Training Toolkit: Courses and Exercises.
Unit 3: Environmental Management

WP 2.1.

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INNOLEA: Innovation for the Leather Industry in Jordan and Egypt
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Disclaimer

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Contents

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1. Introduction

INNOLEA project aims to fill an apparent gap in the area of specialized services for the leather sector with the establishment of four leather centres in local Universities, two in Jordan and two in Egypt, utilizing the experience and expertise of EU partners in the area of services for the leather sector.

Through the creation of these centres and the further tasks that will be implemented in this project, the leather sectors in Jordan and Egypt will be offered access to business development services, such as quality testing, product certification, training, fashion trends, production organization, BtoB and funding opportunities, and subsequently the Jordanian and Egyptian leathers sector will have a valuable ally for its further development.

The project also aims to create and maintain a link between Universities and businesses of the leather sector that will foster innovation and the manufacturing of high value quality products, as well as further cooperation between EU and Jordan and Egypt Universities and leather businesses.

The project also aims to help encourage the Egyptian and Jordanian governments to favour the establishment of leather centres within universities and to promote research and projects between EU and Egypt and Jordan universities in the leather sector, by creating a research innovation and training network, which will continue to operate after the end of the current project.

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2. UNIT 3: Environmental Management

2.1. Objectives

- To improve and update technical competences and skills (on environmental impact control)
- To acquire key skills and competences
- To have a better knowledge about norms and legislation related to treating effluents resulting from leather processing
- To take care of environmental issues in the whole leather process production
- To be aware about wastes produced by the leather tanning and finishing process and their impact on the environment

2.2. Lesson 1: Restricted substances

Authors: Viorica ROSCULET – INCDTP - ICPI

2.2.1. Definitions

SAFE PRODUCT: Shall mean any product which, under normal or reasonably foreseeable conditions of use including duration and, where applicable, putting into service, installation and maintenance requirements, does not present any risk or only the minimum risks compatible with the product's use, considered to be acceptable and consistent with a high level of protection for the safety and health of persons.

SUBSTANCE: a chemical element and its compounds in the natural state or obtained by any manufacturing process, including any additive necessary to preserve its stability and any impurity deriving from the process used.

SVHC: Substances of very high concern

PREPARATION: a mixture or solution composed of two or more substances. Some “preparations” are adhesives, finishing products, dyes, etc.

ARTICLE: an object which during production is given a special shape, surface or design which determines its function to a greater degree than its chemical composition

MANUFACTURER: any natural or legal person established within the Community who manufactures a substance within the Community.

IMPORTER: any natural or legal person established within the Community who is responsible for imports.

DOWNSTREAM USER: any natural or legal person established within the Community, other than the manufacturer or the importer, who uses a substance, either on its own or in a preparation, in the course of his industrial or professional activities.

NON-COMMUNITY MANUFACTURER: a manufacturer of preparations or substances established outside the Community.

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ONLY REPRESENTATIVE FOR A NON-COMMUNITY MANUFACTURER: any natural or legal person established in the Community who represents a non-Community manufacturer of substances or preparations to fulfil, as his only representative, the obligations on importers under the REACH Regulation.

RAPEX: Rapid Alert System for dangerous non-food products, which was established in 2004.

REACH: Registration; Evaluation; Authorisation; Chemicals

2.2.2. General Product Safety Directive (GPSD)

- General safety of products is regulated by Directive 2001/95/EC.
- This Directive shall apply if there are no specific European regulations governing the safety of certain categories of products.
- Commercial products on the domestic market are subject to general safety requirements.

Product safety considers the following aspects in particular:

(1) the characteristics of the product, including its composition, packaging, instructions for assembly and, where applicable, for installation and maintenance;

(2) the effect on other products, where it is reasonably foreseeable that it will be used with other products;

(3) the presentation of the product, the labelling, any warnings and instructions for its use and disposal and any other indication or information regarding the product;

(4) the categories of consumers at risk when using the product, in particular children and the elderly.

The feasibility of obtaining higher levels of safety or the availability of other products presenting a lesser degree of risk shall not constitute grounds for considering a product to be “dangerous”. Furthermore, the law obliges business owners to inform of the risks for the safety of products and services:

The aim of this directive is to ensure that products placed on the market are safe. The competent authorities shall define the necessary procedures and measures that should the manufacturers and distributors should take in order to obtain safe products.

The purpose of the General Product Safety Directive is to ensure that products placed on the market are safe. This Directive shall mean any product, including in the context of providing a service, which is intended for consumers or likely, under reasonably foreseeable conditions, to be used by consumers even if not intended for them, and is supplied or made available, whether for consideration or not, in the course of a commercial activity, and whether new, used or reconditioned.

Manufacturers shall be obliged to place only safe products on the market. Within the limits of their respective activities, manufacturers and distributors must collaborate with the competent authorities, at the request of the latter, in any actions undertaken to prevent risks present in the products they supply or have supplied. The procedures for that collaboration, especially the procedures for dialogue with the manufacturers and distributors in question on issues related to product safety, shall be defined by the competent authorities.

RAPEX

In order to ensure a high level of protection of consumer health and safety, the appropriate means include:

- Establishing
- Updating and monitoring product safety
- Assessments and periodic evaluations of performance of the monitoring activities.

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In order to effectively monitor the market with the aim of guaranteeing a high level of protection for the health and safety of consumers, which entails cooperation between the competent authorities, the Member States shall ensure that procedures are established which include adequate means and measures, which may include, in particular:

- establishing, regularly updating and implementing programmes for monitoring each sector according to categories of product or risk, and also following-up the activities of monitoring, observations and results;
- the monitoring and updating of scientific and technical knowledge on product safety;
- periodic evaluations and inspection of the functioning of monitoring activities and their effectiveness and, if it should be necessary, reviewing the procedure and organising surveillance.

2.2.3. REACH Regulation

REACH (Regulation nº 1907/2006 of the European Parliament and of the Council) is the European regulation relative to the Registration, Evaluation, Authorisation and Restriction of Chemicals. This regulation attributes responsibility to industry for managing the risks associated with substances that it manufactures, imports, sells and uses in its processes. REACH entered into force on1st June 2007.

REACH (Regulation nº 1907/2006 of the European Parliament and of the Council) is the European regulation relative to the Registration, Evaluation, Authorisation and Restriction of Chemicals. This Regulation assigns the industry the responsibility of managing the risks associated with the substances that it manufactures, imports, sells and uses in its processes. To do so, each company must comply with one or more of the requirements established by the Regulation depending on the type of chemicals and preparations that it manufactures, uses and/or imports, their origin (whether they are from the European Union or not) and how they are applied in their industrial process. The future of the footwear industries and of their components, such as tanneries, the manufacture of adhesives, outer soles for footwear, etc., is conditioned within the European Union by this Community regulation.

Depending on the complexity of the business that you run, it may be necessary to employ an accounting professional to manage compliance with the relevant accounting obligations in the Code of Conduct for each type of business activity.

ECHA

The European Chemicals Agency is the official body charged with coordinating all the Member States of the European Union to comply with that Regulation.

- ECHA is the European Union regulatory authority on the safe use of chemicals.
- ECHA is responsible for coordinating all Members States of the European Union so that they can implement the REACH regulation.
- It shows the information on the hazards and safe use of chemicals.
- ECHA has a web page where all the information about the REACH regulation is posted.

General procedure of the REACH Regulation

The REACH system replaces over 40 Directives and regulations and creates a single system applicable to all chemicals. Registration of a substance:

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1. Registration
2. Evaluation
3. Authorisation
4. Chemicals

The main objective is to ensure a high level of protection of human health and the environment. The REACH system replaces over 40 Directives and Regulations and creates a single system applicable to all chemicals. The principal characteristic of this regulation is that it introduces the obligation of registering all chemical substances that are sold within the territory of the European Union and therefore no substance may be put on the market if it is not registered, based on the principle of precaution.

It assigns the industry the responsibility of managing the risks associated with chemical substances. They must guarantee that they only manufacture, sell or use substances that have no adverse effects on human health or the environment. Furthermore, there has to be more information on chemical substances and their associated risks and this must be conveyed to users and consumers. The content of the registration application consists of:

- A technical dossier with general and specific information on the substance;

- A Chemical Safety Report for registrations with tonnages $\geq$ 10 tonnes/year

Registration

Supply Chain in the footwear sector:

1. Manufacturers of substances

2. Importers of preparations

3. Manufacturers and importers of articles

In the supply chain for the footwear sector, the registration of substances must be made by the **manufacturer and importers of substances** who are, for example, the manufacturers or importers of solvents, oxides, tanning agents, etc., the **importers of preparations**, who have to register each one of the substances of which the preparation is made (for example, adhesives, finishes, etc.) and the **manufacturers and importers of articles that contain some substance that is released** in conditions of normal or reasonably foreseeable use (for example, aromas that might be contained in the outer soles or insoles, etc.).

Evaluation

Evaluation under REACH focuses on three different areas:

- Examination of testing proposals submitted by registrants
- Compliance check of the dossiers submitted by registrants
- Substance evaluation.

The European Chemicals Agency is responsible for assessing the registration dossiers. That evaluation will be compulsory for all applications that include any of the tests listed in Annexes IX and X of the REACH Regulation. Once the evaluation is done, registrants may be required to submit further. The result of the evaluation can be:

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- that the substance must be subject to restriction or authorisation procedures,
- the classification and labelling of the substance must be harmonised
- information must be supplied to the other authorities so that they can adopt appropriate measures, for example of risk management.

In line with Article 54 of the REACH Regulation, by 28 February of each year, the European Chemicals Agency has to publish a report on the progress it has made over the previous calendar year on its obligations in relation to evaluations. The European Chemicals Agency is specifically required to include recommendations to potential registrants.

Authorisation

This procedure is used for substances that are of extremely high concern. The main objective of the Authorisation is to ensure the correct functioning of the domestic market and to guarantee that the risks arising from the Substances of Very High Concern are properly controlled. The Commission only grants authorisations for specific uses of a substance in order to guarantee the control of risks and that these substances are gradually replaced by other appropriate substances or technologies where this is economically and technically viable.

The Agency publishes and regularly updates a list of substances (list of candidate substances) identified as being of extremely high concern (carcinogens, mutagens and reproductive toxins), persistent, bioaccumulative and toxic substances; very persistent and very bioaccumulative substances, and some substances of concern which have irreversible serious effects on humans and the environment, such as endocrine disruptors).

The substances included in Annex XIV are subject to authorization. The Commission only grants authorisation for specific uses of substances in order to guarantee the control of risks and to replace them with other substances, if possible. Manufacturers, importers, or downstream users of these substances may not sell them or use them, unless authorisation has been granted for a specific use

Manufacturers, importers or downstream users of a substance included in the Authorisation List can apply for authorisation. Downstream users who do not apply for their own authorisation may use a Substance of Very High Concern included in Annex XIV, provided that it is used in accordance with the conditions of authorisation granted to an agent further up the supply chain for that use.

Holders of an Authorisation, and also downstream users making use of the authorisation given to an agent further up in the supply chain, must include the Authorisation number on the label of the substance or preparation containing the substance for an authorised use.

Restriction

The restrictions are an instrument for protecting human health and the environment from unacceptable chemical risks. The restrictions can limit or prohibit the manufacture, marketing or use of a substance and can be applied to any particular substance in a mixture or in an article, including those not requiring registration. They can also be applied to imports.

2.2.4. Critical substances regulated by the REACH potentially present in footwear

In the footwear manufacturing industry, there are three groups of substances likely to appear in footwear components or in finished products and that generate legal obligations regarding the components that contain them. The substances to be considered are:

Substances of Very High Concern, Substances Subject to Authorisation (Annex XIV of the REACH) and Restricted substances (Annex XVII of the REACH).

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Substance of Very High Concern

Any Member State, or the European Chemicals Agency at the request of the European Commission, can propose a substance to be identified as a Substance of Very High Concern. If it is identified as such, it will be added to the list of candidate substances, which contains all substances that might be included in the Authorisation List (Annex XIV of the REACH).

The proposal is prepared in accordance with Annex XV of REACH, and consists of two basic parts. The first provides the information and evidence for identifying a substance as a Substance of Very High Concern. The second, examined during the monitoring stages in the identification process, contains information on the quantities of the substance in the European Union market and its uses, the emissions and resulting exposure and any possible alternatives to the substance.

After publication of the proposal, anyone who so wishes can put forward any comments or add more information, for example, in relation to the properties, uses and risks of the substance proposed or its alternatives. If no comments are received, the substance will be included in the list of candidate substances. The proposals and comments will be forwarded to the Member State Committee, which decides on the identification of the substance as a Substance of Very High Concern. If the Committee does not reach a unanimous decision, the case will be sent to the European Commission.

The intention of proposing a substance to be identified as a Substance of Very High Concern is made public on the European Chemicals Agency website, in the Registry of Intentions before presenting the proposal. One of the purposes of this Registry is to enable any interested parties to be up-to-date with those substances that could be catalogued as Substances of Very High Concern before being included in the list of candidate substances. This makes it possible to prepare for complying with any possible obligations arising as result of a substance being finally included in the list of candidate substances. Therefore, manufacturers, importers and suppliers of articles are recommended to regularly check the Registry of Intentions on the European Chemicals Agency website.

If no comments are received, the substance will be included in the list of candidate substances. The proposals and comments will be forwarded to the Member State Committee, which decides on the identification of the substance as Substances of Very High Concern. If the Committee does not reach a unanimous decision, the case will be sent to the European Commission.

The inclusion of a substance on the list of candidate substances gives rise to legal obligations for the companies that manufacture, import or use the substance, whether as such, in preparations or in articles.

Manufacturers and importers of articles can obtain information on Substances of Very High Concern and the concentration contained in each from the agents in the supply chain, such as suppliers of components of the articles in or outside the European Union and suppliers of substances and mixtures.

If any of the substances on this list is contained in the articles, the supplier must provide the recipient of the article with sufficient information to allow safe use, including, at least, the substance name if it is found in the article in a concentration higher than 0.1 % by weight.

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If a consumer requests information on the safety of the article that he is buying, the supplier of the article containing a Substance of Very High Concern on the list of candidates in a concentration higher than 0.1 % by weight/weight must give, at least, the substance name. He must provide the corresponding information, free of charge and within 45 days from when the request was received.

The list of Substances of Very High Concern that are candidates for Authorisation was last updated in July 2017. There are currently 174 substances in the candidate list.

Substances subject to authorisation

The REACH Regulation establishes that the European Chemicals Agency must identify, from within the "list of candidates", those substances that are to be included first and foremost in Annex XIV of the REACH Regulation (the "Authorisation List") and recommend the entries in Annex XIV (i.e. transitional provisions and, when appropriate, exemptions and periods of review) for those substances to the European Commission, taking the opinion of the Member State Committee into account. The European Commission will make the final decision on which substances will be included in Annex XIV and with which entries.

Once the European Commission has placed Substances of Very High Concern on the Authorisation List (Annex XIV of the REACH Regulation), companies can submit a request to the ECHA to apply for authorisation for specific uses. REACH allows companies to request authorisation to continue or commence the use of the substances included in the Authorisation List. Those substances included in Annex XIV cannot be used, unless they have authorisation for the specific uses or if the Authorisation is being processed.

Substances subject to restriction

Substances subject to restrictions are listed in Annex XVII of the REACH Regulation. The restrictions relate to the conditions of manufacturing, use and marketing. This means that all manufacturers, importers, distributors, sellers and end users must comply with them. The competent authorities of the Member States shall be responsible for complying with the restriction.

Role and obligations of companies in the supply chain

The REACH Regulation affects companies in the footwear sector. Specifically, footwear manufacturers, producers of components, tanneries, manufacturers of substances and chemical mixtures. That is to say, what is known in general as the “supply chain”. In the supply chain for the footwear sector there are a number of participants identified according to the activity engaged in and the position they occupy in the chain.

The principal function for manufacturers of finished products such as footwear and leather goods (handbags, belts etc.) is to assemble pieces or components. During the assembly, the manufacture, and finishing of the articles, they use substances or chemical mixtures, for example, adhesives, solvents etc.

Therefore, these companies should ask their suppliers for information in order to check if the preparations and components they use contain any Substances of Very High Concern. Furthermore, they should check whether any substance subject to authorisation is used in the manufacture of their articles. They should also

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ensure that their components do not contain any of the restricted substances above the maximum limit permitted.

Communication in the supply chain in the footwear sector

The main tool for transferring the information will be the Safety Data Sheet (SDS). The SDS has to be expanded with an Information annex containing a summary of the Chemical Safety Report (CSR).

The major issue for these "article suppliers" is how to determine whether any of the Candidate List SVHCs are present in their products and at what level. This task is made more difficult by the continuous extension of the Candidate List. SVHCs have been shown to be contained in a range of consumer products, including shoes, but manufacturers and retailers are not always aware of their presence.

In general, there is an obligation to pass on information on these substances if they are contained in the articles. All suppliers of an article that contains any substance included in the list of candidates for Authorisation in a concentration higher than 0.1% by weight, must provide their customers or any consumer who asks for it, with information to allow safe use of the article including, at least, the name of that substance. The relevant information shall be provided, free of charge, within 45 calendar days of receipt of the request. With regard to the obligations of communicating information on the substances contained in articles in general (i.e. communication with receivers and consumers), the following must be noted: This obligation does not depend on the tonnage (i.e. it is also applicable for quantities less than 1 ton/year). The packaging is always considered as an article separate from its content. Therefore, there is an obligation to provide information on the substances contained.

2.2.5. Technical report ISO/TR 16178

***"*Footwear — Critical substances potentially present in footwear and footwear components"** (now under review, will be replaced by ISO/ NP TR 16178, see: www.iso.org).

DEFINITIONS:

Allergen: substance that is capable of inducing an allergic reaction

Allergy: immunologically mediated response to certain specific substances

- NOTE 1. The specific substances are allergens.
- NOTE 2.Type-1 allergy (respiratory allergy) is mediated by IgE antibodies and may cause asthma, rhinitis and urticaria.
- NOTE 3 Type-4 allergy (dermal allergy) is mediated by T-cells and may cause dermatitis.

Detection limit: value from which a substance is considered detectable.

- NOTE. This means that the signal associated to the substance is three times bigger than the background noise signal. The limit of detection is determined experimentally by the laboratory for each substance.

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Quantification limit: value from which a substance is considered measurable

- NOTE. It is the value where the uncertainty of measurement is equal to 50 % of the determined value.

Absence of a chemical: state in which a chemical is lacking from a material, where the test method is unable to detect it.

- NOTE. The amount of the chemical is smaller than the detection limit of the test method.

Critical substance: chemical substance that can be found in footwear or footwear components and that can have an effect on the wearer and/or environmental impact due to its chemical reactivity

- NOTE 1.The effects caused by critical substances vary. They can be carcinogenic or mutagenic effects, allergy, reaction to toxics, etc.
- NOTE 2.Legislations can change; this Technical Report gives the information available at the time of publication. It is the responsibility of the user of this Technical Report to ensure that no changes occur

Critical substances category 1: substances with proven dangerous effect on the wearer

- NOTE. These substances are restricted by regulation at European level.

Critical substances category 2: substances with dangerous effect on the wearer

- NOTE.These substances are restricted by regulation at national level in some countries.

Critical substances category 3: substances with environmental impact

- NOTE. These substances are mentioned in European Ecolabel

Critical substances category 4: substances that are highly suspected to have an effect on the wearer

- NOTE. Possibly, these substances are not restricted by regulation at the time of publication of this Technical Report.

Critical substances category 5: substances that are suspected to have an effect on the wearer

- NOTE. Possibly, these substances are not restricted by regulation at the time of publication of this Technical Report.

Presence of chemicals in footwear materials: A number of chemicals are present in footwear materials. Table 1 of this standard gives:

- materials in which they are supposed to be (for information, see Annex A);
- the list of the critical chemicals, (for information, see Annex B);
- test methods which can be used to provoke and quantify them;

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- the potential risk associated with and assessed by the use of the critical substances category scale (see 2.6). For composite materials, the tests should be conducted on the entire component.
- EXAMPLE 1. Coated textile (cotton plus PVC coating): the test on PVC and the test on cellulosic natural fibres should be carried out.
- EXAMPLE 2. Mixed textile (PES plus cotton): the test on cellulosic natural textile and the test on PES textile should be carried out.

2.2.6. CADS List- allergens and restricted substances

CADS – Cooperation at DSI (Deutsches Schuh Institut) – deals with the subject of hazardous substances in shoes and actively seeks to prevent their use. The association's objectives are the generation and dissemination of knowledge for manufacturing and marketing shoes and shoe materials without hazardous substances as well as for environmentally friendly compatible production.

The CADs list includes the substance to be analysed, their CAS number, limits for the substance and the reach limits, and the material to be tested.

Specifically, these are:

Pool and forward knowledge about hazardous substances as well as current and future statutory regulations;

Develop prevention strategies and actively implement consumer protection

Run a public awareness campaign;

Commission scientific research to analyse the potential hazards of substances used in shoes;

Develop replacement substances and processes or commission their development. Prepare and publish studies about hazardous substances;

Promote theses and dissertations that deal with hazardous substances in shoes and their prevention;

Implement measures suitable for manufacturing and marketing environmentally friendly compatible shoes without hazardous substances.

What is CADS LIST?

The CADs list includes the substance to be analysed, their CAS number, limits for the substance and the reach limits, and the material to be tested.

The group of substances considered by CADS are:

- Azo Dyes
- Biocide
- Chlorinated phenols
- Dyestuffs classified as allergens
- Dyestuffs classified as carcinogenic
- Heavy Metals;
- Organic Tin compounds;
- Other chemicals residues;
- Other phenols;
- Phthalates;

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- Polycyclic aromatic hydrocarbons (REACh);
- Polycyclic aromatic hydrocarbons (EPA)
- Volatile Organic Compounds

2.2.7. Main allergens in footwear and source of allergens in footwear

Main allergens

- Chromium (VI) and Chromium (III)
- Dimethyl Fumarate
- Formaldehyde
- Nickel, cobalt
- Mercaptobenzothiazole
- Thiourea and thiuram compounds
- Carbamates and mercapto compounds
- Rosin
- p-tert-butylphenol formaldehyde resin
- Azo dyes (p-phenylenediamine and 4-aminoazobenzene)

Source: Chromium (III)/Chromium (VI)

More than 80% of leather production worldwide is tanned with trivalent Chromium (III) salts.

Hexavalent Chromium is not used in leather processing, but it can appear as:

- Impurity present in trivalent chromium salts or lead pigments

- Oxidation of trivalent chromium favoured by alkaline conditions in neutralised processes or leather dyeing

- Oxidation of trivalent chromium by the action of free radicals from some fatliquors, under heat and/or light (aging) and low humidity.

Alternative tanning methods to chrome tanning can be applied in order to avoid Chromium VI formation.

Source: Formaldehyde

- **Leather**

  - In tanning and retanning, chemicals based on phenols, naphthalenes and aminated resins (e.g., melamine-formaldehyde resin)

  -Finishing products, additives and preservatives

- **Textile**

  - Special finishing products

  - Preservatives

Formaldehyde can be found in leather because it is comprised in the chemical composition of some tanning and retanning agents based on phenols or naphtalene, as well as in aminic resins, leather finishing products, additives and preservatives. It is also often found in textile products with special finishes. For instance, formaldehyde resin is applied as a preservative and also to improve garment care, in that it avoids stains or wrinkles.

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Source: Nickel, Cobalt and Dimethyl fumarate

Nickel and cobalt: They can be found in any metal part of the shoe

Dimethyl fumarate: It is a preservative, but it is not used in the footwear material production

Source: Rosin and p-tert-butylphenol formaldehyde resins

Natural rubber adhesives (cement), polychloroprene adhesives (neoprene) or contact adhesives are used in the closing operation. Natural rubber adhesives contain rosin resins, and contact adhesives contain PTBF resins. These adhesives can be replaced with water based adhesive or acrylic resins

Source: Rosin

In solvent/water based natural rubber and synthetic adhesives.

Rosin is used in upper preparation operations, such as: closing, folding, and lining.

Source: PTBF resin

- Polychloroprene adhesives (5-7%)
- Some natural rubber adhesive formulations
- Increase the heat stability of adhesive joins

PTBF resin can be found in polychloroprene adhesives and some natural rubber adhesive formulations used for different operations, such as lasting, heel covering, insole manufacturing, insock placing and upper-sole bonding, among others.

Source: RUBBER ADDITIVES

- Thiourea compounds (dibutylthiourea, diethylthiourea, diphenylthiourea)
- Thiuram compounds (tetramethylthiuram disulfide (TMTD), tetramethylthiuram monosulfide (TMTM), tetraetylthiuram disulfide (TETD), dipentamethylenethiuram disulfide (PTD))
- Carbamates compounds (diphenilguanidine, zinc dibutyldithiocarbamate, zinc diethyldithiocarbamate)
- Mercaptobenzothiazol (MBT)
- Mercapto compounds (N-ciclohexyl benzothiacilsulfenamide (CBS), morfolinilmercapto benzothiazole (MMBT), dibenzothiacildisulfide (MBTS))
- p-phenilenediamine derivatives (N-isopropyl-n-phenil-4-phenylenediamine, N-cyclohexyl-N-phenyl-4-phenylenediamine, difenil-parafenilendiamine)

These additives can be found in rubber formulations, since they are used as accelerators for the vulcanisation process, as well as antioxidants.

2.2.8. ECO-label

Eco-label is a voluntary instrument, which offers consumers a guide on environmental issues that include any product offered for sale. Environmental criteria considered in the labeling for consumer products are many

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and are based on assessment of their life cycle (raw materials - process - distribution - use - disposal), as revised in three years, besides ecological criteria are contained and the performance and durability.

By establishing a procedure for eco and specific criteria for different product groups, consumers can choose products that can reduce environmental impact, giving them information on the characteristics of the environmental impact of products labeled organic.

Ensure environmental criteria, performance and durability of textile and leather products undergo the procedure eco, due to "claims" increased buyer, which is becoming better informed, and for products purchased annually (in EU), enforce requirements for health and comfort. Even if a consumer does not perceive the product marketed as a product dangerous to the environment, it is becoming increasingly aware of its potential health benefits, so already we are witnessing the promotion of brands for a better lifestyle and use products, eco-genetic Sano.

In a market where quality textile and leather means both health improvement and better environmental protection, "green products" that minimizes environmental impact and health, ensuring a certain level of quality, can be a fulfilling requirements of today's consumer.

European Eco-label, which is the only sign of environmental quality, certified by an independent organization is valid throughout Europe, is a unique opportunity to meet consumer expectations. In this way it promotes the design, manufacture and marketing your products with reduced environmental impact throughout the product lifecycle.

Application of eco-label on a product means:

- limiting pollution environmental factors (water, air, soil) during the production process;
- limiting emissions of volatile organic compounds (VOCs) during production;
- limiting metal residues and formaldehyde in the final product;
- use recycled packaging;
- control various aspects of product sustainability.

Eco-labeled product recognition is achieved by applying a label on the package or the graphic symbol ,,European flower" (see Figure 2.1), indicating the intrinsic environmental qualities and provides certainty that:

- during the processing of raw material (textile, leather and synthetic) is limited use of substances that have harmful effects on air and water;
- the risk of allergies is low;
- products have colors that withstand repeated washing, drying and forced to withstand sunlight without discolored;
- products have long durability.

Figure 2.1. Graphic symbol of eco-label

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EU Eco-label created by the European Commission in 1993, is a single certification scheme to help consumers to distinguish products and green services, which affect the environment, and it is not granted for food and medical products. It is a voluntary scheme designed to encourage businesses to market goods and services with reduced environmental impact and European consumers - including public and private purchasers - to easily identify them.

European flower can be found throughout Europe as well as Norway, Liechtenstein and Iceland. Community eco- label is part of a broader strategy geared towards promoting domestic production and consumption.

Community eco-label is a ''passport'' that allow free movement of goods within the EU. It is mandatory for products sold in Europe and the export of products to Europe. All EU states have adopted the Community eco-label. Its main advantage is its European dimension. The product is the eco-label awarded by a European Union member state, can be used in all other Member States.

In essence, eco-label is represented only by the above graphic symbol, but it is accompanied by a short descriptive text on the product, packaging, a brochure or other document accompanying the product information and provide information on at least one and three types of environmental impact (Figure 2).

Eco-label for consumer products for specific textile and leather case covers the following product categories:

- textile clothing and accessories: handkerchiefs, scarves, bags, shopping bags, backpacks, belts with a textile fiber content of at least 90% of their weight;
- textile products for interior designing, textile fibers whose content is at least 90% by weight, except the walls and floor coverings;
- yarn, textile fibers and fabrics, knitted textiles for apparel and accessories or interior textiles;
- footwear and leather goods.

Eco-label (see Figure 2.2) is comprised of two parts (columns 1 and 2) and include information for consumers, as follows:

Eco-label	
The registration number of the contract:	• _____ • _____ • _____

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Column 1	Column 2
70 mm	100 mm

Column 2 contains information on the reasons for granting Ecolabel and must cover at least one of the three types of environmental impact:

☐	low air pollution
☐	energy efficient
☐	low toxicity

Figure 2.2. Form and content of eco- label

In terms of specific ecological criteria needed for the textile material, indicate that the following conditions:

- to limit toxic wastes in textile fibers:
  • acrylic: acrylonitrile < 1.5 mg / kg of fiber;
  • cotton: pesticide residues < 0.05 ppm (parts per million);
  • spandex do not use organic tin compounds;
  • greasy wool and other fibers cheratinizate: limitation of pesticides;
  • artificial cellulose fibers: organochlorine substances - (AOX) < 250 ppm;
  • Polyester: Antimony < 260 ppm;
  • Polypropylene: not using pigments Pb (lead).

- to reduce air pollution:
  • acrylic: acrylonitrile < 1 g / kg fiber;
  • spandex: diizocianţi aromatic < mg / kg of fiber;
  • artificial cellulose fibers (viscose)
    - sulfur compounds < 120 g / kg produced filaments;
    - sulfur compounds < 30 g / kg of fiber products.
  • polyester: volatile organic compounds (VOCs) < 1.2 g / kg fiber;
  • polyamide
    - NO_2 (nitrogen dioxide) < 10 g / kg polyamide 6;
    - NO_2 (nitrogen dioxide) < 50 g / kg polyamide 6.6.

- to reduce water pollution during production:
  • flax and other bast fibers: the treatment of waste water from the melting process, the COD (chemical oxygen demand)/ OC (total oxygen consumption) must be reduced by at least 75% (hemp fiber) and 95% (in other fibers);
  • viscosity: Zn (zinc) < 0.3 g / kg fiber;
  • fiber copper: Cu (copper) < 0.1 ppm / year;
  • wool and other fibers cheratinizate:
    - for washing effluents treated off-site: COD < 60 g / kg, 75% discount on treatment;
- the treated effluent on site: COD < 5g/kg, pH 6-9, the discharge temperature < 40 degrees.

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- to limit the use of chemicals in manufacturing of textile products:
  • 90% of products produced by carding and 95% of the sizing, detergents, fabric softeners and complexing agents must be sufficiently biodegradable or eliminated;
  • the content of polycyclic aromatic hydrocarbons (PAHs) in mineral oil < 1% by weight (a product);
  • are prohibited: heavy metal salts, cerium compounds, auxiliary chemicals;
  • emissions of organohalogen compounds from bleaching agents < 40 mg chlorine / kg (100 mg Cl/kg in some cases);
  • concentrations of ionic impurities in dyes must not exceed the following amounts (in ppm):

Ag <100, Ba < 100, Co. < 500 I < 50, Cd < 20, is < 20;

Cr < 100, < 250, Fe < 2500, Hg <4, Mn < 1000;

Ni < 200 Pb < 100 Sb < 50, Sn < 250 Zn < 1500.

• concentrations of ionic impurities in pigments must not exceed the following amounts (in ppm): Ba < 100 I < 50, Cd < 50, is < 100, Cr < 100,

Hg < 25, Pb < 100 Sb < 250 Zn < 1000;

• painting is prohibited by etching with chromium- based dyes;
• water emissions of metal complex dyes based on copper, chromium and nickel - 20% max when dyeing cellulose fibers and 7% for other coating processes:
- Cu < 75 mg (fiber, yarn or fabric);
- Cr < 50 mg / kg, Ni < 75 mg / kg.
• be prohibited:
- azo dyes that cleave aromatic amines listed in GD 177/2004;
- dyes carcinogenic, mutagenic or toxic to reproduction;
- dyes potential sensitisers if resistance to perspiration 4.
• pasta print < 5% volatile organic compounds;
• formaldehyde < 30 ppm for products in direct contact with skin and 300 ppm for other products;
• treat waste water from wet: COD < 25 g / kg / year;
• substances for fireproofing/dressing preparations containing more than 0.1% by weight: carcinogenic, mutagenic or toxic substances are prohibited;
• prohibiting the use of plasticisers and solvents which are carcinogenic, mutagenic or toxic.

- consumer information will be written next to the organic label, following clearly:
  - product produces reduced water pollution;
  - the product contains no hazardous chemicals;
  - product meets specific requirements relating to the whole production process.

Adequacy criteria for use of textile products should consider:

- dimensional changes during washing and drying;
- fastness to washing;
- fastness to wet and dry friction;
- fastness to light.

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Specific ecological criteria of the award green footwear:

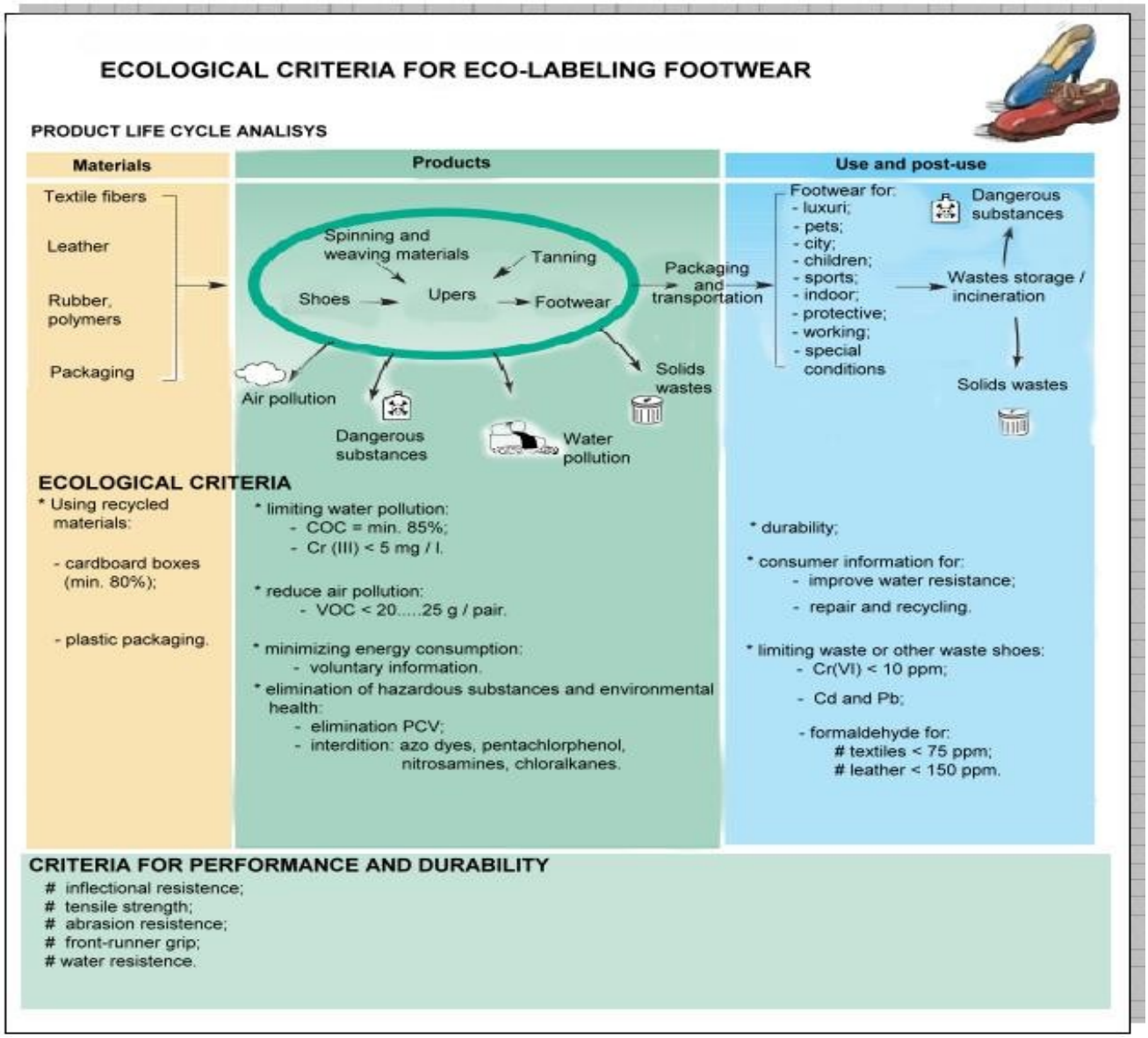

Figure 2.3. Specific ecological criteria of the award green footwear

Regulation (EC) No 66/2010 on the EU Ecolabel

What is the aim of the regulation?

- It concerns the European Union (EU) Ecolabel which is a voluntary environmental labelling scheme.
- By means of transparent ecological criteria, it enables consumers to make conscious choices without compromising on the quality of the products.

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Key points

- The EU Ecolabel may be awarded to products and services which have a lower environmental impact than other products in the same group. The label criteria were devised using scientific data on the whole of a product's life cycle, from product development to disposal.
- The label may be awarded to all goods or services distributed, consumed or used on the EU market whether in return for payment or free of charge, on condition that the ecological criteria have been clearly established. It does not apply to medicinal products for human or veterinary use, or to medical devices.
- The system was introduced by Regulation (EEC) No 880/92 and amended by Regulation (EC) No 1980/2000. This Regulation (EC) No 66/2010 aims to improve the rules on the award, use and operation of the label.

Award criteria

- The label is awarded in consideration of European environmental and ethical objectives. It also promotes the EU's transition to a circular economy, supporting both sustainable production and consumption. In particular:
  - the impact of goods and services on climate change, nature and biodiversity, energy and resource consumption, generation of waste, pollution, emissions and the release of hazardous substances into the environment;
  - the substitution of hazardous substances by safer substances;
  - durability and reusability of products;
  - ultimate impact on the environment, including on consumer health and safety;
  - compliance with social and ethical standards, such as international labour standards;
  - taking into account criteria established by other labels at national and regional levels;
  - reducing animal testing.

The label cannot be awarded to products containing substances classified by Regulation (EC) No 1272/2008 as toxic, hazardous to the environment, carcinogenic or mutagenic, or substances subject to the regulatory framework for the management of chemicals.

Competent bodies

- EU countries must designate one or more bodies responsible for the labelling process at national level. Their operations shall be transparent and their activities shall be open to the involvement of all interested parties.
- They are specifically responsible for regularly checking that products comply with the label criteria. Their remit also includes receiving complaints, informing the public, monitoring false advertising and prohibiting products.

The procedure for award and use of the label

- In order to be awarded the label, economic operators shall submit an application to:
  - one or more EU countries, which will send it to the competent national body;
  - a non-EU country, which will send it to the EU country where the product is marketed.
- If the product complies with the label criteria, the competent body shall conclude a contract with the operator, establishing the terms of use and withdrawal of the label. The operator may then place the

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label on the product. The use of the label is subject to payment of a fee when the application is made, and an annual fee.

The European Commission has created a catalogue of products which have been awarded the label.

The European Union Ecolabelling Board (EUEB).

A 2010 Commission decision (Decision 2010/709/EU) establishes the EUEB. Its members are appointed by the Commission. It is composed of representatives from the EU countries and the European Economic Area, as well as from certain European organisations representing, for example, consumers, business and environmental concerns. The Commission consults the EUEB when developing or revising the award criteria and requirements of the label.

Ecological criteria

- The Commission has adopted a series of decisions establishing ecological criteria for the awarding of the EU Ecolabel to different types of products; for several of these, the validity period expired by the end of December 2016.
- The Commission also adopted Regulation (EU) No 782/2013 replacing Annex III of Regulation (EC) No 66/2010 and amending the maximum fees allowed for financing the evaluation and processing of requests for the Ecolabel made by product manufacturers.

FROM WHEN DOES THE REGULATION APPLY?

- It has applied since 19 February 2010.

BACKGROUND

- For more information, see:

'The EU Ecolabel' on the European Commission's website.

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2.3. Lesson 2: Environmental management in tanneries

Author: Nuno Silva - CTIC

2.3.1. Water management

Tanneries consume a lot of water in the process, optimizing their use becomes essential in companies' strategies. Most of the industrial units have their supplies guaranteed through their own underground sources. During the past few years, the importance of water, as a natural resource, has not been duly considered due to the facilities observed in its abstraction. This way of looking at the situation has led in many cases to the unreasonable use of water resources.

Nowadays, due to environmental but also economic concerns, this situation becomes extremely important and it is necessary to implement measures that promote the rational use of water.

Unreasonable use of water influences negatively the final yield of an operation in terms of product absorption and causes an increase for effluent, resulting in a worsening of total operating costs.

In addition to the economic benefits inherent in abstraction, and especially end-of-pipe treatment, less wastewater with less contaminants will result in the formation of fewer sludge and naturally these measures become relevant to waste prevention.

Water consumption consists of two main components: process water and water required for other uses, such as cleaning, power generation, wastewater treatment, and sanitary facilities. Traditionally more than 75% of the water consumed in a tannery comes from the process, from skin rinses between operations, and other general washes, such as floor washes.

Water consumption in the process varies among tanneries, depending on the type of processes involved, the raw material and the final products. Water consumption is higher in the initial stages of the process than in the finishing phases. In fact, beamhouse processes are the largest consumers of water (about 72% of the total) because, in addition to the baths of physical and chemical treatment, the processes need for successive washes.

Table 2.1. Typical balance of water consumption in the tanning

Operations	Volume (m3/ton of raw hide)
Process until to the beamhouse stage	20 – 25
Process until to the tanning stage (wet blue)	21 – 28
Process until to the finishing stage	34 – 40

If tanneries work with good techniques, technologies and management, it is possible to reduce significantly the water consumption. As an example, a tannery that uses the entire production process in a traditional way, compared to another in which all the cleaner technologies were applied, including effluent recycling processes, the latter will surely reduce the discharge of effluents by about 50% and the consumption of chemicals up to 30%.

For the purposes of comparison and evaluation of these quantitative, it is presented the typical limits of high and low consumption in the beamhouse operations, verified in the tanneries in Portugal. These limits were set at 18 m^3/ton of rawhide, as a value below which a good efficiency in water management is considered,

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and 35 m^3/ton of rawhide, as a value above which excessive consumption of water. There is no correlation between the size of the companies and the way water management is carried out.

There are several techniques or technologies to improve the efficiency of water use and the optimization of water consumption, and they can involve the introduction of several measures, such as:

- Optimization of water consumption and the reduction of the consumption of chemicals used in the process and in the treatment of wastewater. Measure the water used in the different operations and improve the operational control of the used flows (use of adequate instrumentation such as flow meters in the drums and paddle-vat);
- Install timers and water consumption limiters (water faucets and pipes);
- Change the way the washes work, in order to implement an optimized washing system;
- Adapt the water use to the requirements of processes and washes, namely with the installation of pressure reducers. Washing under running water is a major source of waste of water. In these cases, it is important to improve the use of immersion washing methods instead of washing under running water;
- In many cases, baths volumes can be reduced during the different productive operations, obtaining a double benefit, a reduction in the discharged water and an improvement of the efficiency of the process (better chemical exhaustion of the baths);
- Use short baths, e.g. lower water-to-skin ratios (low-float techniques), within acceptable limits in terms of efficiency and skin quality (care must be taken as they may damage the skins);
- Some baths and washing waters (with or without previous treatment) can be use in other tanning operations. Reuse of water can considerably reduce the consumption. However, because the risk of residual chemicals or other components that damage the skins, there is some reluctance to reuse it;
- The use of rainwater in specific applications (toilets, washes, refrigeration);
- Perform periodic tests in pipes and reservoirs;
- Internal dissemination of water saving rules among workers.

2.3.2. Process water treatment

As regards the waters used, there are some important parameters, such as:

- pH;
- Hardness (carbonated and non-carbonated);
- Microbiological contamination;
- Presence of organic matter;
- Colour and smell (may affect final product quality);
- Metals (iron, chromium, copper, others);
- Suspended solids;
- Soluble salts (mainly sodium, potassium, calcium and magnesium chlorides and sulphates);
- Dissolved gases.

2.3.3. Basic water requirements for use in the tanning process

- Soaking: moderate hardness is desirable; a high suspended solids content or microbiological contamination is undesirable;
- Liming: a water with high hardness should be avoided for the normal process, and should not even be used in enzymatic processes;
- Washing after the liming process: a high content of carbonates can origin problems;

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- Pickling and tanning with chromium: the hardness of the water is not problematic;
- Vegetable tanning: the hardness of the water and the presence of iron is harmful; the magnesium and calcium salts may form insoluble tannin compounds; iron salts can cause deposits on the surface of the skin;
- Dyeing and greasing: water should be use without the presence of iron salts; high hardness values generally interfere with the normal functioning of fats and dyes and may even cause uncontrolled precipitation of some more sensitive fats and dyes.

2.3.4. Energy management

The impact of the energy costs on the operating costs of a company in the industrial sector is usually low when compared to the weight of other factors, namely labour costs and raw material costs. Energy management was often neglected, which generates significant losses of energy and contributes to the reduction of business competitiveness.

The concept of Rational Use of Energy has decisively changed the way that energy is view, showing that it is possible to grow without increasing consumption or affecting the quality of production. The key to the issue is Energy Management. Like any other factor of production, energy must be managed continuously and efficiently.

Although the competitiveness argument naturally remains the one that most sensitize the general industry, increasing environmental pressure has reinforced the need to use energy efficiently. In fact, any energy management process will have to start with the knowledge of the energetic situation of the installation. The principle is obvious - to manage is indispensable to know.

When performing an energy diagnosis/audit, it should be borne in mind that industries are a physical place where a series of materials are transforming to produce a good. Therefore, to characterize its behaviour, it is necessary to know a series of production data:

- Operation system, indicating if it varies on weekends or sporadically;
- Degree of utilization of productive capacity referring to the usual time (daily and weekly) and not over 24 hours a day;
- Cost structure, not being easy to cover all the information that would need to know. It is important and necessary to have information on the representativeness of energy consumption over the value of production.

Existing statistical data on the energy consumptions of the Tanning Industry are insufficient for the presentation of the energy situation of the sector, with the detail and rigor desirable.

However, energy consumption in tanneries depends mainly on the following factors:

- Production methods, as well as the capacity and size of equipment;
- The quality and sophistication of electric motors;
- Mechanical movement of hides and skins;
- Drying methods used;
- Equipment and buildings heat losses;
- Air renewal rates in buildings, in order to comply with the Occupational Health and Safety regulations;
- Existence of on-site wastewater treatment;
- Existence of on-site waste treatment and recovery of energy.

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In the tanneries, there is usually a greater thermal component of energy, when compared to the electrical component. The thermal component is usually 2 to 4 times higher than the electrical component. Electricity is consuming essentially in the driving force of equipment, lighting of buildings and offices, while fuels (mainly fuel oil, natural gas and biomass) are consuming in steam boilers.

Table 2.2. Consumption of electricity and thermal energy

Type	Uses	% of total consumption
Thermic Energy	Drying	32 – 34
	Hot water	32 - 34
	Heating installations	17 - 20
Electric Energy	Production equipment (drums and machines)	9 -12
	Compressed air	1,5 - 3
	Lighting	1,5 - 3

These values can vary widely between different companies, and it is important that comparisons be made on the same basis. The sectors that consume more energy in a tannery are the retaning, drying and finishing. In the retaning the baths reach temperatures of the order of 60 ºC (thermal energy) while in the beamhouse and tanning processes, a great part of the operations are made at room temperature. Drying of hides requires the use of drying ovens (electric and thermal energy) and vacuum dryers (electric and thermal energy).

The finishing operations involve the application of chemicals in roller and pistol-dyeing machines, to which succeed drying tunnels. In these drying tunnels passes steam (thermal energy) that exchanges heat with forced air (electric energy). In all phases of the process there are physical-chemical and mechanical operations promoting the electric energy consumption. The drum's rotation consumes a lot of electrical energy.

According to the publications of DGEG (Portuguese Government Energy Department), we have a specific energy consumption value in the Tanning Industry:

Tanned leather for various destinations:

$K = 115$ kgep / 10^3 ft^2

Taking into account data collected in Portuguese industries representative of the sector, the following average value are:

$K = 170$ kgep / 10^3 ft^2

There are a number of measures, which help to promote the efficient use of energy and to reduce its consumption:

- Effective energy management - As a starting point, the company must be able to know precisely the consumed quantities of each type of energy. In most companies, for each type of energy, only total consumption is known;
- Energy market - Having chosen the types of energy to be consumed and the necessary quantity of each type, it is necessary to study the contracting modality for each on. It is appropriate to have a sufficiently wide knowledge of the technical, economic, commercial and legal characteristics of the energy market and it is advisable to have an energy specialist in the company or, if it is a small industry,

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to have an outside specialist. Together with this choice, an analysis of the energy billing should be carried out periodically, proving if it is the most correct according to the different modalities of prices;

- Electric motors - This equipment are one of the main sources of energy consumption, accounting for 70% of electricity consumption in European industry. The cost of using an electric motor is 95% in energy, 3% in purchase and 2% in maintenance. Energy saving starts with the proper selection of motors for each application, and it is necessary to take into account factors such as: ambient operating conditions start conditions or speed, size or power regulation. The greatest savings of electricity are obtained when the engine operate at the maximum efficiency;
- Lighting - The lighting system presupposes in many companies a high percentage of electric consumption. It is necessary to adjust lighting characteristics to each workstation, becoming an important element of economic efficiency;
- Compressed air - For its generation, are used various types of compressors: oil lubricated, tapped with oil-free compression chambers, special pistons and turbochargers. Compressed air systems have the disadvantage of the high cost they assume, due to the poor performance of the current compressors (high losses occurring in the process, especially heat losses);
- Air conditioning / ventilation - In the choice and realization of the systems of air conditioning and ventilation must consider factors such as the occupation and use of the space, location, having special importance the industrial processes that occur. The amount of energy consumed to satisfy the requirement depends both on the selection and design of the generating facility and on the degree of adaptation of its power to the load variations;
- Industrial refrigeration and freezing - In many processes it is necessary to reach temperatures below 0 ºC, or above this value, but always very close to it. We find the most representative case in the tanning industry for the conservation of raw hides (temperatures above 0 ºC). These processes presuppose a high-energy consumption. Therefore, it is important to carry out an appropriate energy optimization process;
- Boilers - The most commonly used heat sources in the tannery come from fossil fuels such as fuel oil, natural gas, others, although biomass (wood and pellets) is also used. Generally, in the transfer of heat to the fluid, a boiler has losses around 20%, but if there is no good maintenance or if it does not operate correctly, these losses can be up to 30%. At the time of determining the effectiveness of a boiler it is necessary to know and control some parameters such as: combustion efficiency, gases temperature, percentage of unburnt product (indicates how incomplete the combustion is), excess air and contents of carbon monoxide, carbon dioxide and oxygen;
- Heat recovery - Some industrial processes, due to their characteristics, can use residual heat from other processes. It is possible to distinguish, mainly, two different sources of heat recovery: boiler combustion gases and condensates;
- Renewable Energies - Once the depreciation rates are deducted, allow becoming practically free (requiring only maintenance costs).

2.3.5. Chemicals management

Effective monitoring of chemical hazards in the workplace requires the efficient transmission of information, by manufacturers or importers, to users of chemicals, namely on potential hazards and on safety precautions to be taken. This flow of information should be accompanied by daily actions by employers to ensure the implementation of the necessary measures to protect workers and therefore the public and the environment.

The amount of chemicals used varies significantly with the specification of the final product, the hides treated and the process chosen. The inorganic chemicals generally used are sodium sulphide, calcium hydroxide, acids,

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carbonates, sulphites and sulphates. The standard organic chemicals are organic acids and their salts. About 20 – 50 % of the hide weight will be added as inorganic standard chemicals and about 3 – 40 % as organic chemicals. The biggest variation is in the amount of tanning agents used:

Table 2.3. Main and auxiliary process chemicals for a conventional process for salted, bovine hides

Chemical consumption	Approx (%)
Standard inorganic chemicals (without salt from curing, acids, bases, sulphides, chemicals containing ammonium)	40
Standard organic, not mentioned below (acids, bases, salts)	7
Tanning chemicals (chromium, vegetable, and alternative tanning agents)	23
Dyeing agents and auxiliaries	4
Fatliquoring agents	8
Finishing chemicals (pigments, special effect chemicals, binders and cross-linking agents)	10
Organic solvents	5
Surfactants	1
Biocides	0.2
Enzymes	1
Others (sequestering agents, wetting agents, complexing agents)	1
Total	100

Besides the main process chemicals, a great variety of substances it is used for auxiliary process purposes. For reasons of workplace health and safety, are applied some barely soluble agents as aqueous suspensions or dispersions, which have to be stabilised with auxiliaries, thus adding even further to the number of chemicals used. These auxiliary agents may demand special attention in any assessment because of the problems of reactivity, toxicity, persistence, bioaccumulation, mobility, and the generation of problematic metabolites. Therefore, it is important to know the quantities used and their behavioural characteristics.

A practical problem faced by tanneries is that many of the chemical products purchased are proprietary products. Many suppliers do not specify the chemical compositions of the products, so tanneries may have to seek additional information from the chemical suppliers in order to determine the environmental impact of the products they use. Safety data sheets generally provide some data on the toxicity of the products to humans and environment, and many tanneries use these as the sole source of information to determine the environmental impact of a certain substance. It is not uncommon for tanneries to use more than 300 different chemicals in the leather making process; that illustrates the difficulty of determining the environmental impact of each of the chemicals.

The above-mentioned potential environmental effects of each substance have been assessed. Suppliers of chemicals, whether manufacturers, importers or distributors, should ensure that:

- The products were classified and their properties evaluated;
- The products are correctly identified / labelled;
- The safety data sheets are properly prepared and available to users until 1 year after delivery (stored for at least 10 years).

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Figure 2.4. Signals on the safety data sheets

Users should ensure that:

- Store products correctly according to appropriate safety rules (eg retention basins, reactivity);
- Use chemicals correctly (eg using the appropriate equipment for individual safety, exhaust systems, transfer with appropriate packaging and with proper identification);
- Have an inventory of the used substances and have all the safety data sheets;
- Evaluate the risks associated with the handling of chemicals and have the required safety precautions (workers, facilities, surrounding area and environment);
- Separate and give the appropriate final destination to packaging waste.

2.3.6. Liquide effluents from the Leather Industry

Regarding their qualitative characteristics, the industrial effluents of the leather industry are extremely heterogeneous depending on the operation or operations in progress.

It is difficult to define their characteristics in detail, although in general they have a number of elements that allow us to distinguish them from urban (domestic) effluents, and from other types of industry. Within the leather industry itself, they are sufficiently different from each other, depending on the type of hides handled, the method of keeping raw hides, the articles to be manufacture and the technology applied.

It can be state that, generally, these effluents present high levels of organic load, suspended solids and several toxic substances. The liming operation it is the responsible for most of the total contaminant load of the final effluent. In comparative terms, between the two processes, vegetable tanning or chromium tanning, we can conclude that the first is, from the bating operation, less polluting, since no significant liquid effluents are generating in the tanning phase itself.

Table 2.4. Contaminant loads in the leather process (salted bovine and ovine hides)

Salted hides of bovine animals (or goats)											
Parameters	**Water consumption**	**COD**	**BOD_5**	**TSS**	**Cr^{3+}**	**S^{2-}**	**Nkj**	**Cl^-**	**SO_4^{2-}**	**Fats**	**Salts**
Quantity/ ton. raw hide	m^3	kg	kg	kg	kg	kg	kg	kg	kg	kg	kg

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Beamhouse (soaking until bating)	7-25	120-160	40-60	70-120	-	2-9	9-14	120-150	5-20	5-8	200-300
Tanning	1-3	10-20	3-7	5-10	2-5	-	0-1	20-60	30-50	1-2	60-120
Retaning	4-8	15-40	5-15	10-20	1-2	-	1-2	5-10	10-40	3-8	40-100
Finishing	0-1	0-10	0-4	0-5	-	-	-	-	-	-	-
TOTAL	12-37	145-230	48-86	85-155	3-7	2-9	10-17	145-220	45-110	9-18	300-520
Salted and dried hides of sheep animals											
Parameters	**Water consumption**	**COD**	**BOD_5**	**TSS**	**Cr^{3+}**	**S^{2-}**	**Nkj**	**Cl^-**	**SO_4^{2-}**	**Fats**	**Salts**
Quantity/ hide	Lts	g	g	g	g	g	g	g	g	g	g
Beamhouse	65-150	250-600	100-260	150-300		6-20	15-30	150-400	5-40	-	-
Degreasing and Tanning	30-100	50-300	20-100	15-30	8-12	-	4-10	40-200	30-50	40-150	-
Retaning	15-35	30-100	15-35	10-20	1-3	-	2-4	20-40	10-20	-	-
Finishing	0-10	0-5	0-2	0-2	-	-	-	-	-	-	-
TOTAL	110-295	330-1005	135-397	135-397	9-15	6-20	21-44	210-640	45-110	40-150	-

Sheepskins with wool											
Parameters	**Water consumption**	**COD**	**BOD_5**	**TSS**	**Cr^{3+}**	**S^{2-}**	**Nkj**	**Cl^-**	**SO_4^{2-}**	**Fats**	**Salts**
Quantity/ hide	Lts	g	g	g	g	g	g	g	g	g	kg
Beamhouse	160-240	550-1100	150-1000	100	-	-	16	400	-	-	600
Degreasing and Tanning	40-70	150 - 300	45-250	15	15	-	2	460	-	40-150	650
Retaning	75-100	80	25-50	80	5	-	3	50	-	-	270
Finishing	-	-	-	-	-	-	-	-	-	-	-
TOTAL	275-410	780-1500	220-1300	195	20	-	21	910	-	40-150	1520

Source: JRC Reference Reports – Best Available Techniques (BAT) Reference Document for the Tanning of Hides and Skins – Industrial Emissions Directive 2010/75/EU (Integrated Pollution Prevention and Control) – 2013.

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2.3.7. Effluents classification and properties

In order to define the type of contamination caused by each process operation, can be classified the different effluents by determination of specific properties:

- **Soaking**: Are generated very high volumes of wastewater. They are characterized by a neutral pH, or slightly alkaline, depending on the chemicals used. They usually contain animal scrawls, blood, soluble proteins, surfactants and humectants, sodium chloride, sodium carbonate or hydroxide, bactericidal fungicides and naphthalene-type preservatives or others;

- **Liming:** This operation generates lower volumes of wastewater than the soaking, although with a substantially higher contaminant load, representing around 50% of the total generated by the tanning industry. They are wastewaters of high alkaline content (pH 12 - 14), and high concentrations in sulphides and sodium sulfhydrates, proteins, calcium hydroxides, hair and some fats;

- **Deliming and Bating:** The volumes of wastewater generated may be significant and contain appreciable amounts of sulphides from the washes after discharging. They are typically rich in soluble calcium salts, pigmentary substances, soluble proteins, enzymes and very often, high concentrations in nitrogen by the use of ammoniacal salts. Its pH is mostly neutral, or slightly alkaline (pH 7.5 – 8.5);

- **Pickling:** If carried out independently of tanning, it produces wastewater, which is not very important in terms of volume but with a considerable contaminant load due to the high concentrations present in terms of organic and inorganic acids and sodium chloride. Its pH 1 - 3 gives strongly acidic waters;

- **Chrome tanning:** Small volume of wastewater rejected. The problems come from the high concentrations of chemicals used. They contain high salinity, abundance of chromium salts, sodium carbonates or bicarbonates, magnesium oxides, tanned leather fibres in suspension and the presence of emulsified fats. The pH values are acidic, pH 3 – 4. These wastewaters are normally treated separately and chrome liqueurs recovered;

- **Vegetal tanning:** Produced wastewater it is reduce in volume due to the reuse of the liquors. Only are rejected the baths with reduced tannin loadings, but even these discharges can be characterized by pH values 3-5, and usually contain natural tannin residues, in addition to phenols, polyphenols, neutral salts, acids and leather fibres.

- **Neutralizing:** This operation generally produces wastewater with abundant volumes according to the characteristics of the washes applied. They have a relatively low contaminant load with varying concentrations of neutralizing and synthetic salts, chromium salts and suspended chromium particles. The pH is in the range 5 – 6;

- **Retaning / Dyeing / Engrase:** Generated wastewaters in these operations are difficult to characterize due to the wide variety of applied processes and technologies. They are generally mildly acidic waters, pH 4 – 5.5, with varying concentrations of mineral, vegetable and synthetic tannins, products derived from phenol, naphthalene or others, dyes, aldehydes, acrylic resins and others, emulsified fats, ammonia, emulsifiers, formic acid and other specific products. The volumes of generated wastewater by these operations are also very variable, depending on the processes and technologies applied.

2.3.8. Effects of various compounds present in effluents generated by the tanning industry

The various elements and compounds present in the effluents can cause harmful effects, such as:

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- **Chlorides:** They are basically rejected in the form of sodium chloride, generally having a harmful inhibitory effect in the development of animal life in watercourses;

- **Sulphides:** Generated in the forms of sodium sulphides and sodium sulfhydrates in the liming operation, producing an extremely unpleasant smell associated with this industry. In acidic medium, the formation of hydrogen sulphide gas (H_2S), which deposits at the bottom of the tanks and pipes, is fatal by inhalation even in small quantities. It is a corrosion accelerator of various materials;

- **Alkalinity:** It acts as an inhibitor of the development and survival of various types of animal and plant species, reducing the effectiveness of some biological used treatments. Their presence also increases the rate of corrosion of various materials;

- **Suspended solids:** They can form deposits in pipes causing eventually total blockage of the current. Its deposition in watercourses can form a mantle inhibiting the development of various animal and plant species. They cause turbidity in the water, preventing the penetration of sunlight, thus reducing the photosynthesis function of the plant species along the watercourse. Depending on their origin and formation, they may be a source of smell and greatly affect the chemical and biochemical oxygen demand values;

- **Chromium oxides:** Chromium may be in various forms. Dichromate has a harmful effect on most organisms, as well as a corrosive effect on industrial drainage lines. The trivalent chromium salts, on the other hand, do not present great indices of danger, being able to be tolerate in small amounts. Hexavalent chromium compounds have great importance to harmful effects on human life (high carcinogenic power and high toxicity);

- **Fats:** In their various forms, they can form deposits in pipes causing eventually total blockage of the current. They usually tend to float in water, forming layers that prevent access to light and oxygen. When emulsified with the use of surface tension reducing agents, they deposit forming sediments;

- **Bactericides and Fungicides:** Usually are generate in small quantities, but still, enough to reduce the conditions of plants and animals' development.

2.3.9. Measures created by industry to reduce the environmental impact on effluents

The industry has been searching to reduce the environmental impact by creating structures and implementing new technologies in order to recycle some of its wastewaters and treat its liquid effluents. As the Portuguese tanning industry is located in Alcanena area, a collective Wastewater Treatment Plant (WWTP) was built to treat the generated liquid effluents.

Companies not located in this area had to create their own solutions, leaving almost the first two stages of the leather process (beamhouse and tanning), only carrying out the third phase (retaning, neutralization, dyeing and engrase) and being obliged to have a treatment for these effluents, usually a more expensive solution.

For the recycling of chromium was create with the capital of the tanneries, a specific installation, the SIRECRO - Chromium Recovery Unit. The unit is a complementary installation of the Alcanena System and it is intended for the recovery of chromium contained in the residual tanning baths from the tanneries. This unit allows the recovery of large amounts of chromium that would otherwise increase the toxic load affluent to physical-chemical and biological treatments. The recovery process of chromium consists of the precipitation of trivalent chromium in the form of chromium hydroxide, pressing followed by dissolution with sulfuric acid and repressing, obtaining as final product the basic sulphate of chromium. This way the chromium cycle closes, allowing reducing significantly the environmental impacts, in addition to achieving a very important savings for the companies of one of the most important chemicals in the tanning industry through reuse.

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Figure 2.5. SIRECRO - Chromium Recovery Unit (Alcanena)

With regard to pre-treatment units (UPI), located at each tannery, there are three types of equipment to:

- Remove solids, such as scraps, hair and grease, avoiding that this type of materials and substances have access to the pipes and to the WWTP, causing obstruction problems;
- To control the effluents quality, by separating the liming baths (after a desulphurisation process, these baths are discharged at specific times and treated at the WWTP) and by separating the tanning baths, which are treated in an outdoor unit (SIRECRO).

A point of great importance is the maintenance and preservation of all the components of a treatment system. It is essential to ensure a good functioning of all the equipment and ensure that the obtained wastewater has the characteristics appropriate to its discharge in the receiving environment, in this case, the AUSTRA (Users Association of the Wastewater Treatment System of Alcanena) collector.

2.3.10. Pre-treatment plant (equipment)

Fixed grids (bar screening) and rotary screens

These devices function as a filter and aim to remove coarse solids, preventing their passage to the collector and to the WWTP. The current procedures for this operation and maintenance correspond to:

- Installation of a solid waste container next to the equipment;

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- Manual/automatic cleaning of the grids and rotary screens, once a day, placing the waste in the container;
- Shipment of waste to the landfill.

Figure 2.6. Fixed grids and rotary screens

Degreaser

This operation has the objective of separating, by density difference, oils, fats and other lighter elements of the effluent. There is a static type degreaser at pre-treatment unit (applies to flow rates up to 20 m^3/h and separates without any auxiliary means). Some units have automatic systems that use compressed air to facilitate the separation of oils and fats.

Liming baths storage tank

This tank must have sufficient capacity to store wastewater from the liming operation and its washes. These waters should be desulphurised with 40 a manganese sulphate solution (catalyst) and with prolonged aeration for 6 - 8 hours (in each case, these conditions should be optimized).

The minimum concentration is 0.1 - 0.2 kg/m^3 for $MnSO_4$ and 0.11 - 0.22 kg/m^3 for $MnSO_4.H_2O$, which may be use in excess to ensure better process performance. This procedure is fundamental to allow a specific pre-treatment of these wastewaters in the WWTP and to avoid problems in the subsequent treatments.

As required by the AUSTRA Regulations, these wastewaters must be discharge to the collector in the period from 0.00 am to 3.00 am. This discharge is done automatically through a programmed timer. It is expressly prohibited to discharge these wastewaters outside the referred period without prior authorization from AUSTRA technicians.

Chromium baths storage tank

This tank must have sufficient capacity to store wastewater from the tanning process (chromium baths). When the same is full, the company to contact AUSTRA, in order to made the collection of the baths to the recycling unit (SIRECRO).

Homogenization tank

This tank serves to store the wastewater (with the exception of the liming and tanning baths), to homogenize its quality and its characteristics. When filled it is discharged to the collector through a pumping system. It should be washed at least monthly with high-pressure water to eliminate residues.

Flow Meter

The flow meter measures the effluent volume drained per unit of time**.** The pipes must remain clean and unobstructed.

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Inspection tank

The inspection tank is sealed and contains a grid to protect the system (can be used for monitoring the discharge conditions of the wastewater).

Sampling

At unplanned time intervals, AUSTRA technicians visit the facilities to verify the correct operation of the pre-treatment unit and to collect samples of the effluent for analysis, and check the compliance with the discharge rules.

Health and Safety

In order to ensure hygienic and safety conditions, the following Personal Protective Equipment must be available to the operator: mask, gloves, rubber boots and protective clothing.

Good practices

Without prejudice to the provisions of special legislation, it is forbidden to dispose of wastewater collectors in the Alcanena System:

- Rainwater;
- Industrial wastewater resulting from the chromium baths in which the content of this metal is higher than the Emission Limit Values;
- Liquid, solid or gaseous products (e.g. gasoline, benzene, naphtha and diesel) which may give rise to flammable or explosive substances;
- Wastewater containing liquids, solids or gases which by their chemical or microbiological nature (e.g. poisonous, toxic or radioactive) or in such quantity, either alone or in interaction with other substances, may constitute a public health risk or a risk for the collectors' conservation;
- Waters with corrosive properties capable of damaging or endangering the structures and equipment of drainage systems, namely with a pH lower than 3.0 or greater than 12.5;
- Sludges and solid or viscous substances (e.g. fats or oils resulting from maintenance or treatment of waste) in such quantities or dimensions as to cause obstruction or any other interference with the operation of the System;
- Sand, sludge, ash, cement or any other product resulting from the execution of civil construction works;
- Any other substances which, in general, could obstruct and/or damage collectors and their accessories, or cause damage to treatment facilities, and which would destroy the final treatment process.

<u>Classes group the industrial units:</u>

- Class 1 - Industrial tannery unit that mainly processes beamhouse operations;
- Class 2 - Industrial tanning unit that processes raw hides - full cycle chromium;
- Class 2A - Industrial tanning unit that processes raw hides - complete chromium cycle, without unharing and liming operations;
- Class 3 - Industrial tanning unit which processes raw skin - complete vegetable cycle or other alternative process;
- Class 3A - Industrial tanning unit that processes raw hides - complete vegetable cycle or other alternative process, without unharing and liming operations;

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- Class 4 - Industrial tanning unit that processes retaning, dyeing and finishing;
- Class 5 - Waste Management Operators (Service Providers);
- Class 6 - Remaining industrial units and other users;
- Class 7 - Municipality.

The pollutant values are also suitable for each class.

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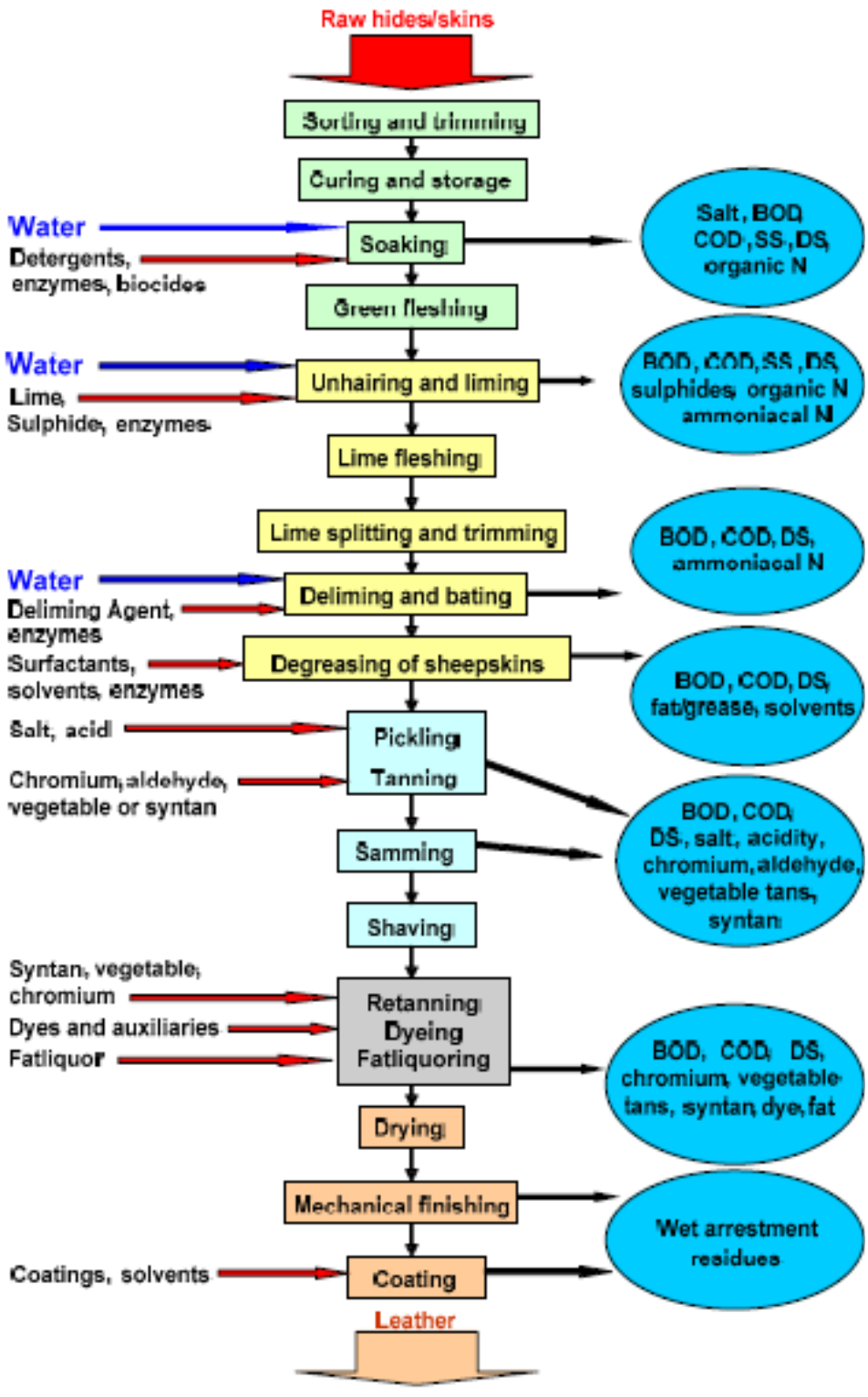

Figure 2.7. Main inputs and aqueous effluents

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2.3.11. Alcanena WWTP (AUSTRA)

The Alcanena Wastewater Treatment Plant is composed of several phases of treatment and built to treat as domestic and industrial wastewater. Much of the inflow to the WWTP corresponding to an industrial component (about 70%). Wastewater flows to the WWTP by four collectors.

Figure 2.8. Wastewater Treatment Plant (AUSTRA)

Treatment of domestic effluent

The domestic wastewater flows to the WWTP passing in a screw and to a well of pumping that is provide with three pumping groups (2 + 1) which pump the liquid to a compact unit with a shredder / degreaser, to removal of sands and fats. From this unit, the liquid goes into the biological treatment - where it joins with the effluent before entering the anoxic tank (without oxygen).

Figure 2.9. Pretreatment of domestic effluent (compact unit with degreaser)

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Treatment of industrial effluent

The industrial wastewater is conducted by three collectors to the initial pumping well of the WWTP. From this, the effluent is elevated to the treatment through Archimedes screws (3 groups) or, alternatively, through electric pump groups (3 groups).

Figure 2.10. Archimedes screws and electric pump groups

From this well, the liquid follows for pre-treatment or, where the pH value is higher than 9.5 (it is always verified that effluent from the liming process, where the pH can reach values of 12), automatically is read pH, and the liquid is sent to the desulphurisation treatment. The treatment is composed of two lines (alternating operation), each with a tank with agitation and oxygen injection (blowers + liquid air). For being an effluent with specific characteristics and with odour production due to the presence of sulphides, industries must discharge between 0.00 am and 3.00 am.

Figure 2.11. Desulphurization system

At this stage of treatment, caustic soda (concentration 50%) may also be added, for a greater oxidation of sulphides. After this phase, controlled by pH regulation through the reading of the redox value (it must be between -100 mV and 100 mV), the liquid follows for a pre-treatment where it joins with the remaining industrial effluent that flows to the WWTP during the day.

This phase consists in the removal of solids from two sanders and the removal of grease in a shredder and degreasing unit:

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Figure 2.12. Solids removal and degreasing

From the pre-treatment, the liquid flows to a flow distribution box for distribution to the first biological treatment. The first biological treatment is performed in two equalization tanks in parallel (with a unit capacity of 5000 m^3). In these tanks, is done aeration by fine bubble diffusers and the controlled oxygen content automatically by set point. The oxygen supplied promotes the degradation of the organic matter, thus reducing the pollutant load at the entrance to the second biological stage. In these tanks, is also added an antifoam.

Figure 2.13. First biological stage

From the equalization tanks, the effluent undergoes a chemical treatment (precipitation with iron chloride / lime coagulation / flocculation with polyelectrolyte) before entering on the primary sedimentation. The liquid from the tanks flows to the second biological treatment while is recirculated the primary sludge to the equalization tanks. Part of the primary sludge is sent to the thickeners.

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Figure 2.14. Chemical treatment / primary sedimentation

Upstream of the second biological treatment, the domestic effluent joint to the industrial effluent. From this point, the treatment of industrial and domestic effluents passes a being together.

The second biological treatment it is performed with a high load activated sludge process, and is composed of two treatment lines, each one by an anoxic tank, an aeration tank and a secondary decanter. In one of the lines, the oxygen system is supplied through six surface aerators; in another line of the oxygen, system is supplied through nine blowers. One of the assembly lines is with an empty part for installation of a tertiary treatment of the final effluent.

Figure 2.15. Second biological treatment

Figure 2.16. Secondary sedimentators

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From the secondary sedimentators, the liquid is discharged at Ribeiro do Carvalho while the secondary sludge recirculates to the anoxic tanks and equalization. Excess sludge (primary and secondary) feed the thickeners (2 units) for further mechanical filter press dehydration (2 units in alternating operation). Most thick sludge is primary sludge. It is added a cationic polyelectrolyte solution prior to introduce into the 2-filter press. The water withdrawn from the sludge in the thickeners, and in dewatering operation, is sent to the beginning of the process. By addition of a so-called Calci (mixture consisting of quicklime, cement and ash), the dehydrated sludge is chemically stabilized. Properly stabilized sludge sent to the sludge landfill, located in the boundary of the Alcanena WWTP, by a truck or tractor with trailer.

Figure 2.17. Thickeners

Figure 2.18. Filter press for sludge dewatering

The air extracted from the initial lifting stations, dewatering unit and degreasing of the domestic effluents, as well as the compact unit of pre-treatment of the industrial effluents delivered in auto cistern, that should be treated in a deodorization unit to combat air contamination with H_2S and other substances that cause unpleasant smell. On the other hand, was recently rehabilitated the installation of treatment of the air extracted from the sludge treatment unit. The installation consists essentially of adsorption and chemical reaction units.

Figure 2.19. Chemical treatment of odors (sludge thickening and dewatering unit)

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Located near Alcanena WWTP, the sludge landfill starts the operation in 1992. It is a controlled landfill where is deposited the sludge produced at the WWTP. After deposition, the sludge is subject to spreading and compaction. Leachates are to a lift station, from where they proceed to the entrance of the WWTP.

Figure 2.20. Sludge landfill

2.3.12. Valuation of by-products and wastes

The leather industry uses animal hides and skins - a by-product of the meat industry - which would otherwise have to be disposed of by other means (either through landfills or by incineration).

Fully processed grain-side leather comprises (very approximately) 20 - 25 % of the weight of the raw hides used in its production. In practice, the proportion varies, depending on the type of leather processed, the source of hides or skins and the techniques applied. Some tanneries produce (and market) by-products such as lower specification leathers. A number of uses for tannery residues have been found in the past, and some may still be available. Tanneries produce also wastes for which there is no use and for which must be found a disposal route.

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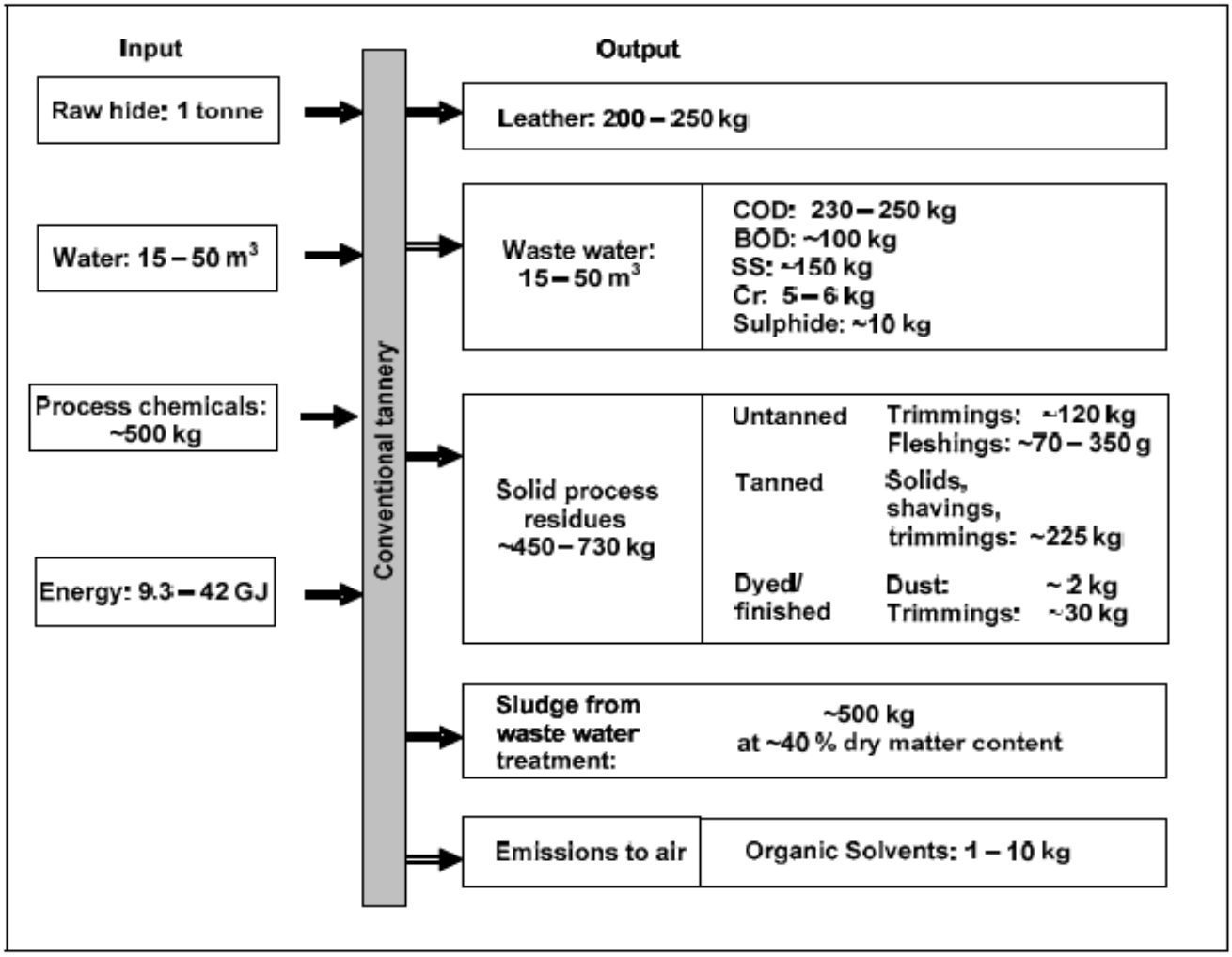

Figure 2.21. Input/output overview for a conventional (chrome-tanning) process for bovine salted hides per ton of rawhide treated

In the first phase of the production process, grains, hair, fleshings and trimmings are generated, which are classified as animal by-products (category 3) and the operator is obliged to carry out their recovery or disposal, according European regulations.

Following the stage of the liming, which removes the fur and removes the epidermis through the addition of lime and other chemical substances, there is also a phase of deliming in which agents are used which react and neutralize lime. This gives rise to products of great solubility easily removable by washing without loss of the relaxed structure acquired in the liming.

In operations carried out after the tanning stage, we have only wastes. Trimmings, shavings, fragments and dusts resulting from operations following the tanning phase, such as shaving, trimming, cutting, sanding, finishing, etc., are classified as waste and must comply with the environmental legislation.

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Typology of wastes

The industrial process of the tannery sector is strongly generating solid wastes. Are generated solid wastes of several types, according to the operation to which is it submitted.

In a simplified way, depending on the stage of the process that gives rise to them, the produced waste can be divided into two groups:

A - Untanned wastes

These wastes come from the beamhouse phase and contain high concentrations of fats, proteins, minerals, sulphides and water. They are biodegradable waste, usually constituted by:

- **Trimmings** - Parts of the raw hides (collagen, hair, fat, connective tissue, blood);

- **Hair and wool** - The wool that results from hair removal can be used in the wool industry. Before that, however, it has washed to remove traces of sulphide that may contain it and the lanolin that impregnates it (there are still some washers in Portugal). The hair is one of the main contaminants of the wastewater of this sector, being one of the responsible for the high organic loads (BOD5 and COD) of the effluents resulting from the operation of beamhouse. This type of pollution can reduce, using a technology of preservation of the hair, through the action of calcium hydroxide followed by a mechanical filtration, preventing their presence in the wastewater. It is a keratin-rich material;

- **Green fleshings, scraps and splits** - They are removed from the flesh side of the fleshing machines. By change the process of producing tanneries, in anticipation of this fleshing to the beamhouse; the carcasses are not contaminated with sulphide. Feast forms the possibility of valorisation of this material and decreases the chemicals consumption in the next productive phases. These wastes are rich in protein and have been applied, like carcasses, to the production of fertilizers, gelatines, pet-food or animal flours, requiring in the different cases some specificities, such as cold storage, traceability and licensing of official entities;

- **Limed fleshings, scraps and splits** - They are contaminated with sulphide. These wastes are rich in protein and have been applied to the production of fertilizers, gelatines, and pet-food or animal flours.

The average composition of fleshings is shown in the following table:

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Table 2.4. Composition of fleshings

Parameter	Unit	Green fleshings	Limed fleshings
Dry matter (DM)	%	44 – 53	21 – 34
pH			11.7 – 12.9
Extractable fat	%	25.6	6.5 – 23
Loss on ignition (1)	%	98 – 99	65 – 86
P (1)	%	0.06	0.2 – 0.7
K (1)	%	0.08	0.03 – 0.05
N (1)	%		1.8
Ca (1)	%	0.13	2.5 – 7.5
Mg (1)	%	0.02	0.06 – 0.14
Organic sulphur (1)	%		0.73
S (1)	%		1.5 – 1.7
AOX (1)	mg/kg	4.2	57.3
Pb (1)	mg/kg	ND – 0.4	ND – 8
Mn (1)	mg/kg		16
Cd (1)	mg/kg	ND – 0.04	ND – 0.16
Co (1)	mg/kg		ND
Cr (1)	mg/kg	ND – 9	3.1 – 34
Cu (1)	mg/kg	1.5 – 1.7	ND – 4.9
Ni (1)	mg/kg	ND – 0.4	ND – 9.7
Hg (1)	mg/kg	ND	ND
Zn (1)	mg/kg	4.6 – 23	21 – 58
As (1)	mg/kg		ND
Na (1)	g/kg		0.2 – 77.3
Gross Calorific Value (1)	MJ/kg		25.611 – 26.500
Net Calorific Value (1)	MJ/kg		24.700
NB: ND = not detectable. (1) related to dry matter (DM). *Source:* [85. Hauber and Knödler 2008].			

B - Tanned wastes

Coming from the post-tanning process steps, they may be divided further into tanned wastes (vegetable, chromium or other alternative agents) and finishing wastes. The composition of these wastes is similar to that of the non-tanned ones, these being fundamentally constituted by water and proteins.

They assume a character of the non-biodegradable type and are therefore more harmful to the environment. It is possible, however, to carry out treatment operations (for example by hydrolysis) which reverse this situation. On the other hand, some types of tanning leave the residues with biodegradable character (e.g. aldehydes).

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- **Vegetal tanned splits and shavings** - These wastes are potentially biodegradable because their composition is proteins and vegetal extracts. Since vegetable tanning is practiced by a minority of national companies, the volume of this waste is reduced;

- **Chromium tanned (blue) splits and shavings -** They result from the splitting of the tanned skins into chrome. An alternative to the controlled landfill, used internationally, is to treat the wastes by hydrolysis, valorising the proteins in the production of fertilizers and recycling the chromium.

- **Chromium tanned trimmings -** They have characteristics similar to blue shavings, but with greater difficulties in the hydrolysis process due to their size. They therefore need a crushing process prior to hydrolysis;

- **Buffing dust and finishing wastes** - Due to their coloration, they are wastes with greater problems to valorisation. A possible destination for these wastes is incineration/pyrolysis. This type of solution allows the use of thermal energy generated and chromium from the produced ashes.

One of the characteristics of the tannery's solid waste is its commercial value, which is aggravated by the maintenance, storage and transportation costs. The industrialist usually pays for his elimination. Some waste, or by-products, can be sold, or used, as raw materials for other industrial sectors. This requires adequate conditions, such as cold storage, dehydration, compaction or grinding. Wastes are separated and handled in different ways, depending on the existing reuse / recycling and disposal options.

Due to the high cost of investment, many treatment options are not economically viable on a small scale.

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Table 2.5. Composition of chromium tanned wastes

Parameter	Unit	Chromium tanned shavings	Offcuts, trimmings	Finished leather waste
Loss on ignition	%	88 – 95 mean 90	90 – 95 mean 92	90 – 95
Dry matter (DM)	%	30 – 50 mean 47	30 – 60 mean 50	
TOC	%	32	30 – 40	
pH	%	3.5 – 4.0 mean 3.7	3.5 – 4.0 mean 3.7	
Extractable fat	%	1.4	2 – 3	
Calorific value	MJ/kg	11 – 20	11 – 20	
Total Cr ([1])	mg/kg	15 000 – 39 000 mean 30 000	10 000 – 35 000 mean 30 000	20 000 – 35 000
As ([1])	mg/kg	0.7		ND – 0.7
Pb ([1])	mg/kg	14.5		8 – 14
Cd ([1])	mg/kg	<0.5		ND – 0.7
Hg ([1])	mg/kg	0.3		ND – 0.5
NB: ND = not detectable. ([1]) related to dry matter (DM). *Source:* [85, Hauber and Knödler 2008].				

C - Sludges from treatment plants

Resulting from the treatment of wastewater, they are a concentrate of the removed pollutants. The stricter the requirements for wastewater purification (emission limit values for certain parameters), the higher the quantity of sludge produced. The quality of the sludge produced depends on the chosen treatment. Show a typical composition for wastewater treatment sludges in the next table:

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Table 2.6. Composition of wastewater treatment sludges

Parameter	Min.%	Max.%
Water content	55	75
Organic matter	40	75
Inorganic matter	25	60
Organic carbon	21	38
Ammonium	0.1	1.6
Nitrogen (organic)	1.3	7.0
Substance extractable with CH_2Cl_2	0.06	0.4
Phosphorous	0.01	0.06
Chromium(III)	0.8	5.0
Aluminium	0	5.0
Iron	0.6	12
Calcium	1.0	15
Sulphur (total)	0.7	7.0

Table 2.7. Amount of organic waste generated during leather production for salted bovine hides

	% of raw hide weight
	Average
Trimmings from raw hides	2 – 5
Lime fleshing	10 – 40
Lime split (1) and pelt trimmings	10 – 20
(Chrome) shavings (1)	20 – 30
(Chrome) split (1)	
(Chrome) leather trimmings	
Buffing dust	0.2 – 1.0
Painting, lacquer and other chemicals	0.5
Sludge from waste water treatment	40 – 50
Packaging	1.5
Notes: (1) Amount depending on splitting in limed or tanned condition.	

Other waste fractions not shown in Table above are salt, organic solvents, residues of process chemicals and auxiliaries, fats from degreasing, finishing sludges, residues from air abatement other than buffing dust, such as activated carbon filters and sludges from wet scrubbers, and residues from waste treatment.

Treatment options for waste with a high organic content include the separation of solids, rendering, leather fibreboard production, animal feedstuff production, composting, soil conditioner and fertiliser production, anaerobic digestion, thermal treatment and landfill. However, depending on specific local conditions, other waste treatment or disposal routes may also be available. Some waste treatment or recycling options may not be viable due to contamination or quality of the waste. This may be due to the contents of process chemicals and pesticides or the origin of the waste. Furthermore, the viability of a certain disposal route strongly depends on the existing infrastructure and the market for waste and by-products.

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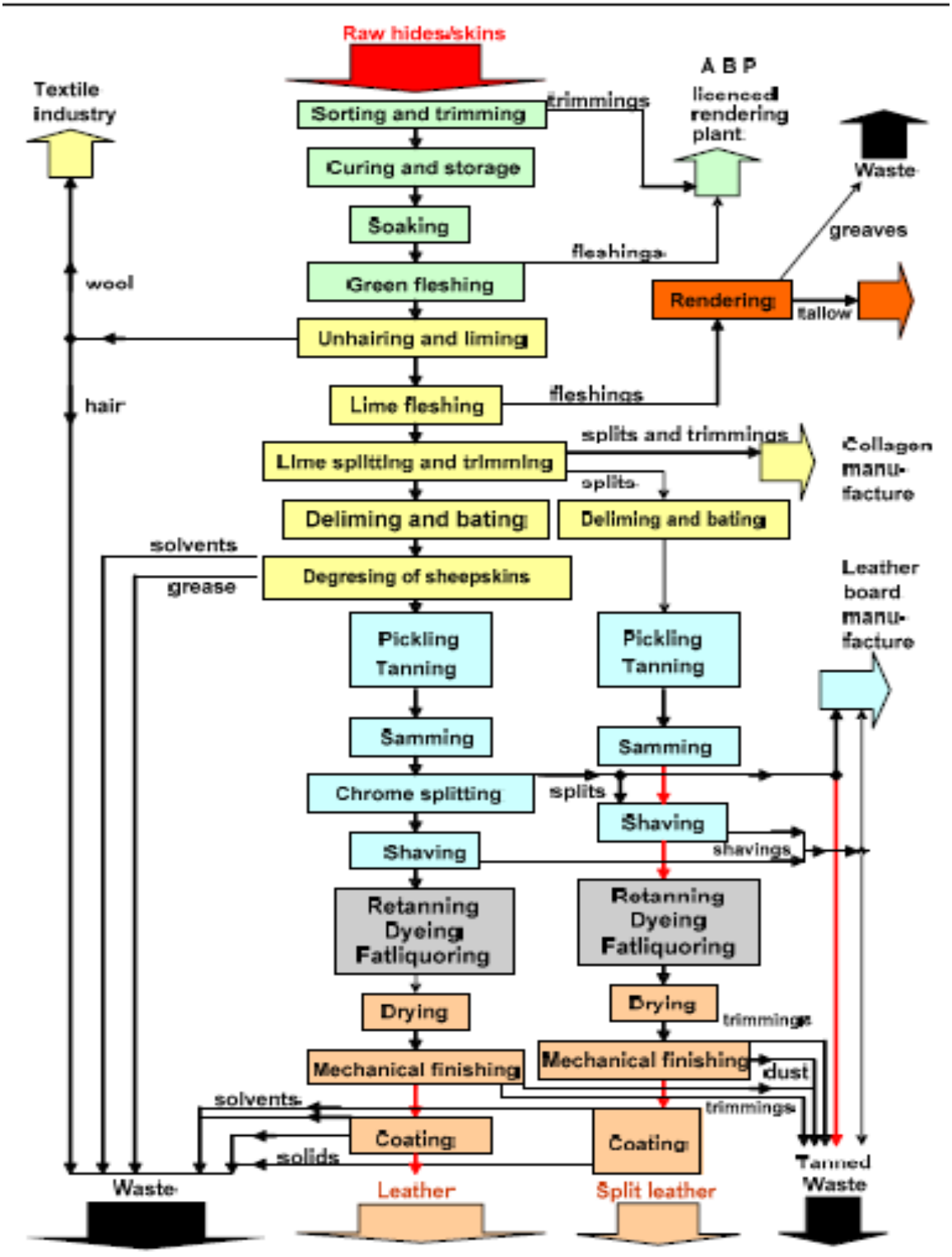

Figure 2.22. Possible arising of co-products, by-products and wastes

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2.4. Lesson 2: Treating effluents resulting from leather processing

Author: Nuno Silva - CTIC

- Environmental impact of the effluent/waste of the leather making process
- Effluent and solid waste management
- Different types of pollutants
- Key indicators

2.4.1. Waste destination

Present the current destination of waste and liquid effluents resulting from the industrial process of chromium tanning in the following table:

Table 2.8. Residues and wastes, their recycling and disposal

Process unit	Type of waste	Contents	Further treatment/disposal/recycling
Trimming	• Parts of the raw hides (trimmings)	• Collagen, hair, fat, connective tissue, blood	• Production of hide glue • Animal feed stuff (1) • Biogas • Thermal treatment • Landfill (1)
Curing	• Solid salt • Brine	• NaCl and possibly biocides	• Reuse (problems with infectious material on salt) • Landfill (1)
(Green) fleshing	• Green fleshings	• Fat, blood, meaty scraps	• Production of hide glue • Recovery of fat • Composting • Biogas • Landfill (1)
Liming and unhairing	• Hair/wool	• Keratin-rich material	• Wool is sold • Reuse as filling material • Production of lanolin from sheep wool • Fertiliser/agriculture/animal feedstuff • Composting • Biogas • Landfill (1)
(Lime) fleshing	• Fleshings	• Fat, meaty scraps • Liming and unhairing chemicals	• Production of hide glue/gelatine protein hydrolysate • Recovery of fat (fleshings only) • Composting • Biogas • Landfill (1)
Lime splitting	• Lime split (flesh-side)	• Collagen plus liming and unhairing chemicals	• Splits can be tanned to produce split leather • Production of hide glue/gelatine • Protein hydrolysate • Sausage casings and other collagen products
Solvent degreasing	• Distillation residues	• Organic solvents and fat	• Recycling of organic solvents • Reuse of fats • Thermal treatment of non-halogenated-organic-solvent-containing waste • Recovery of fat using acid cracking for possible use in the cosmetic industry • Low pH waste waters to be treated
Aqueous degreasing	• Waste water treatment residues	• Surfactants • Emulsified and non emulsified fat • Pretanning agent residues (e.g. aldehyde)	
Tanning/retanning	• Tanning liquors	• For chemical composition of agents, see Section 3.3.5	• Recovery of chromium in tanning liquors
Tanned splitting	• Tanned split	• Leather material of inconsistent thickness and no 'grain' surface	• Split leather • Leather fibreboard production • Protein hydrolysate • Composting • Agriculture

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Process unit	Type of waste	Contents	Further treatment/disposal/recycling
			• Thermal treatment • Landfill (1)
Shaving and final trimming	• Shavings, • Trimmings	• Organic matter with tanning chemicals	• Leather fibreboard production • Protein hydrolysate • Composting • Agriculture • Thermal treatment • Landfill (1)
Fatliquoring	• Obsolete chemicals	• For chemical composition of agents, see Section 3.3.8	• Disposal of chemicals according to their characteristics
Dyeing		• For chemical composition of agents, see Section 3.3.10	
Milling/buffing	• Particulate matter	• Organic matter with contents according to tanning	• Landfill (1) • Thermal treatment • Filler for plastics
Finishing (coating)	• Residues from finishes, • Sludges from finishing agents (over-spray, etc.)	• For chemical composition of agents, see Section 3.3.11 • Solvents • Heavy metals	• Landfill (1) • Thermal treatment
Trimming (final)	• Trimmings with or without finish	• Leather with contents according to tanning and finishing	• Leather fibreboard production for not lacquered • Trimmings other reuse (patchwork, small leather goods, etc.) • Landfill (1) • Thermal treatment
Air treatment	• Depending on the abatement techniques: activated carbon, sludges from wet-scrubbers, filter dust etc.	• Depending on the off-gas stream	• Recovery of organic compounds (e.g. solvents) • Thermal treatment • Landfill (1)
Waste water treatment	• Sludge from waste water treatment	• Depending on the separation of waste water streams	• Use in agriculture • Composting • Biogas • Landfill (1) • Thermal treatment
Waste treatment	• Residues from on-site waste treatment	• Greaves from rendering, residues from anaerobic or aerobic digestion	• Use in agriculture • Landfill • Thermal treatment
Packaging	• Pallets • Paper • Plastics • Containers for chemicals		• Recycling • Landfill (1) • Thermal treatment
Other	• Obsolete chemicals • Scrap metal and defunct equipment		• Recycling • Landfill (1) • Thermal treatment
(1) Legal restrictions apply.			

Other waste fractions

- **Salt** – May be reused in curing or for pickling liquors if it is sufficiently sterilised and clean. In some Member States, landfilling of solid salt is practised;
- **Organic solvents** - May be reused within the process for minor applications such as cleaning; in particular cases, organic solvents can be recovered by distillation for repeated process-integrated use or external reuse. Finally, (non-halogenated) organic solvents can be thermally treated;
- **Residues of chemicals and auxiliaries** - Have to be disposed of in the light of their risk to human health and the environment. Some chemical waste may need to be treat off site in specialised waste treatment plants or taken back by the chemical supplier. Other chemical waste can be classified as non-hazardous waste and disposed of with other non-hazardous wastes;

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- **Residues from degreasing** - Contain fats and (depending on the process chosen) organic solvents or surfactants. Fat and solvents can be recovered or the residues can be treated thermally;
- **Finishing sludges** - Can contain hazardous substances depending on the finishes used. They can be treated physic chemically or thermally or they may have to be disposed of as hazardous waste;
- **Activated carbon filters from air emissions abatement** - May be regenerated several times; final disposal is by thermal treatment or landfill. Leather dust may be thermally treated or it can be disposed of as a waste. Dust may also be compacted before disposal to facilitate handling;
- **Sludges from wet-scrubbers** are a waste for which a disposal route must be found;
- **Packaging material** (containers for chemicals, pallets, and plastics) either be sent back to the supplier, treated thermally or is landfilled.

Liquid wastes from degreasing with organic solvents are the only waste considered hazardous according to the European Waste Regulations. However, the degreasing operation is only used in the processing of sheep, goat or pigskins.
In an attempt to achieve some hierarchy of the remaining residues by their relative danger, we can say that residues with chromium (organic solids and sludge) also have some potential danger.

In the area of Alcanena there are then several companies dedicated to the management and treatment of wastes.

2.4.2. Potential for prevention and recovery in the sector

In a tannery, there is usually an appreciable amount of waste produced in the production process.
The description of the previously production process and its corresponding association to the generation of the residues allows to conclude that the tanning processes can be potentially problematic at the level of the discharges to the environment. The potential for pollution is high and much diversified.
The assimilation of this reality has led to the development of cleaner processes and technologies aimed at preventing pollution. Many of these technologies be successfully applied industrially worldwide, resulting in real benefits for the environment. Thus, the potential of prevention in the sector may be considered high.
In Portugal, there have been some advances in this area, both in terms of applied research and development projects, and in the transfer and implementation of some cleaner technologies in companies.

Measures and technologies for the management and treatment of waste consist of, in order of priority, in:

- Reduction at source: eliminate or reduce the formation of residues in the production process;
- Direct use, or after some processing, of the waste in the productive process itself;
- External recycling, allowing the transformation of useless materials into new products.

Achieve through the waste reduction at source or the prevention of its production:

- Eco product design (design, production and packaging of products with a minimized toxic content, minimum raw material volume or longer shelf life);
- Application of new and less polluting technologies;
- Business management, with change of attitudes of the human resources of the companies.

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2.4.3. Air Emissions

Compared to emissions to water, air emissions occur generally in relatively small quantities. Traditionally tanneries have been associated with odour rather than any other air emissions, although the emissions of organic solvents have been a major problem.
Relevant air emissions are: sulphides from the beamhouse and waste water treatment; ammonia from the beamhouse; tanning and post-tanning operations; sulphur dioxide from post-tanning operations; dust/total particulate from the storage and handling of powdery chemicals, dry shaving, buffing, milling drums and staking.
Modern tanneries should not have significant odour emission problems. Whether a tannery has the following air emissions depends on the type of processes employed:

- Particulate matter;
- Organic solvents;
- Hydrogen sulphide;
- Ammonia;
- Odour.

Emissions to air have effects beyond the tannery site, but also affect the workplace and possibly the health of the tannery workforce. Apart from odours, particular mention should be made of organic solvent emissions, aerosols, and solid particulates (buffing dust and powdery chemicals). The ventilation required for the health and safety of the workforce will limit the effectiveness of containment provided by the buildings.

Particulate emissions

The majority of particulate emissions arise from the dry processes, such as milling, and buffing. Other emissions arise from spray finishing. These emissions may be abated by using filters or gas and particle washers.

Organic solvents

The principal source of organic solvent emissions in tanneries is the coating/dyeing process. Examples of solvents that are used are butyl acetate, ethyl acetate, acetone, methyl isobutyl ketone and methyl ethyl ketone. The consumption of organic solvents may be reduced by the introduction of water-borne coating materials, as well as modern methods of application, such as improved spraying techniques and roller coating. Tanneries employing solvent-based degreasing processes for sheepskins also have organic solvent emissions requiring special abatement. Volatile halogenated hydrocarbons require special attention, as some of these constitute a high environmental risk. Abatement techniques such as activated carbon filters are feasible but their use is not standard practice in tanneries; furthermore, fugitive emissions may be a major part of the total emissions.

Hydrogen sulphide

Hydrogen sulphide gas is both toxic in relatively low concentrations and odorous in miniscule concentrations. It can be released during the handling or treatment of effluent streams that contain high concentrations of sulphide, such as the effluent streams from the unharing process. Under alkaline conditions, sulphides remain largely in solution, but when the pH of the solution drops below 9.5, hydrogen sulphide evolves from the effluent: the lower the pH the higher the rate of evolution.
For this reason, alkaline and acidic liquors should be handling separately in the tannery. In addition, they should be treated separately in the effluent treatment plant until the sulphide has been fully oxidised, unless the mixing is undertaking in an enclosed vessel with air extraction through a scrubber.

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Hydrogen sulphide can be released during the deliming and pickling processes. The addition of small quantities of oxidising compounds (such as hydrogen peroxide or sodium bisulphite) can reduce the amount of hydrogen sulphide being released during deliming. Optimisation of washing processes in order to remove sulphide before deliming and pickling will also reduce the emissions.
Local exhaust ventilation from processing areas (with exhaust treatment) may be necessary to control fugitive releases. Anaerobic bacteria from sulphates may also form hydrogen sulphide during wastewater treatment, and sludge storage and dewatering operations. In addition, hydrogen sulphide may be formed in the sewer system, and in waste disposal sites taking tannery wastes.

Ammonia

Ammonia can be formed in the deliming and dyeing processes. Good housekeeping practices, such as effective washing and process control, can minimise these emissions. Local exhaust ventilation from processing areas (with treatment) may be necessary to control fugitive releases.

Odours

Odours from tanneries can be a major cause of complaints depending on the location of the tannery. They are generated during several operations in the tanning process and from the wastes and effluents from those processes. Odours are not quantifiable, but they frequently give rise to complaints from neighbours.
Both odour emissions and deterioration of the raw material stocks can be controlled by the correct curing and storage of hides and skins. Cool and dry conditions should be maintained in storage facilities for salted materials and doors should remain closed. Temperature-controlled storage is required for unsalted hides.
In addition to hydrogen sulphide and ammonia, there are characteristic mixtures of organic compounds which are noticeable (even more noticeable when hydrogen sulphide and ammonia are controlled) during each stage of the process.

Tannery buildings require good ventilation for safety reasons, due to the potential for hydrogen sulphide and ammonia releases. Air extracted from some areas may need treatment. In tanneries with on-site treatment plants for liquid effluents, these are usually the largest source of odour emissions. Oxidation of substances in solution involves bringing air (or oxygen) into intimate contact with the liquid. This also means that odorous compounds can pass from the liquid into the air.

Odorous can be treated in a bio filter. Because these are biological systems, the concentrations of both ammonia and hydrogen sulphide must be controlled and a chemically dosed scrubber may be necessary as a pre-treatment (or substitute). Other air emissions, such as sulphur dioxide emissions might occur during bleaching. Where energy be obtained from waste incineration.

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Fixed Emissions

In tanneries, the following equipment constitutes sources of fixed emissions:

- Boilers:

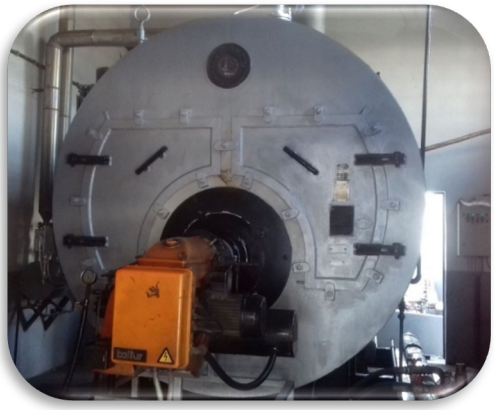

Figure 2.23. Boiler

- Spray-finishing machines:

Figure 2.24. Spray-finishing machines

- Dedusting filters:

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Figure 2.25. Dedusting filters

- Gas scrubber (VOC's):

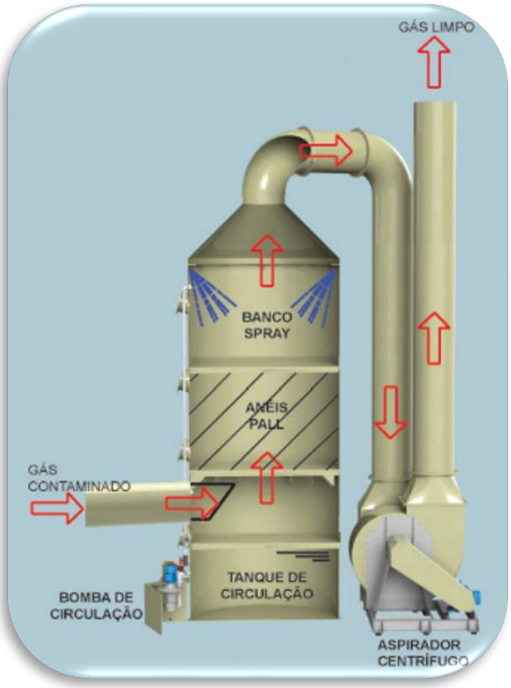

Figure 2.26. Gas scrubber

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- Air Dryer:

Figure 2.27. Air dryer

Diffuse Emissions

Diffuse emissions to air and water occur from various scattered sources such as road transport, shipping, aviation, domestic heating, agriculture and small business. Pollution from diffuse sources occurs over large areas and individually may not be of concern but in combination with other diffuse sources can cause environmental impact.

They must be capturing and channelling to an exhaust system if technically and economically feasible.

Diffuse pollutants released to air includes nitrogen oxides (NOX), Sulphur oxides (SOX), carbon monoxide (CO), Ammonia (NH3) and particulate matter (PM10).

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