Best Available Techniques for the Mediterranean Tanning Sector

INESCOP
SPANISH FOOTWEAR TECHNOLOGY INSTITUTE

Joaquin Ferrer
International Projects
INESCOP

Barcelona, 23rd July 2015

Table of Contents

INESCOP
INSTITUTO TECNOLÓGICO DEL CALZADO Y CONEXAS

Horizon 2020

UNEP

MAP

Strategic Partnership for the Mediterranean Sea Large Marine Ecosystem
MedPartnership

Together for the Mediterranean Sea

GEF UNEP

What is INESCOP?

- Is the Spanish Footwear Technological Institute
- Private and independent service organisation
- Founded in **1971**
- Non-profit making institution

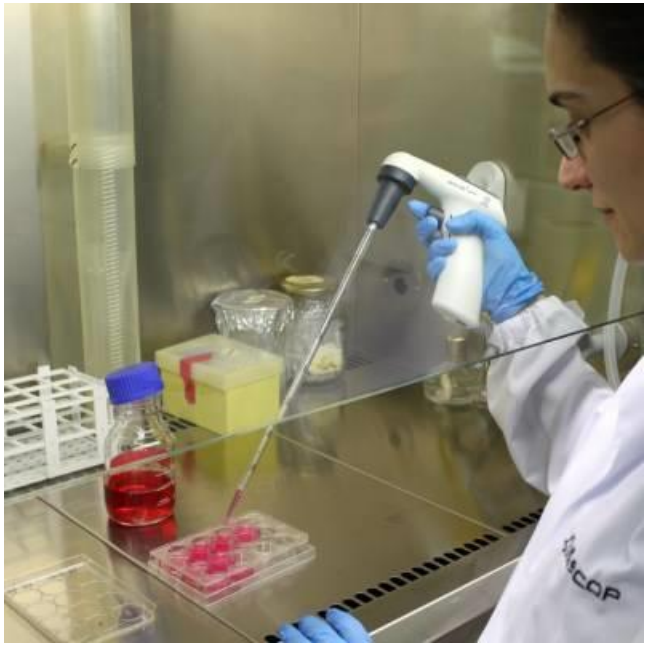
Mission

To offer support to **footwear and related** industries to develop **scientific and technical activities** that cannot be undertaken by themselves

What we do

INESCOP provides direct services, transfers knowledge and technology and carries out research into those topics that are of interest for our industrial sector. The activities span the range of:

- Quality control.
- Technical assistance.
- Standardisation and certification.
- Applied research.
- Development of advanced technology.
- Specialized training.
- Environment.
- Footwear-applied design.
- Information and documentation.



INESCOP
INSTITUTO TECNOLÓGICO DEL CALZADO Y CONEXAS

Horizon 2020

UNEP

MAP

Strategic Partnership for the Mediterranean Sea Large Marine Ecosystem
MedPartnership
Together for the Mediterranean Sea

GEF UNEP

INESCOP Services for the leather sector

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

Human resources

INESCOP has a staff of **140** technicians,
including **95** university graduates,
among which **17** hold a PhD degree in sciences

INESCOP
INSTITUTO TECNOLÓGICO DEL CALZADO Y CONEXAS

Horizon2020

UNEP

Strategic Partnership for the Mediterranean Sea Large Marine Ecosystem
MedPartnership
Together for the Mediterranean Sea

GEF UNEP

Where are we?

Close to the factories

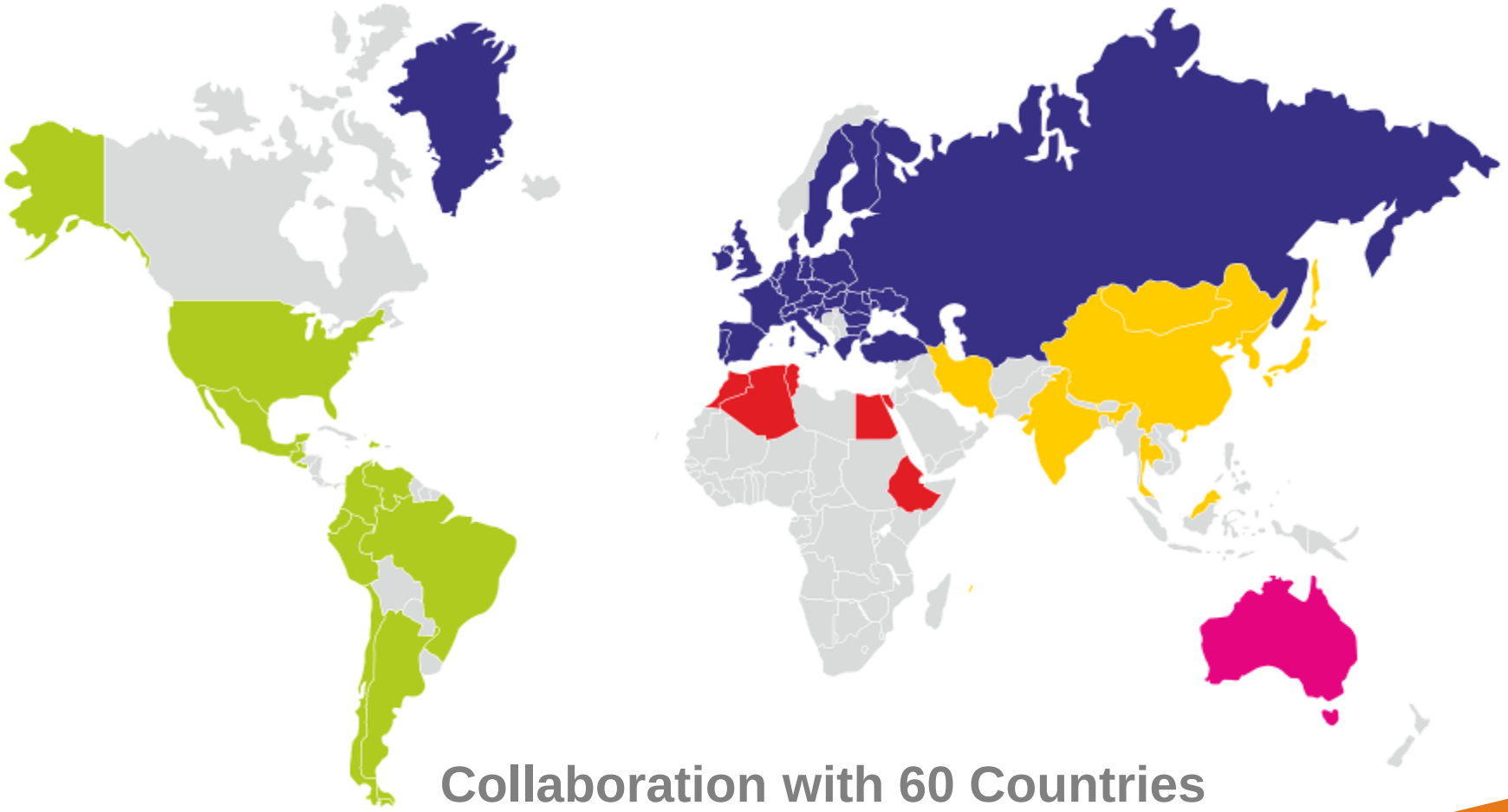
INESCOP
INSTITUTO TECNOLÓGICO DEL CALZADO Y CONEXAS

Horizon 2020

UNEP

Strategic Partnership for the Mediterranean Sea Large Marine Ecosystem
MedPartnership
Together for the Mediterranean Sea
GEF UNEP

INESCOP - Internacional



Collaboration with 60 Countries

INESCOP
INSTITUTO TECNOLÓGICO DEL CALZADO Y CONEXAS

Horizon 2020

UNEP

MAP

Strategic Partnership for the Mediterranean Sea Large Marine Ecosystem

MedPartnership

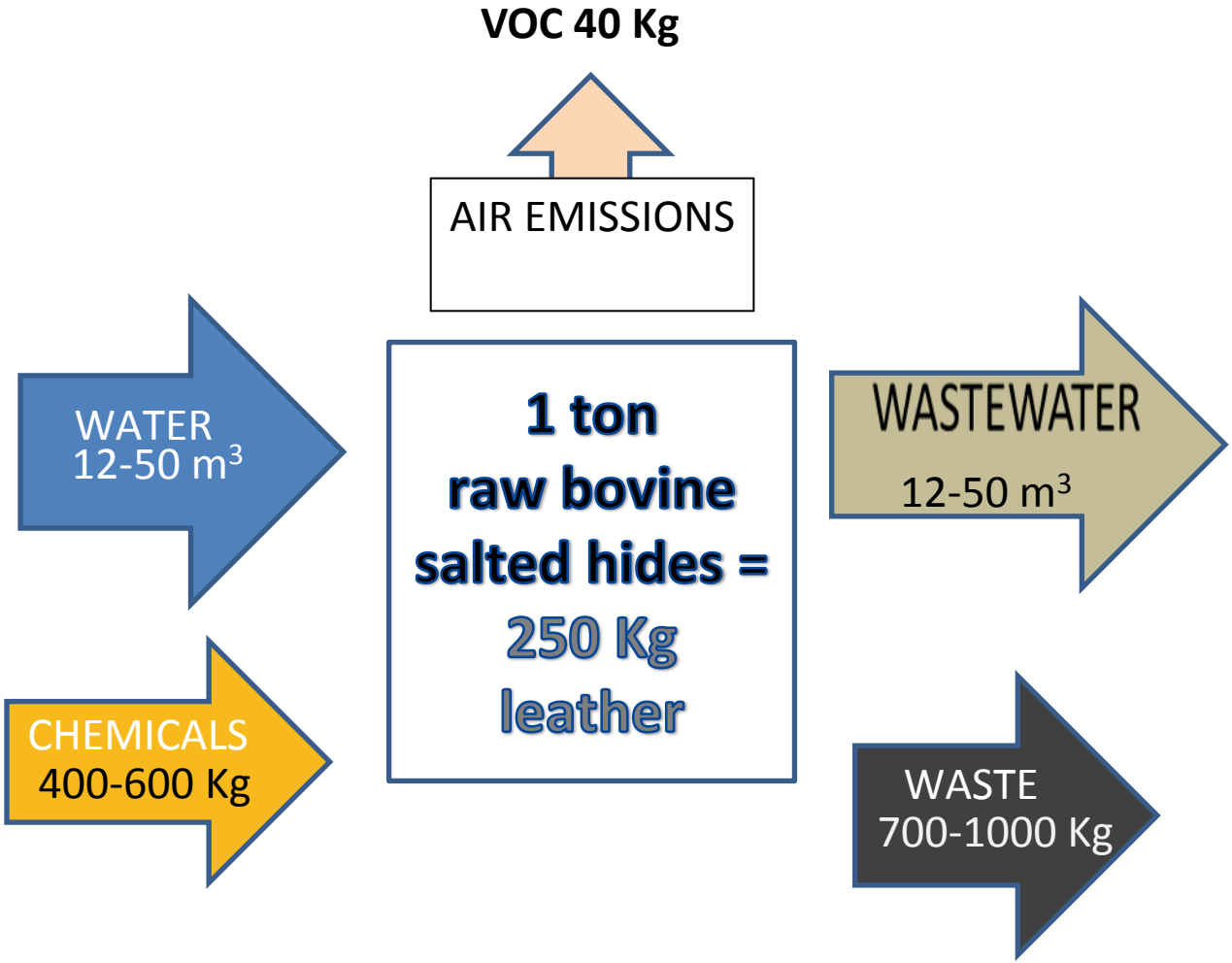
Together for the Mediterranean Sea

GEF UNEP

Best Available Techniques (BAT)

Tanning Sector

Industry benchmarks per ton of processed hide

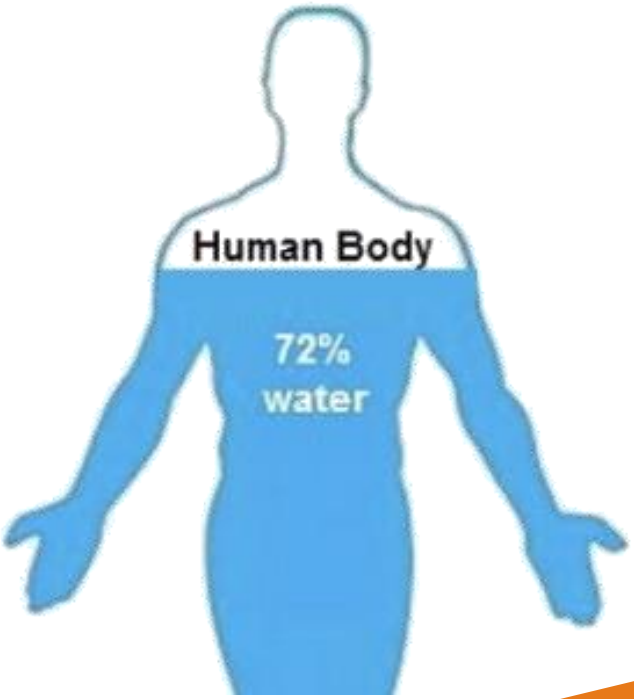


Surface and groundwater pollution

- **Toxic chemicals** - Chromium, sulfides, ammonia, etc.
- **Suspended solids** and;
- **Loads of organic matter**

71% world surface is water

Less than 3% is fresh water



Land pollution

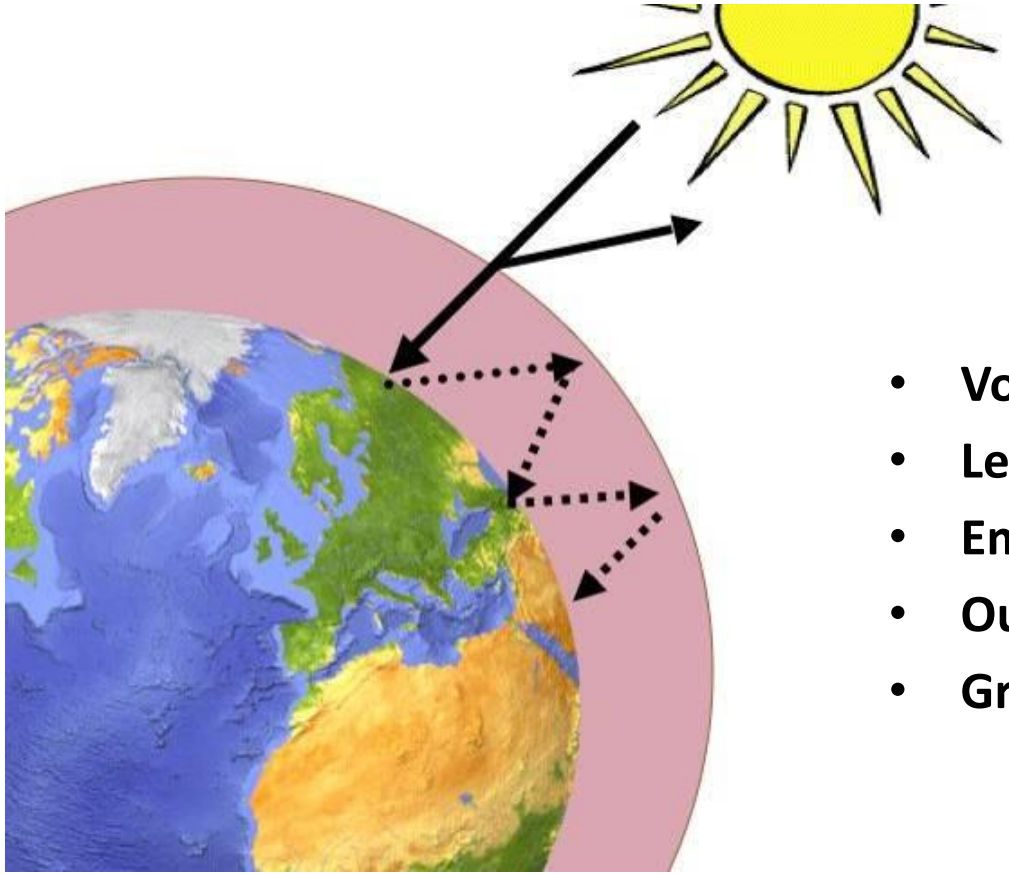
- **Raw trimmings** from raw hides, lime fleshing, degreasing fats, salt…
- Chromium **shavings** and leather **tanned trimmings**,
- **Buffing dust**, process **chemicals** waste
- **Packaging waste** from chemical products
- **Sludge** from waste water treatment.
- And **hazardous substances** → REACH

REACH* in the tanning sector

*REACH is a European Union Regulation for the Registration, Evaluation, Authorisation and Restriction of Chemicals

REACH SUBSTANCES POTENTIALLY USED IN LEATHER MANUFACTURING	
Substances of very high concern (SVHC)	10
Substances subject to authorization (annex XIV)	4
Restricted (annex XVII)	8

Atmospheric pollution



- Volatile Organic Compounds (VOCs)
- Leather dust and other particulates
- Emissions from boilers: NOx, SO_2
- Oudor
- Greenhouse effect

BREF on Tanning BATs

- **BREF:** EU Best Available Techniques Reference Document
- BREF are a consequence of the European **IPPC** Directive (Integrated Pollution Prevention and Control)
- BREF are the **result of an exchange of information on BATs for different industrial sectors** between the European Commission and:
  - European Union Member States,
  - the industries concerned,
  - NGOs promoting environmental protection
- The **first BREF for the tanning of hides** and skins was released in 2003
- The second version was released in **2013**

JOINT RESEARCH CENTRE
Institute for Prospective Technological Studies
Sustainable Production and Consumption Unit
European IPPC Bureau

Summary of the Best Available Techniques for the tanning sector

BAT: the most effective and advanced methods of operation in order to prevent and reduce the environmental impact as a whole

In the Guide a brief summary of **47 Best Available Techniques (BATs)** have been considered more adequate for achieving a high level of environmental protection in the following process stages:

- Storage (2)
- Beamhouse (9)
- Tanning (7)
- Post Tanning (8)
- Finishing (2)
- Wastewater treatment (4)
- Air emissions (3)
- Waste Minimization (2)
- Substitution of chemicals (5)
- Others (6)

10 BATs selected (one per each process stage)

Storage BATs

- Reduction of the time of the storage of raw hides by cooling
- **Mechanical removal of salt**

Beamhouse BATs

- Use of clean hides and skins
- Green fleshing (before any processing o immediately after soaking instead of after liming)
- Hair save using alkali without sulphides
- Low-sulphide unhairing
- pH control for prevention of H_2S emissions
- Lime splitting (instead of after tanning)
- Use of CO_2 in deliming (instead of ammonium compounds)
- Use of weak organic acids in deliming (instead of ammonium compounds)
- **Enzymatic unhairing**

Tanning BATs

- Salt free pickling (using polymeric sulphonic acids instead of NaCl)
- Recovery of degreasing solvents by distillation (sheepskins)
- Recycling and reuse of chromium floats (for pickling or tanning)
- Chromium recovery through precipitation and separation
- Chromium-free leather pre-tanning (aldehides, aluminium, gluteraldehide, titanium, etc.)
- Pretanning followed by vegetable tanning with high uptake of tanning agents
- **Increasing the efficiency of chromium tanning**

Post-Tanning BATs

- Optimising process parameters in retanning (Temperature, float duration, pH)
- Optimisaing dyes uptake
- Optimising fatliquoring
- Process changes to reduce metal discharges (high exhaustion techniques, ageing, etc)
- Use of liquid and low dust dyes
- Low Tempreature Drying (LTD) machines
- **Substitution of nitrogen compounds in post-tanning**

Finishing BATs

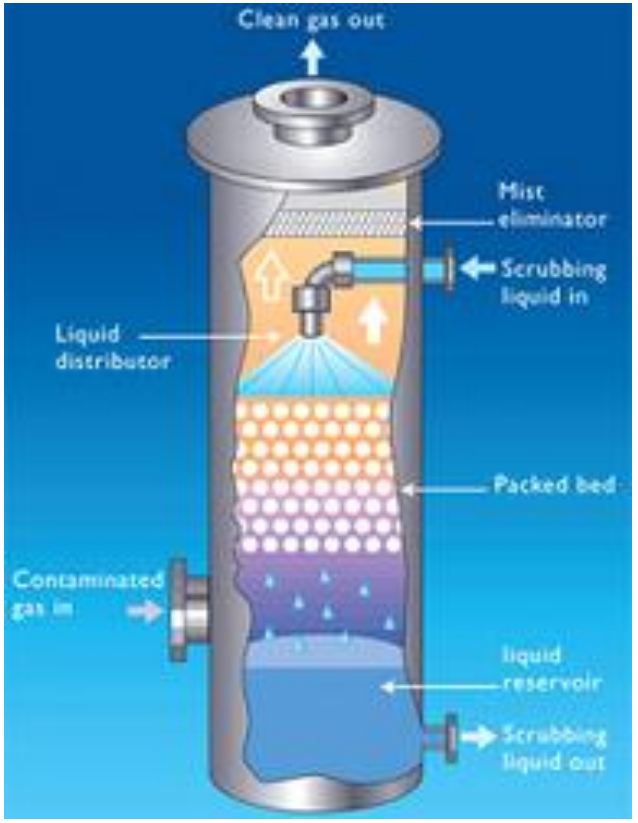
- Improved techniques for spray coating: High Volume Low Pressure (HVLP) spraying technique
- **Curtain or roller coating (non-spraying finishing)**

Wastewater Treatment BATs

- **Mechanical and physico-chemical treatments**
- Biological treatment using activated sludge
- Biological nitrogen elimination
- Post-purification treatments (e.g. sludge dewatering)

Air emissions BATs

- Abatement of ammonia and hydrogen sulphide (wet scrubbers and/or bio-filters)
- Filtration of the emission of dusts and other particulate matter to the air (cyclons, bag filters, scrubbers)
- **Water-based chemicals for coating**



Waste BATs

- Measures for solid waste from wastewater treatment
- **Reduction of disposal of organic waste fractions**

Substitution of Chemicals BATs

- Substitution of halogenated organic compounds in degreasing
- Substitution of halogenated organic compounds in fatliquors
- Substitution or optimisation of halogenated organic compounds in water-, soil- and oil-repellent agents
- Substitution of halogenated organic compounds in flame retardants
- **Substitution of octylphenol and nonylphenol ethoxylates**

Other BATs

- Environmental outputs monitoring
- Decommissioning of tanneries
- Noise and vibration control
- Reuse of treated wastewater in soaking and liming processes
- Rain water management
- **Process water management**

INESCOP
INSTITUTO TECNOLÓGICO DEL CALZADO Y CONEXAS

Horizon 2020

UNEP

MAP

Strategic Partnership for the Mediterranean Sea Large Marine Ecosystem
MedPartnership

Together for the Mediterranean Sea

GEF UNEP

10 most immediate Best Available Techniques (BAT) Tanning Sector

The 10 most immediate pollution prevention options

1. Salt removal
2. Enzymatic unhairing
3. Chromium tanning efficiency
4. Substitution of nitrogenous compounds in post-tanning
5. Non-spraying finishing
6. Wastewater mechanical and physico-chemical treatment.
7. Water-based chemicals for coating
8. Organic waste recycling
9. Substitution of nonylphenol ethoxylates
10. Process water management

Guide on 10 most immediate BAT

One file for each selected BAT. Each file containing:

- Technical description
- Environmental benefits and driving forces
- Cross media effects (if any)
- Economic remarks
- Equipment (if necessary)
- BAT source

BAT 1 (Storage): Removal of salt

- Salting is the most commonly used curing practice
- Removing salt before leather wet treatments implies wastewater benefits:
  - → reduces **salinity** (about 15%)
  - → reduces **total dissolved solids (TDS)** (about 15%)

BAT 2 (Beamhouse): Enzymatic unhairing

- Unhairing is usually carried out by adding **sulphides**
- Separation of the hair from the epidermis can be done by the addition of **enzymatic** products, with environmental benefits:
  - **Sulphides** are **avoided** → wastewater sulphide oxidation is no longer necessary and less sludge is produced.
  - **Reduction of the consumption of water** (less washes are necessary than using sulphide).
  - **Hair is removed in solid form** so the **COD is reduced**.
  - The **toxicity of wastewater is reduced** since the enzymes are not persistent and they are easily inactivated and biodegradable

BAT 3 (Tanyard): Chromium tanning efficiency

- Chrome tanning is the most common type of tannage in the world involving **60-140 ppm of Chromium** in wastewater streams with a water consumption of **50 m3/t hides**.
- Different methods described in this BAT allows **10-14 ppm of chromium** in wastewater with a water consumption about **30 m3/t hides**. Note: after the proper wastewater treatments (BAT 6) the legal limits are met.
- The environmental advantages are:
    - lower consumption of water and tanning agents
    - lower volume of wastewater
    - lower amount of chromium contained in waste and effluents
    - lower amount of chromium in the sludge generated during wastewater treatment

BAT 4 (Post tanning): Substitution of nitrogen compounds in post-tanning

- **Amino resins** are used in the retanning stage (urea-formaldehyde and melamine-formaldehyde) and **ammonia** is used as a dye penetrator.
- These compounds can be substituted by other ones as vegetable or **proteinic retanning agents**, and also **ammonia-free dyes** can be used.
- Environmental benefits:
  - Discharges of **nitrogen are avoided**
  - The substitution of amino resins **avoids** the possibility that **traces of free formaldehyde** may appear **in leather**
  - The substitution of ammonia **avoids** the possibility that **traces of Cr VI** may be formed **in leather**.

BAT 5 (Finishing): Non-spraying finishings

- **Spray** techniques are the most common procedure for leather finishing.
- The leather can be finished using new equipments as a **liquid curtain machine** or a **roller machine**.
- Environmental benefits:
  - The **avoidance of the mist and solid particulate emissions** associated with spraying
  - **Reduced chemical consumption** (Roller coating waste about 3-5% as opposed to 40% for conventional spraying)

BAT 6 (Wastewater treatment): Mechanical and physico-chemical treatment

- The minimum treatment operations should include:
  - screening of gross solids
  - skimming of fats, oils, and greases
  - physical-chemical treatment by flotation or sedimentation using coagulants and floculants
  - chromium precipitation
  - sulphide oxidation (if necessary according to BAT2)
- Only using a mechanical treatment:
  - Reduction up to **40% of gross suspended solids**
  - Reduction up to **30% COD** thus saving flocculating chemicals in the next stage and reducing the sludge generated.
- With the subsequent physical-chemical treatment:
  - Reduction **of COD up to 75%**
  - Reduction of **chromium up to 95%**
  - Reduction of **sulphides up to 95%**

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

- The use of organic solvent-based finishing products is extended involving **atmospheric emissions** and a **workplace health risk.**
- An option is using **aqueous finishes**
- The range for organic solvent-free or at least low-solvent finishing products is increasing as well as their performance.
- Environmental benefits are the **reduction of VOC emission**.
- Beyond the environmental concerns there is a clear **benefit on H&S** operating conditions in the tanneries.

BAT 8 (Waste minimization): Organic waste recycling

- **Waste minimisation** is a must.
- As long as waste are not cross-polluted, **recovery options can be considered** that offer economic as well as environmental advantages.
- The **reduction of wastes** sent for disposal is the main reason for using these techniques, as well as **obtaining useful by-products** as for instance:
  - **Sheep wool** can be used in the **textile** industry
  - **Hair** recovered from BAT 2 can be used as a **soil fertilizer**
  - **Untanned leather waste** can be recycled into **collagen** and **gelatines**

BAT 9 (Substitution of substances): Substitution of nonylphenol ethoxylates

- **Nonylphenol ethoxylates** (NPE) surfactants were used in the leather industry in the past but **today** are **restricted** in the EU due to its toxicity and bio-acummulative character.
- **Substitutes** with better environmental performance are **linear alcohol ethoxilates**:
  - **Lower toxicity** in water
  - Easier **biological degradation**
  - The **need for pre-treatment** to remove the organic fraction before a potential biological wastewater treatment **is avoided**.

BAT 10 (Other): Process water management

- So far **water is necessary** for leather processing.
- Through a good water management (efficient technical control and good housekeeping), the **water consumption** can be **reduced from** commonly employed **40 m3/t** (for bovine hides) to **12-25 m3/t**
- Environmental benefits:
  - **saving water**
  - **saving energy** as a consequence of saving hot water
  - **saving chemicals** due to the use of shorter floats
  - **reducing new wastewater treatment plant size** or if plant is already existing its performance will be increased.

INESCOP
INSTITUTO TECNOLÓGICO DEL CALZADO Y CONEXAS

Horizon 2020

UNEP

Strategic Partnership for the Mediterranean Sea Large Marine Ecosystem
MedPartnership
Together for the Mediterranean Sea

GEF UNEP

Health and Safety

Tanning Sector

Health and Safety in the tanning sector

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

H&S guidelines for tanneries

- For every detected possible danger a table has been prepared containining:
  - Description of the risks
  - Potential consequences
  - Prevention measures

INESCOP
INSTITUTO TECNOLÓGICO DEL CALZADO Y CONEXAS

Horizon 2020

UNEP

MAP

Strategic Partnership for the Mediterranean Sea Large Marine Ecosystem

MedPartnership

Together for the Mediterranean Sea

GEF UNEP

Case Study

INESCOP

INESCOP
INSTITUTO TECNOLÓGICO DEL CALZADO Y CONEXAS

Horizon 2020

UNEP

Strategic Partnership for the Mediterranean Sea Large Marine Ecosystem
MedPartnership
Together for the Mediterranean Sea

GEF UNEP

The convenience for a Technological Institute

- Skilled professionals
- Lab equipments
- Pilot plants for testing
- Close to the factories

→ **Quality Control**
→ **Environmental Monitoring**
→ **Applied Research**
→ **Technology Transfer**

Good for the Environment, Good for Business

LIFE TARELI Project

- Recycling of pickling and tanning baths
- Achieved savings:

» 97% less water
» 55% less salt
» 21% less formic acid
» 14% less chromium

Coordinated by:

INESCOP
SPANISH FOOTWEAR TECHNOLOGY INSTITUTE

LIFE OXATAN project

- **Chromium tanning** (>90% worldwide)
  - Allergy to chromium (dermatitis)
  - Chromium in leather waste & wastewater
  - Possible oxidation Cr (III) → Cr (VI)
- **Oxazolidine tanning:**
  - **Chrome-free** leather
  - Oxazolidine-tanned leather is **more biodegradable**.

Coordinated by:

INESCOP
SPANISH FOOTWEAR TECHNOLOGY INSTITUTE

INESCOP
INSTITUTO TECNOLÓGICO DEL CALZADO Y CONEXAS

Horizon2020

UNEP

MedPartnership

Egypt

- Since **2002**
- Main collaboration with **MTI** (Egypt)
- Creation of the **LTTC** (leather)
- Creation of the **LTC** (footwear)
- Numerous technology transfer actions

Ministry of Industry & Foreign Trade
وزارة الصناعة و التجارة الخارجية

aecid
Agencia Española de Cooperación Internacional para el Desarrollo

Life

L.T.T.C
Leather Tanning Technology Center
مركز تكنولوجيا دباغة الجلود

Leather Technology Center of EGYPT

Tunisia

- Since **1991**
- Main collaboration with **CNCC** (Tunisia)
- Water laboratory and wastewater treatment pilot plants
- Numerous technology transfer actions:

aecid
Agencia Española de Cooperación Internacional para el Desarrollo

Life

Centre National du Cuir et de la Chaussure

LIFE ShoeBAT project

Promotion of best available techniques in the European footwear and tanning sectors

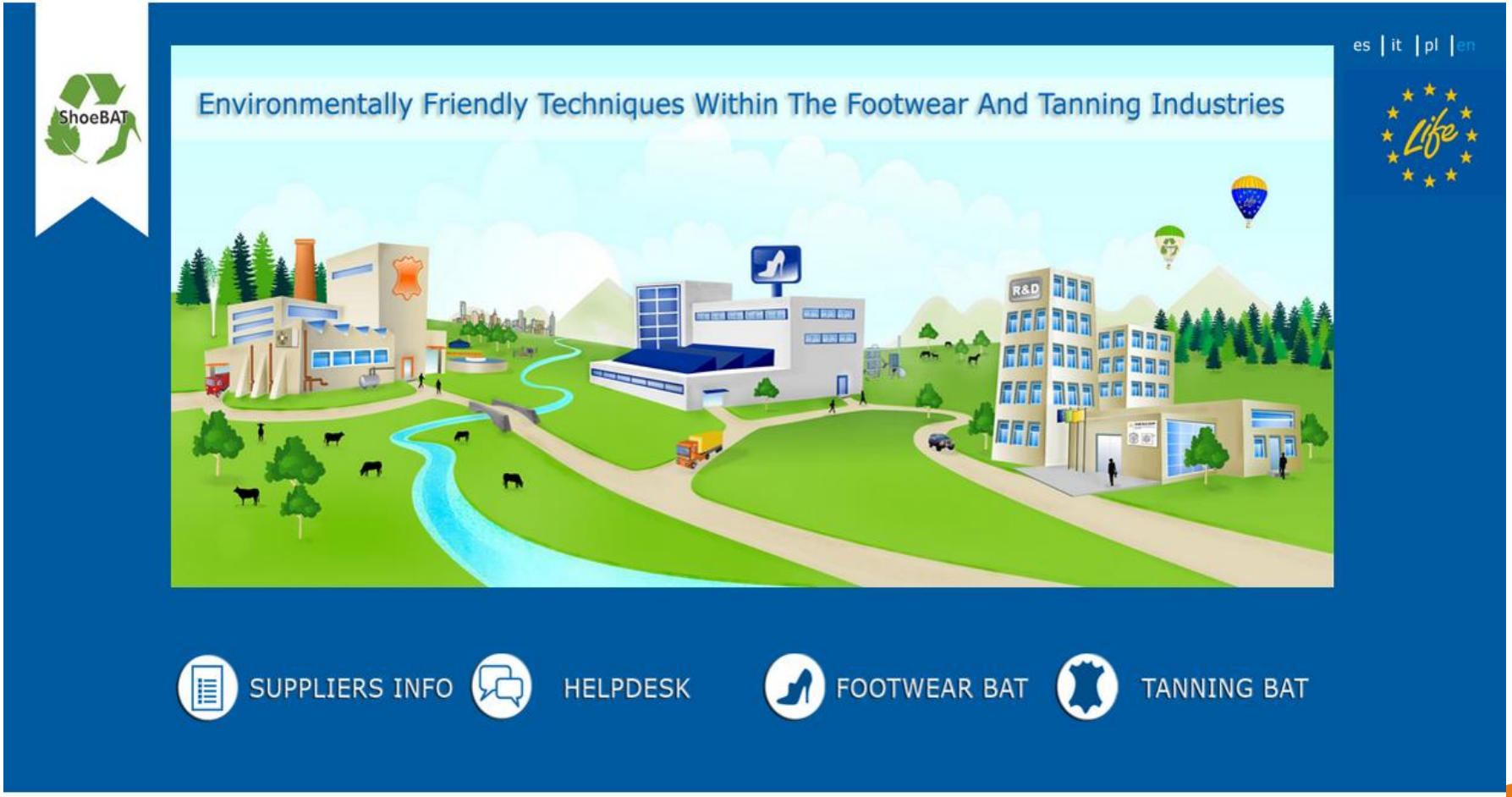
www.life-shoebat.eu

Coordinated by:

INESCOP
SPANISH FOOTWEAR TECHNOLOGY INSTITUTE

LIFE 12 ENV/ES/000243

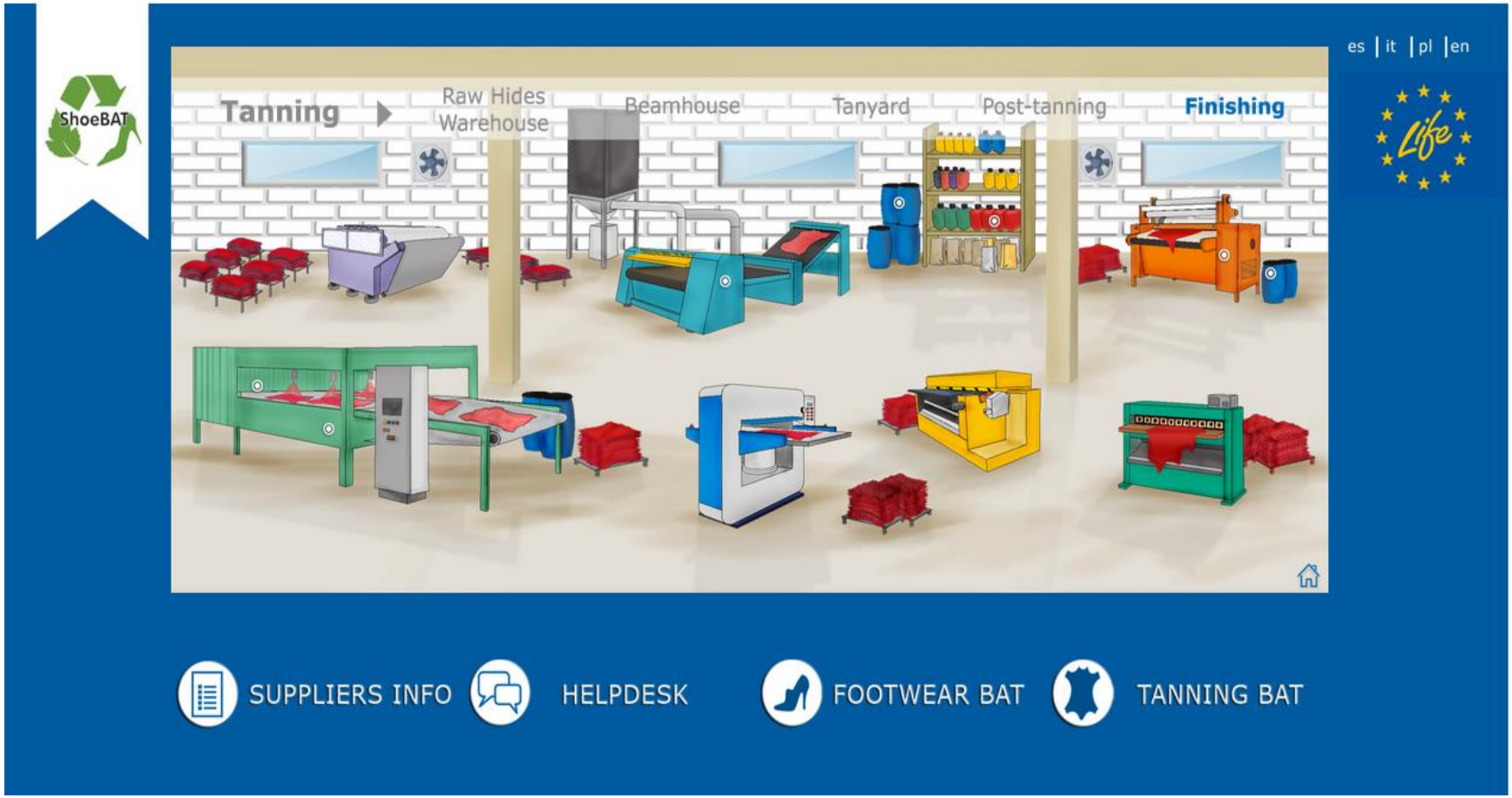
e-platform for BATs



Beamhouse


ShoeBAT
es | it | pl | en
Life
Tanning
Raw Hides Warehouse
Beamhouse
Tanyard
Post-tanning
Finishing
SUPPLIERS INFO
HELPDESK
FOOTWEAR BAT
TANNING BAT

Finishing


ShoeBAT
es | it | pl | en
Tanning
Raw Hides Warehouse
Beamhouse
Tanyard
Post-tanning
Finishing
SUPPLIERS INFO
HELPDESK
FOOTWEAR BAT
TANNING BAT

Thanks for your attention

medioambiente@inescop.es
www.inescop.es

INESCOP
SINCE 1971
Leading innovation