmental impact.

Installation of a high volume/low pressure pistol for finishing: About 50-70% of COV emissions are released by pistol finishing machines. Installing this equipment in the finishing stage will bring about reductions in consumption of finishing products (5%), water (300 m3) and COD (2 tons) and moreover cut down VOC emissions by about 40%.



5.6 Case Study 6. MED TEST. Atef El-Sayed Tannery (Egypt)

Company overview

Atef El-Sayed Tannery is a medium size private tannery recently established in Alexandria. The tannery produces approx. 231 tons/year of wet blue and crust leather for the local market (10%) and for export.

The tannery joined the MED TEST project to identify opportunities for increasing resource efficiency and productivity and reduce pollution loads to minimize investment/operational costs of the planned wastewater treatment plant.

At project's start there was no formalized management system in place. During the implementation of MED TEST project, the company established a management system for quality according to ISO 9001.

Benefits

The MED TEST project identified annual total savings of \$US 97,377 in water, raw materials, fuel and electricity with an estimated investment of \$US 416,850.

Water costs would be reduced by 30% through applying good housekeeping measures, implementation of monitoring and controlling system for water consumption and recycling of pickling bath.

Total electricity costs will be reduced by 62% through improving the power factor, installing soft starters and inverters at machines and improving the lighting system.

The identified measures will entail environmental benefits in terms of reducing wastewater pollution loads by about 5% BOD5 and 7% COD annual loads.

In parallel to the identification of saving opportunities, the site designed and established a management system for quality according to ISO 9001. The company was trained in EMS according to ISO 14001 during the MED TEST in order to be able to integrate CP into the internal quality procedures. This will ensure sustainability of all the identified actions at company level as well as the development of new projects.

Saving opportunities

Measure	Ecor	nomic key figures		Resource saving	s per year
	Savings [USD/yr]	Investment [USD]	PBP [yr]	Water, Chemicals	Energy [MWh]
Good housekeeping	1119	767	0.7	149 m³ water, 25 tons materials	
Electrical system, motors and lighting	3 583	5 0 8 3	1.4		30
New production machines	88750	402667	4.5	5.8 ton product	
Recycling of pickle bath	3925	8333	2.1	220 m³ water, 23 tons chemicals	
TOTAL	97 377	416850	4.3		30

Good housekeeping: The project identified good housekeeping measures, including: regular maintenance programmes, regular cleaning and washing of equipments to control odor generation, better collection of splits from fleshing to reduce waste accumulation and unnecessary washing; using screens to prevent solids from entering wastewater channels; and activating the grounding system to all machines in the tannery to maintain health and safety for employees. The implementation of good housekeeping measures would save 10% of water consumption and reduce the amount of wastewater

discharged to sewage. These measures resulted in reduction of 646 kg/year (5%) BOD and 1,306 kg/year (7%) COD.

New production machines: The company has put in place an investment plan to replace the existing old deteriorated machines with new ones to increase productivity and quality of products as well as environmental performance. New machines are foreseen for toggling, measuring, ironing, spraying, sammying and overhead conveyor for drying the skins that will minimize out of specification products by 5.8 tons/year, reduce time of different tanning processes and ultimately improve labor safety.

Electrical system, motors and lighting: Actions identified to reduce electricity use include: installing power factor correction panel to achieve a standard value in the range of 0.92-0.95;

measuring harmonics for checking distortion in the electrical feeder and protecting the capacitors from damage; installing soft starters and inverters on motors (drums) to reduce their

electricity consumption; improving the lighting system by replacing the current incandescent lamps with energy saving lamps. The implementation of these options will save 62% of total electricity consumption corresponding to 30 MWh/year.

Recycling of pickle bath: Recycling of pickling bath would require installation of a vessel and a filter: this measure will reduce salinity of the discharged wastewater, which is a major problem of the company, achieve 15% water savings and lead to 23 tons/year of chemicals reduction.



5.7 Case Study 7. Waste water treatment plant for tanneries, Igualada, Catalonia (Spain)



Company overview

The company IDR was created in the year 2000 with the objective of building and managing a waste water treatment plant providing service to the tanning sector as well as to the urban wastewater generated by the municipality of Igualada, Catalonia (Spain). The plant entered into operation on September 2005. The total investment on land property, civil works and expenses to start operation was 11.300.000 \in .

The company is currently comprised of 28 tanning companies having each company shares proportional to the generated wastewater. The plant treated in 2014, 350.000 m3 of industrial tanning wastewater as well as 600.000 m3 of urban wastewater coming from the same collector. The treated wastewater is then discharge into another collector that takes it to the wastewater treatment plant of the municipality of Vilanova del Camí where is treated again together with more urban wastewater before being discharged into the Anoia river.

The plant treatment process includes a phase of pre-treatment and a phase of biological treatment of wastewater. The first phase includes a raw filtering system, pumping of industrial and urban wastewater, fine filtering, desanding and degreasing, desulfuration of the industrial wastewater, homogenization, air deodoring of closed rooms and primary decantation. The second phase includes biological treatment, pumping of primary and biological sludge, dehydration of sludge with centrifuges, storage of the sludge in silos and air deodoring of the sludge storage room.

After conducting these actions, the plant treatment yields of different pollutants are the following:

Parameters in grams./liter	Entry		Treated output	% elimination
	Industrial (average)	Urban (average)		
Suspended solids	3,400	0,250	0,080	96,7
COD (Chemical Oxygen Demand)	6,900	0,500	0,350	95,2
Sulfide	0,030	0	0,00015	99,5
Conductivity	16.000	2.700	8.900	4,0
Chromium III	0,068	0	0,00025	99,7

Source: IDR, 2015.

Benefits and cost-saving opportunities

Plant management data and costs (2014)		
	Quantity or cost (€)	
Produced sludge sent for recycling	7.000 Tm.	
Cost of sludge treatment	520.000 €	
Consumed electric energy (3.000.000 kW)	350.000 €	
Personnel wages and insurance	650.000 €	
Reagents (polyelectrolyte, NaOH, Cl3Fe)	440.000 €	
Wastewater treatment Tax	540.000 €	
Maintenance of facilities	248.000 €	
Loan financial costs	990.000 €	
Total cost foreseen for year 2014	3.738.000 €	
Cost of industrial wastewater treatment per m3	10,60 €	

The following summary table is showing the plant main data and costs of management:

Source: IDR, 2015.

The costs of plant functioning previously exposed are divided among users by a quota. This quota is divided in a fixed part and a variable part. In regards to fixed quota, each user pays an annual amount for participation of $30,36 \in$ per share. This fixed quota covers 26% of the plant expenses. As for the variable quota, each user pays an amount proportional to the wastewater discharge on a monthly basis. This variable amount covers 74% of the total of the remaining expense.

The following chart shows IDR plant rates for 2014.

IDR plant rates for 2014			
Fixed quota per year per share	30,36 € (approximately 26 % of total cost)		
Variable quota per discharge per parameter 2014			
Suspended solids	0,823 € / kg.		
COD (Chemical Oxygen Demand)	0,294 € / kg.		
Nitrogen	0,606 € / kg.		
Sulfide	0,729 € / kg.		
M3 + Conductivity	$0,519 \notin$ / unit (conductivity in mscm / 6.000)		
Chromium III	18,022 € / kg.		

Source: IDR, 2015.

The treatment cost per ton of hides produced is the following one:

		Cost treatment Tm. hides
Year	Cost treatment per m3 (€)	(€)
2006	6,81	180
2007	7,58	167
2008	7,74	159
2009	8,34	213
2010	7,73	170
2011	10,00	203
2012	11,17	223
2013	11,34	226
2014	10,60	224

Source: IDR, 2015.

The treatment cost per ton of hides produced has remained constant from the plant initial operation in 2005 until 2009 since users lowering loads per unit produced unit was compensated by the increment

of treatment rates. By 2011 since it was difficult to continue reducing pollution loads per unit produced, rates have evolved according to operational costs.

Annexes

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A2. List of acronyms

AOX adsorbable organic halogen (X) **BAT** best available techniques **BOD** biochemical oxygen demand **BREF** BAT reference document **CO** carbon monoxide CO₂ carbon dioxide COD chemical oxygen demand **CR** corporate responsibility **CSR** corporate social responsibility **EMS** environmental management systems EMA environmental management accounting **EU** european union **EUR** euros **ETP** effluent treatment plant **EIPPCB** european integrated pollution prevention and control bureau **GEF** global environment facility H₂S hydrogen sulfide HVLP high volume low pressure **INESCOP** footwear technological institute **IPTS** institute for prospective technological studies **LWG** leather working group MAP mediterranean action plan MED TEST transfer of environmental sound technology in the south mediterranean region **NAP** national action plan NGO non-governmental organization NaCl salt NOx nitrogen oxides **NPE** nonylphenol ethoxylate **PFOS** perfluoro octane sulphonates **PFOA** perfluorooctanoic acid pH the measure of acidity or alkalinity of a chemical solution, from 0 to 14 **PVC** polyvinyl chloride REACH regulation (EC) no 1907/2006 of the european parliament and of the council on the registration, evaluation, authorization and restriction of chemicals SCPRAC regional activity center for sustainable consumption and production **RECP** resource efficiency & cleaner production SMCP société moderne des cuirs et peaux SOx sulphur oxides SS suspended solids **TDS** total dissolved solids **TKN** total kjeldahl nitrogen TMM tanneries mégisseries du maghreb TNU tannerie du nord utique **TEST** transfer of environmentally sound technology **UNEP** united nations environment programme **UNIDO** united nations industrial development organization VOC volatile organic compound

A3. Health and safety recommendations in tanneries

The following summary tables are showing health and safety recommendations including a description, possible consequences and proposed prevention measures in an average tannery facility in the following dangers:

- Chemical hazards;
- Activities in wet environments;
- Same level or elevated falls;
- Heavy falling objects;
- Collision with moving objects;
- Blows and cuts by objects or tools;
- Projection of fragments or particles;
- Trapping by or between objects;
- Overexertion;
- Thermal contact;
- Direct or indirect electrical contact;
- Fire & explosions; and
- Exposure to noise & vibrations.

DESCRIPTION / STAGES	POSSIBLE CONSEQUENCES	PREVENTION MEASURES
Chemical hazards		
 Contact with chemical substances is made in the different stages of the process by handling or using chemicals, and contact can be made in different ways: inhalation in the form of substances present in the air (gases, dust, vapours, fog and smokes) ingestion, when the workers are eating, drinking or smoking in the work area without washing their contaminated hands by skin contact or absorption, normally through the pores or cuts/wounds in hands, arms, or unprotected body areas 	The consequences of contact with toxic substances depend on different factors; the toxicity of the substance, its ease to penetrate the skin, organs or systems which it affects, the amount of substance or the affected skin surface, and time of exposure. The result of the contact can cause temporary effects, like fainting, headache, eye, skin or lung irritation, allergic reactions, poisoning of the liver, kidney or nervous system, or fainting due to the lack of oxygen. It can also cause long-term illnesses like occupational asthma, ulcers, bronchitis or genetic defects and, in some specific cases, even instant death. Some of the especially problematic substances are: sodium sulphide; chromium salts, which can cause contact dermatitis; aldehyde derivatives, which are irritating and sensitizing; synthetic resins, like urea-formol or urea-acrylics, which are sensitizing; acids and alkalis, which are corrosive, etc. In addition to the adverse effect on the human body, chemicals can be the source and cause of fire,	 For the handling and storage of chemicals in the tannery: Have suitable storage areas equipped with emergency services (shower and eyewash), electrical installation, fireextinguishing means and suitable spill and leak containment buckets Use adequately labelled products according to the safety data sheets Using protective equipment and ensuring the availability of gloves, boots, aprons, safety goggles and respirators for each worker Ensuring adequate hygiene practice, like regular cleaning of work area, floors, walls and machines and removal of waste Where possible, limit the possibilities of exposure to hazardous products replacing toxic products with other less toxic ones Controlling the unloading of paddle vat and drum baths with pipes connected to the

 It is therefore important to know: the characteristics of the chemicals used according to the indications on the labels and the information provided in the products' safety data sheets collective and personal protection equipment that must be used to avoid contact with chemicals 	corrosion and damage to electric installations and structures, and can have detrimental effects on the surrounding environment when they are released in an uncontrolled way.	 drain, Reducing the concentration of pollutants in the surrounding air, using general ventilation and natural airflow, Using low emission equipment, like roller machines instead of spraying units, whenever possible, Using extraction systems in dry shaving machines, wheeling, buffing and dedusting machines and spraying booths
DESCRIPTION / STAGES	POSSIBLE CONSEQUENCES	PREVENTION MEASURES
Activities in wet environments		
Humidity is a risk factor inherent to the majority of processes of the tanning sector and can generate both accidents and illnesses so it is necessary to give greater importance to its control. Many of the beamhouse operations (leather preparation) are carried out by processing hides and skins in big pits or drums. The solutions are usually poured into containers or are transferred through pipes into them and are subsequently emptied through open drains in the work area or pipes. The tasks where the presence of humidity is most important are the following: drum loading and unloading, soaking and unhairing, pre-tanning and tanning, dyeing and fatliquoring, fleshing, splitting, piling and trimming, sammying and cutting into sides, shaving and setting out.	Excessive humidity critically affects the comfort or heat sensation by affecting the environmental humidity; furthermore, certain humidity levels favour the growing of microorganisms with possible detrimental effects on health. Among the effects of humidity are skeletal system diseases (arthritis and rheumatism), respiratory disorders caused by frequent colds and rhinitis, and dermatitis.	To prevent the effects of humidity, it is recommended to wear waterproof clothes and suitable (waterproof and non- skid) footwear and masks. It is therefore important to know: - Waterproof clothes, suitable footwear and masks must be used to prevent excessive humidity affects

DESCRIPTION / STAGES	POSSIBLE CONSEQUENCES	PREVENTION MEASURES
Same-level or elevated falls		
This type of risk can occur in usual work activities and while walking along corridors, entrance doors, etc. due to the floor's state, fixed obstacles, objects that get in the way, etc.	The consequences of this risk are injuries, bruises, scratches, sprains, dislocations, fractures, etc. depending on the type of fall.	 For the prevention of falls during tanning operations the following recommendations shall be taken into account Keep passageways and exit areas clearly marked and free

Heavy falling objects This type of risk is mainly produced in the raw material reception, material storage and preparation in intermediate processes, and storage and dispatching of finished products, due to poor piling up, packaging defects and/or improper way of fastening them, exceeding the capacity both in volume or weight of the vehicle, driving at excessive speed, poor fastening of loads, etc.	The consequences of this risk are injuries, bruises, crushing, etc., due to the impact of chemical product containers, leather batches, etc. on the upper and lower limbs It is therefore important to know: - secure well loads and transport them with care	 To prevent falls of heavy objects the following recommendations shall be taken into account Limit the pile height (boxes, equipment, etc.). Securing materials in warehouses so as to prevent slipping Secure well the loads during transport Use mechanical means in the handling of heavy and/or
		bulky objects
		- Define and mark the area of influence of suspended load and avoid staying under it
DESCRIPTION / STAGES	POSSIBLE CONSEQUENCES	influence of suspended load
DESCRIPTION / STAGES Collision with moving objects	POSSIBLE CONSEQUENCES	influence of suspended load and avoid staying under it

Tage 00		
It is therefore important to know: - maintenance, repairing and cleaning of machines shall be performed with disconnected equipment		 obstacles respecting their widths Regarding operating machines and motor-driven tools with moving elements: Keep protection devices or guards in place, which prevent direct access to operative areas of the moving parts Do not stay in the operation angle of moving parts and avoid contact with them Servicing, maintenance, repair, and cleaning shall be performed on turned-off, disconnected equipment
DESCRIPTION / STAGES	POSSIBLE CONSEQUENCES	PREVENTION MEASURES
Blows and cuts by objects or tools		
Most blows and cuts occur during raw or finished material handling due to the use of machinery and during machinery maintenance operations. In the tanning process, the leathers are subjected to different manual trimming operations using knives or scissors, with the risk of cutting by direct contact with the tool. Furthermore, the majority of machinery used in tanneries has as main element a cylinder fitted with blades (fleshing, splitting, shaving, shearing machines, etc.) which can be accessed in maintenance operations or accidentally while working with them. Finally, the generalised used of rotating drums for tanning and dyeing adds the risk of blows and trapping	As a consequence of these risks, there are frequent injuries such as cuts, tears, pricks, wounds, bruises, scratches, etc. It is therefore important to know: - Use the appropriate tool in each operation and suitable protection for each tool (gloves, goggles, etc.)	 To prevent blows and cuts by objects or tools, the following recommendation shall be taken into account: Use suitable protection for each tool (gloves, goggles, etc.) The machinery shall compliance with the requirements of harmonized standards on machine safety Use the appropriate tool in each operation. Before using a tool, check that it is in a good condition, without debris, with isolation and handles in place, etc. Keep tools clean and tidy in a safe place.
Projection of fragments or particles	-	
In some of the tannery machines there can be a risk of tool particle or fragment projection, like in the band saw, polishing wheel, etc.	Projection of fragments or particles can cause cuts, tears or injuries by particle projection to the face or eyes.	To prevent particle or fragment projection it is recommended to install guards or protective devices in the machines that limit the projection of fragments or particles and use suitable protection for each machine (gloves, goggles, etc.)
DESCRIPTION / STAGES	POSSIBLE CONSEQUENCES	PREVENTION MEASURES
Trapping by or between objects		

This risk can apply to machines that Trapping can cause wounds, cuts, To prevent trapping, the

 have moving parts at the reach of operators. In most of the tannery machinery there is this risk of trapping, given that, in the majority of operations the leather has to be directly held and brought to the operation area manually. In cleaning and maintenance work it may be caused by transmission parts like belts, gears, etc. The machines which have a greater risk of trapping are: In the beamhouse process: fleshing, splitting, shearing machines, etc. in operations prior to finishing: summing, shaving, buffing, setting, shearing, dedusting machines, etc. In the finishing process: ironing, polishing, and splitting 	tears, multiple injuries, etc. It is therefore important to know: keep protection devices or guards in place, which prevent direct access to operative areas of the moving parts 	 following recommendations shall be taken into account: Do not remove guards or protective devices that prevent direct access to moving parts of the machines, Do not stay in the operating angle of moving parts of the equipment and avoid contact with them, Turn off and disconnect machinery during servicing or maintenance.
Overexertion		
In material handling, mainly in unloading or storage, overexertion may occur due to the weight or volume of the materials handled, or to the need to adopt awkward or forced posture with a risk of back injuries.	As a consequence of this overexertion, muscle and bone injuries can occur, which, if the situation is not corrected, can become chronic.	 To prevent these injuries, the following recommendations shall be considered: Avoid awkward postures when handling loads. Decrease the weight of the loads Whenever possible, use mechanical aids to handle materials and, if necessary, loads should be handled by more than one person.

DESCRIPTION / STAGES	POSSIBLE CONSEQUENCES	PREVENTION MEASURES		
Thermal contact				
The risk of thermal contact in tanneries occurs mainly in drying and finishing processes by contact with hot presses and cylinders that can cause more or less severe burns, caused by contact with hot parts of the machinery.	Burns (more or less severe)	To prevent injuries it is recommended to maximise the precautions while operating equipment with hot surfaces, like dryers, ironing presses, boilers and hot water pipes, etc.		
Direct or indirect electrical contact.				
The risk of direct or indirect contact is common to all types of operations and, especially, to the ones conducted with voltage, by incompliance of the basic rules of electrical safety or by faulty	Depending on the intensity of voltage there may be cramps, contractions or tetanisation of the muscles, respiratory arrest, asphyxia, erratically heart beating, ventricular fibrillation, etc. even causing the death of the victim	To avoid these injuries it is recommended to establish suitable maintenance protocols for the facilities and electric appliances, working with the necessary PPE and the most suitable safety material in each		

transmitted.

electrical devices.	under certain negative circumstances.	case.
Fire & Explosions		
In tanneries the fire risk level is considered of medium degree. The high calorific power of the finished product (fur, leather, buffing dust, etc.) is counteracted by a low activation coefficient of these materials. Explosions can happen in tanneries when using solvents due to vapour concentration in certain work areas or the use of pressure equipment, like compressors, boilers, etc.	Depending on the type of fire, there can be consequences for people such as asphyxia, smoke intoxication, multiple injuries, fire burns, etc. Depending on the scope and type of explosion, nearby workers will be affected by severe burns, multiple injuries by projected pieces and materials, etc. even causing the death of the victim under certain negative circumstances.	 To prevent fire, it is recommended: To install the necessary fire extinguishing and detection means and to establish their maintenance procedures, To keep emergency exits free from obstacles and work areas clean, Not to smoke in work areas, To carry out adequate maintenance operations in electrical facilities likely to cause fire, To avoid the accumulation of inflammable/combustible materials To prevent explosions, by carrying out adequate maintenance operations in pressure equipment and use solvent-free products.
DESCRIPTION / STAGES	POSSIBLE CONSEQUENCES	PREVENTION MEASURES
Exposure to noise & vibrations		
Noise as a physical contaminant is also present in tanneries, mainly in beamhouse and tanning processes, and above all in operations prior to finishing due to the great number of mechanical operations performed, which can occasionally exceed 90 dbA. In activities with portable tools, hand-arm vibrations can be transmitted	Depending on the equivalent daily level of exposure, the consequence of this risk, in the long term, can be hearing loss, for high noise level exposure. As additional symptoms there may be temporary auditory fatigue, blood pressure disorders, anxiety, etc. so which can generate specific long-term pathologies.	It is recommended to use hearing protection.