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The framework for sustainable leather manufacture

Second edition

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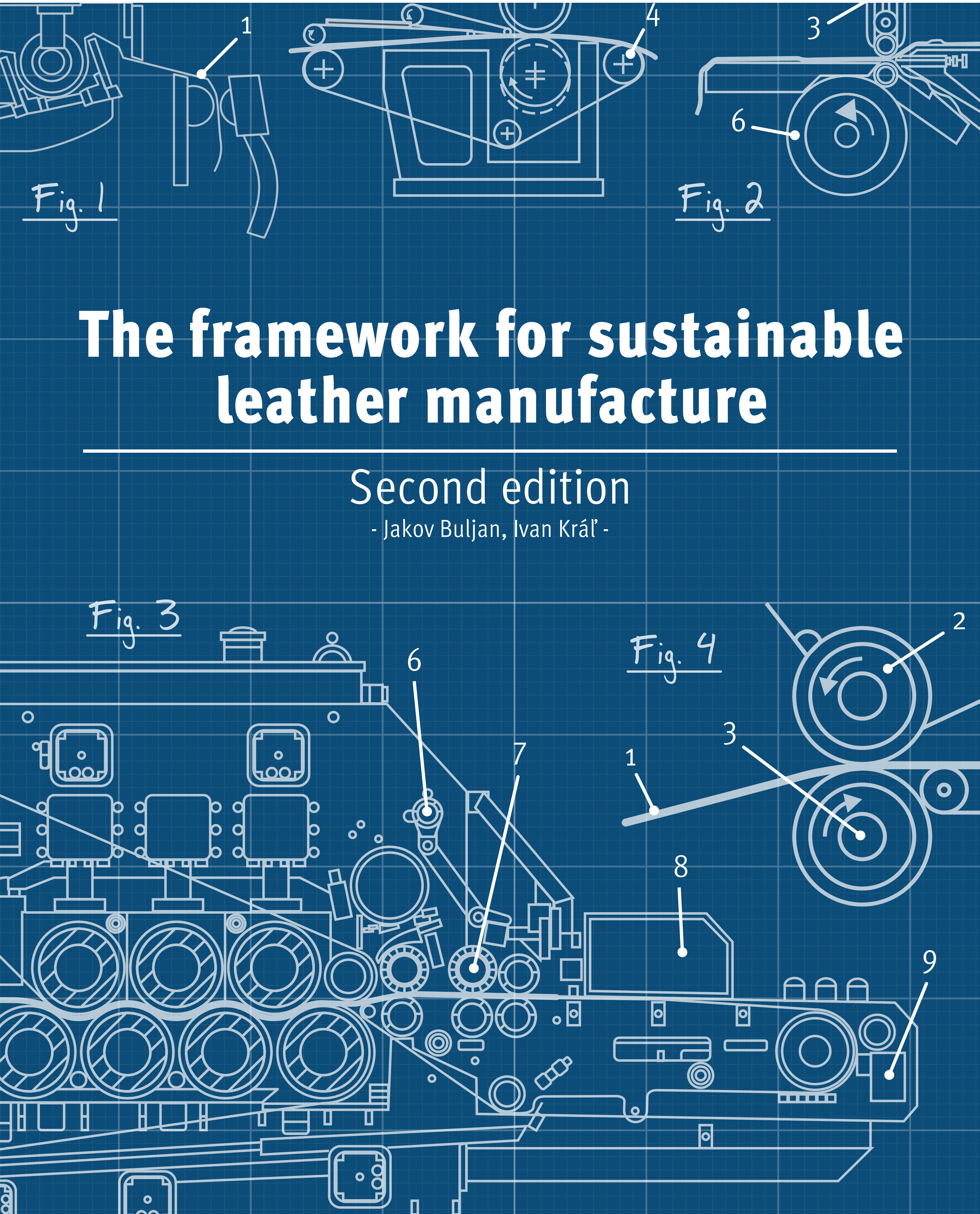
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The information and views as well as tables, drawings, photos, etc. in this paper are primarily intended to serve as background material for UNIDO workshops in developing countries; it is also hoped that they will be used for developing a practical eLearning programme on cleaner tanning technologies.

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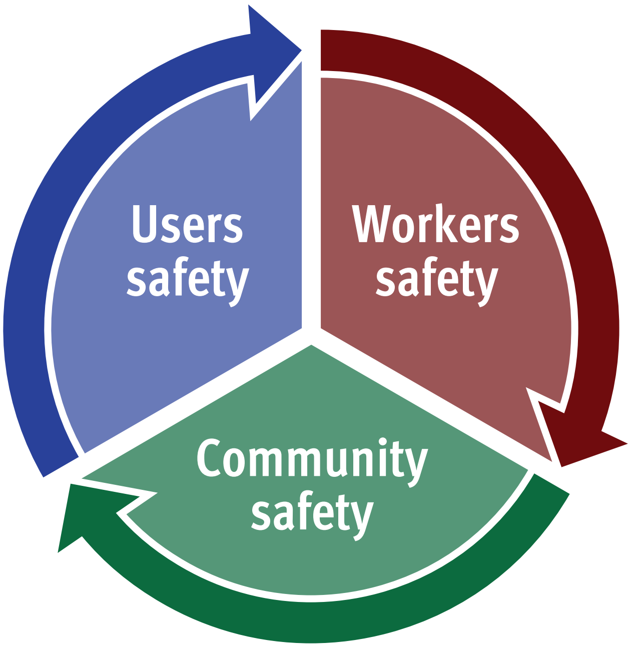
FOREWORD TO THE SECOND EDITION

This paper is a thoroughly revised and expanded version of UNIDO paper *The Framework for Sustainable Leather Manufacture* from 2014. It is primarily prepared to reflect recent developments that took place in defining and computing the leather carbon footprint (CF), about presence of restricted substances in leather (RSLs) and to expand the texts dealing with subjects such as sustainability, vegetable tanning, the future of leather and the promotion of leather as a noble, unique and sustainable material. Specific data on the utilization of solar energy, water saving measures, short term preservation and desalting under recent UNIDO projects, including new photos and charts as well as a new chapter with predictions about the future of leather, have also been added.

On the whole the general intention of the paper is to present and promote the concept of leather as a sustainable (as long as there is livestock to produce meat and milk) and safe material. To be classified as safe, it has to be safe for operators (Occupational Safety and Health at work place, OSH), safe for communities (all emissions treated and safe) and safe for ultimate users. Finally, a tanner (producer) also has to design leather in a way that will facilitate its handling and disposal at the end of life.



PREFACE

> ***If all the forests will disappear, man will be left with only his family tree to weep on.***
>
> Albert Einstein

There is no shortage of papers dealing with some specific aspects of pollution control, including cleaner technologies in leather manufacturing such as operations in the beamhouse, (chrome) tanning or finishing. On the other hand, there is much less widely accessible information providing a comprehensive overview about the scope of preventing and/or reducing the polluting emissions throughout the entire leather-making process.

The evolution that took place during last decades is also to be recognized: the concepts such as Best Available Technology, Not Entailing Excessive Costs (BATNEC) from the early 80s and Cheapest Available Technology Narrowly Avoiding Prosecution (CATNAP) some 20 years later are by now long abandoned and forgotten.

Documents prepared by the Environmental Commission (IUE) of the International Union of Leather Chemists and Technologists Associations (IULTCS) and the Best Available Techniques Reference Document (BREF) prepared in the European Union (both updated from time to time) are globally referred to for guidance on what can be considered a cleaner technology method.

However, while being very useful, they do not quite coincide with the profiles and needs of a large segment of tanners, especially in developing countries. BREF is written in a specific format for conditions prevailing in the EU whereas the IUE set of documents might not be detailed enough for practical purposes.

In the last few decades, under various projects of technical assistance and under the auspices of its well-established Leather and Leather Products Industry Panel, UNIDO has prepared a number of studies dealing with various cleaner tanning methods such as mass balance, desalting of raw hides/skins, hair-save unhairing, chrome balance/chrome management, hair-save liming, detection and avoidance of hexavalent chromium, etc. Now it is believed to be the right time to prepare a single, comprehensive study on cleaner leather technologies, round up and update earlier papers, and supplement the IUE and BREF documents.

In this paper an attempt has been made not only to revisit the traditional "standing" issues (water saving, deliming, chrome management, etc.) but also to present a fresh, neutral assessment of some cleaner methods based on years of practical experience.

In conformity with new trends (and environmental/legislative pressures!) both wet and dry finishings are discussed in more detail than used to be the case.

Energy consumption, traditionally on a side-track (if not totally ignored), is also now looked at more closely.

Serious scientific papers and media headlines about greenhouse effects/global warming and the anticipated public pressures on the leather industry, including current discussions in various leather fora possibly triggered by the UNIDO Leather Panel meeting in September 2012 in Shanghai resulted in a mosaic of information and views under the Life Cycle Analysis (LCA) – Carbon Footprint (CF) chapter.

Indeed, throughout the paper the approach is to present information about experiences gathered and options available to date and to point out their advantages and disadvantages without strong preference and certainly not "imposing" a particular method. After all, there is no general consensus, even about the right terminology. For example, many people think that there is no such a thing like the best available technology because "...a particular technology may be best for one situation but not for another..." and instead "... appropriate technology should be adopted"[1].

In this context, it is useful to remember that there is no unified approach on what is to be classified as a hazardous substance. Possibly (over)simplifying the matter, it could be said that the EU approach is that strong suspicion about potential harmful effect(s) suffices whereas in the USA the negative impact has to be proven.

Finally, it cannot be overemphasised that a significant decrease of polluting loads can be achieved by strict process monitoring and control and/or minor modifications of the traditional, conventional technologies, i.e. without high investments and/or the use of expensive proprietary specialty chemicals.

Some repetitions in the paper are because it is expected that ultimately the paper will be a part of the UNIDO eLearning system where for practical reasons it is useful to have some chapters as nearly independent, stand-alone documents.

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[1] *C. Money.*

1. SUSTAINABILITY

1.1. GENERAL CONSIDERATIONS

Restoring and maintaining the balance between natural resources and consumption and population growth is one of the key elements for the future of humanity. Generally, it is taken for granted that human impact is (easily) measurable.

In reality, there is no universally accepted sustainability[2] measuring system and/or unit. Among those proposed are the Sustainability Development Indicator (SDI), the Human Development Index (HDI), the Environmental Sustainability Index (ESI) and the Environmental Performance Index (EPI). Very interesting is also the IPAT equation:

> **Human Impact (I) =**
> **Population (P) x Affluence (A) x Technology (T)**
> where
> A = consumption per capita and
> T = environmental impact
> per unit of consumption

Possibly the best is the sustainability approach proposed in the UN Brundtland Commission Report (1987) stating: *Sustainable development is development that meets the needs of the present without compromising the ability of future generations to meet their own needs.*

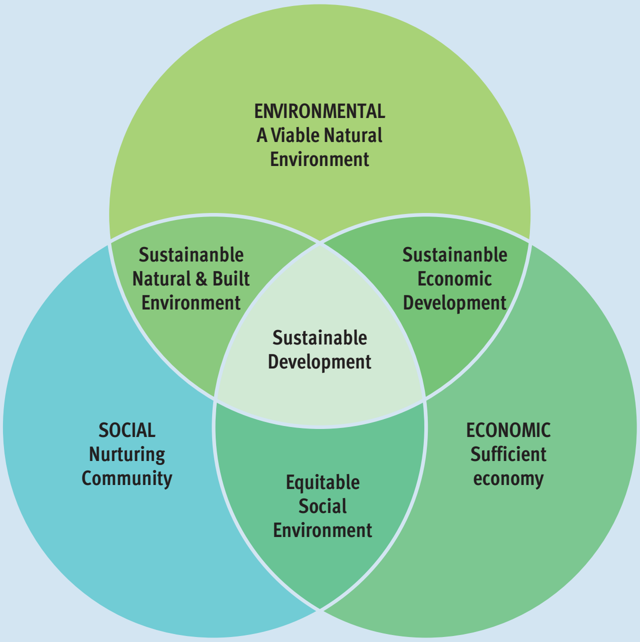
The Daly Rules approach (possibly founded on ecological/thermodynamic principles) suggests the following criteria of sustainability:

- Renewable resources (e.g. fish, soil, groundwater) must be used no faster than the rate at which they regenerate.
- Non-renewable resources (e.g. minerals, fossil fuels) must be used no faster than renewable substitutes for them can be put into place.
- Pollution and wastes must be emitted no faster than natural systems can absorb them, recycle them, or render them harmless.

Some other authors[3] suggest that sustainability indicators should be holistic in nature, measuring sufficiency of well-being for all, sustainability of natural resources and efficiency of converting resources to universal well-being; they believe that complex systems require multiple viewpoints to adequately express the needs of all in the system. In that context sustainability (like in nature) also implies maintaining adaptive capability, development means maintaining opportunity so that sustainable development corresponds to fostering adaptive capabilities and creating opportunities.

In essence, sustainability calls for renewable raw materials, recycling and waste reduction. The tanning sector must adhere to these principles at every stage especially since from time immemorial its perception has been quite bad; its status in virtually all cultures around the world is among the lowest. Even nowadays, the malodours from poorly run tanneries overshadow the fact that, for example, production of one square metre of blue jeans requires about ten times more water than of one square metre of leather.[4]

Figure 1. Correlation among key components of sustainable development



Based on the chart prepared by F. Schmel, UNIDO, Sustainable Development Goals, SDG

1.2. SUSTAINABILITY IN THE LEATHER SECTOR

1.2.1. Raw material base and sustainability

Only the growth rates of goat skins base (rather marginal in importance) exceed the growth rate of human population. However, the growth rates of key parameters of bovine and ovine raw material base (animal herds, pieces of hides/skins or weight/tonnage) are far behind the growth rate of human population production.

Table 1. Comparison of animal growth rates: population, livestock, raw hides (bovine), 1985 - 2010 (25 years)

	Livestock	Production of raw hides	
	Million heads	*Million pieces*	*000 tonnes*
Bovine	0.59	0.88	0.76
Sheep	-0.18	0.76	0.19
Goat	2.40	3.37	3.35

Human Population: 1.41%

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[2] *The Oxford Dictionary of English (OED) defines 'sustainable' as follows: able to be maintained at a certain rate or level ; ...conserving an ecological balance by avoiding depletion of natural resources ; ...able to be upheld or defended*

[3] *See:*
https://www.youtube.com/watch?v=RCN6itoLZvY
https://www.youtube.com/watch?v=-jnH908Ajdo
https://www.youtube.com/watch?v=Q3tJL4JRgn

[4] *Tegtmeyer, Lanxess*

Due to large number of variables/complex relations, it is hard to predict future trends. The key parameters point towards needs (not necessarily demand!) exceeding the raw material availability.

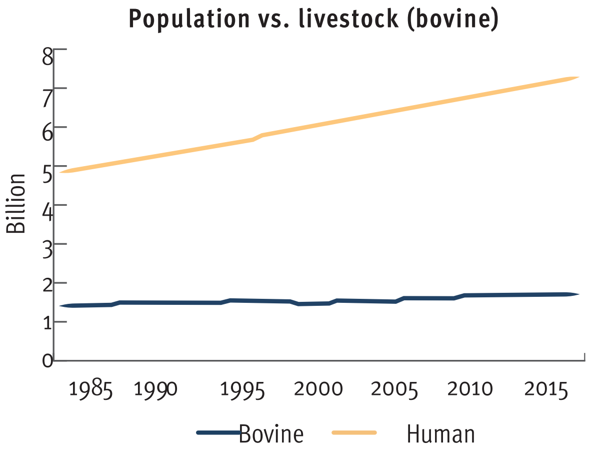
While raw hides and skins, wet blue and crust can be considered commodities, finished leather is normally produced according to an individual buyer's specification.

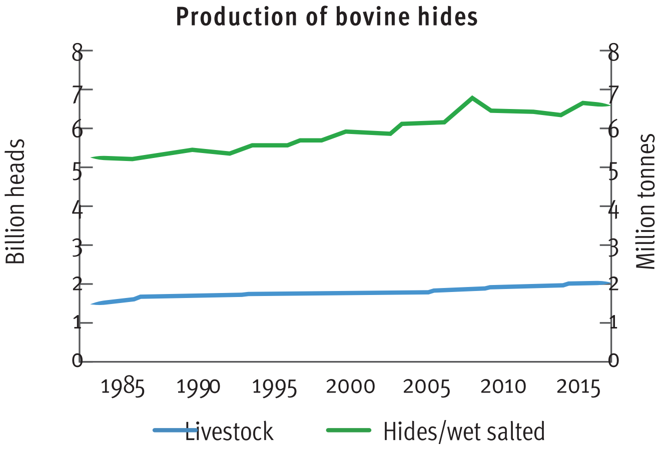
According to a comprehensive computation of mass balance and efficiency of leather manufacturing in a conventional process only about 50% of corium collagen and less than 20% of the chemicals used are actually retained in the finished leather.[5]

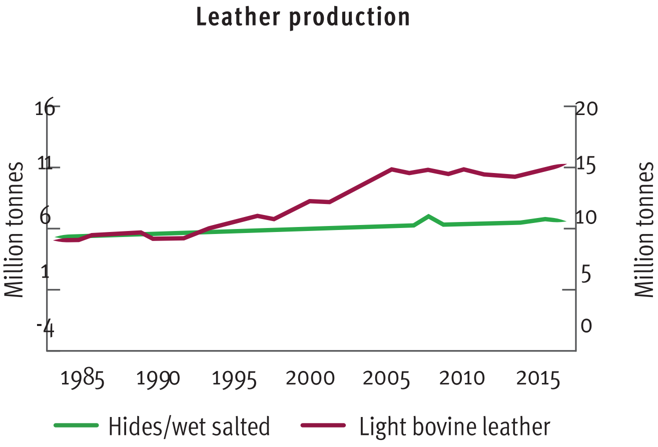
The primary tasks of all cleaner technologies are to reduce the amount and possibly change the nature of pollution emissions, and thus reduce the pressure and costs of end-of-pipe treatment.

Generally, the absorption of new technologies in the leather sector is traditionally slow; established methods last for a long time. The main reason is that despite considerable progress made during the last few decades, leather manufacturing is a mixture of

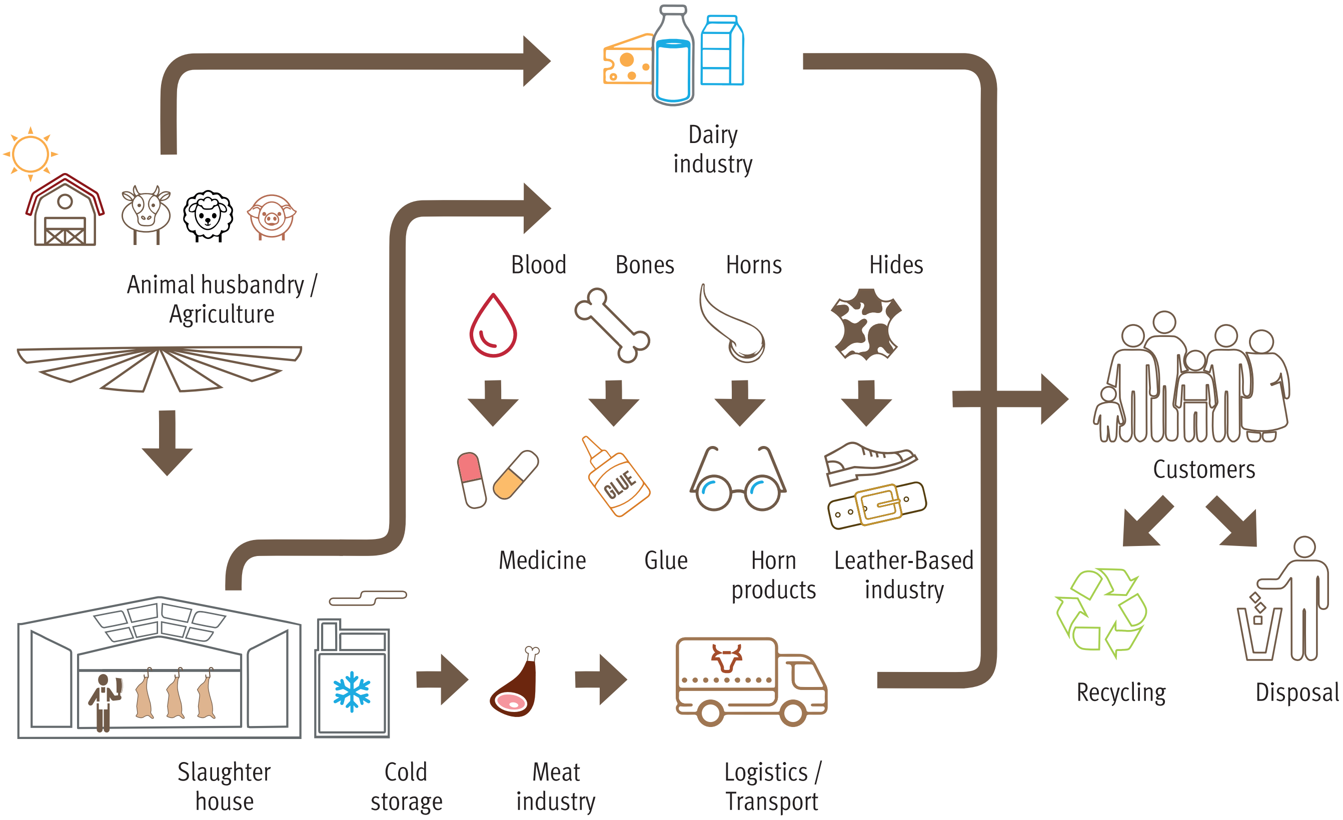
Figure 2. Comparison of annual growth rates: human population, raw hides and leather (bovine) 1985 -2015







Based on charts prepared by F. Schmel, UNIDO


Dairy industry
Animal husbandry / Agriculture
Blood
Bones
Horns
Hides
GLUE
Medicine
Glue
Horn products
Leather-Based industry
Customers
Recycling
Disposal
Slaughter house
Cold storage
Meat industry
Logistics / Transport

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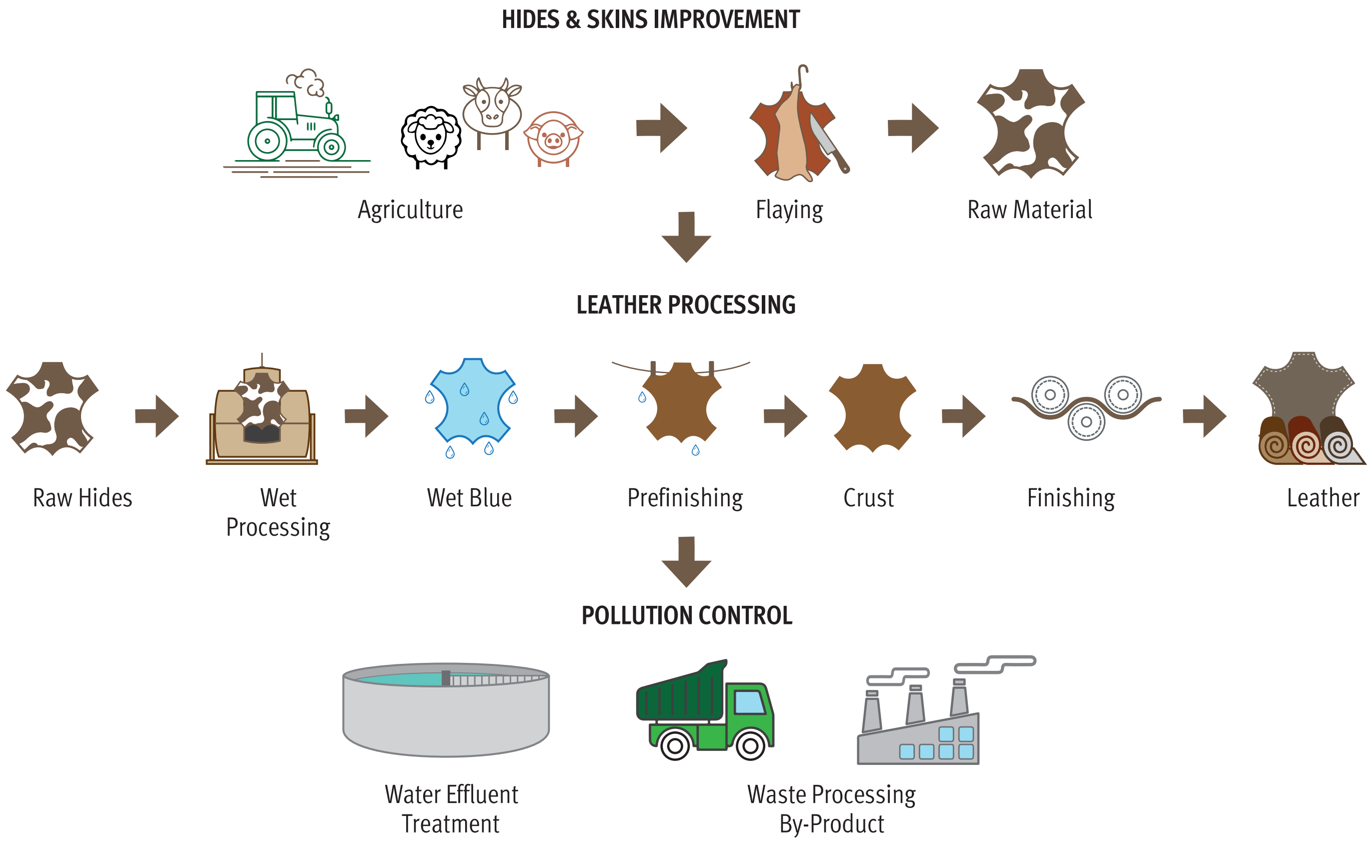
[5] *Mass balance in leather processing, J. Buljan et al, UNIDO*


HIDES & SKINS IMPROVEMENT
Agriculture
Flaying
Raw Material
LEATHER PROCESSING
Raw Hides
Wet Processing
Wet Blue
Prefinishing
Crust
Finishing
Leather
POLLUTION CONTROL
Water Effluent Treatment
Waste Processing By-Product

Based on charts prepared by F. Schmel, UNIDO

science, technology and craft with the nature of some processes are still not fully understood: change of one parameter can considerably affect the fine balance and the ultimate result. Thus, tanners are quite reluctant to modify their existing processes and possibly jeopardize the quality of leather produced. Also, owing to the inherent characteristics of the raw material and desired properties of the finished leather, cleaner tanning methods have their limitations; ultimately, a substantial percentage of all raw material and chemical inputs end up as waste.

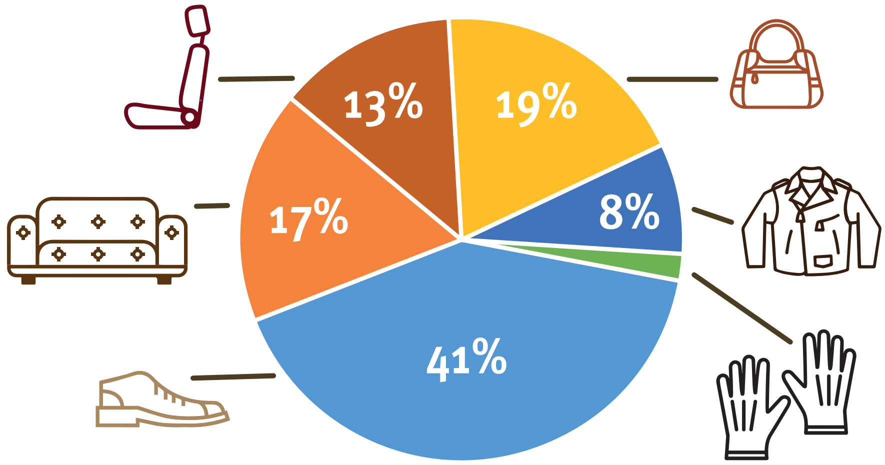
There is no doubt that from the holistic, macro- and long-term perspective, environment-friendly tanning methods are more favourable and cheaper. However, for the individual tanner, cleaner technology methods are usually more expensive due to the cost of more sophisticated equipment and specialty chemicals. The main benefits are better conditions in the plant and a better image with international buyers.

From time to time, most frequently in Europe and mainly among non-specialists, debates surface about comparative environmental advantages of chrome-free synthetic agents and vegetable versus chrome tannage as the prevailing basic tanning method.

The pressure to adopt cleaner technologies normally emanates from environmental imperatives such as the need to meet specific discharge norms, reduce treatment costs or comply with occupational safety and health (OSH) standards. The typical primary targets are:

- Lower water consumption
- Improved uptake of chemicals
- Avoidance of hazardous and/or banned substances (Substances of Very High Concern, SVHC)
- Better quality/re-usability of solid waste and reduced content of specific pollutants such as heavy metals[6] and electrolytes contained therein

Figure 3. The current use of finished leather



Based on Source: https://ec.europa.eu/growth/sectors/fashion/leather/eu-industry_en

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[6] *Although widely used there is no clear technical definition of what it covers.*

1.2.2. The long-term priority targets in achieving leather sustainability

With most consumers, the perception of leather as a natural material is invaluable and it should be preserved and increasingly associated with sustainability, which is why the leather industry itself should insist on very strict sustainability criteria. The following list[7] broadly encompasses the key areas of leather production:

- Resources (hides/skins, chemicals, water, energy)
- Emissions generated during the production process (solid, liquid and gaseous wastes)
- Quality and appeal of the final product, durability
- Product use after end-of life

Availability of the initial raw material, hides and skins was discussed earlier. While the shortage of chemicals needed for leather processing is very unlikely, the emphasis is on much higher uptake than is the case now and, in particular, the need to be fully degradable into non-hazardous components and without any adverse effect on organisms in the water recipient. However, two elements might be critical for long-term sustainability of leather:

- Availability of both fresh water and water recipient/sewage system able to accept the (treated) tannery effluent
- Salt i.e. salinity of tannery effluents

It could be argued that energy should be included as well not because of non-availability, but due to the carbon footprint load (CF) attached to leather if the tanning industry does not switch to energy from renewable sources.

The spread of cleaner technologies and processes is neither spontaneous nor extensive. For all the claims about favourable cost-benefit ratios and/or environmental benefits to be derived from many of these technologies, tanners are not quick in adopting them, be it due to inertia, higher costs or some other limitation.

Contrary to some misperceptions extensive investigations have shown that chrome tanning remains the most environmentally efficient tanning method whereas vegetable and synthetic tanning agents are preferred when specific leather properties are required like in the case of sole and saddlery leathers (vegetable) and automotive leathers which need dimensional stability (synthetic tannage).

In view of ever increasing legal, local and global social pressures[8], no tanner can afford the luxury of not being familiar with the main issues and principles of environmental protection pertaining to tannery operations. Pollution prevention and the persistent promotion of cleaner leather processing, which ultimately leads to lower treatment costs, obviously remains of paramount importance.

1.2.3. Chemicals and sustainability

In recent years there is a striking change in the importance attached to the environmental aspects and sustainability by virtually all reputable suppliers of specialty chemicals to the tanning industry. Here are some examples to illustrate that development:

- Most of the leading suppliers are members of the Zero Discharge of Hazardous Chemicals (ZDHC) foundation which promotes the view that the industry must not produce more waste and emissions than can be degraded by the environment within the same period of time; commits to produce retanning materials that contain little or no salt, no free formaldehyde or phenol; promotes processes designed to reduce the weight of leather and increase its service life and a leather recycling process. In total, a modern, future-oriented leather production should bring economic interests, ecological soundness and consumer benefit into line.
- One supplier launched the Sustainable Leather Management programme, a new initiative claimed to be based on a holistic concept that tackles the challenges of sustainable development systematically along the entire value chain and encompasses the entire life cycle of leather.
- Another supplier undertook helping businesses to reach the ZDHC Joint Roadmap goal in 2020. It vigorously promotes the circular economy concept of which aims to redefine the way products and services are designed in order to look beyond the 'take, make and dispose' model of industrial manufacturing.
- A well-established producer of vegetable (chestnut) extract claimed to be the very first leather chemical company with certified carbon footprint value expressed as kg CO_{2e} per kg of product in accordance with ISO 14025:2010.
- Another chemical supplier promoted a Product Passport stimulating transparency concerning the performance and the effects of chemicals on leather and the environment. The approach is broadly based on the waste hierarchy pyramid.
- Significantly, virtually all chemical suppliers have posts such as Director of Sustainability or equivalent.

While legislative and marketing aspects might be the key drivers behind such moves, it is beyond any doubt that they contribute to both greener production and public perception of the leather industry.

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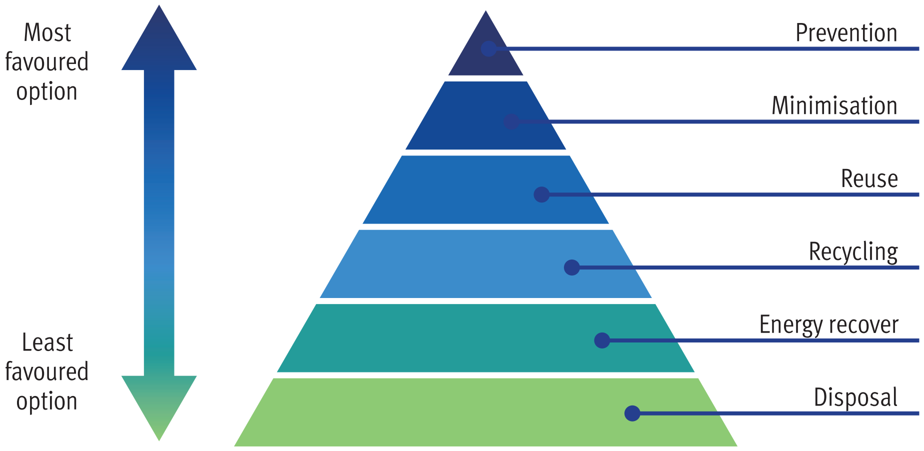
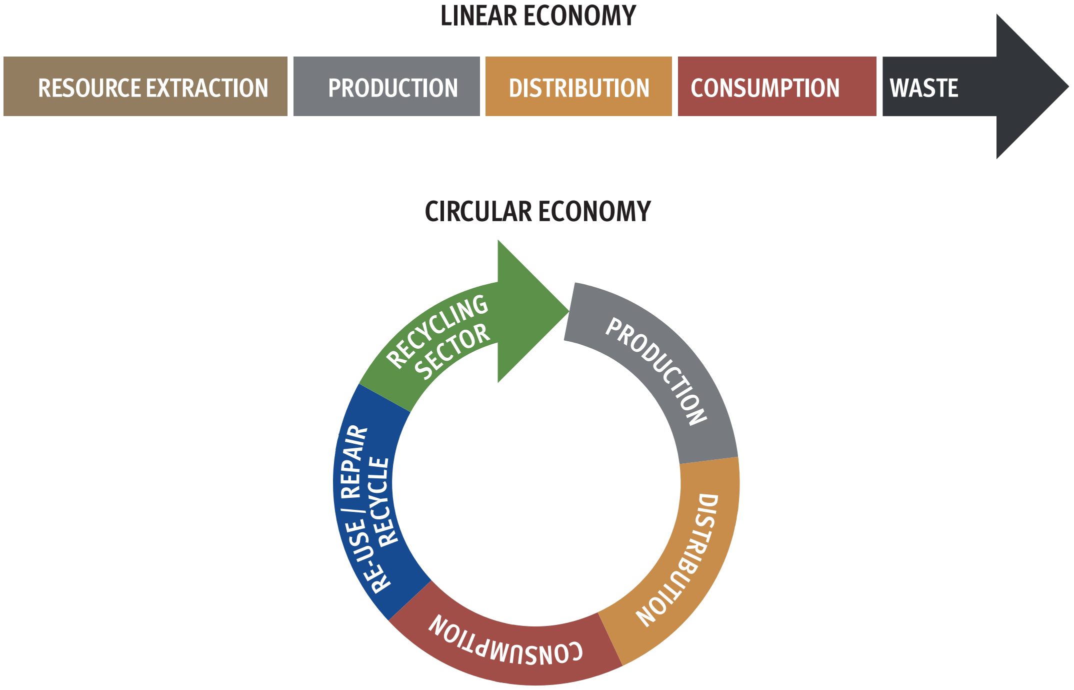
[7] *J. Christner, TFL Ledertechnik, Germany, January 2015*

[8] *In this context refer to the* ***UN Millennium Development Goals (MDG), from Rio conference in 2000 given a fresh impetus by post-2015 UN Development Agenda and the Sustainable Development Goals (SDG) plan.***


Most favoured option
Least favoured option
Prevention
Minimisation
Reuse
Recycling
Energy recover
Disposal


LINEAR ECONOMY
RESOURCE EXTRACTION
PRODUCTION
DISTRIBUTION
CONSUMPTION
WASTE
CIRCULAR ECONOMY
RECYCLING SECTOR
PRODUCTION
DISTRIBUTION
CONSUMPTION
RE-USE / REPAIR RECYCLE

Based on chart by M. Costello[9]

1.2.4. Does sustainability pay for tanneries?[10]

The large majority of companies understand the importance of sustainability yet do not fully recognise how to incorporate it into daily business life. Full integration of sustainability within a business requires considerable time and money; and, inevitably, there is always a question: what are the financial benefits for the tannery?

Incorporating sustainability and innovation in a tannery reframes a company's identity. Tanneries that are continuously building sustainability initiatives create quantifiable goals to be met over defined time periods, incentivise employees to innovate, receive support from management and regularly bring in third-party auditors to review progress.

Sustainability is not usually deliverable in short-term financial results, and change occurs over the medium to long term.

In any case, customers want increased performance from their leather products but are also starting to analyse products' reputations for sustainability.

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[9] *Sustainability in the Leather Supply Chain Conference March 2018: The circular economy aims to redefine the way products and services are designed in order to look beyond the 'take, make and dispose' model of industrial manufacturing.*

[10] *Quoted from the statement by Jon Clark, CEO and Sarah Swenson, Environmental Director of tanners, PrimeAsia, ILM January-February 2015*

1.2.5. Certification of sustainability initiatives

1.2.5.1. The Leather Working Group, (LWG)

Founded in 2005, LWG is a multi-stakeholder group made up of brands, retailers, leather manufacturers, suppliers and technical experts with the objective to develop and maintain an environmental auditing protocol that assesses the environmental performance of tannery operations thus promoting sustainable and environmental business practices. It encompassed more than 400 members made up of brands, leather manufacturers and suppliers. The main LWG working tool is the audit protocol developed and upgraded over several years. The current version (6.5.2) is possibly a bit too complicated. Additionally, some questions and scoring show that the tool has yielded to public issues trumpeted by the media (e.g. chromium, Amazonian rainforest) rather than being entirely based on good science; also, the problem of salinity and salt requires more careful considerations. Certain questions are superfluous and could be seen as an unnecessary infringement on a company's confidential information.

However, there is no doubt that the LWG's auditing protocol has significantly contributed to raising environmental standards, primarily in developing countries, where most of the actual auditing has been done. Gold, Silver and even Bronze rating improve the overall image of the company and apparently create better marketing potential.

1.2.5.2. Some other initiatives

The Brazilian Carbon Disclosure Project (CDP) Supply Chain might be an example of support to and recognition of sustainability gaining global character. It is supposed to help companies build engagement strategies to engage suppliers on a collaborative basis and sustainably develop the value chain. Assessments are carried out via suppliers, who answer a questionnaire on risks and opportunities linked with climate change, water security and activities to reduce deforestation. The CDP scores show each company's progress in each of the four categories: Information disclosure, awareness, management and leadership, which is ascribed as the adoption of best practices.

In March 2018 the Brazil's Leather Certification of Sustainability (CSCB) programme and Italy's Institute of Quality Certification for the Leather Sector (ICEC) have signed a partnership agreement, the Leather Sector - Sustainability Certification Program. One of their proclaimed objectives is to open the dialogue with international NGO's to help evaluate and improve practices, to create and foster communication channels with the most prominent global niche media groups in order to disseminate achievements and promote leather as a sustainable product worldwide.

1.3. INTERNATIONAL UNION OF LEATHER CHEMISTS AND TECHNOLOGISTS SOCIETIES (IULTCS)

Initiated in 1897 and its structure more or less finalized in 1949, IULTCS is presently comprised of more than 20 country member associations, leaders in leather manufacturing, and represents approx. 3,000 individual leather professionals; regardless of legal aspects it is perceived by many as a kind of umbrella organization of the world's leather sector.

IULTCS's aims are the facilitation of global cooperation between leather organizations and the development of standard test methods specific for leather, including their international adoption and correct use. This is operationally achieved through the activities of the Leather Test Methods Commissions, i.e. the IUC (Chemical Test Methods), IUF (Fastness test methods) and IUP (Physical test methods), which have the responsibility to prepare leather test methods for ISO Standards, a well established and reputable mechanism.

> **"The IULTCS is founded for the purpose of encouraging the technology, chemistry, and science of leather on a worldwide basis." (www.iultcs.org)**

Similarly, through its International Union of Environment Commission (IUE), IULTCS addresses the common and special problems relating to environmentally sound leather manufacturing. The IUE Environment document consists of 12 chapters starting with "IUE 1 - Recommendations on Cleaner Technologies for Leather Production" and ending with "IUE 12 - Guidelines for Minimum Environmental Standards". The 10th chapter of the IUE document "IUE Guidelines for Restricted Products in Leather" is in 2018 still in draft stage and is likely to be finalized shortly. In any case, the IUE data on water consumption and pollution load are universally used as reliable references.

More recently, recognizing the need for closer cooperation and support to education, the International Union of Training Commission (IUT) was set up with the task of establishing a framework for global leather education/training facilities and identifying and "validating" a continuous professional development (CPD) programme.

The pitch of IULTCS activities are congresses held every two years in a different country (nowadays one could almost say on a different continent) which serve as a platform where scientists from R&D institutions, suppliers of specialty chemicals and specialists from the industry present the results of their latest research.

Regrettably, without a strong permanent administrative body the IULTCS appears not to be sufficiently involved in preparations and/or verifications of various Restricted Substances Lists (RSLs) by ensuring that they are based on sound science and verified tests.

2. POLLUTION LOAD GENERATED BY CONVENTIONAL TECHNOLOGIES

2.1. GENERAL

Leather manufacturing is a series of operations from preservation to finishing with the aim of converting quickly degradable, highly putrescible raw hides and skins into leather, a stable initial material suitable for use in production of a very wide range of articles: footwear, apparel, dress and protective gloves, furniture, the automotive industry, saddlery, etc.

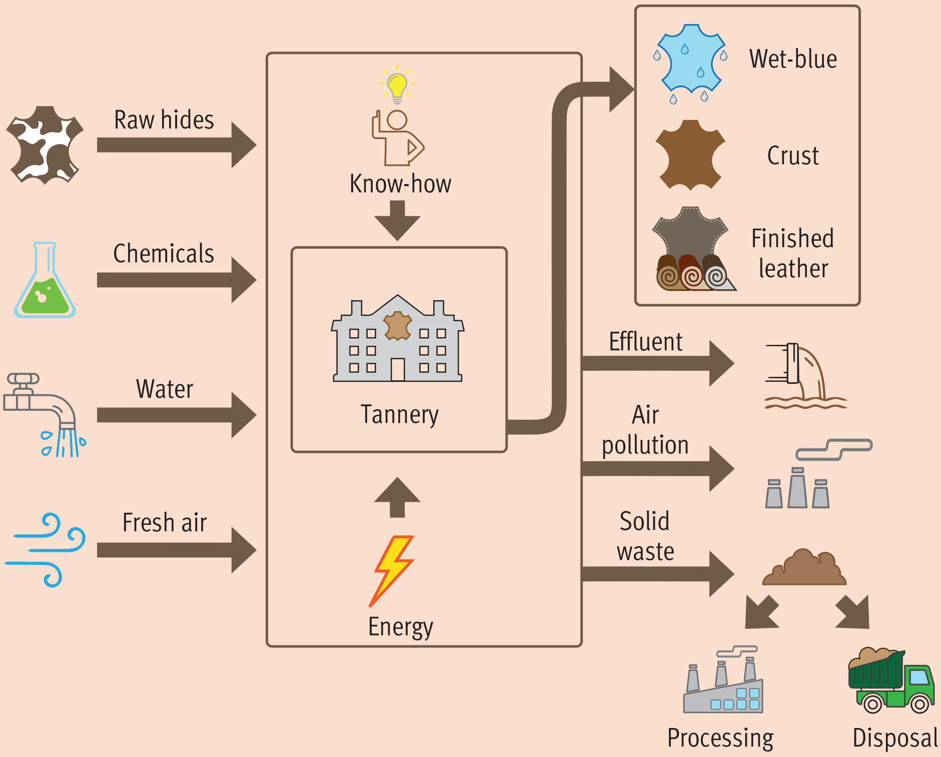
To achieve this aim, it is necessary to apply rather complex mechanical and physical-chemical processes, the tanning step being decisive for giving the stability and character.

While there are already certain synthetic materials that can match or even outperform in some specific areas/purposes (e.g. ski boots), leather's characteristics such as feel, elasticity, permeability of air and perspiration, temperature and water resistance, stability, durability, and attractive appearance make it a highly desirable material with a touch of class and luxury.

Due to varieties in raw materials, processing, chemicals and water consumption, it is no wonder that in the literature figures about pollution load generated during leather production vary a lot and should be interpreted very cautiously. The chart and tables below may give the general idea, the reference being a tonne of wet salted hides.

For the same reason it is practical to indicate the amount of pollutants generated per tonne of raw hide input. While generally lower water consumption is very desirable (nowadays in well-managed tanneries below 30 m^3/tonne), it obviously results in a considerably higher concentration of pollutants.

Figure 4. A simplified chart of the tanning industry



Based on the chart prepared by F. Schmel, UNIDO, Sustainable Development Goals, SDG

2.2. COLLAGEN BALANCE

When evaluating the efficiency of leather manufacture, one of the main criteria is the actual utilisation of collagen. To obtain a true picture of collagen balance, there is a distinction between the corium collagen (true leather-building substance) and total collagen (corium and subcutis/flesh collagen). The 'fate' of both categories throughout the process is shown in the following table.

As said earlier, only 53 per cent of the corium collagen and about 50 per cent of the total collagen content of the raw hide end up in the finished leather. The rest is very often disposed of as solid waste, since for various reasons (lack of markets, commercial viability, inadequate technology etc.) the recovery of valuable components such as collagen, fat or chrome is not practised.

Figure 5. Sources and types of pollutants generated in leather processing

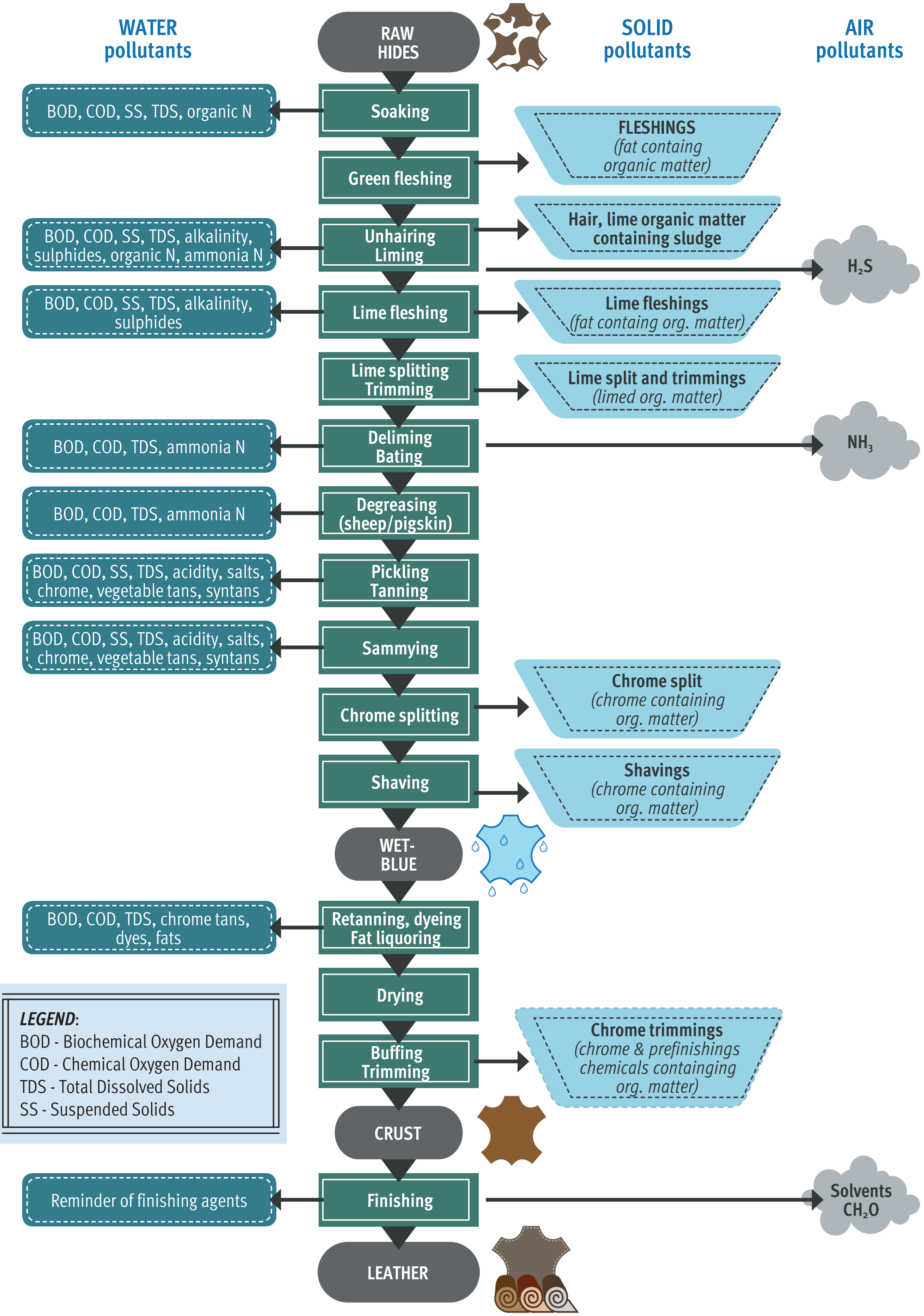
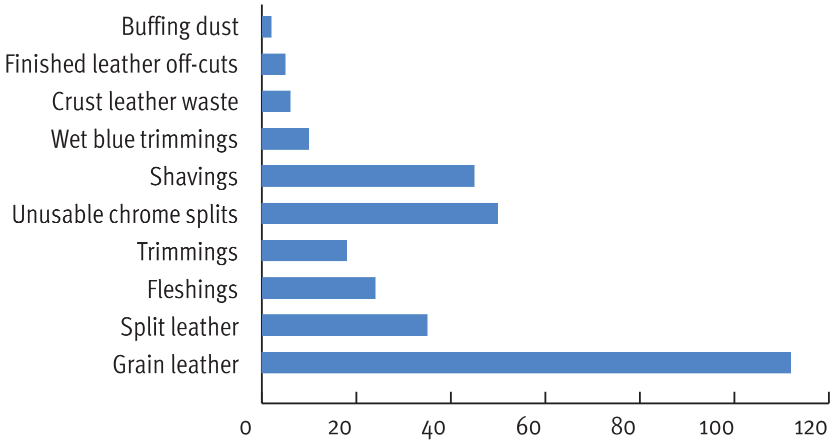

WATER pollutants
RAW HIDES
SOLID pollutants
AIR pollutants
BOD, COD, SS, TDS, organic N
Soaking
FLESHINGS (fat containg organic matter)
Green fleshing
BOD, COD, SS, TDS, alkalinity, sulphides, organic N, ammonia N
Unhairing Liming
Hair, lime organic matter containing sludge
H_2S
BOD, COD, SS, TDS, alkalinity, sulphides
Lime fleshing
Lime fleshings (fat containg org. matter)
Lime splitting Trimming
Lime split and trimmings (limed org. matter)
BOD, COD, TDS, ammonia N
Deliming Bating
NH_3
BOD, COD, TDS, ammonia N
Degreasing (sheep/pigskin)
BOD, COD, SS, TDS, acidity, salts, chrome, vegetable tans, syntans
Pickling Tanning
BOD, COD, SS, TDS, acidity, salts, chrome, vegetable tans, syntans
Sammying
Chrome splitting
Chrome split (chrome containing org. matter)
Shaving
Shavings (chrome containing org. matter)
WET-BLUE
BOD, COD, TDS, chrome tans, dyes, fats
Retanning, dyeing Fat liquoring
Drying
LEGEND:
BOD - Biochemical Oxygen Demand
COD - Chemical Oxygen Demand
TDS - Total Dissolved Solids
SS - Suspended Solids
Buffing Trimming
Chrome trimmings (chrome & prefinishings chemicals containging org. matter)
CRUST
Reminder of finishing agents
Finishing
Solvents CH_2O
LEATHER

Figure 6. Collagen distribution in leather and solid waste (kg)- splitting in chrome (kg/1 000 kg of wet salted hide, 26.5 kg/hide)



Where the utilisation of collagen by-products is concerned, lime splitting is the superior technology.

Approximate full chemical mass balance from preservation to finishing

Salting (ca. 40% of the hide fresh weight) + resalting (during longer storage up to 10%) plus chemicals in leather processing, including reprocessing (cca 45% on w.s. weight), total approximately 90% of fresh hide weight. It means that the ratio of **chemicals used vs. fresh hide/skin weight is ≈ 0.9:1.0**

After adding the amount of chemicals typically used for purification of tannery effluents (coagulation, flocculation, sludge conditioning), it can be safely said that the actual ratio of **chemicals used vs. fresh hide weight is ≈ 1 : 1.**

The obvious is often overlooked: somewhat paradoxically the same amount of pollutants at lower water consumption means lower hydraulic load (volume) but higher concentration of pollutants not always easy to treat.

With the view of keeping it short and concise, there are many simplifications and omissions of details; thus, for an in-depth understanding of the complexities of specific processes it is recommended to consult the extensive literature on this subject.

Finally, although contrary to widespread misperception that vegetable tanning is environmentally harmless (in reality, its effluent has a very high and difficult to treat COD), here it is mainly dealt with combined chrome tanning only because it is by far the most prevailing leather tanning method.

Table 2. Initial organic content of salted hides

(Calculated on 100 kg of salted hides)

Component	kg
Water	45
Proteins	33
- Albumins	4.5
- Keratins	4.5
- Collagen	24
Lipids (triglycerides)	4.0
Carbohydrates (mucopolysaccharides)	0.5
Total dry organic matter	**37.5**

Source: Manzo et al., Mass balance in chrome tanning

Table 3. An example of mass balance in leather processing

Example of mass balance of chemicals in leather processing Kg/ ton of wet salted hide			
Chemicals	**Added in process**	**in/on leather & splits**	**Wasted**
Chrome oxide, Cr_2O_3	25	12	**13**
Organic tannins	25	20	**5**
Fatliquors	22	17	**5**
Dyestuffs	5	4	**1**
Acids, bases, salts	191	-	**191**
Tensides	3	-	**3**
Enzymes	5	-	**5**
Finishing products	100	12	**88**
Total	**452**	**72**	**380**

Source: J. Buljan et al., Mass balance in leather processing
Note: EU (BREF 2013) figures about chemicals added are even higher whereas one supplier (BASF) suggests a very wide range of 168 – 493 kg/t of w.s.w.

Table 4. Estimated pollution load from the global input of 10 million tons w.s.w./year

Parameter	Typical pollution load, conventional process *kg/tonne of w.s. hide*	Approximate global discharge *Thousands of tonnes/year*
Biochemical oxygen demand, BOD_5	90	900
Chemical oxygen demand, COD	180	1800
Suspended solids, SS	90	900
Chromium, Cr^{3+}	7	*56
Sulphides, S^{2-}	7.5	75
Total Kjeldahl Nitrogen (TKN)	12.5	125
Chlorides, CL^-	225	2250
Sulphates, SO_4^{2-}	63	630
Oil and grease	6	60
**TDS	450	4500

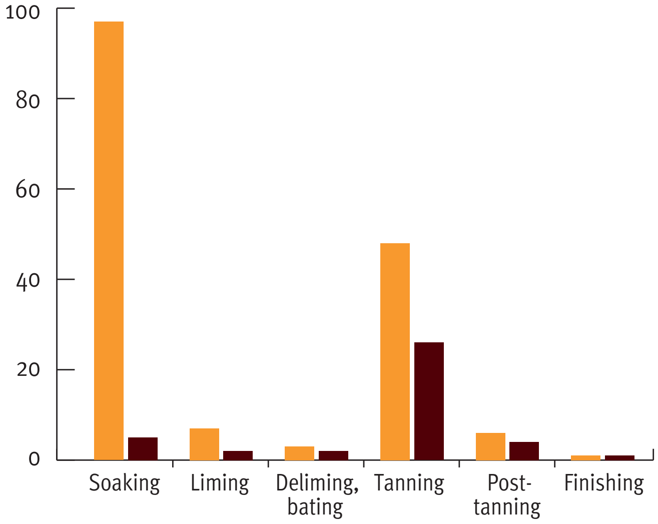
**After allowing 20% for chrome-free tannages **Mainly chlorides and sulphates*

2.3. SOME POLLUTANTS OF SPECIFIC IMPACT

Salt/chlorides

Salt/chlorides mainly emanate from the soaking and tanning stages of salted or brine-cured hides and from pickling; they are highly soluble and stable, unaffected by waste water treatment thus making the final, treated effluent unfit for irrigation or livestock watering. At present their treatment and disposal is possibly the hardest challenge of the leather industry in arid regions.

Figure 7. Comparison of the mean chloride loads



Sulphates

The main source of sulphates is the deliming process (ammonium sulphate), followed by the tanning (chrome powder) and post-tanning stages as well as catalytic oxidation of sulphides in beamhouse effluent.

Many process chemicals contain "hidden" sodium sulphate (e.g. retanning agents).

Sulphide

The residual sulphide in effluents is easily oxidized into sulphate. The real issue is the risk of the formation of highly toxic hydrogen sulphide due to:

i) poor segregation of streams and mixing of alkaline with acidic spent floats as the pH of the effluent drops below 9.5

ii) anaerobic conditions and reverse reaction (action of sulphur-reducing bacteria, long waste water pipework/ collection network).

Substances with specific water-polluting potential

Substances with specific water-polluting potential due to:

- acute toxicity on mammals
- aquatic toxicity on fishes, dolphins, algae and bacteria
- biological degradability (hydrolysis, photolysis, oxidtion, etc.)
- soil mobility
- ability to accumulate biologically
- carcinogenic effect
- mutagenic effect
- teratogenic effect (i.e. causing malformations or functional damage to an embryo or a foetus).

Most of these substances are on the Restricted Substances Lists (RSL) and/or Substances of Very High Concern List (SVHC), see chapter 15.

3. TANNERY ENVIRONMENTAL MANAGEMENT SYSTEMS (EMS)

3.1. GENERAL

> **The International Organization for Standardization (ISO) in its ISO 14001:2004 defines the Environmental Management System (EMS) as part of an organization's management system used to develop and implement its environmental policy and manage its environmental aspects. It emphasises that the overall aim of this Standard is to support environmental protection and prevention of pollution in balance with socio-economic needs, and stresses the importance of an effective EMS being well integrated into the organization's management system.**

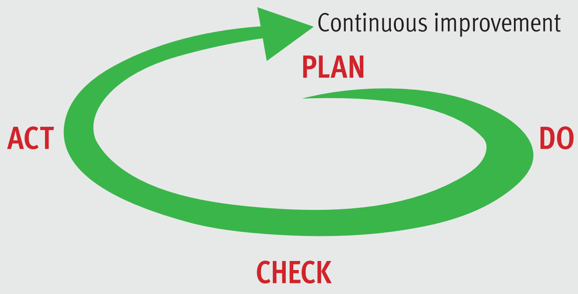
Environmental labelling and life-cycle assessment belong to the same ISO 14000 family of voluntary standards.

The motivation for the establishment and implementation of an EMS (certified or non-certified) is normally based on a combination of the following elements:

- Better overall environmental performance, avoidance of non-compliance costs
- Better insight into environmental aspects of tanning operations, pollution and wastes generated which are, in different form and levels, of interest to the environmental protection bodies, NGOs, inhabitants of the adjacent residential areas, etc.
- Improved basis for decision-making
- Pressure, direct or indirect, by the buyers concerned about their own public perception
- Drastic reduction of frequency of injuries at work; serious injuries do not happen at all.
- Due to better working conditions and reduction and/or elimination of harmful or irritating substances, in the long run there are less chronic illnesses and absences from work.
- Improved company image
- Closer involvement and eventually better motivation of all personnel, a feeling of shared responsibility for pollution prevention and safety at work
- Lower volume and lower costs of disposal of non-utilizable wastes; sometimes there can be a reduction of operational costs.

ISO 14001:2004 is based on the Plan-Do-Check-Act methodology, in short PDCA, which could be represented by the following diagram:

Figure 8. The PDCA cycle



Based on the chart prepared by F. Schmel, UNIDO

Since the process is continuously revisited and reviewed, every EMS is a process of continual improvement.

It is quite interesting that ISO 14001 does not include the Occupational Safety and Health (OSH) at the work place aspect although in practice, at the shop-floor level, environmental protection and pollution prevention are so intertwined with OSH that they simply cannot be viewed apart. In the ISO system OSH is addressed under ISO 18000.

EMS in a tannery implies irreversible departure from the practice of addressing the environmental issues in a reactive and ad hoc manner, which often delegates them to a junior level manager to handle them as a temporary nuisance. EMS calls for a coherent, systematic, thoroughly designed, documented and planned approach with clearly defined strategic goals as well as specific medium- and short-term targets and explicit distribution of implementation responsibilities, regular reviews, verifications, improvements, etc. including dissemination of information and extensive training activities at all levels.

It is essential that, wherever applicable, environmental protection targets and performances are defined and set in measurable terms.

While large tanneries might turn to external inputs and standardized procedures for setting up or upgrading the existing EMS, medium and smaller units can opt for developing their own EMS tailored to their specific needs. Properly designed and implemented, they can produce satisfactory results that can be easily verified and ultimately accepted by external auditors (giving higher credibility) and/or representatives of environmental enforcement authorities and the NGO. It is hoped that this framework will be of use for such purposes.

The main components of a tannery EMS

- Commitment of management, including senior management;
- Definition of an environmental policy that includes the continuous improvement of tannery operations;
- Planning and establishing the procedures, objectives and targets, in conjunction with financial planning and investment;
- Implementation and operation of procedures paying particular attention to:
  - structure and responsibility
  - training, awareness and competence
  - communication
  - employee involvement
  - documentation
  - efficient prwocess control
  - maintenance programmes
  - emergency preparedness and response
  - safeguarding compliance with environmental legislation;
- Checking performance and taking corrective action paying particular attention to:

  - monitoring and measurement
  - corrective and preventive action
  - maintenance of records
  - independent (where practicable) internal and external auditing in order to determine whether or not the EMS conforms to planned arrangements and has been properly implemented and maintained.
- Review of the EMS and its continuing suitability, adequacy and effectiveness by senior management;
- Preparation of a regular environmental statement;
- Non-mandatory validation by certification body or external EMS verifier;
- Development of cleaner technologies;
- Consideration for the environmental impacts from the eventual tannery decommissioning at the stage of designing a new plant, and throughout its operating life;
- Application of a full scale benchmarking

Adapted from BREF 2013

3.2. BUILDING UP YOUR OWN EMS

A good starting point for building your own EMS can be the elements of benchmarking related to environmental and occupational safety and health at work (OSH) contained in the UNIDO paper titled Benchmarking in the Tanning Industry (2011). The outline of ten "cock-pit check lists":

Check list No.	Area - Component
1	Tannery location, infrastructure
2	Production parameters
3	Cleaner technologies
4	Energy management and consumption
5	Quality assurance, reprocessing, delivery time, failures
6	Product development, strategies
7	Occupational safety and health at work, machinery maintenance
8	Effluent treatment, solid waste, air emissions
9	Financial indicators
10	Human resources and staff welfare, Corporate Social Responsibility, CSR

A company maintaining a continuous dialogue with the local community will be in a better position to resist unfounded pressures of local politics that, regrettably, often (mis)use environmental issues for their own purposes.

Environmental Management System (EMS) in a tannery serves as a very practical management tool for systematic and coherent strategic planning, implementation, verification, review and improvement of environmental and occupational safety and health at work place (OSH) aspects of its operations. This approach is in sharp contrast with ad hoc, crisis management and nearly spontaneous reactions to pressures by legislative enforcement authorities or by the general public. Genuine support and commitment by top management, team work with all benefits of close interaction of all organizational units, circulation of information, continuous training at all levels, and accountability and responsibility in defining and meeting specific targets (e.g. waste minimization/recycling/reuse) are essential components of a good EMS.

Introducing cleaner technology methods is certainly a dynamic and continuous process. One of the key tasks of any EMS in a tannery is to keep pace with the scientific developments and techniques, and acquire, adapt and implement them to suit local conditions.

3.3. QUALITY ASSURANCE, REPROCESSING

Possibly the most complex challenge for every leather manufacturer is to maintain the capability to supply the end-user with a consistent product despite the fact that the properties of the main input, the raw hide, vary considerably even within the same weight, breed and sex category. Consistently adhering to delivery schedules is of equal importance with providing the demanded quality of product. Therefore, the continuous and very careful monitoring of all process parameters is a condicio sine qua non for achieving and maintaining the desirable quality level and consistency.

Good monitoring and control are also the indispensable components of cleaner technologies; when strictly applied and followed they reveal that in most tanneries the actual consumption of chemicals exceeds the theoretical, recipe-based computation at times by as much as 10-15%. There are many possible sources for this difference, the most typical being material handling waste, overdosing (including over-spray in finishing), low exhaustion and probably the most crucial, the reprocessing/refinishing of batches not meeting specifications.

Additional labour, energy and time losses, possibly compounded by the diminished trust of the customer for failing to deliver the goods on time, are further undesirable consequences of reprocessing. To quote an experienced leather industry specialist: "The costs of chemicals, labour, rejects, re-works, energy and pollution control/treatment are amplified by waste."

What is more, the unavoidable wastes due to lower reactivity of some processes/chemicals (e.g. vegetable tanning, retanning with syntans, fat liquoring and dyeing), as well as some general chemicals (e.g. acids) not absorbed in the process, add to the amount of chemicals which end up in the drain instead of the leather, thereby increasing the pollution load.

Modern controls in leather manufacturing, preferably partially or fully automated, monitor and correct parameters such as weights, volumes, pH, temperatures, run-times, preparation and dosing of chemicals, rinsing as well as leather properties, comparing and correcting them to coincide with standard/reference values in order to reduce deviations and ensure that the final product complies with the given specification.

Listing all quality parameters that need to be controlled and monitored exceeds the purpose and concept of this paper.

4. WATER MANAGEMENT

4.1. CONSUMPTION AND AVAILABILITY

> **The largest material input in leather processing is water; its consumption by weight is by far higher than any other component of the production process, including the main raw material, hides/skins themselves.**

Water consumption consists of two main components: water needed for physical-chemical processes (process water) and water needed for cleaning, energy generation, waste water treatment and sanitary purposes (technical water). The focus here will be on the process water.

Variations in water consumption presently range from less than 15 m^3/ton to more than 80 m^3/ton of wet salted hides for nearly identical raw material category and basically the same type of finished leathers produced (e.g. shoe uppers). The latter, wasteful scale of water consumption still persists in some pockets where water is drawn from rivers, lakes or drilled wells with hardly any control and virtually free of charge.

The following estimates provide a realistic picture about water consumption in the conventional process of bovine hides.

i) IULTCS/Environmental Commission, IUE

Table 5. Typical water consumption ranges

	Water
Values per t of rawhide	*m^3/t*
BOVINE SALTED RAW HIDE PROCESS	
Beamhouse (soaking to bating)	**7/25**
Tanning operations	**1/3**
Post tanning	**4/8**
Finishing	**0/1**
TOTAL	**12/37**

ii) EU-BREF, 2013

Table 6. Water consumption in process stages (conventional processing)

Process stage	**Waste water discharge per unit of raw hide (m^3/t)**
Total to end of beamhouse	20 - 25
Total to wet blue	21 - 28
Total to finished leather	34 - 40

Water shortages are no longer limited to arid regions in developing countries with inadequate infrastructure as more and more tanneries in industrialized countries in moderate climates are also affected. Water scarcity is turning into a serious global issue.

Recent examples are current and anticipated difficulties in both water supply and effluent discharge in Spain and Italy. Even in otherwise water-rich Austria, a too small water recipient is a constraint for further expansion of already large tannery operations. Some conferences are almost entirely dedicated to topics such as access to fresh water and optimisation of water usage.

4.2. WATER SAVING STRATEGIES

> **The growing water shortage, especially in arid regions, compounded by increasing charges as well as changes in perception of water as a freely available resource to one among chemicals essential for the process, has brought about a dramatic reduction in water usage. On the global scale in the past 25 years water consumption for production of leather from bovine hides has declined by about 37%: from approximately 60 m3/ton of hides to 38 m^3/ton[11].**

Water use can be reduced at many points of the leather making process and good water management should be seen as one of the key components of modern leather technology and the overall factory management.

In addition to reducing pressure on the water supply, water conservation has other important benefits: lower water consumption implies smaller sized plants (especially treatment plants), lower consumption of chemicals, and, as a rule, lower operating costs, including the cost of energy.

However, contrary to some (mis)perceptions, reduction in water use does not reduce the pollution load *per se* - the same amount of pollutants is just concentrated in smaller volume.

There is a considerable scope for simple, low cost and yet effective ways to save water and reduce manufacturing costs even in a tannery following conventional technology. Considerable differences in raw material, product range, technology followed calls for specific, tailor made water management plans. Generally, the first, mandatory steps include:

- Separately monitoring and measuring water use in various departments (beamhouse, wet finishing, finishing, utilities etc.) as well as effluent streams and total flow;
- Calculating the tannery's current water footprint and defining target consumption benchmarks for individual sections
- Switching from continuous, "running water" to batch washes;
- Introducing strict (ideally automated), control of the volume of processing water;
- Adherence to the principle: reduce, reuse, recycle e.g. lime washes for the first soak
- Modification or replacement of existing vessels and some equipment with more efficient ones (e.g. drums & driving gears) making them suitable for low/short floats;
- Close inspection of installation, pipework and equipment for any losses and leakages;
- Close assessment and reduction of use of technical water (fleshing, cleaning, etc.)
- Use of high pressure cleaners for floors, drums, equipment

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[11] *J. Knoedler, 2014*

4.2.1. Measurement of water consumption and establishment of water balance

The first step in assessing the actual water consumption at each process step is to check how much water is used per unit of raw material processed. The quantity of incoming water and water leaving the tannery should be measured and compared. If the difference between incoming and outgoing water is more than 10-15%, then there are some "invisible" losses in the system; usually it is through valve and pipe leaks, especially in the old, underground pipe-work. Verifying the accuracy of the readings should not be overlooked either.

Normally the next step is to introduce regular i.e. daily/weekly/monthly water audits. The current period's water use has to be compared against production for the identical period in the past; the actual consumption also has to be compared with the theoretical/recipes' projections. Monitoring and control for each department or section or even machines greatly facilitates spotting the sources of excessive consumption and/or losses.

Tip: The easiest way to identify leakages is to check water meters while the factory is non-operational e.g. during weekends

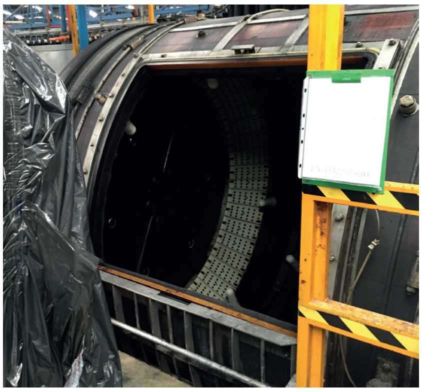
Obviously, water consumption always needs to be matched with and computed per unit of raw material processed (input weight of hides and skins, pelt, wet blue, crust, etc.) as well as per unit of final products (e.g. area of leather in m^2); the assessment should also include at least the amount of chemicals used.

4.3. SOME PRACTICAL EXAMPLES OF WATER SAVING MEASURES

4.3.1. Washing

Water used for washing in various steps represents around 30 -50% of all water used in the process and that is why it is the very first target within the water savings measures. In practice the main cause is washing with running water washes i.e. with rotating drum, slatted door and open water valve. This way it is very difficult to control the process and the flow rate. Instead, batch washing with a closed door can bring about water savings of more than 50%.

Figure 9. Plastic sectors inside the drum, fixed with stainless steel screws

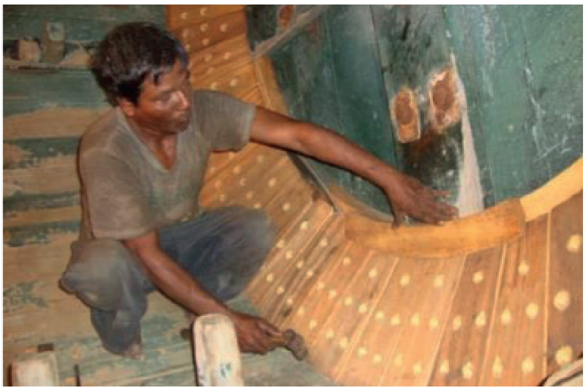


Source: Mr. N. Niedzwiedz

Additional water reduction and more uniform quality is achieved by thorough drainage after each process step, including washes; float residues in vessels require more water for washing. False perforated bottom ends in paddles or plastic/wooden perforated sectors (with more drainage valves per sector), significantly improve drainage of floats.

Recent developments in processing vessels (cross circulation) facilitate better washing as well as thorough drainage.

Figure 10. Installation of wooden sectors to improve drainage of floats



4.3.2. Low/short float techniques

There is no general rule on float length and each process needs to be carefully assessed in order to achieve the best quality vs. optimum use of water, chemicals and energy. Short float means a higher concentration of chemicals, rapid penetration and higher exhaustion rates. Strict monitoring and control of the key parameters such as pH, temperature, time, as well as penetration, will further contribute to better uptake of chemicals and reduce the amount of water needed for washing. Consistent quality and reproducibility and avoidance of reprocessing are further benefits.

However, high efficiency in any process does not necessarily result in good quality. Excessive float reduction in some specific processes can result in grain defects and damages due to mechanical action. While some modern vessels, new materials and techniques reduce this danger, this risk should be always considered.

Obviously wherever possible pits and/or paddles that utilize 300% – 1000% floats should be replaced with drums.

Tip: Paddles and pits are needed for certain processes such as the first soaking of dried skins, processing of long-wool and some special skins.

4.3.3. Recycling and water reuse

Many relatively clean rinse and wash waters can be recycled to other processes where the low concentration of residuals chemicals will have little adverse impact. Typical examples of water reuse:

- Part of the main soak can be reused for the “dirt soak”.
- Part of the second lime wash can be reused to start a new lime liquor; alternatively, it is used for the first wash.
- Deliming liquors (after pH adjustment with drained pickle float), can be reused for liming. Caution, risk of forming H_2S!
- Drained pickle float is used for pH adjustment of deliming liquors.
- Drained pickle float can be reused for building up the new pickle (as a rule this process is started by adding salt and sodium formate, followed by first acidification with formic acid and (only if badly needed), the final pH is adjusted with sulphuric acid). Cost and quality considerations permitting, weak organic acids and their salts can be also used.
- Recycling of spent tanning floats (covered in detail in Operations in the Tanyard: Chapter 10).
- Water from wetting back wet blue leather is mixed with fresh water for the next wetting back batch.
- In some cases (e.g. processing of fresh hides and segregation of streams), fully treated effluents can be reused for the dirt soak.

Generally, each reuse should be properly tested prior to reuse in full production.

Reusing and float recycling per se are quite simple processes especially in new tanneries where it is expected that sufficient space is left to accommodate screens (e.g. self-cleaning fine filters), storage tanks, skimming devices, pumps and piping with good access for maintenance and repairs. This may however be quite difficult in old tanneries with limited space. Obviously, recycling systems require higher levels of supervision.

Recycling of process liquors e.g. liming, tanning is an additional way of reusing such effluents and residual chemicals to reduce water requirements and pollution from the process and should be adopted whenever feasible. However, in practice, float recycling is not as often as one would expect it. The explanation can be that i) as said earlier, it requires additional space for storage tanks and/or ii) the risk that it may affect the leather quality prevails over possible savings in water and chemicals.

4.3.4. Recycling and water reuse

Green fleshing not only opens up of the hide structure and allows for better penetration of chemicals during soaking and liming, but also reduces the water needed for soaking, liming and washing after liming by up to 15%.

Lime splitting allows the trimming away of by-products (e.g. shoulders, flanks, splits) prior to further processing and reduces or minimizes water and chemicals use.

4.3.5. Fleshing, vacuum dryers, finishing

In some tanneries fleshings are collected and transported with the aid of water, which in some cases water used can reach 1 – 2 m^3/t of w.s.w. Use of fleshings pumps with an efficient collection system can effectively reduce water consumption for this operation.

Old vacuum dryers are typical examples of “hidden” and often overlooked water consumers. Similarly, while water consumption in the finishing department is comparably very low, scrubbers and chemicals for container cleaning may use more water than actually needed.

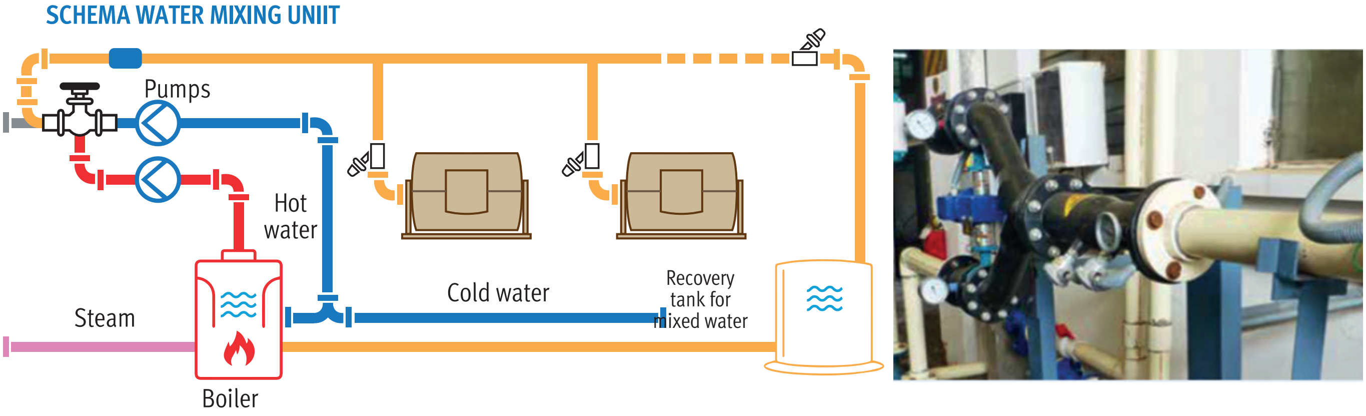
Finally, floor cleaning and leaking valves in sanitary units also need appropriate water consumption control.

UNIDO assisted Kanpur Leather development project, India
The very first step: installation of reliable water flow meters

A comparison of various types of water flow measuring equipment (Kanpur, India)

PARAMETER	ORDINARY	ELECTROMAGNETIC	AUTOMATED HOT & COLD WATER MIXING AND DOSING
Type	Mechanical	Electromagnetic	Electromagnetic, PLC controlled
Accuracy	Average	Very good	Very good
Possibility of manual error	Average	Average	Low
Ease of operation	Manual control required	Easy	Very easy
Life	Relatively short (strainers are required)	Long	Long
Investment (About 8 processing vessels)	Rs. 80,000 (= USD 1,200)	RS. 300,000 (= USD 4,600)	Rs. 1,000,000 - 1,500,000 (= USD 15,500 - 23,000)

A hot and cold water mixing and dosing system



SCHEMA WATER MIXING UNIIT

Source: UNIDO Kanpur Leather development project (India)

4.4. WATER CONSUMPTION TARGETS

It is important to emphasize that for many technical reasons (raw material, technology, leathers produced, climate, etc.) it is not possible to set a kind of norm regarding water consumption. Thus, the following values are primarily for general guidance in establishing specific targets in individual tanneries.

Table 7. BAT-associated consumption levels for water for the processing of bovine hides

Process stages	Water consumption per ton of raw hide (⊥) (m^3/t)	
	Unsalted hides	Salted hides
Raw to wet blue/white	10 to 15	13 to 18
Post-tanning processes and finishing	6 to 10	6 to 10
Total	16 to 25	19 to 28

(1) Monthly average values. Processing of calfskins and vegetable tanning may require higher water consumption.

Table 8. The theoretically lowest water consumption, stage-wise

Process stage	Waste water discharge m^3/ton of w.s. hide
Soaking	2
Liming	4.5
Deliming, bating	2
Tanning	0.5
Post-tanning	3
Finishing	0
Total	**12**

4.5. ZERO LIQUID DISCHARGE (ZLD) CONCEPT

This concept is being developed at industrial scale in several tannery clusters in the state of Tamil Nadu, India. Essentially, the ZLD systems concentrate dissolved solids present in effluent by Reverse Osmosis (RO) and a type of Multi Effect Evaporation (MEE) until only damp solid waste remains. Solid waste is disposed of and nearly all water is reclaimed and reused. Accordingly, some of the existing Common Effluent Treatment Plants (CETPs) have been supplemented by RO and MEE, together with auxiliary steps (tertiary treatment, water softening etc.).

The main aim of the ZLD is actually removal of TDS (salinity) from the combined effluent. Due to very high investment and operation costs, including the problem of disposal solid residue (mainly sodium chloride) its wider acceptance is quite unlikely. In the best case RO+MEE might be limited to treatment of only highly concentrated saline streams (soak, pickling).

4.6. Rainwater management

The aim here is twofold:

i) To minimise the amount of rainwater that becomes contaminated and requires treatment as the main effluent.

ii) To maximise the amount of rainwater collected separately to be used either in the leather process itself or for cleaning.

The main source of rainwater contamination is paved yards with residues of spills of chemicals and that is why their area should be as small as possible and the inflow/outflow blocked by physical barriers. At the same time, it is recommended to install rainwater separators for rooftop rainwater.

Figure 11. One of the three reservoirs of rainwater at Packer Leather, Narangba, Queensland, Australia

Source: World Leather, Oct/Nov 2014

4.7. Banned substances in tannery effluents

In addition to the controlling of traditional parameters such as COD, BOD$_5$, TKN, chrome, sulphide, etc., an important trend in European legislation is stricter regulation of the presence of biocides and pesticides in tannery effluents such as DDT, hexachlorohexane, aldrin, dieldrin, endrin, isodrin, naphthalene, etc. especially since some prohibited substances, notably organochlorine compounds, are stable enough to survive waste water treatment processes.

Only registered and approved biocides can be used and their choice is becoming more and more limited; it is not surprising that it is claimed that some biocides and pesticides prohibited in Europe may be imported with hides and skins from countries where their use continues.

Virtually all pesticides found in the tannery waste water are residues of pesticides used to treat live animals whereas biocides are regularly used in preservation and soaking, pickling, tanning, and post-tanning processes.

5. RAW MATERIAL PRESERVATION, SALINITY

Although the preservation of raw hides and skins, be it of short- or long-term nature, normally takes place before they enter a tannery, the method of preservation is of such impact on its overall environmental performance that it needs to be considered more closely.

Raw hides and skins are subject to autolysis (i.e. degradation due to activity of enzymes within the cell) and attack by microorganisms present in the air, hair, dung, floor, etc. The flesh side is more vulnerable to attack than the grain. The pace of both autolysis and bacterial degradation increases with temperature. Preservation protects the raw material by:

i) inhibiting enzymes' activity
ii) arresting the growth of microorganisms

Short-term preservation can last up to a maximum of three weeks, the methods applied are chilling, icing, application of biocides or the combination thereof.

Long-term preservation methods practised are drying (mainly skins) and salting/brine curing, which can preserve up to six months; the latter method dominates in (inter-continental) trading.

Short- and long-term preservation cannot be compared directly as they are not equally applicable.

Preservation is usually carried out at the slaughterhouse but it can also take place at the hide dealer's premises, at the hide market or even in a tannery located close to the slaughterhouse. In certain cases, it might be necessary to repeat the step at the tannery, e.g. if chilled hides are salted for longer storage or if the initial salting was not sufficient to dry the hides.

5.1. TRADITIONAL PRESERVATION METHODS

5.1.1.Drying

Moisture removal kills and/or inactivates bacteria and enzymes. While frame drying is mainly adopted for hides and sometimes for skins, suspension-drying is only suitable for skins. Direct exposure to sunlight has to be avoided as it may cause the flesh and grain layers to dry rapidly and form a hard crust which prevents the internal layers of the hides from drying, thus prompting putrefaction in those areas. Generally, if drying is too slow, decomposition sets in, if too fast or in the sun, the fibre network is damaged and proteins denaturate.

While the percentage of skins preserved by drying is substantial, in the case of hides it is insignificant.

5.1.2. Salting (conventional, brining)

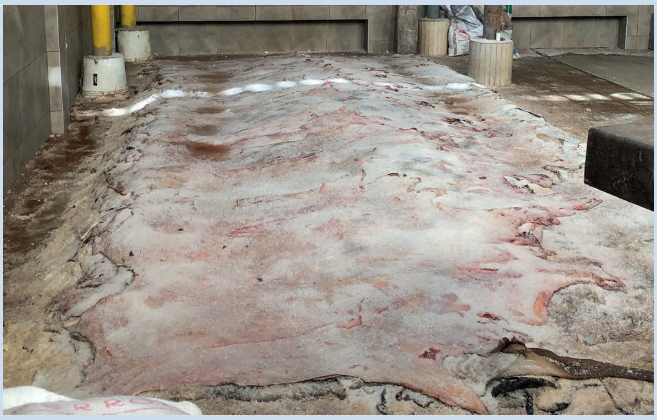
Salt inhibits the growth and bacterial activity by lowering the moisture content in the raw stock. After flaying hides and skins are firstly cooled, spread out (hairside to the floor), uniformly covered with salt, stacked, sandwiched with more salt and left to drain for about a week until solid salt indicates the saturation point. Eventually hides are resalted and packed for long-term storage and/or transport. The total amount of salt (sodium chloride) applied is usually about 40%, but with resalting in the dealer's or even tannery premises it may reach 50% on the fresh (green weight).

A preservation technique of brining in saturated salt brine is mainly used in the USA. Saturated brine contains 35.9 g of salt per 100 grams of water at 20 oC; salt saturation is calculated from the hide moisture and ash content. Typically, a brine cured hide of 38 kg contains about 15.4 -16.3 kg of water, 16.3-18.1 kg of hide substance and 3.6 -4.5 kg of salt.[12]

Hides are placed in raceways and made to swim by mechanical means. Usually, after brining some more salt is sprinkled for safety. Brining is faster than conventional salting; the salt solution fully penetrates within 12 hours. The brine is continually recharged with salt plus a preservative and reused indefinitely. There is always excess brine to be treated or evaporated. Brining in drums is also possible.

Some Australian hides and most sheepskins are drum salted with no added water which minimises salt use and effluent. Drums, mixers and processors are used with about 20% salt on hide weight; more is required if the hides are wet. Air drying of sheepskins in Australia in open sheds using solar and wind energy is a good example of environmentally friendly and salt avoiding curing. Regrettably, increasing numbers of skins are now salted for processing with the wool on.

Figure 12. Brined and salted USA hides in Xuzhou Nanhai Leather Factory, China



Preservation by salting is not quite foolproof; the rawstock can be contaminated by slow-growing halophilic bacteria causing red and purple heat. That is why, especially in cases of longer transportation and storage (possibly under unfavourable conditions), selected biocides may be included in the salt. Several proprietary products are on the market. They are based on potassium dimethyldithiocarbamate (> 0.3 % hide weight for brine curing), p-dichlorobenzene, sodium silicofluoride, and borax. Also, boric acid and sodium metabisulphite might occasionally be used.

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[12] *Leather technologists pocket book, SLTC, David G. Bailey*

Hide dealers stock hides and skins to accumulate adequate quantities of the same origin, weight category, quality, etc. but also for speculative reasons (rising price trends). Tanners, on the other hand, stock the raw material to optimise the consistency of their batch processes and the quality of the finished leather to meet the customer's specifications.

Total Dissolved Solids (TDS) – mainly chlorides and sulphates (colloquially salinity) – in effluent is the major environmental concern in arid and semi-arid regions of the world as it makes the receiving water recipients (rivers, lakes) unfit for both livestock watering and irrigation. High salinity in irrigation water causes high osmotic pressure which results in reduced water availability and retarded plant growth of crops. Also, while the presence of calcium and magnesium ions in tannery effluent that ends up in irrigation water stabilises the soils, high concentrations of sodium can cause dispersion of clay.

While a certain percentage emanates from other operations such as pickling, deliming, tanning and wet finishing, the main source of TDS, especially of sodium chloride, is salt from preservation. Unfortunately, TDS in tannery effluent cannot be removed by conventional treatment (reverse osmosis, RO considered excessively expensive). **The environmental damage caused by salting prevails over its positive aspects.**

Worldwide, based on approximately 10 million tons w.s. weight processed and computing the salt at the level of 40% of fresh hides & skins' weight and after allowing for hides processed unsalted, it can be estimated that at least 3.0 million tons of common salt per year is discharged into water recipients. There are strong voices on the international scene against shipping wet-salted hides from one side of the world to the other and arguments that hides are to be processed at least as far as wet blue or wet white stage as close to source as possible.

Table 9. Preservation by salting

Advantages	Disadvantages
• Widely available at modest cost • Simple, easy to apply • Very reliable if carried out properly • Very limited capital investment • Facilitates elimination of interfibrillary, non-collagenous matters in soaking and preparation for liming/tanning • Allows long storage & transportation, (large) stock holding, more uniform lots both for sale and processing	• More expensive than fresh or icing • Investment cost high if mechanised • (e.g. brining) • Disposal of polluted/excess salt a problem • **Heavy pollution of waste water (salinity), that cannot to be removed by normal treatment because of extremely high energy costs** • **Reverse Osmosis (RO) normally not affordable.**

5.2. ALTERNATIVE, ENVIRONMENTALLY FRIENDLY SHORT-TERM PRESERVATION METHODS

In addition to the drying mentioned earlier, the only alternative to salting is the processing of fresh (green) hides and skins i.e. short-term preservation by cooling, using crushed ice or refrigerated storage, by using biocides and the combinations thereof.

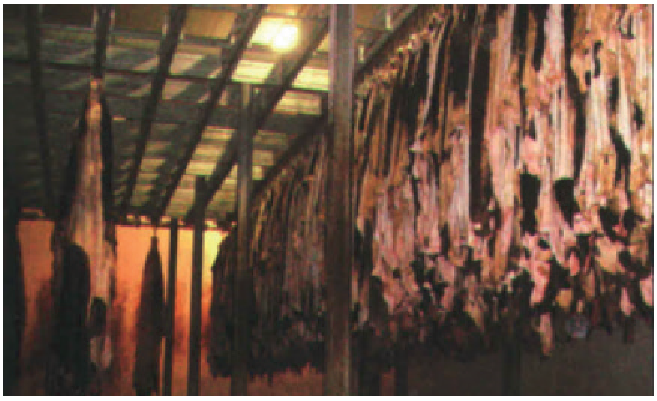
Rapid post-mortem cooling is essential for short-term preservation. It can be carried out in a few ways:

- Immediately after flaying hides are spread on a clean smooth floor with the flesh side down;
- Immediately after flaying hides are put into a mixer containing chunks or cubes of ice;
- Immediately after flaying hides are passed through a tank of glycol-cooled water and, generously iced, placed into a storage container;
- By using CO2 snow. Very convenient where cold storage facilities are already available; with good ventilation there is virtually no health or safety risk.
- By using refrigerated storage units: the hides must be hanging and without touching each other.

The cooling chain must not be interrupted during transport and storage. The temperatures to which hides and skins should be chilled depend on the required duration of preservation. In moderate climates the maximum time span between cooling down and processing for fresh, unchilled hides is 8 – 12 hours. If the refrigeration temperature is reduced to 2°C, hides and skins can be stored for three weeks without suffering damage.

The number of tanneries in Europe that process fresh hides is growing due to increased environmental pressure; biocides are not used in the preservation of raw bovine hides. Some of those used in the past such as PCPs, DDT and HCH are not permitted anymore. On the other hand, distances and infrastructure allow fast movement of goods within Europe.

Figure 13. Cold storage for fresh raw hides



Source: Feltre, www.feltre.com

In Brazil, with huge feed lots and large scale abattoirs, only fresh hides are processed. However, there are claims that more biocides are needed in the course of processing fresh hides; also, the soaking of fresh hides requires some adjustment in the process. The investment cost of ice-making machines is generally lower than for chilling units and cold stores. The technique is considered economically viable when the cooling chain is no longer than two days.

UNIDO assisted Leather development project Kanpur, India: processing chilled hides

To avoid exorbitantly high investment and operational cost of Reverse Osmosis (RO) and Multi Effect Evaporation (MEE) of saline effluents now implemented under ZLD concept in India, there is a coordinated effort by some tannery clusters, hide traders and abattoirs in the Kanpur area to abandon conventional preservation by salting and switch to **short term preservation by chilling.**

Procedure:

After flaying in the slaughterhouse, hides are hung in the cold store at about 4°C preferably in a conveyor for easy handling. They are folded, stacked and transported in refrigerated containers and delivered to the tannery, ideally to be processed shortly upon arrival. In any case they should not remain folded and stacked for more than five days.

The main aspects of processing:

- The weight of raw hides can be assumed to be the same as that of wet-salted where the weight loss due to dehydration is compensated by the mass of salt.
- Soaking needs to be 4 – 5 hours in drums or paddles
- Float of only 70 % (compared with 150% for wet-salted) is sufficient
- The amount of bactericide is the same as for wet-salted, about 0.1% while about 0.5% of wetting agent is required to facilitate cleaning and washing
- Addition of about 0.5% of sodium carbonate is recommended to increase the pH level in preparation for liming (pH up to 11)
- Liming can be continued according to usual practice

Energy requirements for chilling of 1000 hides in a 40 feet container is about 100 kWh/day.

The main benefit of chilling, i.e. avoiding use of salt is that the amount of (TDS) in the tannery effluent is reduced by 30-40%. The corresponding savings in environmental costs is of the order of Rs. 1260/tonne (mixing with urban sewage) or up to Rs. 4600/tonne of raw material in the case of using RO+ MEE (ZLD concept) now imposed in India.

At the moment it seems that the target with biocides is to ensure one-week preservation without salt or drying; in rural areas of some

A comparison of storage costs of 1 tonne of buffalo hides for 15 days (Kanpur, India)

PARAMETER	CHILLING	(WET) SALTING
Power requirement	50 units for chilling + 50 units for 15 days storage in a refrigerated container = 100units	Nil
Salt	Nil	300 kg
Cost of curing	Rs. 800/tonne	Rs. 900/tonne
Labour cost	Rs. 30/tonne	Rs. 60/tonne
Capital expenditure	Chilling rooms, cold store, and refrigerated containters	Floor space for applying salt
Days in storage	Limited to 15 days	About 60 days

Chilled hides in a cooling box

Table 10. Short-term preservationv

Advantages	Disadvantages
• No salt in the waste water from soaking • Reduced soaking time & lower energy consumption • Water consumption 2-3 m^3 per ton less than for salted hides • Some claim that the hides are softer, more regular neck parts, easier to process • Better yield (1 – 1.5 %) also claimed; • Lower stock holding, lower working capital needed	• Limited time available between slaughter and processing: ideally 5 -7 days, maximum three weeks • Difficult to build homogeneous batches be it in the abattoir, by a dealer or in a tannery • Process adjustment needed for unsalted hides • In practice contingency salting of excess raw material in the tannery may be required • No flexibility to buy raw material and accumulate the stock when prices are lower • Transport costs high(er) if refrigerated trucks are used • High energy consumption/costs for refrigeration • Noise from engine-powered refrigeration units • Hard to organize in countries without large abattoirs and with poor infrastructure • Not suitable for international/transcontinental trade • Higher risk of deterioration, damage

developing countries up to three weeks are needed. However, there are concerns about uneducated people using potentially hazardous chemicals with limits on our ability to train or manage applications.

Biocides are hazardous – they need to be as they are controlling living things – but it is important to consider "sustainable" use and not just reduction. Using less is not necessarily better; if the sufficient amount is not used, hides are not preserved and the consequences are well known. Substitution with "greener" biocides is not necessarily better since hazardous substances typically correlate with weaker biocides so that higher amounts/percentages are needed. Also, it is known that it is not the inherent hazard but the level of exposure (volume and time) that is crucial.

As said earlier, in Australia sheepskins are drum salted with no added water which minimises salt use while drums, mixers and processors are used with about 20% salt on hide weight; more is required if the hides are wet.

Hides for local processing are preserved using the short-term method in drums using up to 1% sodium chlorite ($NaClO_2$) dissolved in low volumes of ice chilled water. Depending on ambient temperature and transport and storing modes they can be stored for several days. The same method is also used in Brazil.

Long-term preservation as well application of silicates in pickling and tanning has not been accepted by the industry.

6. BEAMHOUSE

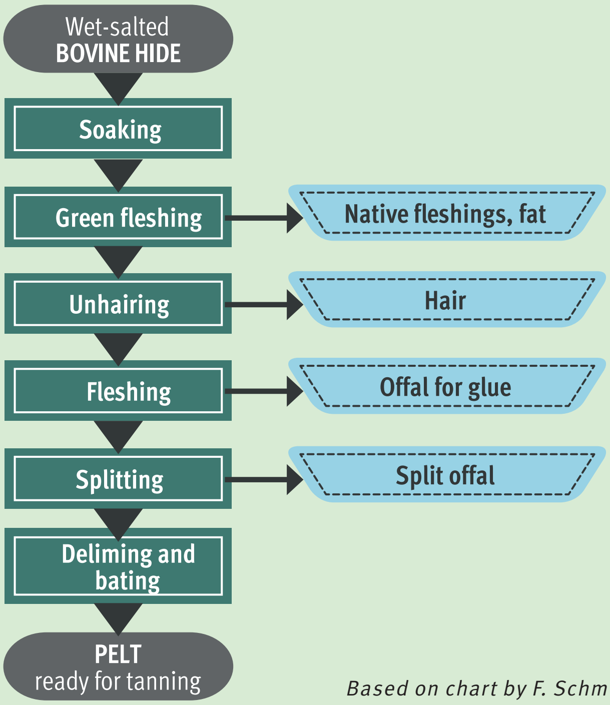
> **The traditional saying rightly claims that (good) leather is made in the beamhouse. Indeed, while the type of tannage (e.g. chrome vs. vegetable tanning) gives the leather its basic character, other properties like the fullness, elasticity and stretchability are defined by (fine) tuning of each of the beamhouse stages. The mistakes made here, be it excessive or insufficient liming/opening up, partial or full deliming let alone at the extremely sensitive and risky bating operation, are irreversible.**

The aim of unhairing and liming is:

- Removal of hair and epidermis
- Removal of any residual interfibrillary components
- To open up the fibre structure in preparation for the tanning process

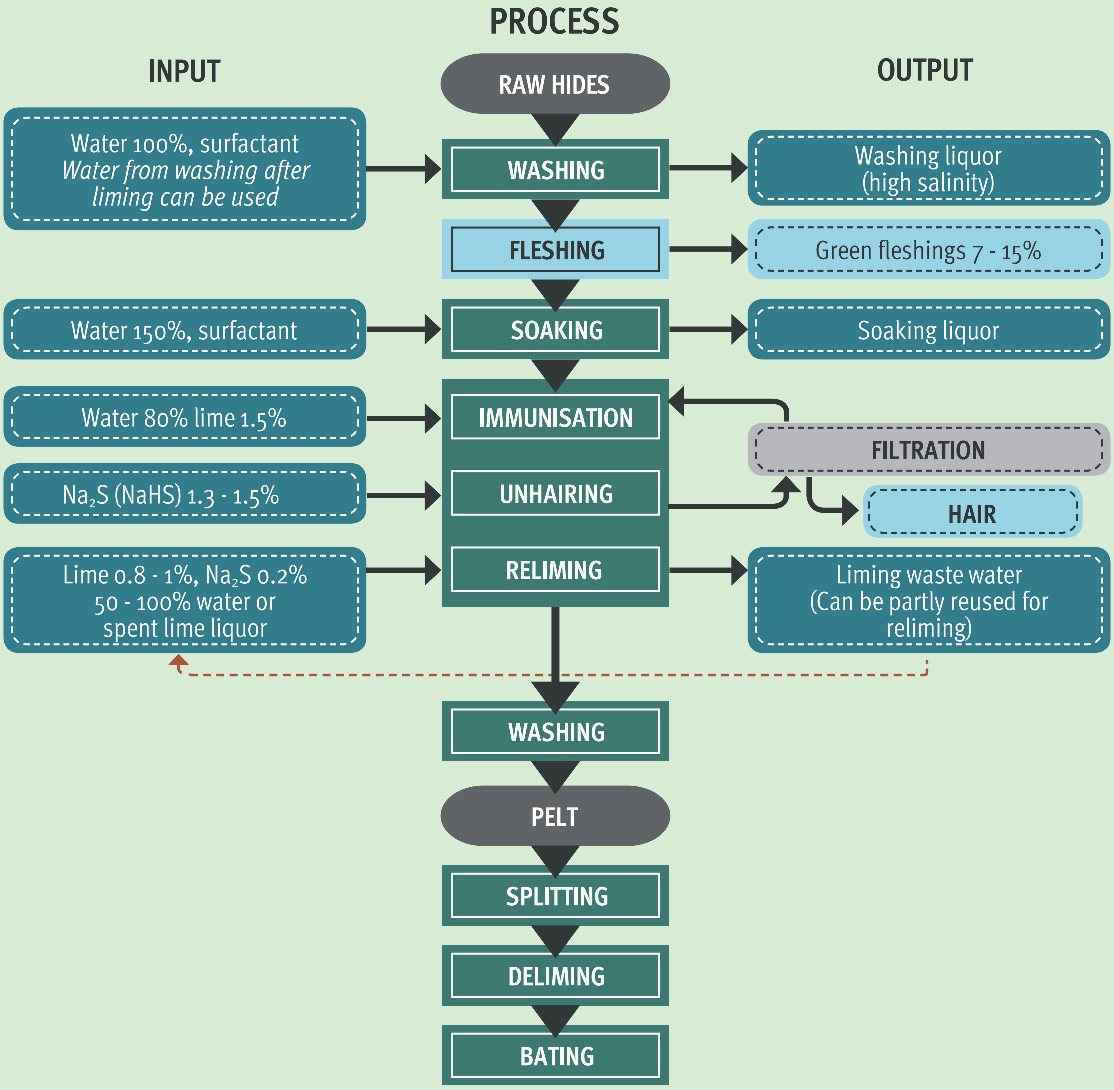
Thus, the beamhouse operations in essence are a purification process for removal of non-collagenous substances.
As usual, there are many variations of the nature and sequence of the processing steps. The next chart shows one of them with the alternative of fleshing before ("green") and after liming.

Figure 14. The sequence of typical operations in the beamhouse


Wet-salted
BOVINE HIDE
Soaking
Green fleshing
Native fleshings, fat
Unhairing
Hair
Fleshing
Offal for glue
Splitting
Split offal
Deliming and bating
PELT
ready for tanning

Based on chart by F. Schmel

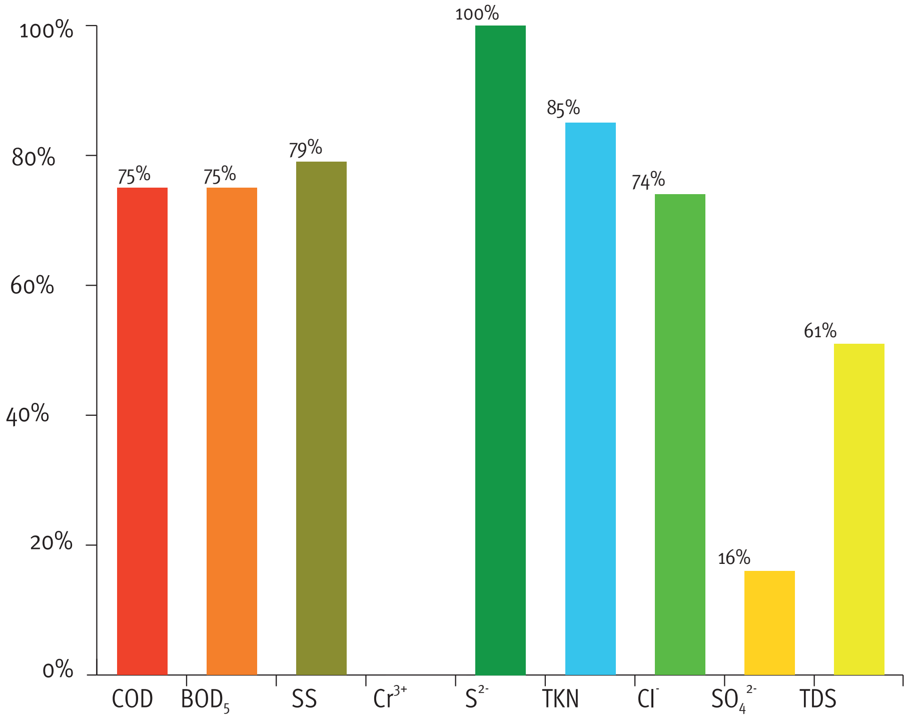
Figure 15. The process sequence, input/output in the beamhouse


PROCESS
INPUT
OUTPUT
RAW HIDES
Water 100%, surfactant
Water from washing after liming can be used
WASHING
Washing liquor
(high salinity)
FLESHING
Green fleshings 7 - 15%
Water 150%, surfactant
SOAKING
Soaking liquor
Water 80% lime 1.5%
IMMUNISATION
FILTRATION
Na₂S (NaHS) 1.3 - 1.5%
UNHAIRING
HAIR
Lime 0.8 - 1%, Na₂S 0.2%
50 - 100% water or
spent lime liquor
RELIMING
Liming waste water
(Can be partly reused for reliming)
WASHING
PELT
SPLITTING
DELIMING
BATING

The appearance, wastes and bad smells emanating from the beamhouse in old and inadequately run tanneries are the main culprits for the poor perception of the tanning industry as a whole.

The next figure shows the typical share of the beamhouse in the overall tannery emissions:

Figure 16. The share of the beamhouse in the total emissions, conventional process



Based on chart by M. Bosnić

More about the main beamhouse operations is given in the following chapters.

7. SOAKING

7.1. PURPOSE AND MECHANISM

The purpose of the soaking process is to bring the hides and skins to a condition very similar to that shortly after flaying. It is important to have them fully rehydrated and to remove any manure and dirt as well as the major part of any preservation substance used, usually common salt.

Furthermore, the major part of interfibrillary matter consisting of non-collagenous proteins (albumins, globulins and elastin) as well as glycosaminoglycans (di-/polysaccharides) are removed thus making the raw material better prepared for further processing. The hyaluronic acid (HA), a long, non-branching polysaccharide chain is one of glycosaminoglycans that retard the opening up process. While the concentration of salt in the interfibrillary space decreases, the HA acid causes increase in viscosity and the hide swells. The removal of the HA makes the hide more flaccid.

The soaking process varies a lot to suit the type of raw material (cattle hides, sheep, goat skins) and the preservation method (fresh/chilled, brined, wet or dry salted, dried), the typical water consumption for the first („dirt soak“) being 200-300% on w.s. weight but in case of heavy contamination with dirt and manure adhering to hide, it can be much more; for the second, the main soak, normally it does not exceed 200%.

Soaking is carried out in low speed rotating drums (hides) or paddles (woolly and/or dried skins). In industrial types of leather processing, soaking in pits has been virtually abandoned. Rewetting is normally supported by applications of appropriate surfactants and sometimes enzyme based auxiliaries.

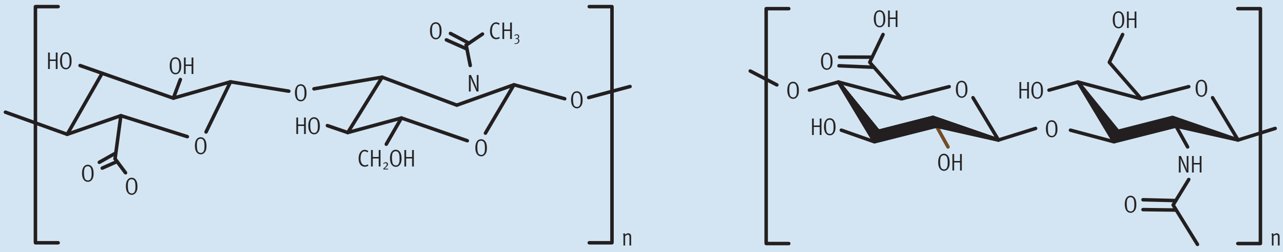
Alkalis (e.g. 0.2 – 2 g/l of sodium hydroxide), surfactants, and enzymes may be added to improve the efficiency of the soaking process; alternatively, weak acids such as formic acid or sodium bisulphite can be used for the same purpose. Biocides may be added to the float, normally at the rate of about 0.1 % of the w.s. weight to minimise bacterial damage and emissions of foul odours especially if the float temperature is higher than desired.

It is recognized that the soaking of fresh hides requires more intensive support (e.g. combination of soda ash, surfactants and proteolytic enzymes) to achieve the necessary removal of interfibrillary matter.

Generally, the thoroughness of the soak can be controlled by monitoring parameters such as weight gain, float density (typically 4 – 6 ° Baumé at the end) or removal of hyaluronic acid. Actually, it seems that the removal of hyaluronic acid is essential for opening up the hide structure and the use of soda ash, suitable enzymes and surfactants greatly accelerate that process.

The waste soak liquor contains soluble proteins, suspended matters like dirt, dung and blood washed out from the hides, plus chemicals or residues of chemicals added such as alkalis, surfactants and biocides, giving a very high COD. However, worst of all, the salinity of the soak liquor varies from about 11,000 – 23,000 mg/l as Cl^- (see the previous chapter, Preservation).

Figure 17. The structure of hyaluronic acid



Based on source: G. Stockman et al. Buckman Laboratories/Black et al. Prime Tanning Company, USA, WL, Feb/March 2010

7.2. CLEANER METHODS IN SOAKING

Generally, the range of techniques to reduce emissions includes:

- Use of unsalted hides or skins, i.e. preserved by one of the short-term preservation methods or drying
- Desalting - partial salt removal from wet salted hides and skins
- Use of clean hides or skins only
- Avoidance or substitution of hazardous, environmentally unfriendly substances
- Optimisation of water consumption and process control
- Green fleshing

The synergistic effect of combining 1.5 A direct and 2.0 A alternative current followed by 1 g/L bronopol (2-bromo-2-nitropropane-1,3-diol), a widely used antimicrobial agent for application in the hide soak liquors is still at the early research stage.

7.2.1. Green fleshing

Ideally, fleshing should be carried out in the abattoir itself thus facilitating the hide preservation and lowering the transport load but that is seldom the case. Fleshing can be carried out at several stages of the process:

- green fleshing of fresh or chilled hides/skins
- green fleshing after (first) soak
- pickle fleshing (not common, mainly skins)

Tanners traditionally prefer fleshing after liming since in that condition fleshing is much easier.

The soaking of hides can be combined with “green fleshing”, usually after the dirt soak – especially if there is a good scope for utilisation of native fleshings (Green fleshings are free from liming and unhairing agents). Also, fleshing at this stage allows for a more rapid and uniform penetration of chemicals into the hide. For example, it is estimated that in the EU with green fleshing the consumption of chemicals and water in the beamhouse are reduced by 10 – 20%.

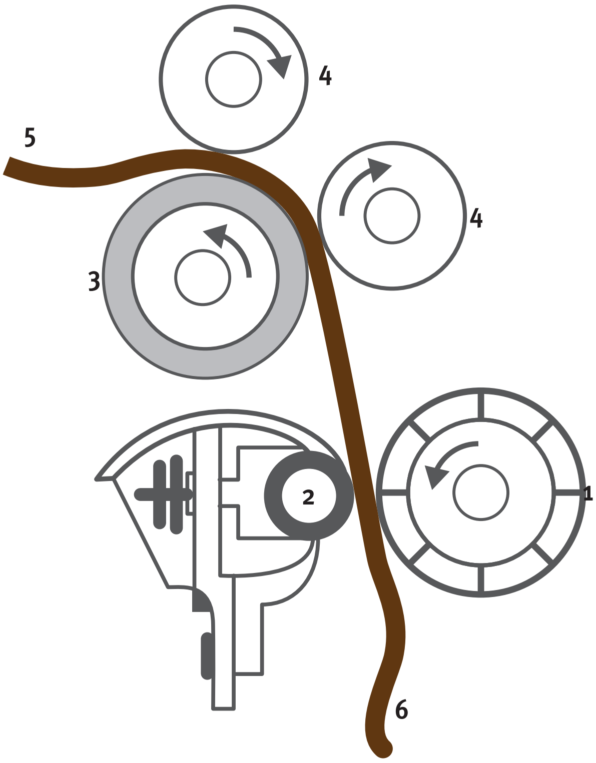
The basic machine for fleshing is the same for green fleshing and fleshing after liming. However, for green fleshing a demanuring cylinder needs to be installed. Also, green fleshing requires a well-set machine and experienced operators to avoid damaging hides as well as additional, after lime fleshing. Finally, green fleshing may not be viable with hides very dirty with dung without additional machine operation for dung removal.

Chemicals are not needed for fleshing. Sawdust may be used for a better grip on slippery hides; however, the amount of water used to wash away the fleshings from the fleshing machine is very often overlooked.

In the case of (heavier) European or USA hides about 10-40% of their weight is removed as wet limed fleshings; from lighter hides in developing countries it is considerably less. The amount of green fleshing is lower than that from lime fleshing.

Disposal options greatly differ for green and limed fleshings and change in accordance with local legislation and availability of treatment facilities. Thus, they vary from rendering and landfill (after treatment) to production of hide glue or fat recovery. For example, in the EU the demand for green fleshings has suffered a great set back due to very strict regulations concerning animal by-products.

Figure 18. Operating principle of the fleshing machine



1 = knife cylinder

2 = pneumatic pressure roll

3 = backing roll

4 = transport rolls

5 = inlet - pelt to be fleshed

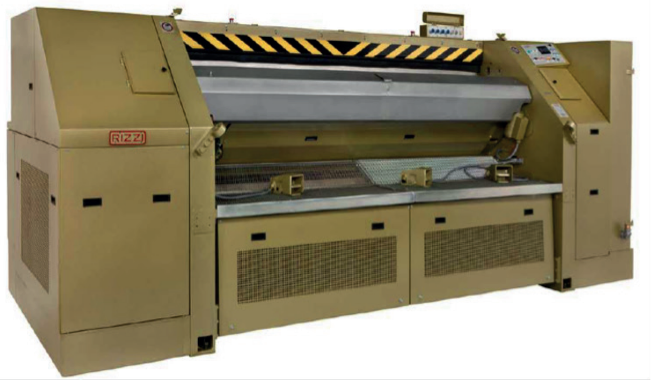
6 = outlet - fleshed pelt

Based on source: BASF Pocket Book for the Leather Technologist, 4th edition

Figure 19. Green fleshing in Australia

Source: C. Money, Australia

Figure 20. Through feed fleshing machine



Source: www.rizzi.it

7.2.2. Salt removal

Dry salted hides are opened out for processing in such a way that they are shaken or tumbled, so that loose salt crystals fall off and are not taken into the soaking process.

Loose salt can be recovered by shaking. This operation can be carried out mechanically by using purpose-built equipment. Approximately 6 – 8% of the original salt content of the hide is eliminated, corresponding to about 5% of the total salt discharge from the tannery.

The overall salt emission level depends on the amount of salt dissolved in the raw material. About 5% of the salt usually found in the effluent streams is recovered. To test the efficacy of the technique, the treated batch of hides/skins may be shaken again and the loss in weight must not exceed 1%.

Salt disposal can be a serious constraint since its reuse for preservation or pickling is not possible due to bacterial contamination, landfilling is often forbidden (high solubility) and the cost of salt recovery (purification by dissolving followed by evaporation) is high in comparison with the cost of fresh salt.

According to European experience, if all measures listed are taken, the emissions from soaking can be reduced to the levels shown in the following table.

Table 11. The scope for reducing emissions from soaking

Parameter per tone raw hide	Unit	Salted hides (calculated on salted weight)	Fresh or chilled hides
Water volume	m^3/t	4	2
Total solids	kg/t	130	45
Suspended solids	kg/t	10	10
BOD_5	kg/t	10	12
COD	kg/t	23	23
Total Kjeldahl nitrogen	kg/t	1.5	2
Cloride (Cl)	kg/t	55	5

Satisfactory results, especially in smaller tanneries, can be achieved with some improvisation as it was done under a UNIDO project in India: an existing old wooden drum 2.4 m x 1.8 m was modified by drilling holes of 85 mm in diameter and spacing of 130 mm and the drum fitted with an electrical motor of 3.75 kW.

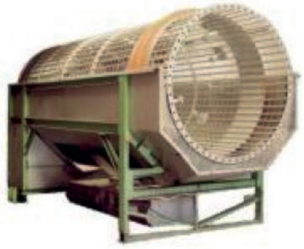
The best results were for wet salted lots of 250 - 400 kg at the speed of about 3 RPM (velocity 0.35 m/s) for 15 - 20 minutes. The amount of salt collected on the stone floor was about 5 -7% of the weight of raw stock during the dry season but less during the monsoon season.

Another method was adopted in a tannery was processing heavy buffalo hides. A brush-type desalting machine with a working width of 2100 mm, a cylindrical roller fitted with 5 nylon brushes, the width of each brush 125 mm, the speed of the brush roller 400 RPM and a 3.7 kW motor was installed. The salt on the flesh side is removed by the bristles of the nylon brushes and drops down a sloping wooden plank to the rear of the machine.

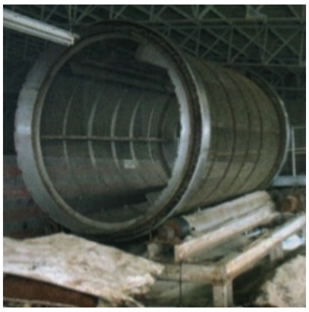
Finally, to reduce the strain of pure manual shaking, a simple wooden frame (750 mm x 750 mm standing at 750 mm) that can be easily lifted and shifted was designed and made from local wood.

Hides (four workers) and skins (two workers) are beaten three

Figure 21. Drums for desalting of hides

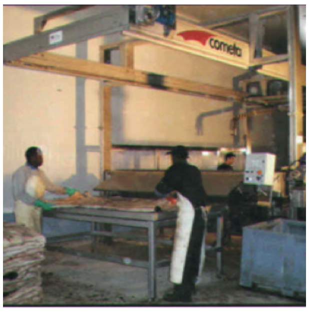


Source: www.rizzi.it



Olcina, World Leather June/July 2009

Figure 22. Desalting machine



Source: Feltre, www.feltre.com

Figure 23. Old wooden drum converted into a desalting drum

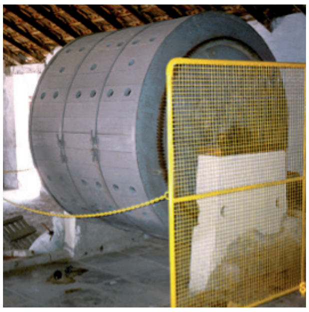


Figure 24. Brush type desalting machine

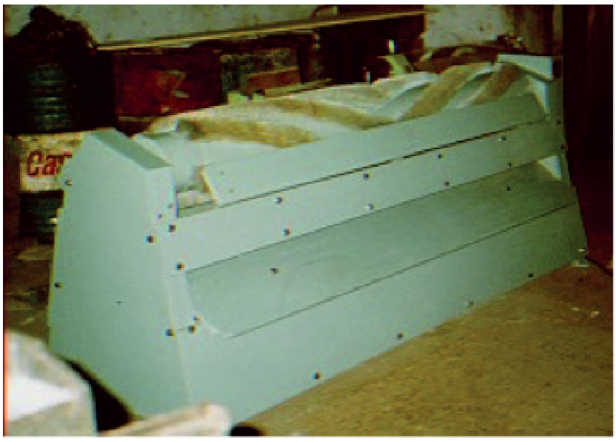


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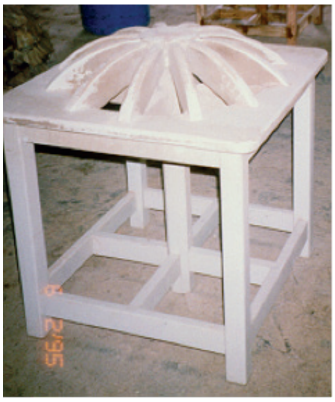
Figure 25. Dome type DODECA wooden frame for manual desalting



times on the frame and the salt is collected manually from the floor. On average, it takes two hours to desalt one tonne of raw material.

It must be emphasised that all desalting measures mitigate the problem of salinity to a very limited extent and are certainly not a complete answer to this challenging issue.

Furthermore, although the salt from preservation from soaking is by far the largest source of the Total Dissolved Solids (TDS) load in effluents, it is not the only one: some contamination emanates from other stages of the conventional tanning process, such as deliming, pickling, tanning and retanning.

UNIDO assisted Kanpur Leather development project, India

Hide and skin desalting was carried out using equipment described earlier (desalting drum, Dodeca wooden frame, brush type machine) and salt shaker, a cage made of stainless steel, 2.7 m diameter length 5m, adjustable inclination, rotated by 15 kW motor.

Brush type desalting machine and inclined salt shaker

Overview of performance of four desalting methods used in Kanpur

PARAMETER	SALT SHAKER	BRUSH TYPE DESALTING MACHINE	DESALTING DRUM	DODECA WOODEN FRAME
Salt removal	80 - 100 kg/t	70 - 80 kg/t	50 - 70 kg/t	50 - 80 kg/t
Time needed for 1 tonne	30 minutes	60 minutes	60 minutes	120 minutes
Manpower	2 man-hours	2 man-hours	2 man-hours	4 man-hours
Investment cost	Rs. 3,000,000	Rs. 240,000	Rs. 200,000	Rs. 25,000
Sustainability	Hides	Hides and skins	Hides	Skins

Environmental benefits

TDS EMISSIONS IN SOAK	FIRST SOAK	SECOND SOAK
Average TDS of soak liquor without desalting (300% float)	53,780 mg/l	27,580 mg/l
Average TDS of soak liquor after desalting (300% float)	33,250 mg/l	15,000 mg/l

The main benefits of desalting:

- Instead of two, one soaking suffices
- The water/effluent volume need for soaking is halved
- Due to lower salinity tanneries can be linked to somewhat smaller urban WWWs
- For tanneries with RO+MEE (ZLD), the recovery rate at RO will be increased, membrane life extended, less salt residue produced, less energy consumed

Unfortunately there is still no satisfactory solution for reutilization or disposal of the collected salt.

Cost benefit analysis of desalting

INVESTMENT COST (capacity 2 tonnes/day)	RS. 240,000
Operating costs • Electricity: Rs. 26/t • Labour: Rs.105/t • Depreciation Rs. 80/t	Rs. 126,540 per annum
Cost saving (for tanneries with zero liquid discharge, ZLD) • Savings in effluent treatment costs @ 1500 l/t: Rs. 90/tonne • Cost savings in evaporation due to increased recovery rate in RO plants by 2 %: Rs. 540/tonne	Rs. 378,000 per annum
Cost saving (for tanneries with dilution) • Savings in effluent treatment costs @ 1500 l/t: Rs. 90/tonne • Cost savings in reduced sewage for dilution by $50m^3$/t: Rs. 700/t	Rs. 474,000 per annum
Annual net savings	Rs.251,500 - 347,500 per annum
Pay back period	8 - 10 months

8. UNHAIRING, LIMING

8.1. LIMING WITH HAIR-BURN UNHAIRING

As said earlier, the main aims of the liming process are:

- **removal of hair (wool) and epidermis**
- **removal of any interfibrillary components remaining after soaking and "opening up" of the fibre structure, including an acceptable level of swelling**
- **partial saponification of the natural grease**

The well-known stability/non-solubility of keratin and its resistance to chemical attacks is due to strong bisulphide cross linking (intermolecular or intramolecular) of cystine, the amino acid richly present in keratin's structure. Some strong reducing agents such as the traditionally used sodium sulphide – Na_2S and sodium hydrosulphide – NaHS are able to break down the disulphide bond[13]:

$$\underset{\text{Cystine}}{\text{R-S-S-R}} \longrightarrow \underset{\text{Cysteine}}{\text{2 R-SH}}$$

In the conventional liming – hair burning process, the liming chemicals either destroy the hair and epidermis completely or loosen them to such an extent that they can be removed mechanically without any difficulty. At the same time, they bring about a certain amount of swelling (plumping) of the fibre structure and partial saponification and emulsification of the hide fat. The liming is usually carried out with hydrated lime – $Ca(OH)_2$ and sodium sulphide – Na_2S and/or sodium hydrosulphide – NaHS, which has a less pronounced plumping effect.[14]

In addition to high water consumption, soaking and liming with hair-burning are the most polluting part of the entire process of leather manufacturing in terms of nearly all the key parameters (BOD, COD, Suspended Solids, TDS/salinity and nitrogen).

8.2. HAIR-SAVE UNHAIRING

Hair-save unhairing of hides in pits or sweating skins has been used since the time immemorial; hair-save lime-sulphide unhairing dates from the 1880´s and was widely practiced. Modern commercial methods were developed with the advent of drums fitted to recirculate the liquor and separate the loosened hair. The main reasons for use of hair-save in modern times are:

- significant decrease of organic pollution load, including nitrogen; **a quarter of the overall nitrogen releases stem from liming and unhairing!**
- significantly lower volume of sludge for reuse or disposal
- lower costs of effluent treatment (chemicals, energy)

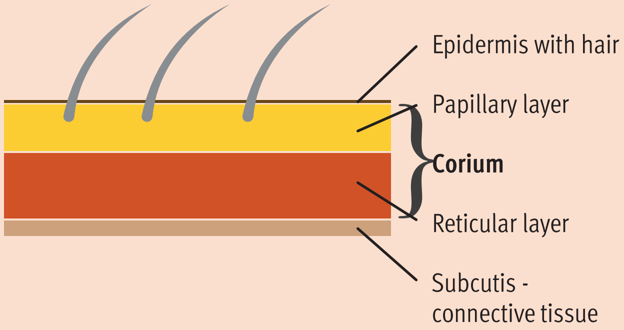
The presently prevailing hair-save process utilises conventional chemicals normally used in the hair-burning system (lime and sulphide), but applies them in a somewhat different manner resulting in proven environmental benefits. Enhanced leather properties are also likely whereas claims about improved area yields are not quite convincing.

The principle of the method is quite simple: the hair fibre is firstly partially immunized by an alkali (lime) to be subsequently removed by the action of sulphide and ultimately recovered by filtration.

First step: Removal of intact hair by manipulating the pace of adding lime and sulphide

Second step: Opening up of the fibre structure by conventional lime/sulphide process

Figure 26. A schematic cross-section of bovine hide



Based on drawing by M. Bosnić/J. Buljan

This process sequence is possible because the fully developed keratin in hair, nails and the upper part of the epidermal layer is highly resistant to chemical or biological attack, except from sulphide which breaks down the disulphide bonds. The immature keratin found in hair roots, hair root sheaths, and the lower layer of the epidermis is more easily degraded and dissolved.

The resistance of keratin to chemical degradation can be substantially increased by immunisation i.e. treatment with an alkali, but without sulphide. The alkali transforms the sulphur cross-links into different, highly resistant thioether bonds. Mature keratin is much more easily immunised than immature keratin. This increases the difference in degradability between hair and hair roots, thus simplifying the hair-save unhairing process.

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[13] *Strong oxidative agents such as $NaClO_2$ or Na_2O_2 are also able to break this bond but for various operational limitations, including OSH aspects, that kind of oxidative unhairing has not been accepted by the industry.*

[14] *A few years ago, it was suggested to consider using 1,4-dimercapto-butan-2,3-diol (DMB) as the reducing agent in the first step followed by a proteolytic enzyme in the second step of unhairing. It was claimed that lime was not needed and there was no risk of development of hydrogen sulphide. It seems that high costs prevented further development and large scale testing of this method.*

The point at which the hair breaks is decisive to the success of the process; the lower the breakage down the hair shaft in the follicle, the better the process. Any hair debris remaining in the follicle is a problem, especially with black-haired hides.

Immunisation can be achieved by using sodium hydroxide, lime or calcium hydroxide; it usually takes 1-1.5 hours. Most commercial systems for hair-save unhairing are based on immunisation.

A careful balance between insufficient immunisation and over-immunisation must be maintained. In the event of over-immunisation, the hair cannot be loosened satisfactorily in the subsequent unhairing stage. Obviously, the amount and use of a reducing agent, the amount of alkali as well as the time and temperature of immunisation are critical for the success of the process.

The hair is loosened by intensive mechanical action during the chemical unhairing process. This mechanical action entails a risk of abrasion, and hence damage to the grain. Suitable measures must be taken in order to prevent this (for example, by adding slip agents).

After loosening, the hair must be separated from the liquor as soon as possible in order to minimise the pollution load since prolonged immersion may to some degree dissolve the hair substance and reduce the filterability of the hair. Temperatures up to 30°C are considered safe, whereas at 35°C the hide substance is drastically damaged, especially in the grain layer. In tropical countries where fresh water temperatures may be higher than 30°C, it may be necessary to use paddles instead of drums for unhairing and/or adding ice to reduce heat induced by friction.

For reasons not fully understood it seems that the hair-save unhairing method works better on hides preserved by salting than on fresh hides; again, given the almost insurmountable environmental problems associated with salinity, this aspect should not impede switching to processing fresh/chilled hides wherever possible.

8.2.1. PAINTING

Painting is a traditional hair-save method for calf, sheep, hair-sheep and goat skins; also, it is obligatory where the hair/wool is valuable. Skins are painted by hand or machine on the flesh side with a paste consisting of sodium sulphide, lime or kaolin (china clay) or organic thickeners and water. Typically, lime is added to the solution containing about 10% sodium sulphide (9 °Bé) until about 15 °Bé is reached; the final density of the paste of about 20 °Bé or more is achieved by adding kaolin (china clay).

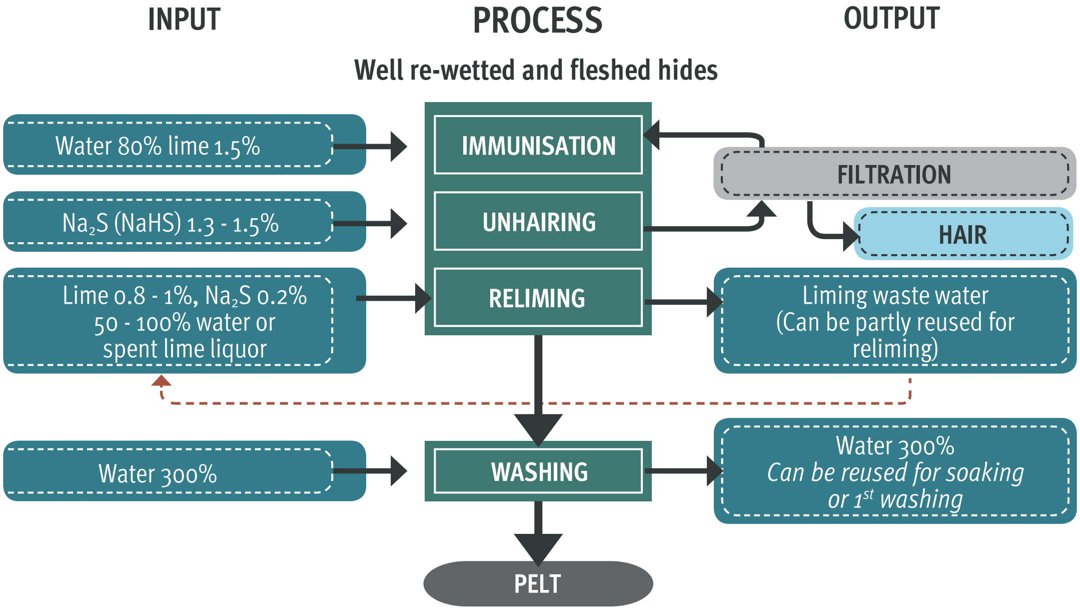
Although very seldom, painting on the grain side is also used for special types of rawstock to produce a particularly smooth and fine grain; the hair is completely destroyed.

After painting, the skins are stacked in a pile, hair side against hair side. The unhairing chemicals penetrate the skin from the flesh side and destroy the hair roots. It is then a simple task to scud off the hair that is not in contact with the unhairing chemicals. Mechanical unhairing and re-liming are necessary; painting is labour intensive, requires more space and usually takes more time.

Figure 27. A pile of painted sheep skins

8.2.2. HAIR-SAVE LIME-SULPHIDE UNHAIRING

Figure 28. Process diagram of hair-save liming with float recirculation


INPUT
PROCESS
OUTPUT
Well re-wetted and fleshed hides
Water 80% lime 1.5%
IMMUNISATION
FILTRATION
Na_2S (NaHS) 1.3 - 1.5%
UNHAIRING
HAIR
Lime 0.8 - 1%, Na_2S 0.2% 50 - 100% water or spent lime liquor
RELIMING
Liming waste water (Can be partly reused for reliming)
Water 300%
WASHING
Water 300% Can be reused for soaking or 1st washing
PELT

The minimum sulphide dosage in hair-save lime-sulphide unhairing is approximately 0.25-0.5% sodium sulphide flake (60% Na_2S) or 0.6-1.2 kg S^{2-} per tonne salted raw hide.

The critical concentration of sulphide in the liquor, below which the hair remains unaffected and above which it is destroyed, depends on several variables: length of float, lime dosage, pH, temperature, process time, intensity of mechanical action and hair length. Approximate ranges are as follows:

Table 12. Approximate sulphide dosing ranges

% float	% sodium sulphide flake (60% Na_2S)	kg S^{2-}/tonne raw hide
50-100	0.5	1.25
200	1.0	2.5
300	1.5	3.7

In practice, 200% float at a dosage of 1.5 - 3% Na_2S (iron-free) flake (equivalent to 3.7-7.4 kg of S^{2-} per tonne raw hide) is used.

Thus, the basic recipe in summary is as follows[15]:

Immunisation:	Max. 150% water 28°C
	1.5 % lime
	45 minutes (15 min. rotation)
Unhairing:	+ 1.5 % sodium sulphide flake (60% Na_2S)
	After $1^{3/4}$- 2 hours filtration until clear
Reliming:	+ water up to 180-200%
	2% lime

Run at low speed (2-3 rpm) for approximately 14 hours

In order to obtain a perfectly clean pelt grain, a minimal amount of enzyme is added to the reliming liquor. The advantage of the method is that proprietary products are not used and the chemical costs are comparatively low.

8.2.3. UNHAIRING WITH ORGANIC SULPHUR COMPOUNDS

Three types of organic sulphur compounds are used in proprietary products based unhairing systems:

- Mercaptoethanol
- Salts of mercaptoacetic acid (thioglycolic acid)
- Formamidinesulphinic acid

These compounds are strong reducing agents, acting in the same way as sulphides. The advantage of their use is that they considerably reduce the amount of sulphide consumed and discharged with the waste water; also, their oxidisation results in harmless substances. On the other hand, these chemicals are much more expensive so they are mostly used in instances where effects other than environmental improvement are sought. For example, liming with these compounds yields a lower degree of swelling than using lime and sulphide only with possible positive effects on the area yield and the smoothness of the grain.

The use of mercapto products requires the application of occupational health standards and the same protective measures as the use of sulphides. Free mercaptans in the air are actually more toxic than hydrogen sulphide, but for several reasons (such as higher oxidation rate during the process, lower tendency to generate free mercaptane, and the latter's higher boiling point) the risk of mercaptane vapours being released into the atmosphere is considerably lower than is the case for hydrogen sulphide. Owing to their high oxidability, thio-compounds have to be thoroughly mixed when being added to the float. In any case, suppliers normally provide detailed guidelines for their use.

8.2.4. ENZYMATIC UNHAIRING

Enzymes are biological catalysts in the form of proteins, typically working under mild conditions. Enzymatic processes are hard to control; commercial preparations containing proteolytic enzymes attack the collagen of the grain layer to a certain degree, leading to looseness of grain and grain sueding. Moreover, enzymes alone cannot completely eliminate the ground and fine hair. Thus, it is unlikely that an unhairing process exclusively based on the use of enzymes will ever be practically possible. Also, enzyme preparations are expensive and in most cases the environmental benefits they offer are insufficient to justify the cost.

Enzymes, however, are extensively used to support alkaline immunisation-sulphide unhairing to eliminate ground and fine hair and to obtain cleaner pelts.

With the combination of the sulphide and an unhairing enzyme, the hair is broken in the zone just above the root–the pre-keratinous zone. The following are the key considerations:

- Enzymes are applied at low levels (e.g. 0.15 %)
- Enzymes target epidermis and interfibrillary matter but often grain enamel is also damaged
- Simultaneous reduction of lime (to cca 1.5 %) and of sulphide (to cca 1.0 %) is not essential but cannot be ignored
- Enzymes are rather expensive
- Good process control is essential

Finally, enzyme unhairing has been used on long-haired goatskins since the grain layer on these is more resistant to enzymatic attack than grains on skins or hides of other species.

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[15] *Generally, it is taken that the concentration/purity of lime – Ca (OH)2 is 100%, Na2S 60-62 % and NaHS 95 %. Lime is added as a suspension but very often directly from bags.*

8.2.5. *X-Zyme technology*

Vigorously promoted for several years, X-Zyme technology claims to offer a completely new enzyme-based soaking and unhairing solutions using carbohydrase followed by a protease. Within a 2-step process a glucosidase (a carbohydrate-splitting enzyme, i.e. without proteolytic activity) targets glucose aminoglycans (GAGS) by degrading dermatan sulphate proteoglycan (DSP). In the liming process a specific protease is applied to remove hair and the basal membrane of the epidermis and facilitates hair-saving and semi hair-saving methods. This enzyme has a relatively narrow activity optimum (pH 9.2 – 10.5) which makes it easy to turn it on and off.

Enzyme technologies normally help reduce the pollution load emanating from the beamhouse.

8.3. HAIR SEPARATION AND FLOAT RECIRCULATION EQUIPMENT

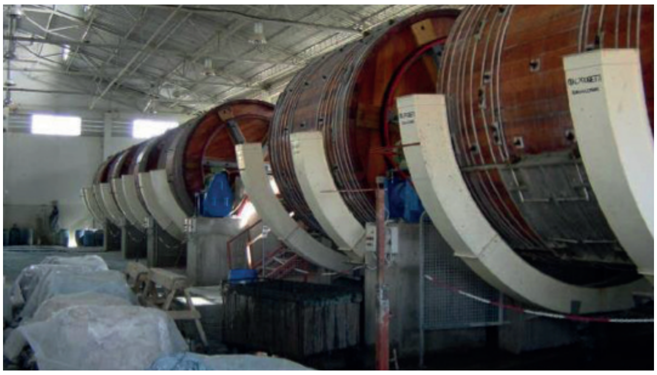
Modern hair-save unhairing processes require equipment for recirculating the float and separating the hair.

Hair separation is preferably carried out at the same time as hair loosening so as to minimise the degradation of the hair. Modern drums equipped with recirculation as well as temperature, and pH regulations are commercially available. The float is pumped out of the drum laboratory box and fed back in through a hollow axle.

In older drums without a recirculation laboratory box, a recirculation and filtering system can be fitted provided that the drum axles can be used for float circulation.

For that purpose, it is necessary to install perforated plastic or wooden elements inside the drum (on one or both sides, if the drum is big enough) and drill holes of not less than 80 or 100 mm diameter on the external side and fix of a manual valve; again, depending on the drum size, semi-circular float collecting gutters are fitted on one or both sides of the drum (see pictures below).

Figure 29. A battery of drums with semi-circular float collection gutters



It is important that the filtering capacity is sufficient to maintain the appropriate recirculation speed and complete filtering process within the required time. The typical flow capacity of commercial recirculation-filtering systems is 600-1000 l/min.

Various types of sieves (e.g. wedge wire screen, vibrating wedge wire screens rotating drum sieve, mesh gauge is 0.5-1.0 mm) can be used to separate the hair; the float may be pumped to the sieve through the vessel's existing circulation pump or via separate pumps recovering up to 90% of the loosened hair. Nowadays most of the screening systems on the market are combined with dewatering devices.

In the screw type press with compactor, the hair separation takes place in the filtering pipe with a semi-circular section of the perforated plate with a screw scraping the inner surface; the hair is dewatered in the rubber cone section.

Dewatering of separated hair is not always easy, but it is important for further handling.

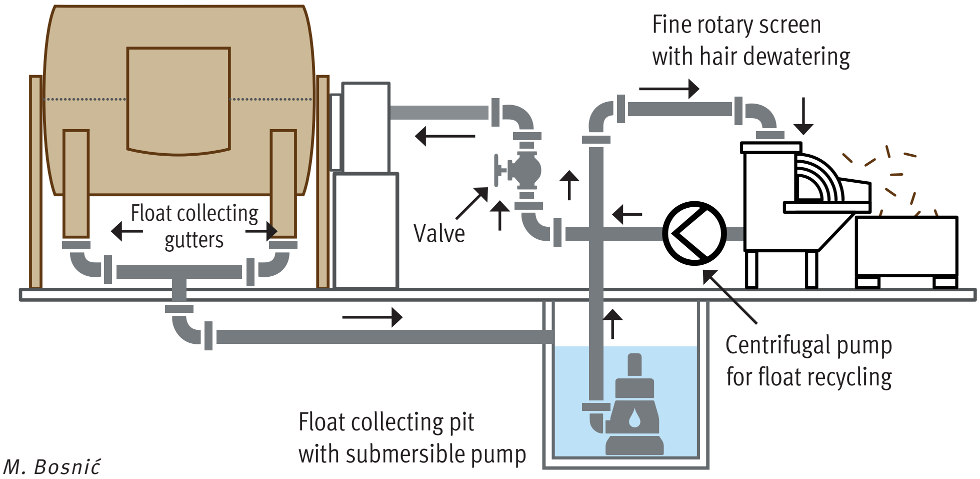
The cost of introducing hair-save unhairing depends on the host factors such as tannery size, the scope of retrofitting existing drums vs. purchase of modern drums with recirculation systems, availability of chemicals, etc.

However, meeting specific pollutants' discharge limits (primarily for nitrogen), may prevail over other considerations and induce the tannery to switch to hair-save. In any case, every cost-benefit analysis of hair-save unhairing has to consider the specific local conditions.

The claims about increased area yield do not appear sufficiently supported by reliable figures.

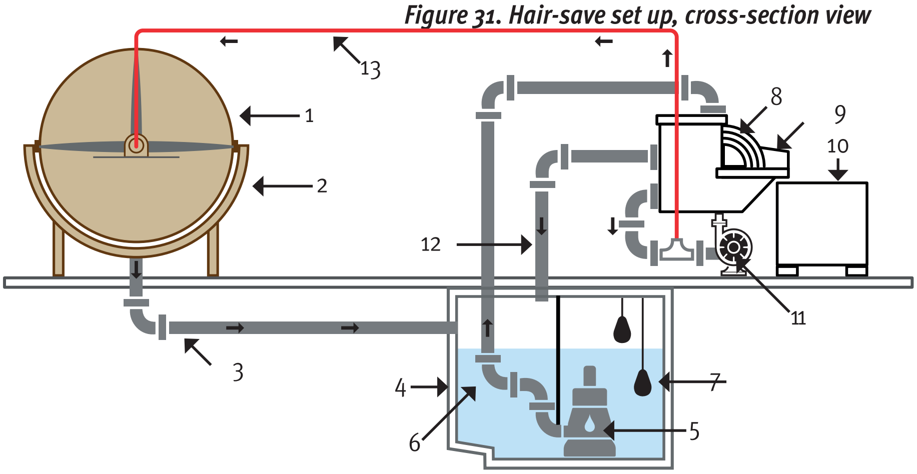
Generally, it is believed that the costs of chemicals for hair-dissolving and lime-sulphide hair-save are of the same magnitude; if the latter is enzyme-assisted, the cost is likely to be somewhat higher but worth the additional cost. As a rule, the costs of using specialty, proprietary hair-save systems are higher, sometimes substantially.

Figure 30. Hair-save system with rotary drum filter and collecting pit


Fine rotary screen with hair dewatering
Float collecting gutters
Valve
Centrifugal pump for float recycling
Float collecting pit with submersible pump

Based on chart by M. Bosnić

Figure 31. Hair-save set up, cross-section view

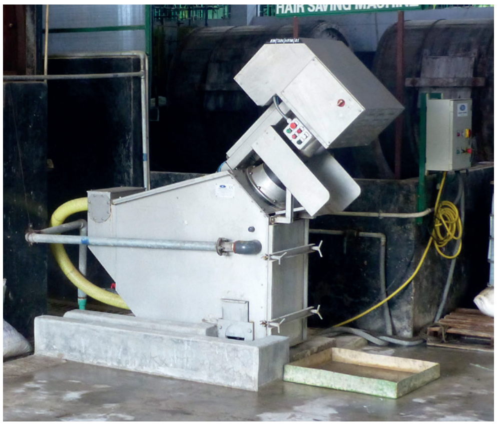


LEGEND

1. Liming Drum
2. Collecting Gutter
3. Collecting Pipe
4. Lifting Tank
5. Submersible Lifting Pump
6. Lifting Pipe to Rotary Screen
7. Floating Level Switch
8. Fine Self Cleaning Screen
9. Hair Squeezer
10. Container for Dewatered Hair
11. Centrifugal Recycling Pump
12. Overflow
13. Lifting Bath to the Drum

Based on chart by M. Bosnić

Figure 32. Screw type screen with compactor and container



Source: I. Král

UNIDO assisted Kanpur Leather development project, India

The introduction of a hair-save system decreased the organic pollution load (SS, COD, BOD and sulphides), significantly lowered the volume of sludge for reuse or disposal and lowered the costs of effluent treatment (less chemicals and energy required).

The following table shows the cost benefits of installing a hair-save unhairing system for a tannery of processing capacity of about 5 tonnes per day.

Investment cost	**Rs. 1,320,000**
Estimated annual savings (after excluding operation and maintenance expenses)	Rs 303,360
Payback period	approx. 4 years

8.4. PREVENTION OF H_2S EMISSIONS FROM EFFLUENTS

Effluents from the unhairing and liming processes contain high concentrations of sulphur compounds derived from the sodium sulphide used in unhairing. If the pH of these effluents is allowed to fall below 9.5, hydrogen sulphide gas will evolve. These liquors may be oxidised (biologically or by adding chemicals using manganese sulphate as a catalyst) before being mixed with acid effluent or being discharged to the general mixing tank, which generally has a pH of 8.5 – 9.

Sulphide-bearing effluents from the beamhouse are normally treated separately to reduce the sulphide levels in the waste water treatment plant and to prevent the release of hydrogen sulphide when acidic effluents are mixed with effluents containing sulphide.

If sulphide-bearing effluents are to be mixed with acidic or neutral effluents before full oxidation of the sulphide is achieved, the mixing must be carried out in an enclosed tank, with air extraction through either a carbon filter or a scrubber dosed with either hydrogen peroxide or alkaline sodium hypochlorite.

Precautions to avoid the formation or emission of hydrogen sulphide are taken for some or all of the following reasons:

- to avoid toxic gas concentrations within the tannery;
- to prevent emissions of hydrogen sulphide as an air pollutant;
- to reduce odour nuisance, which can occur even in very low H_2S concentrations.

Low emissions of sulphides might even arise if no agents containing sulphide are used because some degradation products from keratin are alkyl sulphides.

Thiols, which are added or are formed by the degradation of sulphur containing proteins, are found in waste water effluents. Some are highly volatile, so they could cause an odour problem in the waste water treatment and may need abatement measures.

8.5. OXIDATIVE UNHAIRING

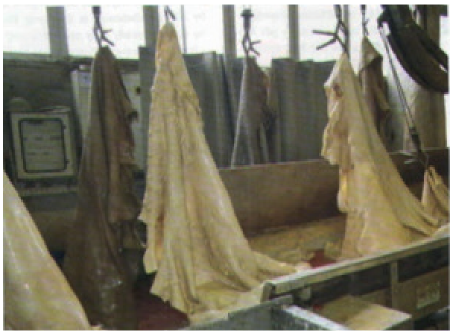
It is reported that oxidative unhairing is already implemented in Italy at the industrial scale: it uses hydrogen peroxide for oxidation and sodium hydroxide as the source of alkali and it is carried out in a propylene drum fitted with an internal water jacket for temperature control. It is claimed that the pelts are comparable to those from the traditional unhairing and liming process.

There is a fresh attempt to revive oxidative unhairing, tried many years ago as a continuous process at industrial scale (Darmstadt process). Attempts were also made using sodium hypochlorite. More recently oxidative (hair-save) unhairing has been investigated in Italy under the EU cofunded project and by the end of 2016 reportedly tested at the semi-industrial scale: the method uses hydrogen peroxide for oxidation and sodium hydroxide as the source of alkali (with calcium hydroxide there is a risk of hair immunization) and is carried out in a propylene (PPE) drum fitted with two cooling systems and advanced temperature, pH etc. monitoring and control systems. Depilation is carried out at pH 12.6.

At the end of liming the liming bath is treated (acidification with H_3PO_4, centrifugation, neutralization) and recycled for the next batch.

It is claimed that the pelts are comparable to those from the traditional unhairing and liming process, there is no malodour problem, dyeing is more uniform and the only minor issue are stretches on the sides. Environmental benefits are lower Suspended Solids and lower COD, slightly lower water consumption whereas the presence of phosphorus is seen as advantage.

Figure 33. A comparison between hides from oxidative and conventional unhairing/deliming



Source: Oxidative unhairing, R. Daniels, Gruppo Dani, WL Oct/Nov 2013

8.6. THE SCOPE FOR HAIR UTILISATION OR DISPOSAL

Nowadays, environmental and possible cost benefits prevail over the problem of coping with yet another solid by-product. The quantity of hair recovered in relation to the weight of raw hide varies considerably. Basically, it depends on hair length and hide thickness, which are properties linked to animal breed, gender, age, season, etc. Typical ranges are given in the table below.

Table 13. The amount of hair in relation to hide/skin weight

	% drained hair	% hair dry matter
Heavy bovine hides	10 - 15*	3 - 5*
Light bovine hides	15 - 20*	5 - 7*
Calf skin	20 - 40**	10 - 13**
Sheep or goat skin	60 - 90**	20 - 30**

*Calculated on salted weight ** Calculated on dry weight

The dry matter content of the drained hair is approximately 33% whereas at the end of the process it is 15-20%. After dewatering to 15% dry matter, the hair does not give rise to any odour when deposited as waste.

To avoid rapid putrefaction of the proteinaceous matter in the float adhering to the hair and development of malodour, the hair must be dewatered as swiftly as possible. The sulphide content in fresh, wet hair is approximately 80-100 ppm and it oxidises easily; within three to four hours the sulphide content is less than 10 ppm and after a day the sulphide completely disappears. For some uses, including agriculture, the hair has to be washed primarily to remove the residual salt (sodium) very harmful for the soil. Full stabilization is achieved by simple drying.

Numerous proposals for bovine hair utilization, often speculative or founded on the strength of laboratory scale tests, have been advanced:

- Felt production (historical use)
- Agricultural fertiliser (orchards, market gardens, nurseries)
- Animal feedstuff (cannot be used as a sole protein, lacks lysine and methionine)
- Gasification – fuel source
- Biodegradable flowerpots
- Some limited use in cosmetics

A more recent concept is a growth of keratin degrading bacteria and use of microbial keratinase to accelerate hair degradation within the composting process, the optimum reported to be at 50°C and pH 9.0. At the moment there are only two areas of wider applications for hair recovered from hair-saving processes:

- agricultural fertiliser & composting
- animal feedstuffs

Currently, in both areas, applications of partially or fully hydrolysed hair prevail by far. Uses of non-hydrolysed bovine hair, mainly based on its fibrous properties (e.g. felting) are insignificant.

Several companies in different countries produce organic nitrogen fertiliser prepared from partially hydrolysed, pelleted hair. As a source of slow-releasing organic nitrogen, hair is a valuable soil conditioner usually marketed as a special product primarily for orchards, market gardens, nurseries and private gardens.

Composting, typically in windrows, is another approach: the hair that is not degraded is useful because it endows the compost with a long-term effect.

Hair protein can be used in the production of animal feedstuffs. Owing to a deficit of two essential amino acids, lysine and methionine, it cannot be used as the sole protein component in the feed.

Waste hair has also been in specific market niches such as in the production of biologically degradable flower pots or anti-weed soil covering. To a limited extent, hair has also been used in the production of foaming agents for fire-extinguishers.

8.7. IMPACT ON POLLUTION LOAD

A wealth of information is available on the environmental load and impact of hair-save unhairing, much of which is provided by the suppliers of commercial systems. The following table presents a considered evaluation of what can be achieved in practice:

Table 14. Pollution load: hair-save vs. hair pulping, decrease in %

	Discharge from hair-save unhairing* kg/tonne raw hide	% reduction compared to hair-pulping	
		In unhairing liquor*	In total tannery waste water
Total solids	60	30	8
Suspended solids	15	70	43
BOD_5	20	50	28
COD	50	50	28
Kjeldahl nitrogen	2.5	55	22
Ammonium nitrogen	0.2	25	2
Sulphide (S^{2-})	0.6 - 1.2	50 - 60**	50 - 60**

*Including waste water from washing

** The percentage reduction of the discharge is greater than the corresponding reduction of the dosage

The sulphide discharge indicated in the table corresponds to 15-30 mg/l in the total waste water (at a water consumption rate of 40 m^3 per tonne raw hide). The discharge with the waste liquor varies greatly depending upon processing conditions; actual results are better or poorer than those cited in the table.

It is evident from the table that introducing hair-save unhairing is only a partial solution to waste water problems; seen in relation to the total tannery discharge, sulphide and suspended solids are the quantities most reduced and, to a lesser extent, BOD_5 and COD. Despite reducing the sulphide discharge, subsequent treatment is still essential. Under these circumstances, each tannery must decide for itself whether hair-save unhairing is a worthwhile proposition. In any case, if substantial improvements in the waste water discharge are to be achieved, hair-save unhairing must be accompanied by the use of cleaner technologies in all other stages of processing.

Table 15. Overview of hair-save technologies

Advantages	Disadvantages
• Lower BOD, COD • Lower Nitrogen • Lower suspended solids • Cleaner grain • Can be cheaper in the long run	• Hair disposal problem • Requires a fundamental change in the process • Short hair roots • Higher investment costs

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8.8. SUMMARY ON HAIR-SAVE UNHAIRING

Introducing hair-save unhairing is not necessarily an advantage for every tannery; each individual tannery must decide for itself whether it is worthwhile to introduce the method as the optimum solution, which depends on specific local conditions.

The starting point in any consideration should be a cost-benefit analysis encompassing:

- savings in overall effluent treatment costs, especially those related to treatment and disposal of sludge;
- possible additional costs of the method selected;
- necessity to attain pollutants discharge standards, especially nitrogen and TDS limits;
- possible impact/improvements in leather quality;
- favourable image/marketing effects (“eco-leather”, eco-labelling);
- economic implications of hair disposal.

In evaluating a method, occupational safety and health (OSH) aspects must also be taken into consideration.

In the course of introducing hair-save unhairing, other processes in the tannery should, as far as possible, remain unchanged.

Environmental authorities may set specific requirements. As far as possible, these should be known well in advance so as to have adequate time in which to implement the new method.

Before any new technology is introduced, it is important to ascertain whether, in terms of environmental and occupational safety, it is equal to, better than or maybe inferior to the technology it is going to replace. If needed, information on product toxicity must be obtained from the supplier.

When evaluating a new technology, factors not directly related to the tannery (e.g. production of chemicals) should also be taken into consideration (‘life cycle thinking’).

As with all cleaner technologies, hair-save unhairing presents only a partial solution to a tannery’s environmental problems. A tannery that produces nothing but finished leather is utopian; cleaner technologies will never make end-of-pipe treatment unnecessary.

Hair-save unhairing must be seen as a partial, but important element in the general optimisation of the production, including environmental aspects and better housekeeping.

Combining hair-save unhairing with the partial recycling of lime float and the use of second, final washing float for the first (dirty) soak is possibly the optimum approach from both practical and environmental aspects.

Sulphide elimination is rather easily achieved through an end-of-pipe treatment, usually by catalytic oxidation.

Only about 22% of the total nitrogen content in waste water is eliminated by hair-save unhairing. If nitrogen is a key problem, the hair-save unhairing must be supplemented by deliming without ammonium salts (for example, using carbon dioxide).

Nearly all methods on the market claim to improve leather quality and increase area yields. These claims, however, cannot be taken at face value; they have to be verified in industrial trials over several months.

Float collection and filtration after chemical unhairing is in practice the easiest method to implement using existing equipment. It thus entails relatively low investment costs. Cheap and simple screens can be selected, yet this approach is not optimal in terms of hair quality and reducing the waste water load.

At present, the most realistic possibilities for utilising the hair recovered seem to be as a soil additive or animal feed. Slow degrading hair protein is especially beneficial in soils in dry regions prone to desertification since it increases the humus content of the soil.

9. DELIMING AND BATING

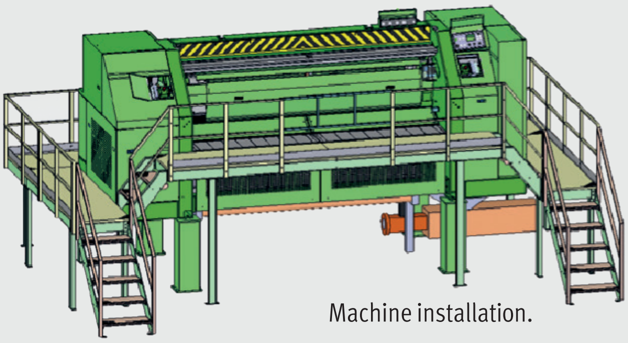
Mechanical operations have a significant impact on the character and volume of polluting solid, liquid and air emissions. While technical details can be found in standard textbooks, here are only some illustrations and points relevant for reducing the pollution load.

9.1. FLESHING

The environmentally preferred green fleshing has been described in an earlier chapter. Here it is important to take note of water sprinkled to clean the transport rollers and the working area that also facilitates the transport of fleshings by the screw feeder; too often this water is overlooked in computations of total water consumption.

Figure 34. Hydraulic heavy duty fleshing machine for calves, butt and cattle hides

(A screw feeder for removal of fleshings, automatic opening of water jets)



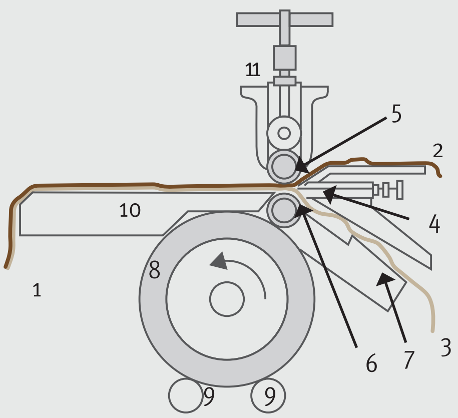
Machine installation.

Source: Rizzi

9.2. SPLITTING

The machines used for lime splitting or tanned splitting are basically the same but there are differences in the hardness and roughness of the rollers. The splitting machine can be used for either lime splitting or splitting after tanning, but not for both operations at the same time.

Figure 35. Operating principle of splitting machine



1. Unsplit hide
2. Grain or top split
3. Flesh or bottom split
4. Bandknife with guide
5. Transport roll
6. Section roll
7. Doctor roll
8. Rubber roll
9. Backing roll
10. Table
11. Thickness adjustment

Source: Based on BASF Pocket Book for the Leather Technologist, 4th edition

A condensed overview of splitting in limed condition is given in the next table.

Table 16. Overview of ex-lime splitting

Advantages	Disadvantages
- Lower consumption of chemicals in subsequent processes - Shorter processing time due to lower pelt/leather thickness - Shorter processing time brings about lower energy consumption - Permits the use of different tannages for grain and splits - More non-tanned vs. (chrome) tanned solid waste, wider range of utilization options - Facilitates environmentally preferred CO2 deliming - Better area yield	- Limed pelts are hard to handle - Handling of pelts with a pH of about 12 and with residual sulphide requires specific OSH measures - Lower accuracy in comparison with splitting of wet blue - Shaving of lime split leathers might be more demanding (especially of splits) - Splitting of thin hides may result in a loss of split yield - Generally, it results in a somewhat higher amount of shavings

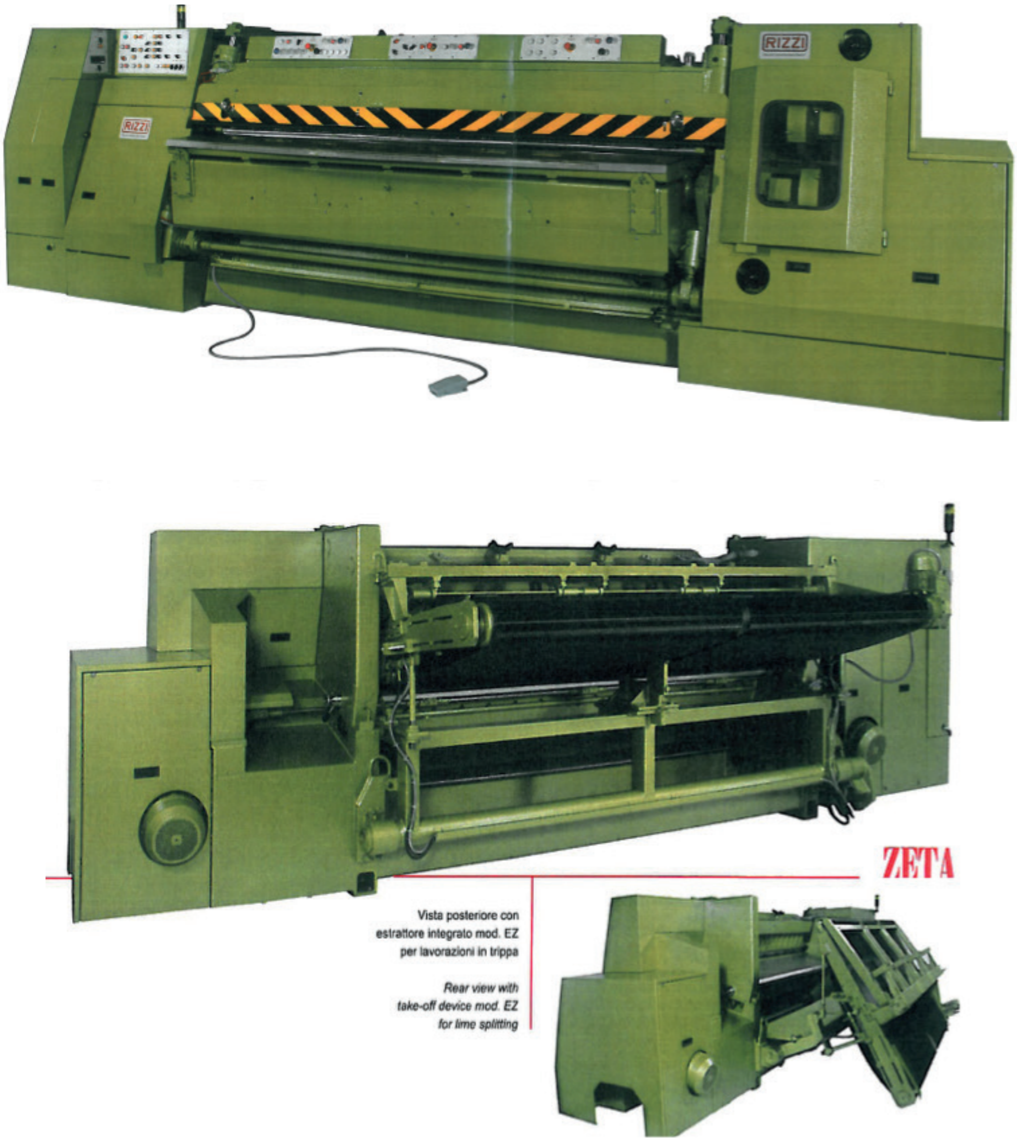
Hides for upholstery and automotive leathers are usually split in limed condition.

The ratios between splitting thickness and area and thickness in the wet blue stage shown in the table below can be considered quite representative.

Splitting	1,000 kg raw hides	Wet blue, area, m^2	Wet blue, thickness, mm
2.2-2.4 mm	1,000 kg	116	1.6 - 2.0
2.8-3.0 mm	1,000 kg	108	2.0 - 2.4

Note: Chrome uptake/ chrome content in 2.0-2.4 wet blue is less by 0.1-0.2% compared to 1.6-2.0 mm wet blue

Figure 36. A splitting machine for both ex-lime and wet blue splitting



Source: Rizzi

9.3. DELIMING

The aims of deliming:

- Removal of residual of chemicals used during unhairing and liming

Calcium salts have to be removed to avoid the formation of insoluble and damaging salts during later stages, primarily of calcium sulphate, $CaSO_4$; also, the removal of sulphide should prevent the formation of hydrogen sulphide as the pH drops.

- Reduction in pH in preparation for further processing

To lower the pH of the pelt from about 12.5 to the level suitable for activity of enzymes used for bating (mostly it is pH 7-8). The reduction of pH also brings about a reduction in swelling.

To reduce the alkalinity and remove the calcium from the limed hides, a combination of washes and deliming agents is used.

While chemicals such as ammonium sulphate, ammonium chloride, hydrochloric acid, formic acid, sodium bisulphite or metabisulphite are traditionally listed as suitable for this purpose; in practice ammonium sulphate is commonly used.

Mineral acids are cheap, but with these it is hard to control the pH. There is a high risk of pelt damage because it is difficult to ensure uniform dosing and distribution. With organic acids there is no ammonia and they are relatively safe, but again it is hard to control the pH and the penetration can be slow.

Ammonium sulphate is widely available, inexpensive and has excellent buffering at the pH for typical bating enzymes. However, despite such properties, replacements have been sought not only due to OSH considerations (harmful ammonia gas develops at the initial stage of deliming), but above all for its significant contribution to nitrogen and TDS load in effluents. Reacting with lime ammonium sulphate forms calcium sulphate $Ca(SO_4)_2$ which, if the float is not long enough, remains in the solution.

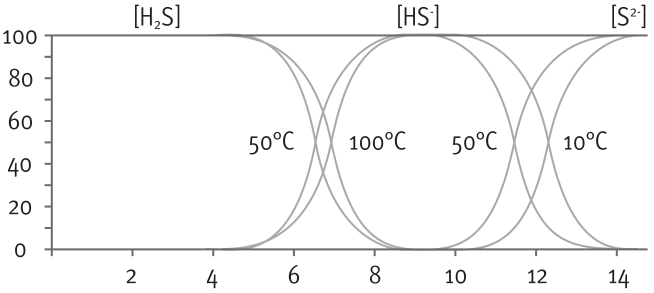
The amount of ammonium sulphate normally added is about 2 – 3% on the wet salted weight.

9.3.1. Polluting emissions

- **In practice, one of the main issues concerning is the large contribution of ammonium salts to the overall ammonia nitrogen (NH_4-N) load in tannery effluents. Furthermore, the content of nitrogen exceeding the desirable TOC: TN: TP ratio of 10:1:0.2 reduces the efficiency of the activated sludge treatment. Very often, despite adding carbon and phosphorus nutrients and despite extensive nitrification/denitrification steps, it is very hard to meet nitrogen discharge limits without eliminating or reducing the amount of ammonium salts in deliming.**

- Residual sulphides from liming can, if the pH falls below 9.0-9.5 result in highly toxic, free hydrogen sulphide gas and this is the case in CO_2 deliming (and in pickling).
- Ammonium salts used for deliming in alkaline float produce harmful, malodorous ammonia gas.

Figure 37. Relationship between pH and release of H_2S gas



x = pH value
y = molar concentration (% of total)

Based on chart by M. Bosnić, derived from the BASF Pocket Book for the Leather Technologist, 4th edition

9.4. CLEANER TECHNOLOGIES OPTIONS

9.4.1. Replacing ammonium salts with weak organic acids

Lactic acid, formic acid and acetic acids, esters of organic acids, magnesium lactate, non-swelling aromatic acids, etc. can be used to substitute ammonium compounds in the deliming process. With a float of 200% they are added at about 1.5% of pelt weight during about 1 – 1.5 hours. It is also believed that less agent is needed for the subsequent bating process.

However, replacement of ammonium salts with weak organic acids is not quite satisfactory because:

- While the NH_4-N load is significantly decreased, there is an increase of COD load in the effluent
- There is no buffering effect comparable to that of ammonium sulphate
- The use of commercial products is several times more expensive than deliming with ammonium salts.

Table 17. Discharge of ammoniacal nitrogen during deliming

Deliming agent	Discharge of ammoniacal nitrogen per unit of raw hide (kg/t)
2 % ammonium sulphate	4.5
1 % carbon dioxide + some ammonium sulphate	1.1 - 1.2
1 – 1.5 % carbon dioxide	0.02

9.4.2. Deliming with carbon dioxide gas (CO_2)

As in nature, carbon dioxide dissolves readily in water and the weak organic acid (carbonic acid) formed has a high affinity to lime reducing the pH of the float and hides. The reaction between lime and carbon dioxide produces a water-soluble salt: calcium bicarbonate, Ca $(HCO_3)_2$.

There are different, rather simple techniques to introduce the CO_2. Ideally, it is introduced into the drum recirculation system but it can also be injected into the float directly and even into headspace: since CO_2 is heavier than air, it settles onto the float surface. The process control is not very sophisticated. Obviously, there is little to no release of ammonium gas.

Carbon dioxide is usually supplied in cylinders; installation of a pressurised storage tank for CO_2, diffusers and a warming chamber may be necessary. The consumption of CO_2 is of the order of 0.75 – 1.5% on the pelt weight. Some degreasing effect action as well as improvement in dye bonding in later stages are also claimed. The leather quality is not affected. The cost depends on local availability and prices - in Europe it is comparable to deliming with ammonium salts.

However, there are some differences in the deliming process:

- The final pH at the end of the process can be somewhat lower (pH 6.7 – 6.9) against pH 8.8 – 9.2 with ammonium salts; yet with careful control it can be adjusted to the same range
- Some adjustments of the bating process might be needed
- The time needed for deliming is longer

With CO_2 as a deliming agent there is not only a substantial decrease of ammonium nitrogen (NH_4-N), but also of the Total Kjeldahl Nitrogen (TKN) pollution load in effluents.

Limitations and undesirable effects:

- In some cases, especially with thicker, unsplit hides (more than 1.5 mm) deliming with CO_2 has to be supported with reduced quantities of ammonium salts or organic acids or esters.
- If the final pH of deliming is lower than the pH after ammonium deliming, hydrogen sulphide (H_2S) – well known for its malodour

and high toxicity – can be generated and released. This can be prevented by the addition of 0.1 – 0.2% of hydrogen peroxide (H_2O_2), which in turn can be corrosive to wooden drums. It is claimed that some advanced dosing systems can eliminate this problem. In any case, a good ventilation system and treatment of extracted H_2S should be in place.

- Should the pH fall below 7, there might be some residues of melanin in the grain layer so that black and red hides may appear dirty.

While evaluating the costs of ammonium salts-free deliming, substantial savings in the waste water treatment costs - mainly in nitrification/denitrification - have to be taken into account.

Table 18. Emissions in waste water from deliming and bating

Emissions to waste water kg/tonne of raw hide	Ammonium salts	CO_2
BOD	3	3
COD	6	6
TS	45	30
TKN	5	1.5
NH_4-N	4.1	0.1 - 0.2

Source: EU BREF 2013

Table 19. Overview of carbon dioxide, CO_2 deliming

Advantages	Disadvantages
• No ammonia gas or discharge to effluent • About 50% lower BOD • Good penetration on light skins • No risk of acid shock • No risk of lime blast • Automated, easy to use • Limited changes	• pH too low for conventional bating enzymes • Suitable only for skins, light and/or split hides, not for heavy, thick hides • Use of hydrogen peroxide needed for hydrogen sulphide in situ removal • It requires installation of CO_2 cylinder(s) • Longer deliming times may be needed

9.5. OSH AT DELIMING

Due to ammonia gas and hydrogen sulphide gas associated risks, appropriate protection measures (prevention, neutralization, ventilation, etc.), including proper staff training have to be in place. Fixed and portable meters with coloured indicator tubes are a must.

Table 20. Overview of various deliming systems

Deliming system	Advantages	Disadvantages
Ammonium salts	Cheap Buffers at pH for typical enzymes Easy to use, low(er) BOD	Very poor environmental performance (harmful gas, TDS, Nitrogen)
Carbon dioxide	No risk of acid shock and lime blast No ammonia, relatively safe	Not suitable for heavy, thick hides Use of hydrogen peroxide needed for hydrogen sulphide in situ removal
Organic acids	No ammonia, cheap	Close pH control, can be too slow
Mineral acids	No ammonia, cheap	Close pH control, risk of damage

9.6. BATING

The purpose of bating **is to remove all residual and partially degraded proteins and interfibrillary matter from the pelt leaving it clean and open for pickling and the tanning process. This is done by using specific, commercially produced enzymes.**

Enzymes are biological catalysts, usually but not always highly specialized for a certain type of substrate. It could be said that they work on a "lock & key" principle. Those that act on proteins in pelts during bating are called proteases and are of pancreatic (mainly) or of bacterial origin. Commercial bating agents are often mixtures of a few enzymes. They contain only 1 – 5% of active ingredients, the rest being inert carriers (wood flour, kaolin) and salts (ammonium chloride in most cases) as buffering and deliming agents.

As biological catalysts, active enzymes work best under their optimal temperature and pH conditions. For example, fungal enzymes work better under acidic and neutral (and thus within a wider range), bacterial enzymes work better under neutral or slightly alkaline conditions whereas for the optimum effect, pancreas based proteases need pH 8-8.5. Bating agents for tanneries are mostly tuned to work at pH 7-8 and at a temperature of 35°C.

Again, since enzymes are basically proteins they irreversibly denature and are effectively destroyed at a temperature of about 70°C.

In addition to factors mentioned earlier, crucial for the impact is the enzyme activity value (Loehlein-Volhard Unit, LVU) expressed as the number of enzyme units in 1 g of bating agent where one enzyme unit has the capacity to digest 1.725 mg of casein.

In practice, the rating of bating agents is from 500-1000 LVU (weak, for technical and harness leather), 1000-1500 LVU (medium strong, for most types of leather) and 1500-2000 LVU (strong, glove and clothing leather). For dosing, normally 0.5 – 2.5%, concentration in the float is actually more important than the amount of enzyme calculated on the weight of hides.

Potential inhibitors of bating enzymes activities can be biocides, surfactants, salt and excess deliming salts.

The thumb print and blow test are a tanner’s traditional tools for the evaluation of the bating effect.

The environmental impact of bating is not significant. However, in addition to BOD and COD in effluent, there can be hydrogen sulphide and ammonium gas emissions from residues from the deliming process and TDS load from non-active components of the commercial bating agent.

10. OPERATIONS IN THE TANYARD

10.1. GENERAL

Tanning is a process that transforms hides and skins into a usable material namely leather. Depending on the tanning chemical(s) used that bind to collagen, leather has excellent or at least better resistance to microbiological degradation and heat, keeps the shape and dries easily

Tanning with basified chrome salts (chrome tannage) presently utilized in 80-90% of leather produced worldwide is very fast and reproducible; it lends flexibility, high tensile and tear strength, good heat resistance (for shoe upper leather more than 100 °C), good vapour and air permeability, dyeing properties and general versatility that cannot be matched by any other tanning agent.

Table 21. Overview of the main tanning systems

Type of tannage	Tanning agent used	Auxiliaries used
Chrome tannage	Basic sulphate complex of trivalent chromium	Salt, basifying agents (magnesium oxide, sodium carbonate or sodium bicarbonate), fungicides, masking, agents (e.g. formic acid, sodium diphtalate, oxalic acid, sodium sulphite), fatliquors, syntans, resins, etc.
Other mineral tannages	Aluminium, zirconium and titanium salts	Masking agents (1), basifying agents, fatliquors, salts, synthans, resins, etc.
Vegetable tannage	Polyphenolic compounds leached from vegetable material (e.g. quebracho, mimosa, oak)	Pretanning agents, bleaching and sequestering agents, fatliquors, formic acid, syntans, resins, etc.
Synthetic tannage (resin-syntans)	Sulphonated products of phenol, cresol, naphtalene, cresylics, polyacrylates, melamine resins etc.	Fixing agents, either acid or alkali, fatliquors
Aldehyde tannage	Glutaraldehyde and modified aldehydes	Alkali, bleaching agents, tanning agent carrier
Oil tannage	Cod oil and marine oils	Catalysts such as manganese, copper or chromium. Sodium bicarbonate or other alkali, aldehydes, emulsifiers

(1) The auxiliary used varies depending on the mineral used and the type of cross-link with collagen

Source: BREF 2013

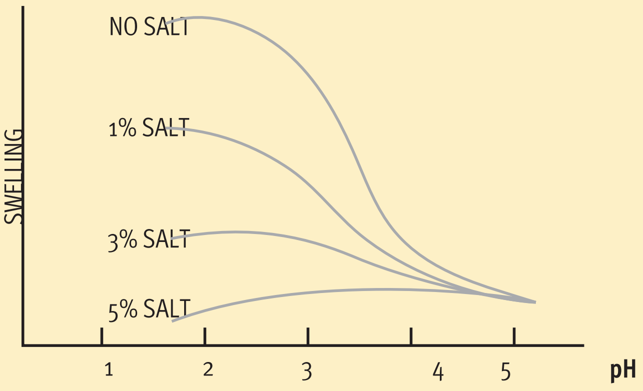
10.2. THE MAIN FEATURES OF THE CHROME TANNING PROCESS[16]

10.2.1. *Pickling, tanning, basification*

The conventional chrome tanning consists of three main steps: pickling, tanning and basification that used to be considered and carried out separately whereas nowadays they overlap more often than not. Sammying, draining and, later on, other operations in wet-finishing like splitting and shaving are also important for the overall chrome management.

Pickling is the preparation of pelt for tanning itself by acidification in saline solution. Under standard conditions this is achieved by the combination of sulphuric and formic acid (1.0 - 1.8%) or of sulphuric acid and sodium formate and not less than 5% in practice 6-7% on pelt weight of sodium chloride, NaCl to prevent acid swelling of the collagen[17]. If deliming is not quite complete, some hydrogen sulphide gas may be released into the air. Adding hydrogen peroxide or sodium metabisulphite to the float can prevent these emissions. Factors to consider are the type of acid and its penetration, the choice of (neutral) salt and its concentration, the float and hide's

Figure 38. The swelling of collagen in relation to % of salt



Source: Practical Leather Technology, World Leather

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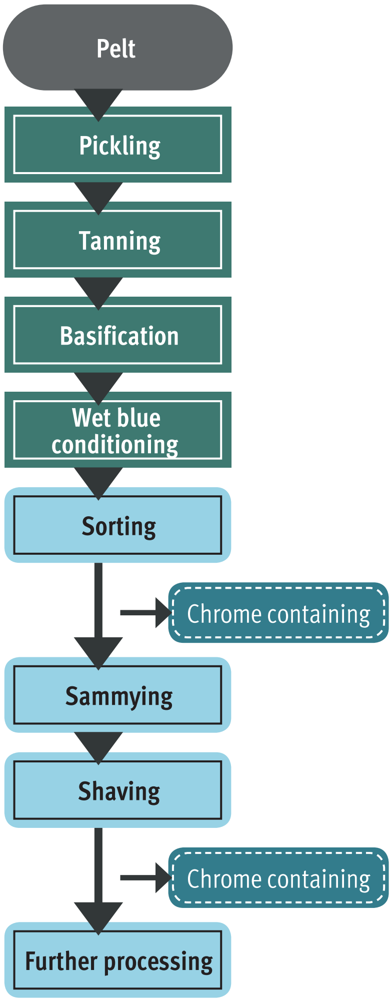
[16] *For more detailed review of the process and computations of chrome balance see UNIDO papers* ***Chrome balance in leather processing and Chrome management in the tanyard.***

[17] *It should not be overlooked that NaCl has a hydrotropic effect on pelts especially below the iso-electric point (pH 5.5) and that makes the hides softer; also, its hygroscopic effect helps to keep the moisture level under control (e.g. in wet blue leather.*

Figure 39. Flow chart of the main steps in the tanyard



Source: Based on BASF Pocket Book for the Leather Technologist, 4th edition

cross-section pH and temperature.

Good draining and rinsing followed by "horsing" for better stabilization and fixation of the tan are very important for better chrome uptake. For example, a lower pH supports chrome penetration and even distribution whereas the type and salt concentration influence the swelling control; incidentally, a higher concentration of chlorides in the pickle contributes to the opening of fibers and softer skin better than sulphates.

In the case when skins are to be stored and/or transported for a longer time, about 0.2% of commercial fungicides such as TCMBT or p-chlorometacresol are also added. A short float (40 – 60% float) is recommended; the time needed to bring the pH to 2.8 - 3.0 is about 1-2 hours.

10.2.2. *Recycling of pickle floats*

Most commercial chrome tanning products are supplied and used in powder form. They contain about 25% Cr_2O_3 of 33% basicity – the chrome offer in the conventional process is usually 8-12% of the chrome salt corresponding to about 2.0 - 3.0% Cr_2O_3 on pelt weight. Under standard conditions, 60 - 80% float is used. Some surfactant auxiliaries may be added to improve the dispersion and penetration.

Basification – gradually raising chrome basicity from 33% to 66% – increases the reactivity of chrome complexes and neutralises pickling acids. The commonly used basification agent is sodium hydrogen carbonate ($NaHCO_3$) in the amount of 0.8 - 1.2% on pelt weight added in several portions until the final pH 3.8 - 4.2 in the float is reached. Due to its low solubility and reactivity some tanners prefer magnesium oxide (MgO) as a self-basifying agent, dosage being 0.6 - 0.8%; alternatively, they use chrome tannins containing a self-basifying component so that there is no need to add the basification agent separately. The temperature at the end of tanning and basification operations lasting at least 6 - 8 hours should be 35 - 40°C. After drumming, the leather is unloaded, drained and sammed.

Conventional chrome tanning is a rather simple, low risk process; deficiencies such as poor penetration and fixation, inadequate shrinkage temperature, and stains are easily avoidable.

Table 22. The main controls of chrome tanning

Process conditions	Float length, Cr concentration, pH, temperature, time, mechanical action
Process control checks	Liquor density (Baumé) and pH, pH of the hide , Cr penetration, temperature (especially during basification), chrome content and shrinkage temperature
Common problems	Inadequate Cr penetration, poor fixation, shrinkage temperature too low, raw streaks
Post tanning aspects	Use of fatliquors and fungicides, ageing, sammying

10.2.3. *Emissions*

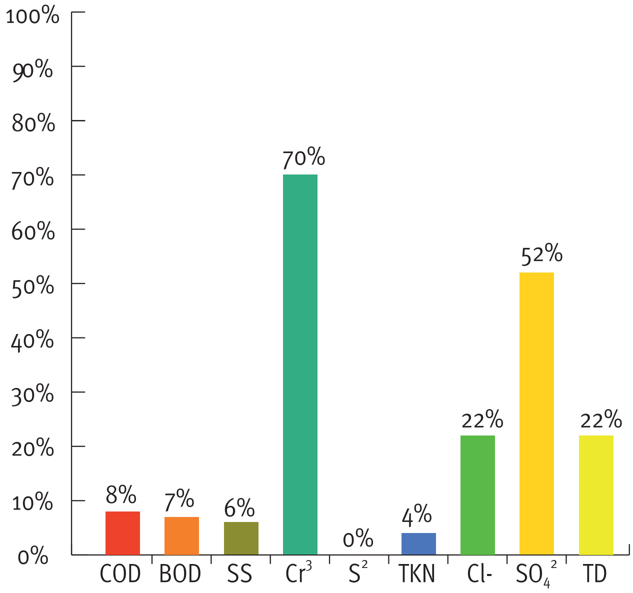
The main focus is on waste chrome which is contained in:

Liquid waste:	**Spent floats from tanning and re-tanning, wet finishing (leaching!) as well as waste from sammying and draining.**
Sludge:	**Dewatered slurry resulting from sedimentation of suspended solids during primary (physico-chemical) effluent treatment.**
Tanned (solid) waste:	**Shavings, buffing dust and unusable (mostly wet blue) split, as well as crust and finished leather trimmings.**
Other:	**A mixture of salts, natural grease, traces of fungicides, residues of auxiliary agents**

Limits on total chrome discharge in effluent vary widely between 0.05 and 10 mg/l for discharges into water bodies (direct discharge) and 1-50 mg/l for discharges into sewage systems (indirect discharge), the prevailing limit being 2 mg/l. Due to strict environmental regulations, disposal of chrome-containing solid wastes in some countries may pose a significant disposal problem.

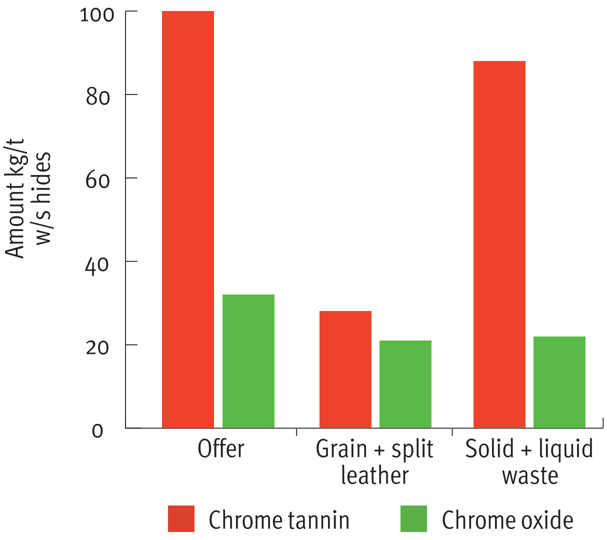
The balance is based on a general application of chrome tannin containing 25% Cr_2O_3 and neutral salts. It is calculated for the use of: (a) 2% Cr_2O_3 on pelt weight for tanning; and (b) 1.2% Cr_2O_3 on shaved weight for re-tanning. In these models, it is also assumed that chrome reacts with pelt collagen in the form of basic chrome sulphate.

Figure 40. The share of the tanning department in total emissions



Based on chart by M. Bosnić

Figure 41. Chrome balance in leather manufacturing



Based on source: Mass balance, J. Buljan et al., UNIDO

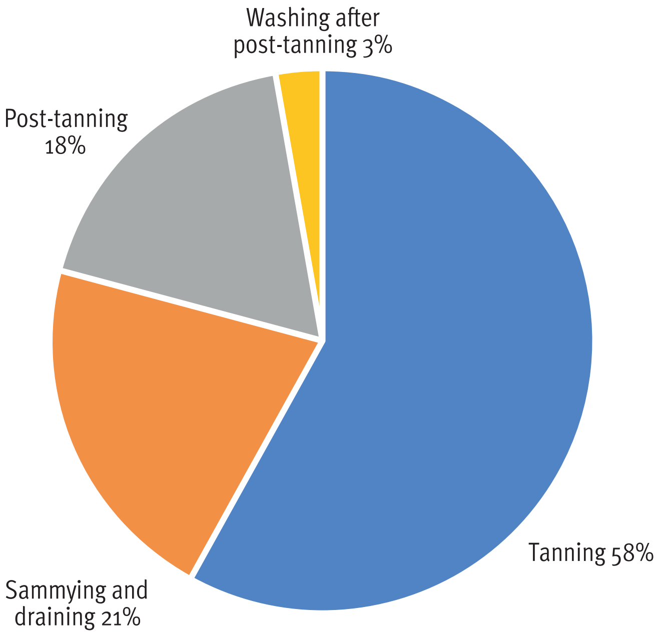
One example of the amount of chrome discharged in effluent from individual operations under standard technological conditions is shown in the following table.

Table 23. Chrome discharged in effluent from individual operations

Operation	Cr_2O_3 kg/t w.s. hides
Offer	**21**
Discharge	
Spent tanning float	4.1
Sammying and draining floats	1.5
Post-tanning floats	1.3
Washing float after post-tanning	0.2
Total discharge	**7.1**
Utilization %	**66**

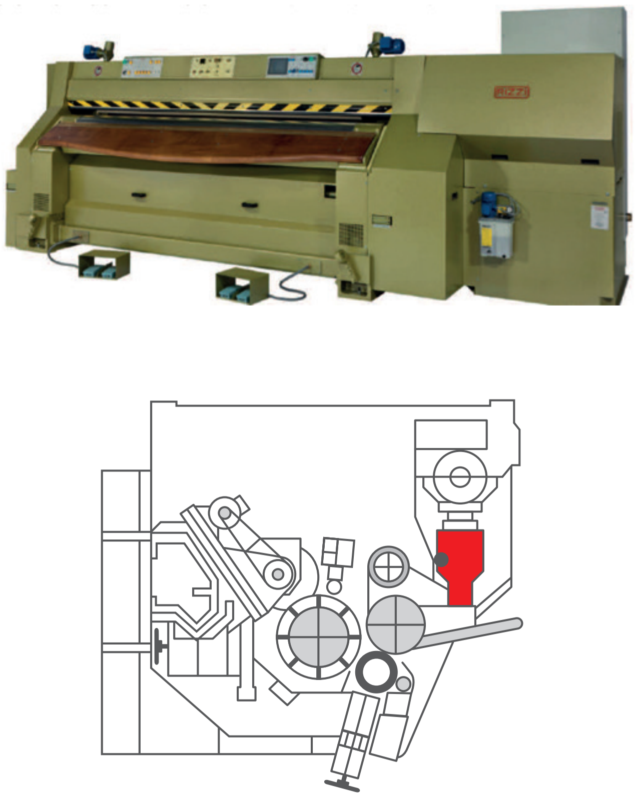
In general, chrome uptake under typical technological conditions is 60 - 80% of the offer. The share of chrome oxide discharged in effluent from individual operations is illustrated in the next Figure.

Figure 42. Share of Cr_2O_3 discharged in effluent from individual operations, under standard technological conditions in %



While the main portion of the chrome in effluent comes from the tanning float, significant amounts are discharged from sammying and re-tanning. Thus, chrome management has to consider all operations in the tanyard and the wet finishing department; maximising chrome uptake should be the first priority in any chrome management improvement project.

Figure 43. Shaving machine with cross-section schematic view



Source: Rizzi

10.3. BETTER CHROME TANNING

10.3.1. Pickling

The main goal of better pickling is to significantly reduce or entirely avoid the salt (sodium chloride) used to prevent acid swelling and thus reduce the overall Total Dissolved Solids (TDS) load of tannery effluents having such a negative impact on ultimate water recipients.

Various low- and salt-free pickling systems have been proposed and tested such as use of non-swelling polymeric sulphonic acids, partial substitution of chloride by using e.g. aromatic sulphonic acids, etc., but to date they have not been widely accepted by the industry. It seems that the main reasons for this are neither higher costs nor higher COD, but their perceived impact on chrome tanning and dyeing and ultimately leather characteristics. Thus, recycling of pickling floats in combination with recycling of tanning floats for the time being remains the best option.[18]

10.3.2. Tanning

To improve the efficiency of the chrome tanning process, it is essential to increase the chrome uptake and thus reduce the chrome concentration and the total amount of chrome in residual, spent floats. In principle, there are two basic approaches to achieve this goal, both of them with certain variations and advantages and limitations:

- Optimisation of the parameters of the conventional process
- Modifying the tanning process (conventionally called high exhaustion systems)

A combination of the optimisation of process parameters and modifications of the tanning process constitutes the basis for a modern, environment friendly high-exhaustion chrome tanning process, but for better understanding they will (firstly) be reviewed separately. Obviously, the lower chrome input also results in lower discharge of dissolved solids (TDS) in mixed effluent.

10.3.2.1. Optimisation of the parameters of the conventional process

Here a tanner significantly improves the chromium uptake without introducing any new chemicals. The main parameters that affect process efficiency and should be optimised are:

- mechanical action
- offer and concentration of the chrome tanning agent
- pH
- temperature
- reaction time

Thorough liming also contributes to better chrome uptake whereas splitting after liming improves the chrome penetration and reduces the consumption of chemicals.

Mechanical action

Drum dimensions and rotation speed are essential to ensure intensive agitation required to achieve good chrome penetration and completion of the tanning process within a reasonable/desirable time. At the same time, as with pickling, drum motors and transmission systems must be able to cope with very short floats.

Offer and concentration of the chrome tanning agent

Evidently, the higher the chrome concentration in the float, the faster the chrome penetrates into the fibre structure and the faster the reaction between collagen and chrome. For safety and quality, tanners traditionally tended to use more chrome powder than theoretically needed; this attitude is in direct conflict with the need to improve the exhaustion rate (better with the lower chrome offer).

With an offer of about 2% Cr_2O_3, a shrinkage temperature of 110°C can be achieved but the efficiency – exhaustion rate is only 65%. For a shrinkage temperature of 100°C, an offer of only about 1% Cr_2O_3 suffices and the efficiency is evenis up to 80%. However, not to risk inadequate boil fastness and an uneven cross-sectional distribution, a chrome offer of less than 1.7% Cr_2O_3 is not practiced.

Leather tanned with an offer of about 2% Cr_2O_3 contains 4 - 5% Cr_2O_3. In practice, a chrome content of about 3.5% Cr_2O_3 is needed in order to achieve a shrinkage temperature of 100°C.

Reaction time, pH and temperature

Under constant conditions, the longer the tanning time, the higher the chrome content in leather while its shrinkage temperature increases. Better chrome uptake, increased chrome content in leather and higher shrinkage temperature can also be achieved using a higher pH because it results in higher astringency of chrome complex species.

Increasing either the temperature or the pH of chrome tannage increases chrome fixation and the higher chrome content raises the shrinkage temperature. However, it should be remembered that the temperature increase primarily governs chrome fixation whereas a pH increase primarily governs the rise in shrinkage temperature.

The relationship between chrome uptake and shrinkage temperature also depends on the pace of temperature and pH rise during tannage:

- The earlier the heating is started, the higher the chrome uptake; however, the initial temperature must be below 30°C.
- The heating pace has little or no effect on the shrinkage temperature.
- The pace of basification has little or no effect on the chrome uptake.
- Early basification is likely to yield a lower shrinkage temperature, but late basification will have neither a positive nor a negative effect on shrinkage temperature.
- Slow, regular increments in pH during basification result in the

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[18] *There are claims that use of some weak acids and their salts in pickling, in addition to avoiding sulphuric acid, also results in lower water consumption, less salt in effluent, no need of extra cooling of pickle bath, better tear resistance etc.*

maximum shrinkage temperature.

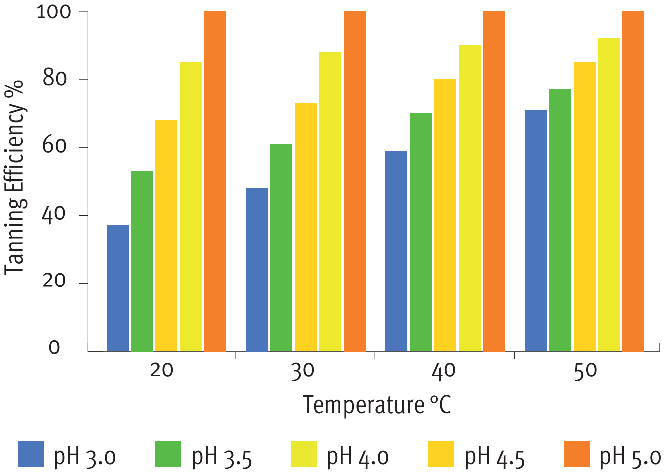
Furthermore,

- Better chrome uptake and reduced chrome concentration in effluent can be achieved by finishing the tanning at the highest possible pH and temperature. End values of up to 40 - 45°C (even 50°C has been reported!) and pH 4.0 - 4.2 are advantageous.
- It is recommended to use a low chrome offer combined with high chrome concentration in the float and extend the tanning time as long as possible at high(er) drum speeds. A chrome offer lower than 1.7 % Cr_2O_3 is not recommended for commercial applications.

Figure 44. Parameters to be optimised in the chrome tanning process

Reduce	Increase
Chrome offer	Mechanical action
The pace of pH change	Temperature
The pace of temperature change	pH
	Reaction time

Figure 45. Effect of the final pH and temperature (°C) on tanning efficiency in % of chrome offer fixed on collagen



In any case, efficient tanning, without imparting leather quality, requires the skill of balancing, i.e. supporting the reaction between the chrome complex and collagen and avoiding chrome precipitation.

10.3.2.2. Modification of the tanning process - High exhaustion

Here again, to improve chrome uptake and reduce chrome concentration in effluent there are basically two approaches:

- Masking of the chrome tanning complex
- Increasing collagen reactivity

Chrome utilisation in a high-exhaustion tanning process goes up to 98%, a dramatic increase in comparison with conventional tanning (about 65%). As a (very desirable) corollary there is also a significantly lower level of chrome concentration in residual floats; also, in a high-exhaustion tanning procedure, chrome leaching at later stages is minimal. Leathers from both conventional tanning with a chrome offer of 1.9% Cr_2O_3 and high-exhaustion tanning with a chrome offer of 1.3 % Cr_2O_3 contain approximately the same amount of chrome - in the range of 4.0 - 4.5 % Cr_2O_3.

Masking of the chrome tanning complex

Masking is the incorporation of certain reactive groups (ligands) into chrome tannin complexes with the aim to reduce their affinity to collagen and enhance the chrome penetration rate to permit basification to a higher pH value without risking precipitation of chrome complexes. It also gives a smoother grain.

There is a wide range of readily usable masking tanning auxiliaries available on the market. They can be of a rather different nature: formate, acetate, oxalate, dicarboxylic acids (short- and long-chain), aliphatic dicarboxylates, low molecular weight polyacrylates and syntans, etc; and with specific properties and performances. They may be applied at the start of the tanning process or even form a part of the basification system. The amount of the masking agent can vary from 0.5 to 1.0%.

Excessive masking has some negative effects such as slower polymerisation of chrome complexes and too low afinity and bonding to collagen. Too high a temperature may result in an uneven and drawn grain.

More recently (e.g. BREF, 2013) it has been reported that strong masking makes chrome precipitation difficult and that if an aromatic dicarboxylic acid like phthalic acid is used, complete precipitation is not possible. There are also doubts about whether high exhaustion based on such masking agents can be considered a cleaner method at all.

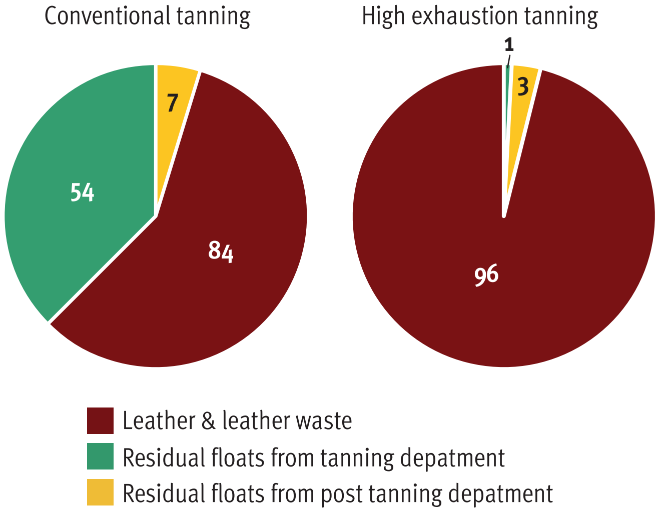
Increasing collagen reactivity

Higher collagen reactivity is usually achieved by increasing the number of carboxyl groups on the amino acid side chains of the collagen so as to provide more sites for crosslinking. Glyoxylic acid and commercially available tanning auxiliaries based on glyoxylic acid are being used. Dosing to the pickling float is often practiced.

Fixing the chrome with special polymer acrylate, chrome concentration in residual floats is around 10 mg/l while it ranges between 200 - 500 mg/l when a conventional post-tanning procedure is applied; the chrome discharge from post-tanning operations in effluent is reduced to less than 0.4 kg Cr/t w/s hide:

With high exhaustion the discharge is only 4% of the chrome offer i.e. nearly one tenth of that in conventional tanning. Ultimately, the chrome offer can be reduced by 35% and the amount of residual chrome of only 0.4 kg Cr/t w.s. hide or only 13 mg/l in mixed waste water streams at the water consumption level of 30 m^3/t w.s. hide.

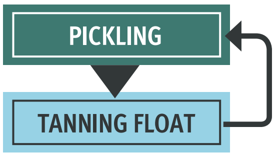
Figure 46. Comparison of chrome distribution



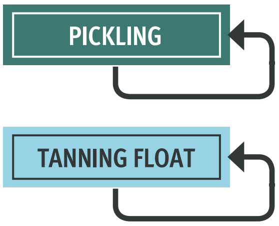
10.3.2.3. *Direct chrome recycling*

Recycling spent floats directly from chrome tanning back into processing is the simplest means of reusing chrome. There are many, many variations of recycling practiced to suit local conditions such as space/infrastructure available, type and quality of leather produced, costs of chemicals, labour and, in particular, chrome discharge limits. Here are some examples:

Recycling of spent tanning float to pickling

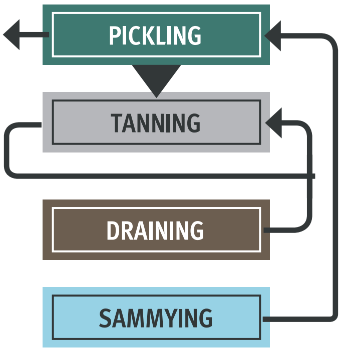

PICKLING
TANNING FLOAT

Separate recycling of spent pickling and tanning floats


PICKLING
TANNING FLOAT

Another option: Spent tanning float plus draining water is recycled in the following tanning run. Waste water from sammying is recycled in the following pickling run and discharged each day.

Separate recycling of spent tanning floats and sammying water


PICKLING
TANNING
DRAINING
SAMMYING

In all cases it is important to remove leather fibre and other undissolved impurities by filtering the recycled floats, which is why all of them require installation of storage tanks, pumps and filters.

The build-up of neutral salts normally stabilizes after five cycles; there are no indications of the accumulation of less reactive or inactive chrome complexes. However, in direct chrome recycling balancing the float volumes might be a problem because the float volume required in the pickle is lower than the total volume of spent tanning float, draining and sammying effluent. It is often overlooked that usually the discharge of the spent float after deliming and bating is incomplete and that the water content in pelt is higher (70%) than that in wet blue (55%). Furthermore, adding pickle acids and basifying agents also increases the volume of recycled spent floats. This excess float must be discharged with other effluents or, much better, used in re-tanning or taken for chrome recovery by precipitation.

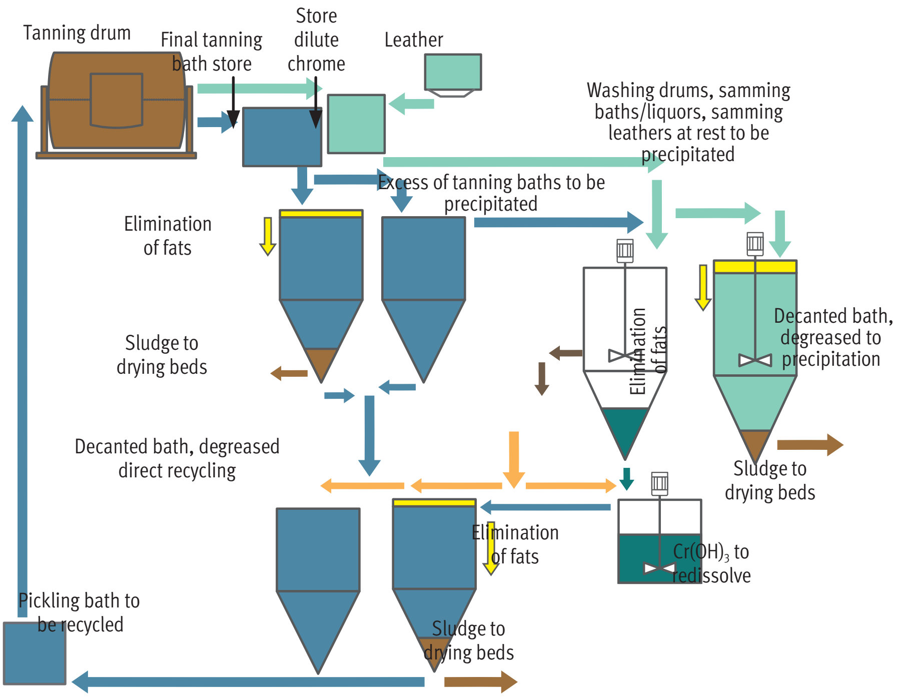
Table 24. Overview of direct chrome recycling

Advantages	Disadvantages
• Significant reduction of Cr in waste streams • TDS reduction • Simplest form of reuse, low capital cost • No additional chemicals needed, low running costs • Can be operated indefinitely • Leather quality not affected	• Build up of chrome liquor volume • Some changes of tanning process are needed • Requires very high level of process control • Tanned leather is darker

Recycling efficiency depends primarily on the completeness of float collection, the rate of float excess to be discharged and the recycling technique used. An efficiency of 90% following the conventional chrome tanning is easily attainable; with a good collection system and more sophisticated recycling techniques 95 - 98% efficiency is possible. This results in a decrease of chrome load in effluent to 0.30 - 0.75 kg Cr/t w.s. hides and a chrome concentration in mixed waste water streams in the range of 10 - 25 mg Cr/l for water consumption at 30 m^3/t hides.

A practical case of a comprehensive direct recycling system in a South American tannery is shown in the next flow-chart.

Figure 47. A practical example of direct chrome recycling system


Tanning drum
Final tanning bath store
Store dilute chrome
Leather
Washing drums, samming baths/liquors, samming leathers at rest to be precipitated
Excess of tanning baths to be precipitated
Elimination of fats
Sludge to drying beds
Elimination of fats
Decanted bath, degreased to precipitation
Decanted bath, degreased direct recycling
Sludge to drying beds
Elimination of fats
Cr(OH)3 to redissolve
Pickling bath to be recycled
Sludge to drying beds

Based on source: J. M. Salazar, Recycling chrome liquors. Leather International, Nov/Dec, 2008

Producers of high quality leathers in Europe tend to prefer high exhaustion over direct recycling claiming that there is a certain change in colour of tanned leather (wet blue) that affects the subsequent drum dyeing (especially in pale colours) and that the content of impurities (proteins, grease) increases. They also believe that the economies are in favour of the high exhaustion method.

10.3.2.4. Chrome recovery and reuse

An indirect method of chrome recycling is chrome recovery from spent tanning floats by precipitation, re-dissolution with acid and subsequent (re)use thereby avoiding an increase in float volume. Also, if the recovered chrome contains too many impurities, it can simply be dumped. Any alkali precipitates chrome salts; however, the stronger the alkali, the faster the rate of reaction and the slower the rate of coagulation.

Rapid: Precipitation with sodium hydroxide or sodium carbonate, polyelectrolyte for enhancing coagulation/flocculation followed by thickening and dewatering (of the voluminous sludge) by filtration and ultimately re-dissolution with sulphuric acid. Such chrome recovery systems can be installed in (three) phases, from a very basic to a complete one producing chrome liquor of high quality.

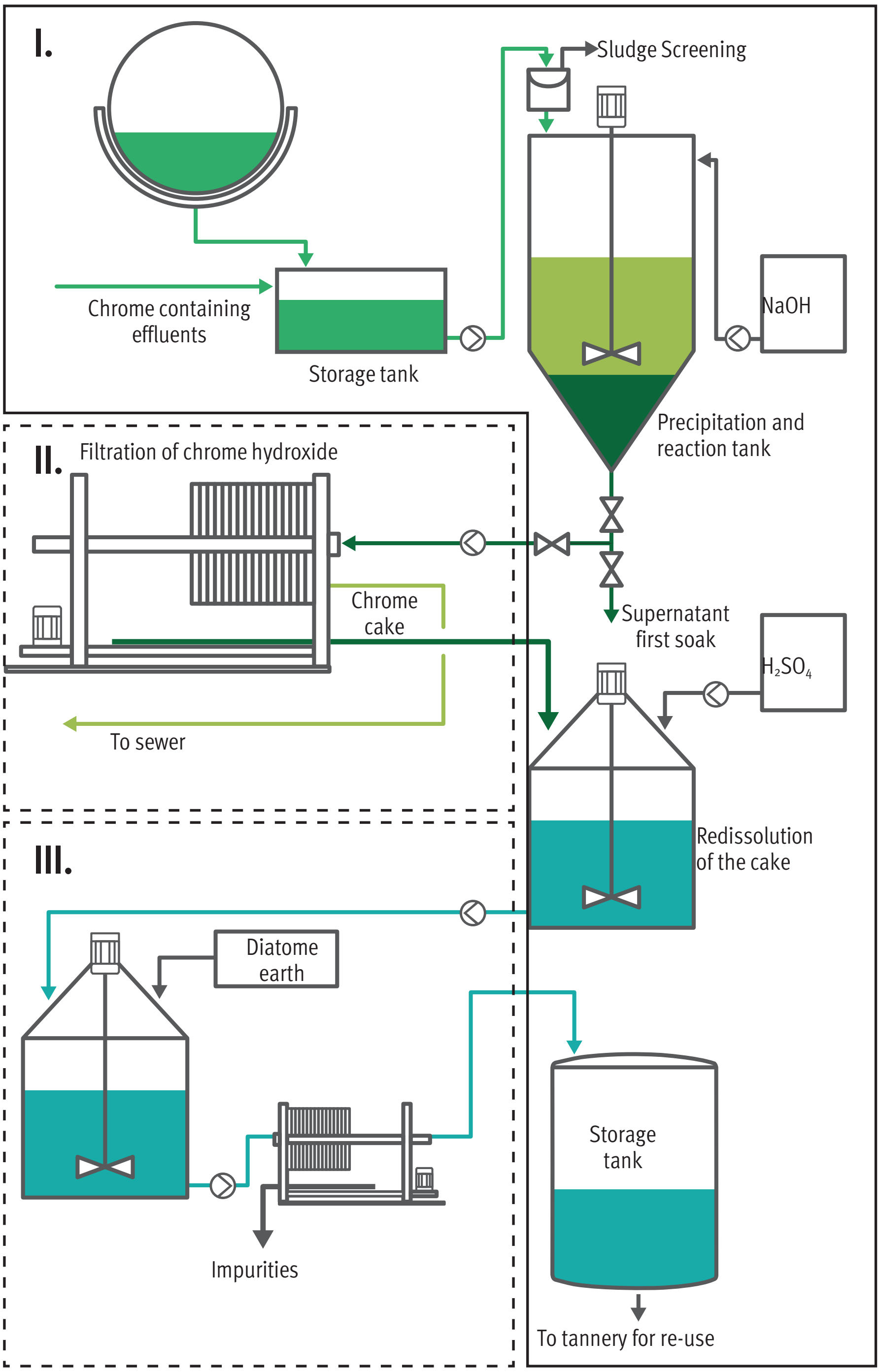
For very small tanneries and/or testing purposes, a good solution can be a mobile, platform mounted chrome recovery unit.

Slow: Precipitation with magnesium oxide, suspension settling, decantation of the supernatant and subsequent acidification of the relatively dense precipitate. This is a great advantage in that there is no need for filtration, but purity and low solubility of MgO can be an issue.

Some important points to be observed during the process:

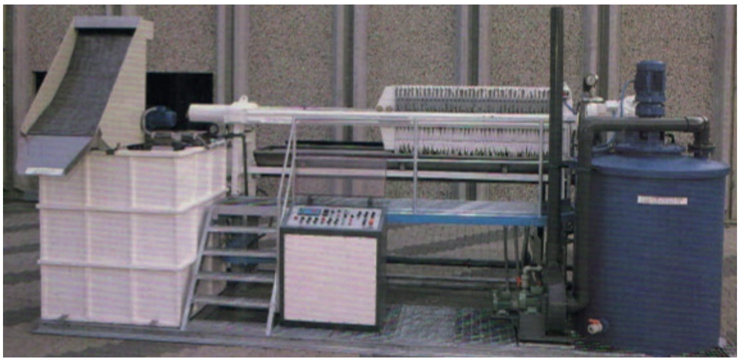
- Good screening and fat removal by skimming
- Exact dosing of alkali
- The size and structure of MgO particles, continuous stirring of the slurry
- The optimum pH range is 8.5 - 9.0; the pH value should not exceed 10.0 because chromium hydroxide starts redissolving. However, in case of floats from high-exhaustion tanning, it is sometimes useful to raise the pH over 10.0, reducing it thereafter to 8.5- 9.0
- The right temperature for precipitation is 35 - 40°C; for high-exhaustion tanning 60 - 80°C may be needed (the greater the concentration of masking agents, the higher the temperature required).
- The chrome filter cake or slurry are dissolved by concentrated sulphuric acid added at a rate of 2 kg or more per kg chrome oxide on a continuous basis while stirring until pH 2.5 is reached.
- The cake should be redissolved as soon as possible, as it becomes less

Figure 48. Chrome recovery by precipitation with sodium hydroxide/carbonate


I.
Sludge Screening
Chrome containing effluents
Storage tank
NaOH
Precipitation and reaction tank
II.
Filtration of chrome hydroxide
Chrome cake
To sewer
Supernatant first soak
H_2SO_4
Redissolution of the cake
III.
Diatome earth
Impurities
Storage tank
To tannery for re-use

Based on chart by M. Bosnić

Figure 49. A platform mounted chrome recovery unit with a filter press



Source: Italprogetti

soluble on standing.

- After adjusting its basicity, the tanning liquor is stored ready for re-use in a separate tank. The problem of staining while using the recovered chrome is a consequence of insufficient reduction of astringency in the reused spent float or inadequate solubilisation of the chrome precipitate.

Except for high quality leathers, mixing 70% fresh with 30% recovered chrome gives satisfactory results; this ratio coincides well with 25 - 30% of the chrome offer that is actually recoverable.

Approximately 30% of the chrome offer can be reused and saved by means of a recovery technique using precipitation when conventional tanning is applied and 2.4% of the chrome offer is discharged. In the case of a high-exhaustion tanning, approximately 9% of the chrome offer can be reused and saved, while discharging is only 0.7%. The effects of the chrome recovery/reuse on decrease of chrome discharged in effluent at the typical offer level of 2.0 % Cr_2O_3 on pelt weight, i.e. 2.2 % Cr_2O_3 on w.s. weight, are shown below.

Table 25. Influence of chrome recovery/reuse upon tanning/re-tanning efficiency and amount of chrome discharged in effluent

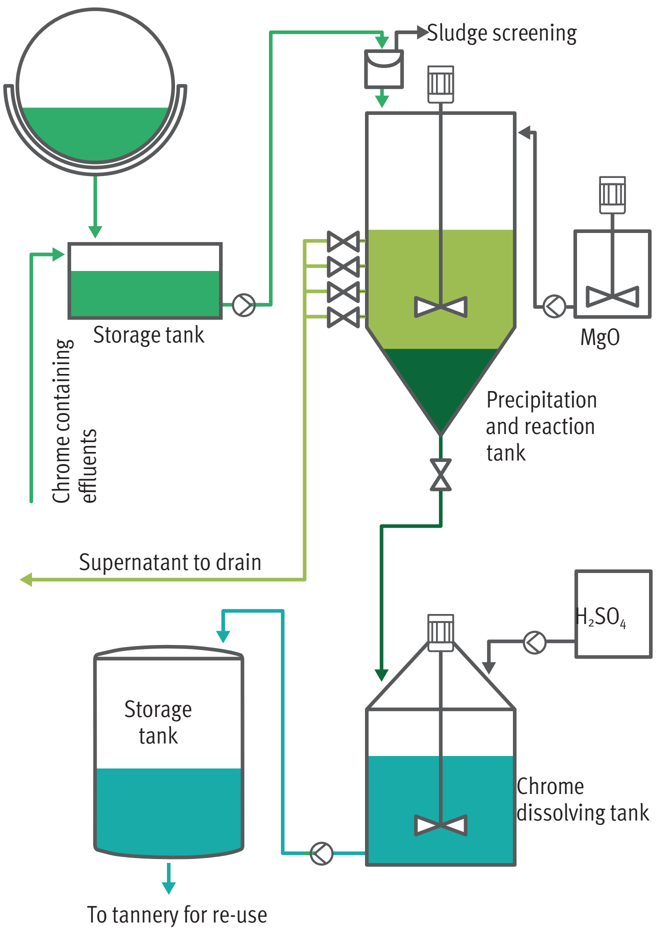
	Tanning/Retanning	
	Conventional	High-exhaustion
Efficiency %	97.6	99.2
Load discharge kg Cr/t w.s. hides	0.36	0.12
Concentration in mixed effluent, mg Cr/l at 30 m3/t w.s. hides	12	4

Correctly performed chrome recovery/reuse reduces the chrome load in effluents to 0.12 - 0.36 kg Cr/t w.s. hides, whereas the chrome concentration in the effluent ranges between 4 and 12 mg Cr/l. Chrome in unrecovered spent floats, leather fibres (buffing dust), the supernatant and/or filtrate with a chrome content of 1 - 10 mg/l are sources of the residual chrome concentration in effluent; to bring it down to 1 mg Cr/l (the norm prevailing in Europe), the residual floats from washing, neutralisation and fatliquoring must also be precipitated.

Table 26. Overview of chrome recycling by precipitation

Advantages	Disadvantages
• Significant reduction of Cr in waste streams • More similar to using fresh chrome than recycling, very little changes • No volume build up • No additional chemicals needed, low running costs • Can be operated indefinitely • Leather quality not affected	• TDS increase • Requires higher level of process control • Additional chemicals needed, higher running costs • More complex plant than for recycling, higher investment costs • Tanned leather is darker

Figure 50. Chrome recovery by precipitation with MgO



Based on chart by M. Bosnić

Recovery without reuse

For nearly full elimination from residual floats/effluent emanating from neutralisation, re-tanning, fatliquoring and dyeing, the chrome they contain has to be precipitated but due to presence of organic substances this chrome cannot be reused. For this purpose calcium hydroxide, sometimes in combination with ferric and/or aluminium salt and an organic polyelectrolyte is commonly used.

In other words, it is not easy but the amount of 0.03 kg Cr/t w.s. hides or the concentration of 1 mg Cr/l at water consumption of $30 m^3$/t w.s. hides are attainable.

10.3.3. Summary

In the traditional tanning process ultimately less than 50% of the chrome input is to be found in leather while the rest is disposed in solid/liquid waste streams. Also, normally only 60 - 80% of the chrome offer is utilised in tanning.

In practice, in addition to the optimisation of the key parameters of the conventional process there are three principal approaches to maximising chrome utilisation: high exhaustion based on the modification of the tanning process; direct recycling of tanning floats; and chrome recovery/reuse after its precipitation and re-dissolving. The main features of the key points are summarised below.

Optimisation:

Mechanical action, chrome concentration, chrome offer, pH, temperature and reaction time are the main parameters to be optimised. A chrome offer as low as 1.7% Cr_2O_3 on pelt weight is possible; short float, gradual basification and end-values up to

40 - 45°C and pH 4.0 - 4.2 are advantageous.

High exhaustion: based on modifications to the tanning process:

High exhaustion is achieved by masking the chrome tanning complexes and increasing collagen reactivity. Actually, a combination of process modifications and process parameter optimisations are the basis for modern high-exhaustion chrome tanning processes. Depending on the pelt thickness, the chrome offer can be reduced from a standard level 2.0% Cr_2O_3 to 1.3% Cr_2O_3 on pelt weight, chrome utilisation can go up to 98% without affecting the leather quality and leaching in post-tanning operations is also minimised; however, an improved drum drive system and an increased level of process control are needed. Chrome discharge can be reduced to only 0.4 kg Cr/t w.s. hides.

Direct recycling of spent floats:

Direct recycling is the simplest form of reusing chrome using several recycling techniques. Depending on the process control and sophistication level efficiencies, recycling rates between 90 and 98% can be attained. A certain constraint is a build-up of excess liquor volume.

Chrome recovery/reuse:

Chrome recovery/reuse is an indirect way of recycling chrome. The residual chrome contained in spent floats is recovered by precipitation with an alkali and separation of the suspension to be ultimately re-dissolved in acid for reuse. Dewatering filtration is needed if the alkali used is sodium hydroxide or sodium carbonate but not for magnesium oxide. However, with this method there is an increase in the TDS level in effluent.

Table 27. Advantages and limitations of high-exhaustion chrome tanning

Advantages	Limitations
• Savings in chrome used • Reduced level of chrome in waste streams • Reduced level of sulphates in waste streams • Reduced level of water consumption • High chrome fixing, leaching minimised • Sammying possible immediately after leather unloading • Flexible, applicable to any type of leather • No loss in leather quality	• Deliming should be as complete as possible • Longer running time needed • Higher temperature required • Slip agent needed to avoid abrasion of grain • Improved drum drive • Increased level of process control needed • Higher running costs

Table 28. Advantages and limitations of chrome tanning with float recycling

Advantages	Limitations
• Savings in chrome used • Reduced level of chrome in waste streams • Reduced level of neutral salts in waste streams • Reduced level of water consumption • No additional chemicals needed • Simplest form of reuse • Can be operated indefinitely • Flexible, applicable to any type of leather • No loss in leather quality	• Build up of excess liquor volume • Mechanical pretreatment of waste streams required • Some change to tanning procedures needed • Increased level of process control needed • Some differences in leather colour possible • Some capital costs needed • Slightly increased running costs

Table 29. Advantages and limitations of chrome tanning with chrome recovery/reuse

Advantages	Limitations
• Savings in chrome used • Reduced level of chrome in waste streams • Close to using fresh chrome • Minimum procedure changes in tanning • Treating all liquors • Flexible, applicable to any type of leather • Can be operated indefinitely	• Mechanical pretreatment of waste streams required • Increased discharge of neutral salts • Additional chemicals and man power required • Increased level of process control needed • More complex plant needed • Higher running costs • Higher capital costs

The choice of the chrome maximisation method depends on individual conditions in the tannery and no explicit recommendation can be given about the best option; each tannery has to devise an optimal technology for applying the chrome liquor recovered. For example, if the tanning of grain leather is carried out using a powder tanning agent, the chrome liquor recovered can be used for split tanning.

10.4. THE COMPARISON OF CHROME BALANCE:

i) Conventional tanning and/or chrome retanning: with a chrome offer of 15-17 kg Cr/t w.s. hides, 40-45% of the chrome offer remains in the leather, 26-30% in the solid waste and about 30% in effluent, while 21-24% of the chrome offer can be recovered and reused.

ii) High-exhaustion tanning and/or chrome retanning: with a chrome offer of 10-13 kg Cr/t w.s. hides, 57-60% of the chrome offer remains in the leather, 32-38% in the solid waste and 3-8% in effluent while only 1-5% of the chrome offer can be recovered and reused.

The lowest practically attainable amount of chrome in effluent lies somewhere between 0.3 - 0.4 kg Cr/t w.s. hides so that at

30 m^3/t w.s. hides, the chrome concentration ranges between 10 and 14 mg Cr/l.

Since the limit is mostly within the range of 1-4 mg Cr/l worldwide, in addition to chrome recovery it is also necessary to precipitate chrome from all waste streams from both tanning and post-tanning operations. Calcium hydroxide combined with ferric and/or aluminium salt and some organic polyelectrolyte is considered the most suitable precipitant. Only after precipitation can a concentration of about 1 mg Cr/l at 30 m^3/t w.s. hides (corresponding to an amount of 0.03 kg Cr/t w.s. hides) can be attained.

In that context the Best Available Technology – Associated Emission Levels values indicated by EU-BREF 2013 might be of interest:

Table 30. BAT-AELs for total chromium and sulphide emissions through indirect discharges of waste water from tanneries into urban waste water treatment plants

Parameter	BAT-AELs
	mg/l
Total chromium (as Cr)	< 0.3 – 1
Sulphide (as S)	< 1

10.5. WET BLUE LEATHER

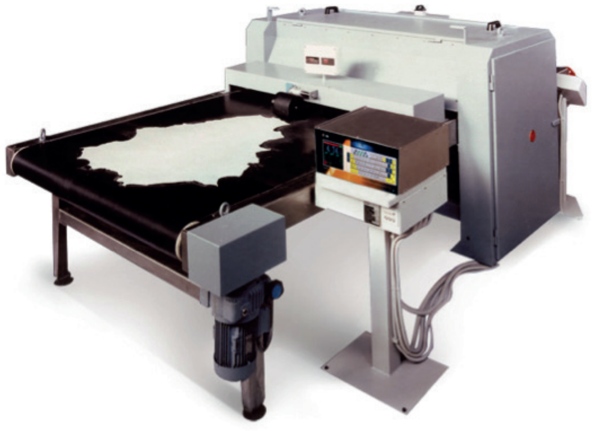
Chrome tanned leather, not neutralized and certainly in wet condition has become a well-established commodity in world trade. The key parameters (volatiles, oil & grease, ash chromium oxide, hide substance) are nearly standardized[19]. However, more and more wet blue hides are made according to detailed specifications for a particular buyer.

In addition to considerations mentioned earlier, a very important environmental/OSH aspect in the case of wet blue is the application of fungicides essential for long(er) transportation and storage.

Nowadays the main active components in wet blue fungicides are:

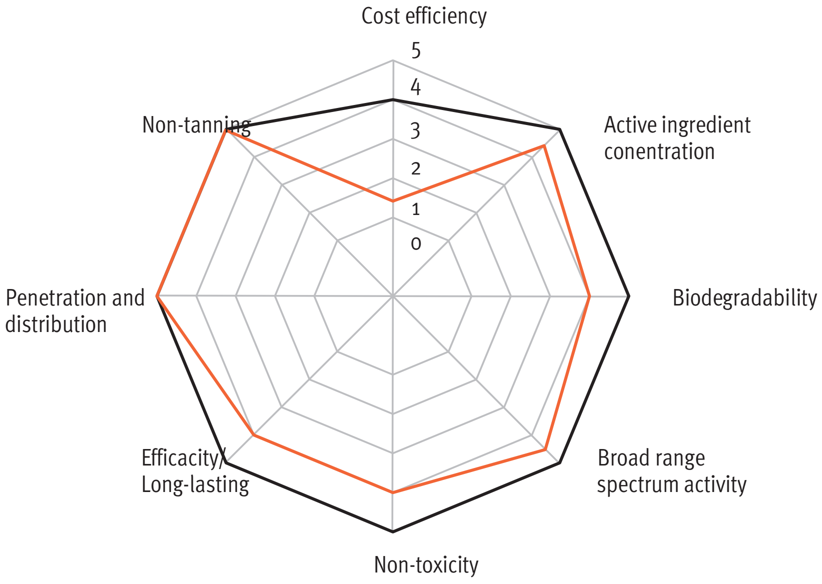
- para-chloro-meta-cresol (PCMC)
- ortho-phenylphenol (OPP)
- 2-(thiocyanomethylthio)benzothiazole (TCMTB)
- 2-n-octylisothiazolin-3-one (OITZ)
- 2-benzimidazolyl-methylcarbamate (BMC)
- 2-mercaptobenzothiazole (MBT)

Figure 51. Electronic area measuring machine for leathers at pickled or wet blue stage



Source: http://www.gerelettronica.com

Figure 52. A comparison between properties of an ideal and an existing, high quality preservation agent



Based on source: Sustainable Leather Management (SLM). C. Tysoe, H. Rehbein, Lanxess, WL April/May 2011

Tanners have to make sure that the use of fungicides conforms with national and international regulations. For example, the OPP and PCMC are used in both cosmetic and food industries and are relatively safe for humans and the environment; yet the OPP is on some Restricted Substances Lists. The TCMTB is more toxic and does not control some moulds.

Advances have been claimed in combining two or more products using eutectic technology. While the conventional products are prepared in water in emulsion or dispersion form, eutectic technology makes it possible to convert two or more products which are normally solid at room temperature to a single, stable and ultra-concentrated liquid.

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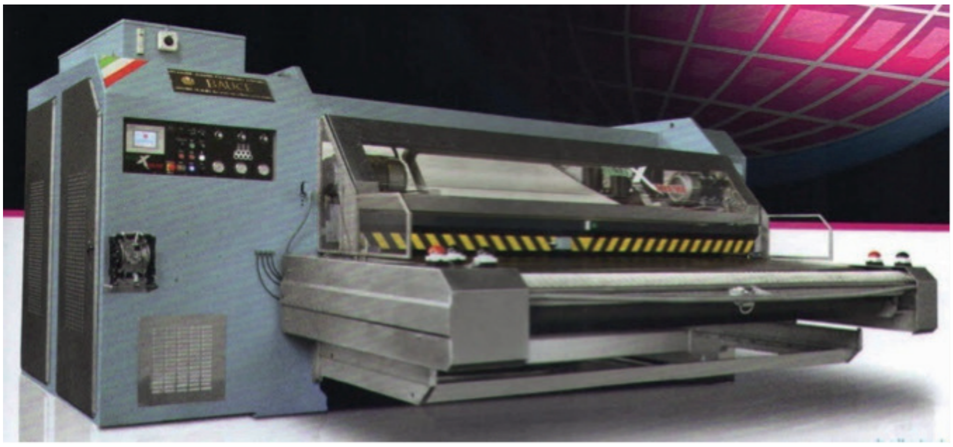
[19] *See the INTERNATIONAL CONTRACT No. 6 - HIDES & SKINS, ANNEXE C - WET-BLUE HIDES & SKINS, WET- BLUE SPLITS by the International Council of Hides, Skins & Leather Traders' Associations (ICHSLTA).*

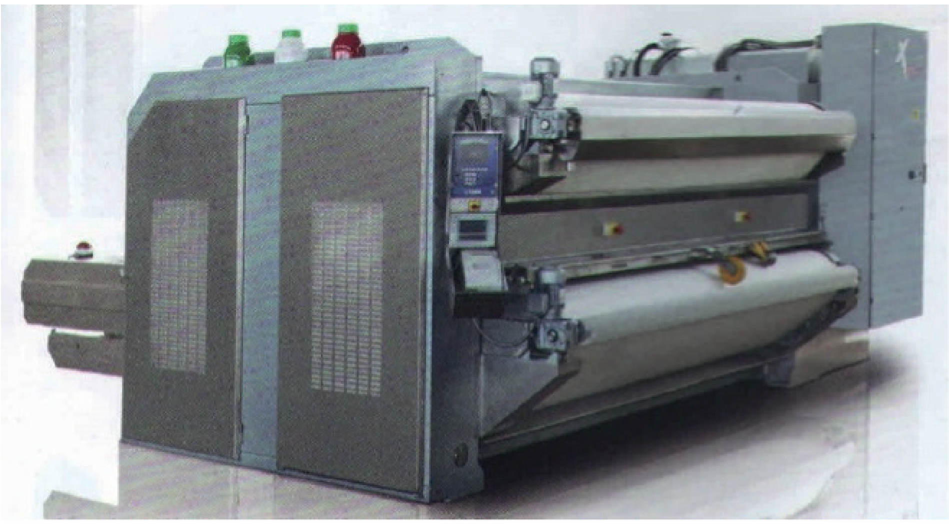
Figure 53. Wet blue sammying machine, seven cylinders, six sammying points

(Suitable for hides with hump)

Front view

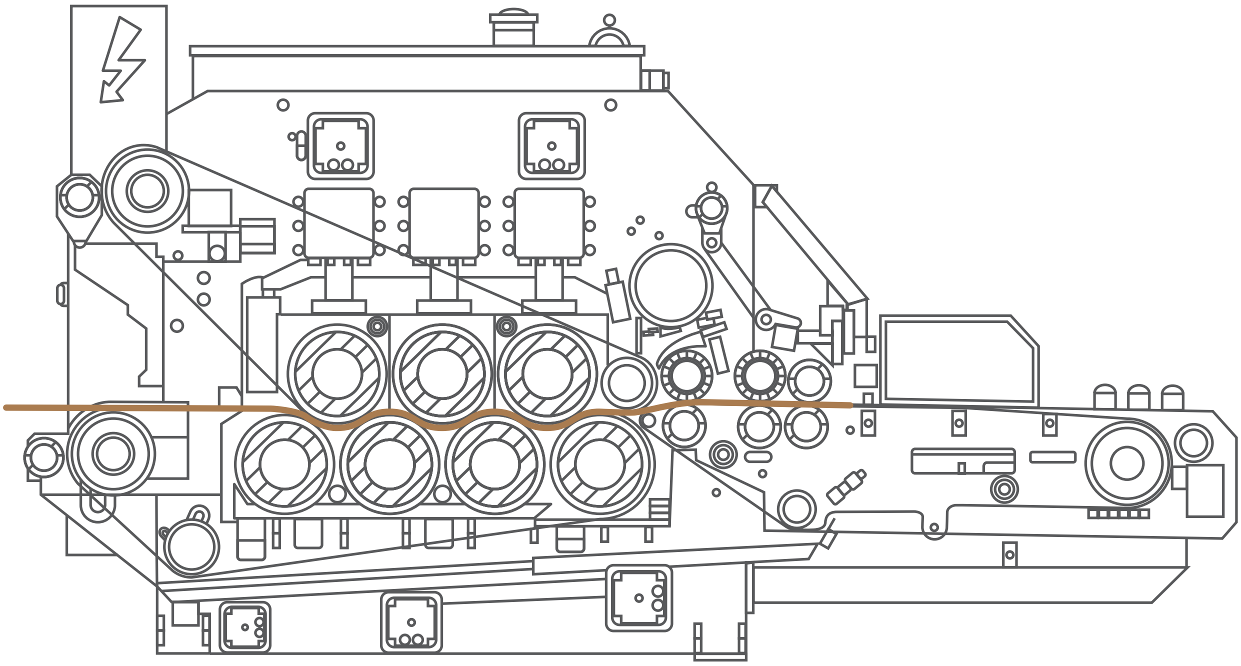


Rear view



Source: Bauce TRI.MA, World Leather Dec 2014

Cross section



Based on source: Bauce TRI.MA, World Leather Dec 2014

11. PRETANNING AND WET WHITE CONCEPT

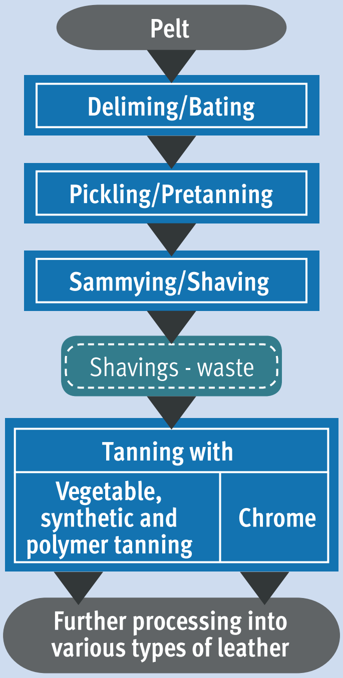
11.1. CONTEXT

The original driving force behind the wet white concept was the minimisation of the production of chrome-containing solid waste. It introduces a pretanning step with the view of making an intermediate product (shrinkage temperature normally around 80°C) with a partly stabilized structure that should permit mechanical operations, transportation and storage.

More recently the pretanning – wet white concept was largely driven by the growing demand in the automotive sector for chrome-free products to meet the requirements of the EU Directive 2000/53/EC regulating waste disposal from scrapped vehicles (End of Life Vehicles).

Many chemicals and their combinations have been proposed and used for pretanning: aluminium and titanium salts, silicon dioxide gel, polyacrylates, syntans, glutaraldehyde derivatives and other tanning agents. The bonding of aldehyde based agents is mainly on amino groups of collagen. The minimum dosage is 1.25% aluminium oxide, 1.0 – 1.5% glutaraldehyde or 0.75% titanium oxide.

Figure 54. Flow chart of pretanning and wet white tanning


Pelt
Deliming/Bating
Pickling/Pretanning
Sammying/Shaving
Shavings - waste
Tanning with
Vegetable, synthetic and polymer tanning
Chrome
Further processing into various types of leather

Source: Based on BASF Pocket Book for the Leather Technologist, 4th edition

11.2. PRETANNING WITH MODIFIED GLUTARALDEHYDE, I, TFL

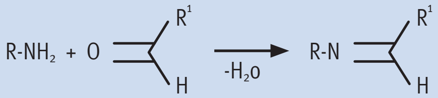
Tanning with glutaraldehyde (GA) only gained industrial relevance with the introduction of GA with moderated reactivity to collagen (modified glutaraldehyde).

The aldehyde tanning agent binds not only to amino groups in the lysine side chains of collagen, but, under tanning conditions, also with itself undergoing a so-called aldol reaction that can lead to polymerisation of monomeric GA. Eventually a very wide variety of different structures is formed.

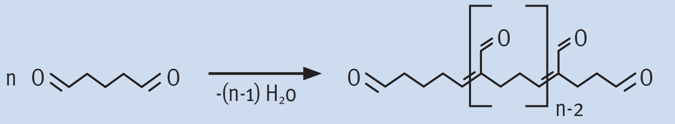
The mechanism of GA tanning, shrinkage temperature as function of offer and OSH aspects are shown in the following figures.

Figure 55. The mechanism of GA tanning, shrinkage temperature as function of offer

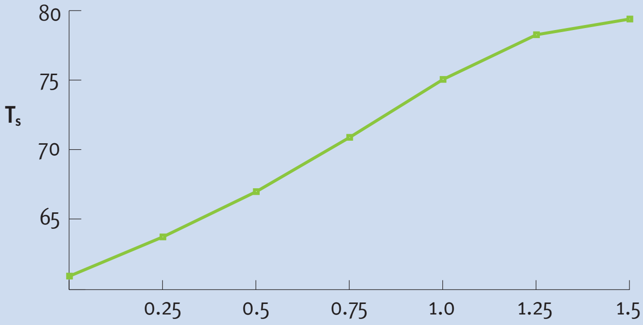
Panel 1: Reaction of aldehydes with amines to Schiff's bases



Panel 2: Aldol condensation reaction of glutaraldehyde



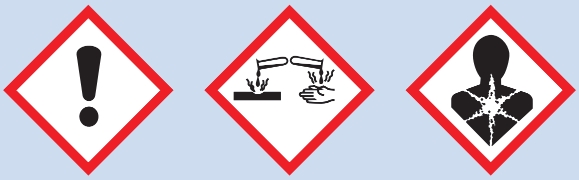
Panel 3: Shrinkage temperature T_s in °C as a function of glutaraldehyde offer



Note: The measurements were performed after basification to pH 5.0.

Industrial tanning is carried out with offer of about 3-4% of the commercial product with concentration of 20-25% corresponding to 0.75-1% glutaraldehyde. The reactivity towards collagen and the rate of aldol condensation increase when the pH is raised from pH 3.0 to pH 4.2–5.0 during basification. The formation of covalent bonds during tanning is irreversible. The typical shrinking temperature is in the range of 72-75 °C.

Panel 5: GHS labelling of a typical pre-tanning agent based on gluteraldehyde (20-25%)



- The first "irritant" pictogram is related to the harard statements H302 (Harmful if swallowed), H332 (Harmful if inhaled) and H335 (May cause respiratory irritation).
- The second "corrosive" pictogram is related to the statement H314 (Causes severe skin burns and eye damage)
- The third "health hazard" pictogram is related to H317 (May cause an allergic skin reaction) and H334 (May cause allergy or asthma symptoms or breathing difficulties if inhaled).

GA is irritant and corrosive and should be handled accordingly; however, it is not classified as a carcinogenic, mutagenic and/or reprotoxic substance. Some GA residue can be found in wet-white leather but is not detectable in crust; reportedly there is no restriction on its presence except by some ecolabels.

It appears that in EU there are some restrictions for the use of GA as a biocide but not as a tanning agent.

Finally, it is interesting to note the content of some aldehydes in some food items.

Panel 4: Natural content of aldehydes in food items

Food Item	Aldehyde contained	Concentration up to	Health rist of aldehyde
Coffee	Furfural	250 ppm	Carcinogenic (low potential)
Bread		14 ppm	
Ginger	Citral	13.500 ppm	No health risk
Lemon peel oil		130.000 ppm	
Vanilla pods	Vanillin	23.200 ppm	No health risk
Cinnamon	Cinnamaldehyde	30.000 ppm	Potentially mutagenic/ carcinogenic (data needed)
Fruit	Acetaldehyde	400 ppm	Genotoxic

NOTE: The listed health risk refers to the pure aldehyde, not the food item.

Panel 6: Occupational exposure limits for glutaraldehyde in different countries, TWA = Time-weighted average, STEL = Short term exposure limit.

Country	TWA (8h)	STEL (15min)	Ceiling
Netherlands, Belgium			0.06 ppm
UK, Austria	0.05 ppm	0.05 ppm	
Germany	0.05 ppm		0.2 ppm
France	0.1 ppm	0.2 ppm	
Russia		1.2 ppm	

Panel 8: Glutaraldehyde content during tanning process. Values based on 4% pretanning agent and 50% float (full substance hide).

Process step	Content of glutaraldehyde
Offer	16000 ppm
In the pretanning float (pH 3 / 8h)	~ 1500 ppm
After basification (pH 4.2 / 4h)	~ 800 ppm
On the wet white	Not detectable to 60 ppm
On the crust	Not detectable to 5 ppm

Source: C. Gabagnou et al., WL, December 2015/January 2016

11.3. PRETANNING WITH POLYCARBAMOYLSULFONATE (PCMS), X-TAN

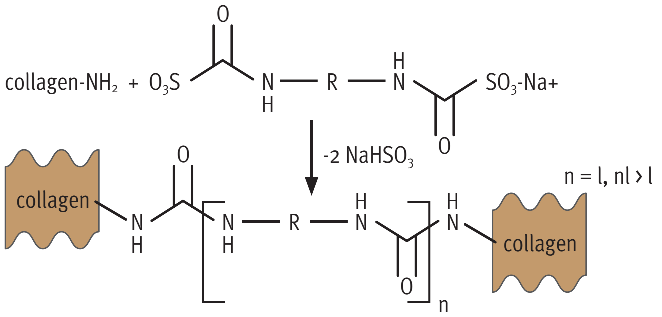
The system is vigorously promoted as metal- and aldehyde-free organic tanning under the proprietary brand name X-TAN. It is claimed that:

- It uses non-hazardous, easily degradable chemicals
- Significantly reduces the salt load in effluent
- The process can be easily modified to suit specific customer's needs
- X-TANned leathers are transport and storage stable and can easily be converted into a very wide range of products requiring good dyeability and biodegradability

The bonding mechanism and some process parameters are shown in the next figure.

Figure 56. Schematic view of the PCMS bonding mechanism

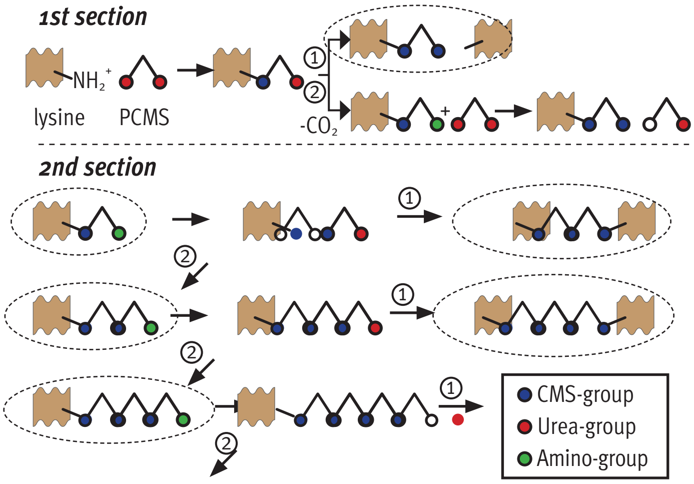
Panel 1: Simplified schematic view of the basic cross-linking reaction of X-Tan with collagen.



R = hydrocarbon residue with a divalent or a polyvalent functionality

Based on source: C. Tysoe et al. Lanxess Deutschland GmbH, World Leather Oct/Nov 2011

Panel 2: Simplified schematic view of the two possible reactions of PCMS and the chain elongation process resulting in a statistical mixture of various lengths

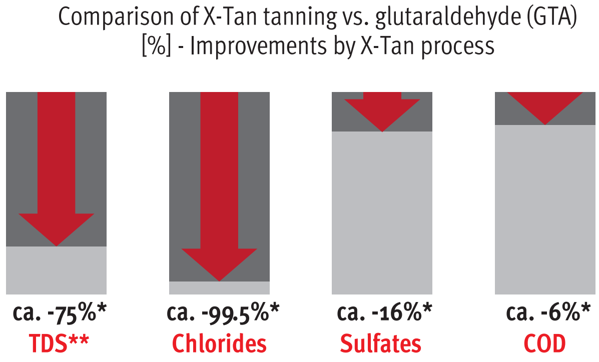


Circled structures are the most likely resulting molecules

There is no pickling, the tanning agent is added directly into the float after ammonia-free deliming and bating. No reaction occurs in the acidic-to-neutral pH range facilitating quick, full penetration. The process is triggered at pH above 8 by adding an appropriate base. Later on, further pH adjustment is required to offset the effect of sodium bisulphite formed in the reaction. A high percentage of non-cross-linked lysine groups of collagen remains free as fixation sites for syntan and dyes.

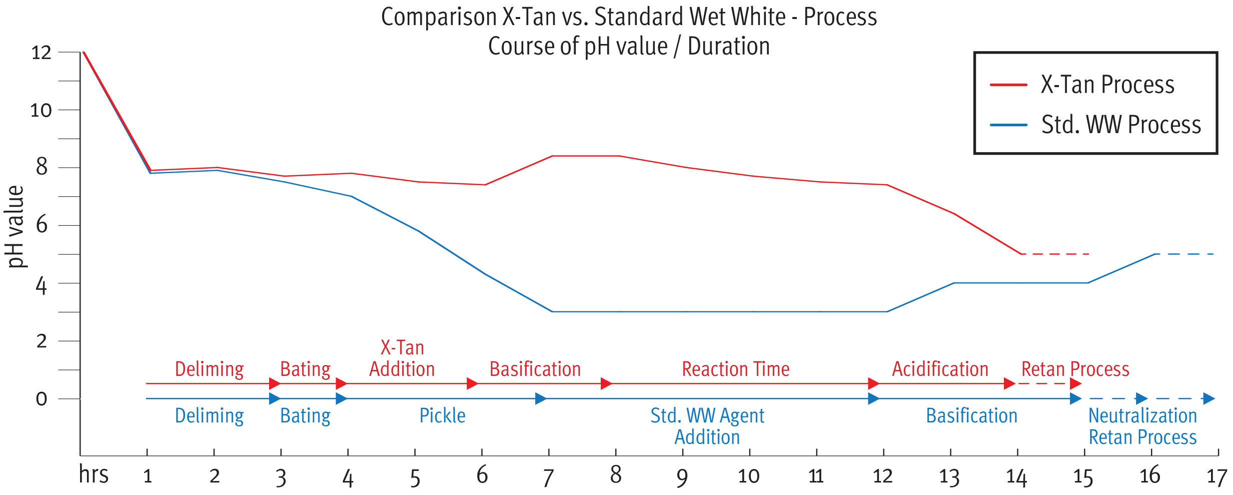
Additional advantages claimed for the intermediate product obtained are good physical properties, easy sammying and shaving (including metal-free shavings), full reaction/exhaustion of the tanning substances and their environmental friendliness, lower TDS and COD in comparison with glutaraldehyde tannage, good temperature stability, storability and re-wet ability, virtual whiteness, resistance to yellowing, uniform colours and, in particular, good tear resistance.

Panel 6: Effluent benchmark of the X-Tan process with standard GTA tannage



* Based on internal measurements
** Total Dissolved Solids

Panel 5: Schematic comparison of X-Tan vs. conventional wet white tannage process (pH vs. time)

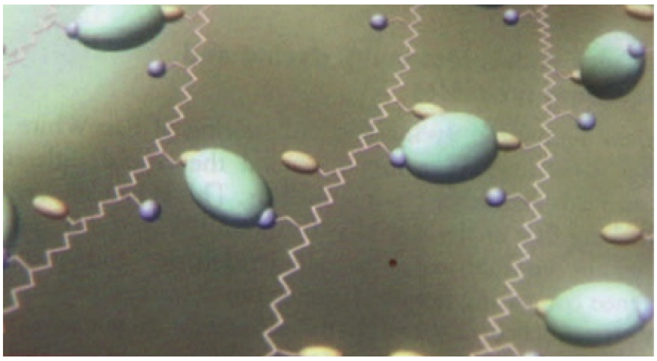


11.4. EASYWHITE TAN

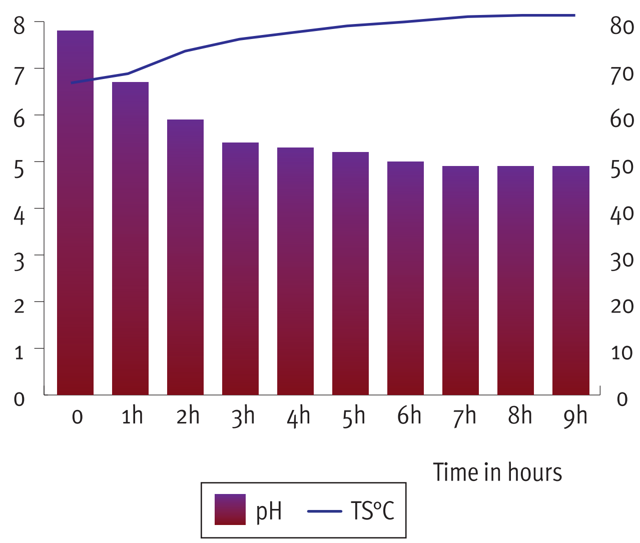
The chemicals supplier that promotes EasyWhite Tan claims that it combines the advantages of the three established tanning methods (chrome, vegetable and glutaraldehyde) albeit without their disadvantages. The tanning agent is metal- and formaldehyde and glutaraldehyde- free. Initially it was developed for automotive leathers but is reportedly also applicable for white sport shoes and water repellent leathers.

The process is apparently very simple: following conventional deliming and bating but without pickling, the tanning agent is added in one single addition to a very short float (10-30%) at pH 7-8.5 in one single addition, no other auxiliaries needed. The pH decreases steadily and continuously until the process is completed after approx. 8 hours of tanning time at pH 5.0. There is no basification or separate fixation.

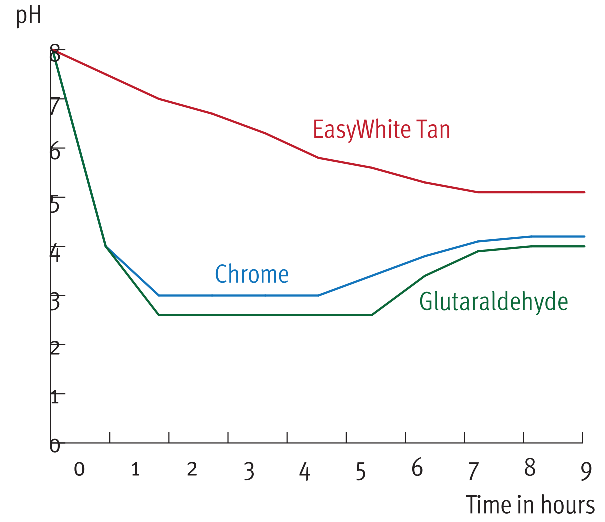
Figure 57. The suggested tanning mechanism of the EasyWhite Tan method, process parameters, versatility



Panel 1: Process progression regarding pH, time and shrinkage temperature



Panel 2: pH development between standard tanning process and EasyWhite Tan



Based on source: C. Reineking, Clariant Produkte, WL February/ March 2011; M. Bartle, C. Reineking, Clariant, WL Dec 2011/Jan 2012, R. Gamarino, C. Reineking, Clariant Produkte, WL

Panel 4: Comparison of article versatility of different tanning systems

Article	Chrome Tanning	Glutaraldehyde Tanning	Easy White Tanning
Automotive	●	●	●
Upholstery	●	◑	●
Vegatable Types	◑	○	●
Sports Shoe	●	○	●
Garment	●	◑	◑
Waterproof Shoe Upper	●	○	◑
Shoe Upper	●	◑	●

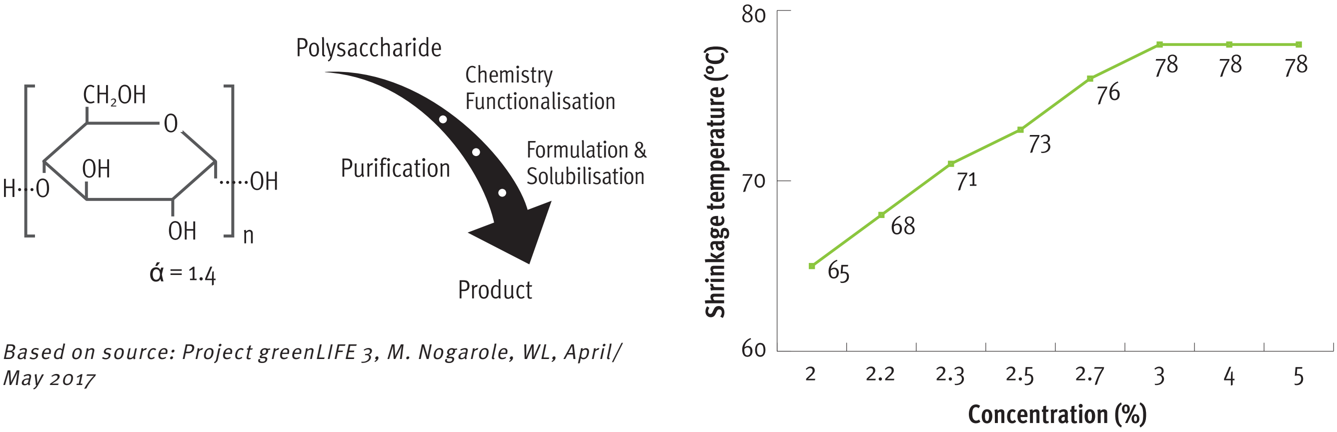
● Excellent ◑ Recommended ○ Not recommended

11.5. PRETANNING WITH POLYSACCHARIDES

Very recently an attempt was made to transform by-products such as polysaccharide into a tanning material.

The tanning process is reportedly very short and can take place in acid or neutral medium thus avoiding pickling. It is claimed that shaving is easy, the leather produced is light resistant, has good tensile strength and resistant to tearing. Accordingly, this tannage is suitable for light, grain leathers.

Figure 58. Pretanning with polysaccharides, shrinkage temperature



Based on source: Project greenLIFE 3, M. Nogarole, WL, April/ May 2017

11.6. AL-SILICON TANNING

Al-silicon tanning is reportedly a 2-component system based on compounds of aluminium and silicon with natural polycarboxylic acids and organic acids that meets all the requirements for automotive leather and supposedly withstands the high temperatures during shoe production. Both very soft leather for fashion garments and very tough leather for bikers can be made.

11.7. GENERAL ASSESSMENT OF THE WET-WHITE TANNING CONCEPT

The strong opinion of many tanners is that alternative tannages cannot deliver the same properties and performance characteristics as chromium tannages. Chromium-tanned leather is more “nourished”, rounder and fuller than wet-white, and has superior performance with regard to tensile strength, shrinkage temperature, lightfastness, etc. Metal-free tannages also leave much to be desired in areas such as availability, robustness, and cost. For this reason, even where customers in various sectors look to move away from chromium, they often reconsider as the alternatives have negative implications for the quality of their products.

This is not say that there is no place for metal-free tannages; leather production is about imparting the properties desired by the customer to the leather, and tanning systems are not always interchangeable when it comes to providing specific product performance.[20]

Promotors of wet-white (X-TAN) also assert that wet-white and chrome do not compete with each other; they have different performances and are two alternative tanning methods. They claim that the new generation of organic tanning represents a significant advance over traditional wet-white technology:

- There are two different reaction possibilities of the product: the primary one with lysine groups leather (1,000 times more reactive) and another reaction with water. During application any product excess is rapidly, completely and harmlessly degraded reacting with water.
- It is easy, safe, and robust and lowers the effluent COD load; since no pickle is required there is no acid hydrolysis of the collagen, which again protects tensile and tear strength.
- Chlorides are reduced by ca. 99.5%, TDS by ca. 75%, shorter process time, less energy.
- Transport and storage stability is greatly improved making international tradability of this commodity a reality, use of good fungicide is essential.
- If the wet-white were to accidentally dry out, they re-wet quickly with no adverse effect on final leather properties.

Similarly, responding to the criticism of the wet white concept, the supplier of EasyWhite claims:

- Stahl EasyWhite Tan is a leather tanning system for the creation of chrome-free leather that uses 40% less water during tanning and the salt in the wastewater is reduced by at least 80%. The tanning float can be easily reused and is chrome-free.
- Leather is very soft and smooth, yet it remains dimensionally and thermally stable; the collagen fibres are less damaged during the tanning process, resulting in a tighter grain and making it suitable for both dark and white and pale coloured leathers.
- It considerably simplifies and shortens the production process as two demanding steps, pickling and basification, in the tanning process become superfluous.

A great advantage of the wet white (pretanning) concept is that only the part of pelt that will end up as leather is tanned which a priori reduces the amount of tanning agent used. For example, only about 9.5 kg Cr_2O_3/t w.s. hides are needed for the main chrome tanning stage instead of the usual 21 kg Cr_2O_3/t.

It is also much easier to utilize and/or dispose of solid waste or, rather, by-products (unusable splits and shavings) resulting from mechanical operations of pretanned material; for example, being organic materials, they can have excellent value as fertiliser. However, only pretanned by-products have some limitations as they tend to become putrid and gluey.

Since pretanning changes the physical and chemical characteristics of the leather, it can also be used as a mechanism to improve chrome uptake and thus reduce the chrome input, reportedly from 8% to 5% on the basis of pelt weight. Pickling and pretanning can be combined, although pickling is not always necessary. Depending on the chemicals used, pretanning does not necessarily change the main leather characteristics nor limits the choice of further processing (chrome, vegetable or resin tanning).

Achieving accurate splitting and shaving in wet white condition can be somewhat difficult; some believe that this is compensated by a comparably tighter grain.

Retanning of wet white material requires higher amounts of retanning agents (e.g. syntans or vegetable tanning agents) than for chrome tanning. Some pretanning agents can be the cause of serious environmental concerns; for example, the hazards associated with aluminium due to its good solubility. Furthermore, in pretanning with glutaraldehyde fungicides are required in doses higher than those for chromium tanning and precipitation of chromium during effluent treatment is affected if aldehydes are present in the effluent stream.

Furthermore, some opponents claim that the tanning materials are sourced either from the petrochemical industry (synthetic materials) or from increased land use (vegetable-based materials). In some cases there is a large increase in hard to treat, recalcitrant COD in effluent.[21]

For a variety of reasons, including difficulties associated with splitting and shaving, commercial acceptance of wet white technology is low.

Table 31. Overview of pretanning – wet white concept

Advantages	Limitations
• Chrome-free trimmings, shavings • Easier disposal of unusable splits • Tanned is only part of the pelt that will end up as leather • Slightly lower water consumption • Lower consumption of chemicals, less salt • Better chrome uptake in the main tanning • Better grain tightness • White leather, good dyeability, uniformity • If accidentally dried out, they re-wet quickly with no adverse effect on final leather properties.	• The costs (additional operations, chemicals) might be higher • Splitting & shaving might be difficult and less accurate (sponginess) • The colour of the (final) wet blue can be different (greener) • Slightly higher carbon footprint (CT) in comparison with wet blue • Higher dosing of fungicide required • Tanning materials emanate from the petrochemical industry (synthetic) or increased land use (vegetable) • Commercial acceptance of wet white still rather low

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[20] *Based on “A future for chrome?” Dr Kerry Senior, ILM, August, 2017*

[21] *See “Goodbye to chromium and all that!” The Toggler, ILM 2014*

12. OTHER TANNAGES

12.1. MINERAL

Aluminium III, Zirconium IV and titanium IV (white) and titanium III (coloured) based.

Aluminium, zirconium and titanium tannages differ from chrome tanning because there are cross-links with various groups (covalent, ionic, hydrogen bonds). These tannages cannot be considered as substitutes for chrome tanning since they produce leathers of very different (generally inferior) characteristics.

Aluminium (III) tanning gives a nice white leather but inadequately water- and/or heat-resistant; thus, nowadays its use is limited to specific purposes (glacé leather for gloves, fur production), pretanning, or in combination with chrome tanning to increase the uptake of chromium. Aluminium tanning is also combined with vegetable tanning to increase the shrinkage temperature. The typical ratio is 6-7% mimosa tannin and 1% Al_2O_3; a similar dosage or less for additions in chrome tanning. Aluminium salts can also be combined with aldehydes such as (modified) glutaraldehyde.

Zirconium (IV) tanning, mostly with zirconium sulphate, gives white, strong and stable leather. Tanning starts at a lower pH (1.3 – 1.5) than for chrome tanning; citric acid can be used as a complexing agent to achieve a lower pH. To prevent swelling at least 7% salt is needed based on pelt weight. In practice the use of zirconium salts is limited to combinations with other tanning agents, primarily chrome.

Titanium salts, usually sold as proprietary titanium-aluminium complexes based products are good pretanning and retanning agents. Again, they are mostly used successfully in combination with other mineral tanning agents. Ammonium titanyl salts increase the nitrogen load in the waste water.

12.2. ORGANIC

The main categories are:

- traditional vegetable tanning (with wood, bark or leaf extracts);
- those based on reactive organic compounds (formaldehyde, glutaraldehyde and modified glutaraldehyde) normally in combination with vegetable or synthetic tanning agents;
- oil tannage.

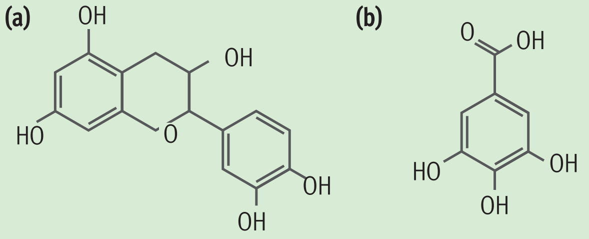
12.2.1. Vegetable tanning

Vegetable tanning's main traditional use is in the production of sole leather for high quality shoes, leather goods, harnesses, saddlery and much less for upholstery; these products are still perceived as elite, luxury items such as fashion leather bags, special upholstery and for exclusive automobiles. However, use of vegetable tanning extracts is nowadays almost a regular feature in various combinations of tanning, primarily in retanning but sometimes in pretanning too.

In addition to properties dependent on the type of hide or skin, the characteristics of vegetable tanned leather mainly depend on the nature of vegetable tanning material, the percentage of tannins offered and the levels of acids and salts in the tannage.

Vegetable tanning uses plant extracts from either hydrolysable pyrogallol (myrobalan, oak, sumac, chestnut, etc.) or from the condensed, catechol based tannins (mimosa, quebracho) group. Tanning is typically carried out with combinations of catechol and pyrogallic tanning agents. The famous E.I. (East India) process mainly used a combination of myrobalan (Terminalia chebula) and avaram (Assia auriculate) or myrobalan and mimosa (Acacia mearnsii).

Figure 59. The structure of epicatechin (a) and gallic acid (b)

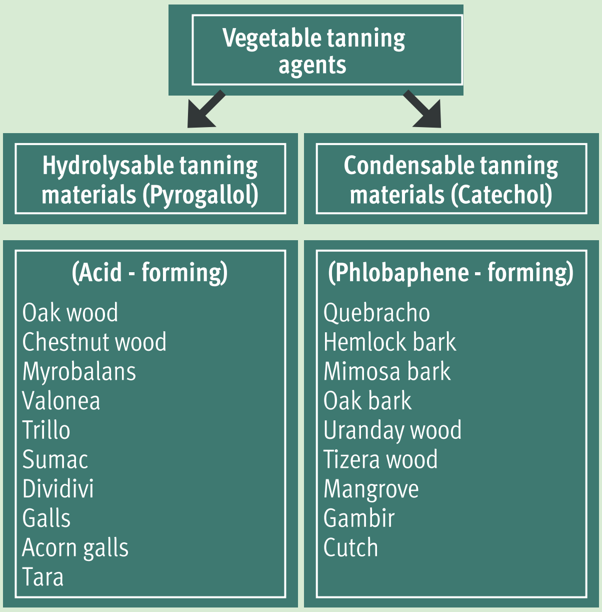


Based on source: F. Diaz, Stahl, WL, Oct/Nov 2011

Vegetable tannins are polyphenols with optimum tanning properties with a molecular weight of 600 to 3000. Below 600 there is no real tanning effect while the polymer above 3000 is almost insoluble and can hardly migrate through the hide.

The widely used vegetable tannin extracts are mimosa, quebracho (the soluble type), chestnut (sweetened), myrobalans and valonia; tara tannin extract is gaining in importance as an efficient agent in the prevention of conversion of trivalent into hexavalent chromium (finished) leather. Typically, they are spray dried or concentrated to contain 60 – 70% of active tanning matter, the rest being various gums, sugars, organic acids and mineral salts. Different tannin extracts lend quite different properties and appearance to leather; for optimum results they are often combined.

Figure 60. Vegetable tanning agents



In addition to its traditional uses in combined tannages to lend fullness, to improve burnishability and glazing and give fix cationic dyes and some resins, vegetable tannins are increasingly used in retanning of chrome tanned leathers to supress formation of CrVI.

In contrast to chrome tanning, vegetable tanning requires large amounts of tanning agent (extract), typically 40 – 50% on pelt weight; the overall uptake rate is about 50 – 70% of the tanning extract offer. Thus, while one tonne of raw hide gives about 200 – 250 kg of chrome-tanned leather, it gives 600 – 650 kg of sole leather. Water consumption is about 3 – 5 m^3/tonne of pelt weight, the traditional pit tannage having a higher consumption than the drum processes.

Since the unusable splits, shavings and later on buffing dust do not contain any minerals, they can easily be utilized and/or disposed.

The main quantities of vegetable tannins are now obtained from tree plantations (renewable sources); this is not valid for quebracho trees that grow scattered in the forests of South America. A dramatic increase in the use of vegetable tannins could result in consumption exceeding the supply.

More recently there were suggestions to consider spruce and birch, traditionally used in Russia for making leather of outstanding properties; vast spruce and birch forests in Russia and Scandinavia would ensure a nearly unlimited supply of renewable sources. The fact that up to five times more spruce agent than mimosa is needed to achieve the same level of tanning compounded by apparently complicated logistics possibly explains why this option has failed to attract commercial interests.

Another concept, branded Wet-Green, based on the utilization of residues from olive harvesting and olive oil production having (pre) tanning potential[22], is being promoted. However, to date there are no signs of wider acceptance at the industrial scale.

The main tanning can be seen as a two-stage process: penetration and uniform distribution of small tannin particles through the cross section resulting in fibre stability to swelling, pH changes and osmotic effects followed by increase of tannin fixation and deposition. The effectiveness of the latter is improved by the concentration of tannin (usually up to 21% corresponding to 18 °Be), increasing acidity (pH below 3.2), increasing astringency (the choice of the right type of tanning agent) and higher temperature (but not exceeding 37 °C).

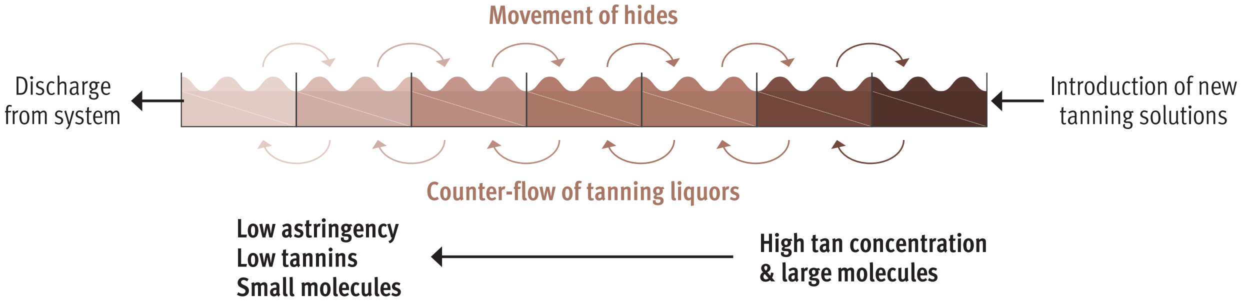
Panel 1: Sources of Tannins

Barks	Woods	Fruits & pods	Leaves	Roots	Plant galls
Wattle (Acacia sp)	Quebracho (Shinopsis sp)	Myrobolam (Terminalia chebula)	Sumac (Rhus sp)	Canaigre (Rumex hymenosephalus)	Oak (Quercus sp)
Oak (Quercus sp)	Chestnut (Castanea sp)	Valonea (Quercus Aegilop)	Gambier (Uncaria gambier)	Rhubarb (Rheum rhabarbarum)	Allepo (Quercus infectoria)
Eucalyptus (Eucalyptus sp)	Oak (Quercus sp)	Divi-divi (Caesalpinia coriara)	Dhawa (Anogeissus latifolia)		Tamarix (Tamarix articulia)
Avaram (Cassia auriculata)	Cutch (Acacia catechu)	Algarobilla (Caesalpinia brevifolia)			Pistacia (Pistacia sp)
Babul (Acacia Arabica)	Wandoo (Eucalyptus wandoo)	Tara (Caesalpinia spinosa)			Chinese (Rhus semialata)
Willow (Salix caprea)		Teripod (Caesalpinia digyna)			
Mangrove (Rhizophora sp)		Cashew husk (Anacardium occidentale)			

Based on source: F. Diaz, Stahl, WL, Oct/Nov 2011

12.2.1.1. *Traditional counter-flow pit tanning system*

Due to the duration extending from several weeks to even months, the centuries old pit tannage is almost entirely replaced by drum and combined pit and drum tannage; one alternative is the Liritan pit system that includes pretanning with sodium hexametaphosphate (Calgon).



Derived from WL April 2006

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[22] *Presumably based on reaction of oleuropein (a secoiridoid glycoside) ultimately reacting with lysine groups on protein.*

Slow vegetable tanning pits at the Concerie Riunite GB SpA, Italy

12.2.1.2. Rapid vegetable tannage

The rapid tannage is a rather simple system: tanning extracts and auxiliaries and possibly some water are all added to the same vessel. The mechanical action by drum rotation supports penetration whereas heat build-up improves the tannin uptake.

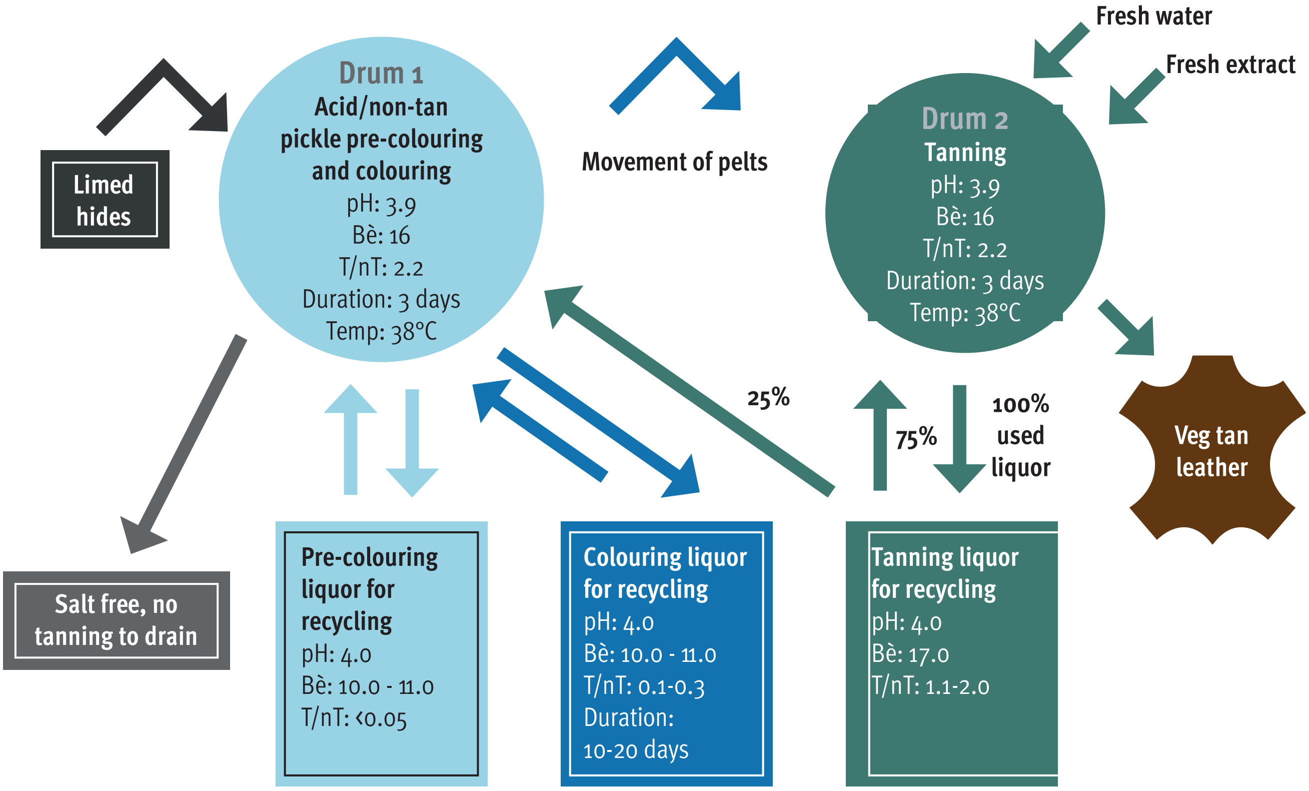
The first step is conditioning (no float!) with non-swelling syntan, bisulphite and formic acid, followed by washing and pretanning with 8-10 % of replacement syntan and finally, a no float main tannage with initially non-astringent and (10-18%) and then with astringent vegetable powder (10-18%). However, there are many variations of this basic process.[23]

12.2.1.3. Pit-drum tannage and semi-rapid vegetable tanning

It was developed to combine the best of both systems. First processes, deliming and light pretannage, are carried out in the drum. The hides are then transferred into a chain of counter-flow pits with steadily increasing concentration of vegetable extract to be transferred to the drum for the final tanning step for which fresh extracts and some water are added; part of the exhausted float from the drum is discharged into the last, strongest concentration pit.

The semi-rapid method (the flow shown in the last diagram) represents a refinement of the well established pit-drum tanning using completely exhausted vegetable tanning float to replace salt within an acid pickle. It reportedly achieves full uptake of tanning extracts from residual floats and can be tuned according to the type of leather to be produced.

Panel 6: Semi-rapid vegetable tannage. High exhaustion, salt free


Fresh water
Fresh extract
Limed hides
Drum 1
Acid/non-tan pickle pre-colouring and colouring
pH: 3.9
Bè: 16
T/nT: 2.2
Duration: 3 days
Temp: 38°C
Movement of pelts
Drum 2
Tanning
pH: 3.9
Bè: 16
T/nT: 2.2
Duration: 3 days
Temp: 38°C
25%
75%
100% used liquor
Veg tan leather
Salt free, no tanning to drain
Pre-colouring liquor for recycling
pH: 4.0
Bè: 10.0 - 11.0
T/nT: <0.05
Colouring liquor for recycling
pH: 4.0
Bè: 10.0 - 11.0
T/nT: 0.1-0.3
Duration: 10-20 days
Tanning liquor for recycling
pH: 4.0
Bè: 17.0
T/nT: 1.1-2.0

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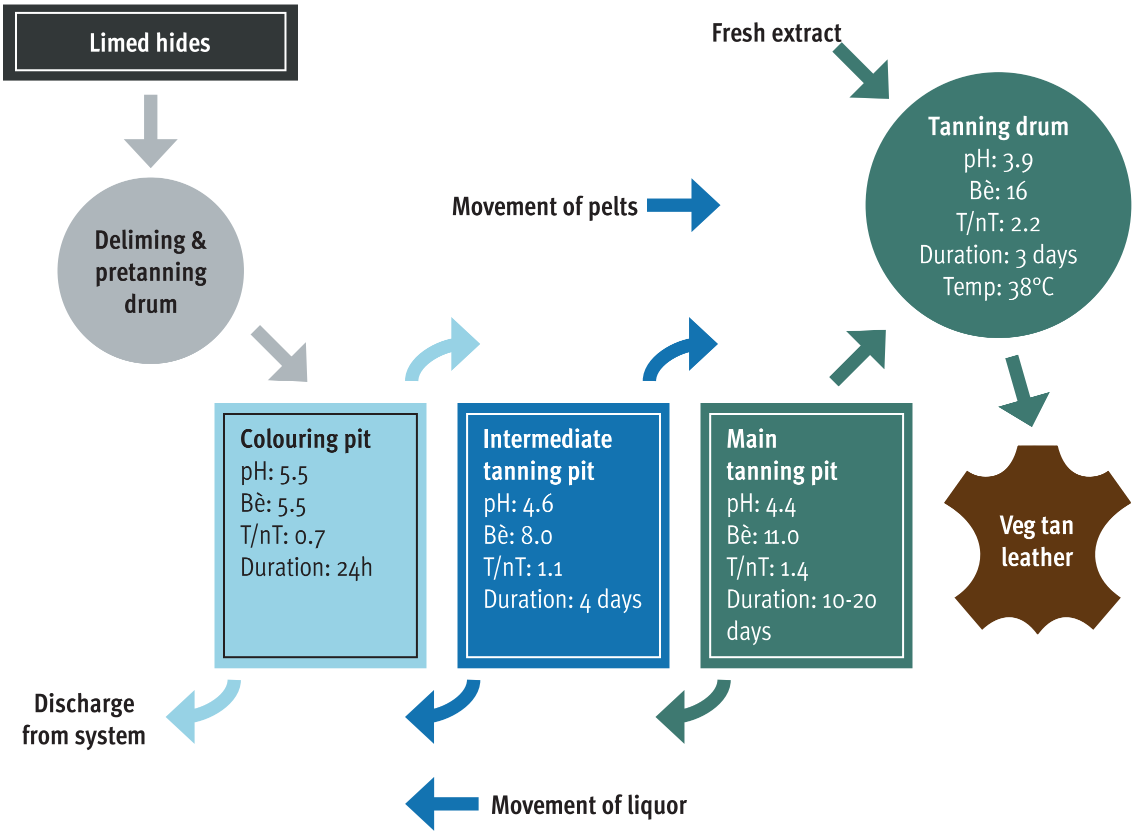
[23] *Colin Jones, Northampton, UK, WL April 2006*


Limed hides
Deliming & pretanning drum
Fresh extract
Movement of pelts
Tanning drum
pH: 3.9
Bè: 16
T/nT: 2.2
Duration: 3 days
Temp: 38°C
Colouring pit
pH: 5.5
Bè: 5.5
T/nT: 0.7
Duration: 24h
Intermediate tanning pit
pH: 4.6
Bè: 8.0
T/nT: 1.1
Duration: 4 days
Main tanning pit
pH: 4.4
Bè: 11.0
T/nT: 1.4
Duration: 10-20 days
Veg tan leather
Discharge from system
Movement of liquor

Drum-Pit and Rapid Tannage: Advantages/disadvantages

Drum-Pit tannage

- Long process time
- High investment in stocks
- High investment in equipment
- Larger building area
- Process needs analytical control
- No mechanical damage
- High yield
- Low pre-tanning costs
- Better colour control
- Easier temparature control
- Large batches

Rapid tannage

- Short process time
- Low investment in stocks
- Low investment in equipment
- Smaller building area
- Process controll by formula
- Mechanical damage
- Low yield
- High pre-tannage costs
- Lack of colour consistency
- Difficul temparature control
- Small batches

Drum-Pit and Rapid Tannage: Advantages/disadvantages

Drum-Pit tannage

- Total or partial delimed
- No acid/salt pickle
- Superficial pretannage
- Tannage with astringent blend of vegetable extracts
- High liquor/pelt ratio (typically 6:1)
- Minimum mechanical action
- Long tanning time (20 days)

Rapid tannage

- Full delimed
- Acid/salt pickle
- Pretannage to equilibrium
- Tannage with blend of sweet (non-astringent) extracts
- Low liquor/pelt ratio (typically 0.3/1)
- Short tanning time (1-2 days)

Source: E. Poles, Silvachimica, WL Dec 2012/Jan 2013

12.2.1.4. Pit-drum tannage and semi-rapid vegetable tanning

Unavoidable by-products of the expanding cultivation of olive trees are the substantial quantities of leaves and twigs that contain precursor molecules that by catalytic reaction can be transformed into an activated molecule with the propensity to bind to hide and skin collagen.

As a tanning agent, the (aqueous) olive leaf extract is reported to combine the advantages of organic synthetic reactive agents by creating stable covalent chemical bonds with those of the usual vegetable tanning. It is claimed that leathers tanned in such a way, using usual tannery vessels and without any specialty chemicals are comparable with common wet whites except that some savings in retanning and dyeing are possible. The shrinkage temperature is about 70 °C. Not unlike other vegetable tanned leathers, wet greens are susceptible to iron stains; storage for longer than 2 – 3 weeks requires application of fungicides. Solids from the process, including sludge, are suitable for thermal application. Finally, it is hoped that, following some stabilization, a new commodity, green crust, easy to wet back for further processing could be developed. This would be a further asset to this already exceptionally sustainable concept.

12.2.1.5. *Other uses of vegetable extracts, tara*

Tara is a bushy tree that grows wild on the mountainous chains of Peru at an average altitude of 1200 metres, but nowadays also in plantations. The fruit and pods are picked up and are processed into a number of products, including tara powder – a pyrogallic (re)tanning agent mainly used in the production of light-coloured, lightfast, tight-grain leathers, well complementing wattle extract. More recently it is considered very effective in supressing the development of hexavalent chromium in chrome tanned leathers.

Figure 61: Semi-rapid vegetable tannage. High exhaustion, salt free

12.2.2. *Emissions and pollution load*

The main components of emissions and pollution load in effluent are:

- Residues of the tannin extract are not bound to leather
- Soluble non-tannins are present in the readily usable tannin extract
- A very high COD load (up to 220 kg/tonne hide) of low biodegradability (recalcitrant COD)
- Dark, unpleasant colour and phenolic compounds of these effluents
- Large amounts of sludge from both tanning and later on from (biological) treatment

Contrary to widely spread misperceptions, vegetable tanning agents, syntans, and aldehydes can cause serious damage to surface waters due to their low biodegradability and their toxicity to aquatic life.

Table 32. Waste water volume and pollutant loadings per tonne of raw hide or skin from vegetable tanning including pickling, washing, and bleaching

Quantity per tonne of hide or skin	Counter current pit	Drum	Salt-free pickling
Water volume, m^3	3 - 4	3 - 4	
Total solids, kg	110 - 200	65 - 100	
Suspended solids, kg	10 - 15	10 - 15	
BOD_5, kg	40 - 75	25 - 35	
COD, kg	120 - 220	70 - 110	
Chloride (Cl^-), kg	50	?	4

12.2.3. *Cleaner methods*

The main aim of cleaner methods in vegetable tannage is the increase of the uptake of vegetable tannins, the corollary of which is a simultaneous decrease of pollution load and, in particular, of recalcitrant COD. For commercial reasons another target is the shortening of the (long) tanning process. This is generally achieved by:

- Switching to drum or pit-drum tanning (mentioned earlier)
- Using short floats and closed loops in drum tanning releasing very little waste water
- Pretanning with various chemicals and auxiliaries (polyphosphates and/or syntans) improving the penetration and uptake; their cost is more than compensated by shorter processing time.
- Ex-lime splitting (already traditionally adopted for vegetable tanning)

12.3. CHROME-FREE TANNING – TANNAGES WITH SYNTANS AND OTHER SYNTHETIC ORGANIC COMPOUNDS

The drive for chrome-free leather principally comes from the automotive industry; it is claimed that particular properties like low dry-shrinking of leather are important to them. The pressure exerted on the public by certain groups and organisations with strong misperceptions about chrome tanned leather and poor understanding of deficiencies of some chrome-free tannages, including, in particular, their inferior environmental performance is also very relevant.

Chrome-free tannages are generally based on the use of reactive organic compounds in combination with vegetable or synthetic tanning agents. Syntans are sulphonated condensation products of hydroxyl-substituted aromatic compounds (phenol, cresol or naphthalene) with formaldehyde and often with amides.

Chrome-free tannages are normally preceeded by pretanning. Glutaraldehyde derivatives are used both in pretanning (production of wet white) as well in the main chrome-free tanning. For technical and safety reasons, in the leather industry in Europe glutaraldehyde is mainly used in the form of a modified glutaraldehyde product.

Rather new developments are polycarbamoylsulfonate (PCMS), X-TAN and EasyWhite pre-tannages. They have a well-known positive impact of the usability of solid waste but the nature of their effluent load might be of a disadvantage.

12.3.1. Environmental aspects of chrome-free tannages

Syntans with a lower impact on the environment (low levels of free phenol) are available commercially, but there are still some that are hardly biodegradable:

Normally, syntans have a very high COD, their degradation both in the course of effluent treatment and recipient water bodies is very slow (aerobically and anaerobically) and even the degradation products are strong and highly persistent and mobile pollutants.

Glutaraldehyde is only degraded to a limited extent, has high toxicity and, if the concentration is high, it may influence negatively biological treatment.

12.4. OIL TANNAGE

Oil tannage has been used for the production of a specific type of leather (chamois) such as leather for traditional Bavarian (Germany) folks costumes and hunting garments (preferably from deer hides) as well as for the washing of car windscreens:

In the original formulation tanning was carried out by using highly unsaturated cod oil that was driven into the hide and oxidized by strong mechanical action. Subsequently the excess cod oil was wrung and washed out with sodium carbonate. The dried leather had a specific yellowish colour and very pleasant feel. It could also be dyed.

Later on, the original procedure was modified by introducing a pretanning step with glutaraldehyde and the oil oxidation was accelerated by blowing the warm air into the vessel. There are also commercial oil tanning agents mostly used for washable gloves and garment leathers with high tear resistance.

A disadvantage of oil tannage is that the cod oil releases a pungent smell and waste water discharge is highly COD loaded.

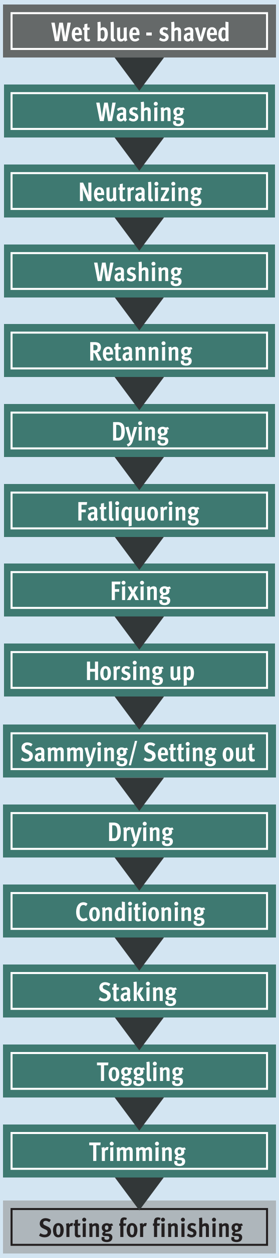
13. WET FINISHING

13.1. GENERAL

While the tanning stage basically converts a putrescible, easily degradable hide into a stable material, wet finishing lends more specific properties to leather (softness, basic colour, water repellence, etc.) important for its appearance and ultimate use. This explains why in practice there are so many variations of wet finishing (post-tanning) operations.

The main stages of typical wet finishing are neutralisation (deacidification), retanning, dyeing and fatliquoring. As a rule, all of them are carried out in the same processing vessel (usually a drum) to be followed by a series of mechanical operations.

Figure 62. One of many variations of operations in preparation of wet blue for dry finishing


Wet blue - shaved
Washing
Neutralizing
Washing
Retanning
Dying
Fatliquoring
Fixing
Horsing up
Sammying/ Setting out
Drying
Conditioning
Staking
Toggling
Trimming
Sorting for finishing

13.2. NEUTRALISATION

The purpose of neutralisation is to remove free acids present in tanned leather in order to prepare it for the subsequent stages i.e. retanning, dyeing and fatliquoring.

Since the pH is normally not raised to the neutral point, in reality it is deacidification. For soft leather and better dye penetration deacidification is carried fully throughout the cross-section whereas partial deacidification, only to a certain depth, gives firmer leather. Excessive neutralization results in a loose grain and empty handle; on the other hand, too low a pH results in the undesirable leaching of chrome.

Mildly basic chemicals are commonly used and consist mostly of sodium carbonate/bicarbonate, sodium bisulphite and metabisulphite, sodium tetraborate (borax), sodium formate/acetate; dosing of a single or a combination of agents is up to 4% on the shaved weight.

Polyphosphates are usually used for deacidification of vegetable tanned leathers. In addition to retanning and/or filling properties, some syntans also have a neutralising effect.

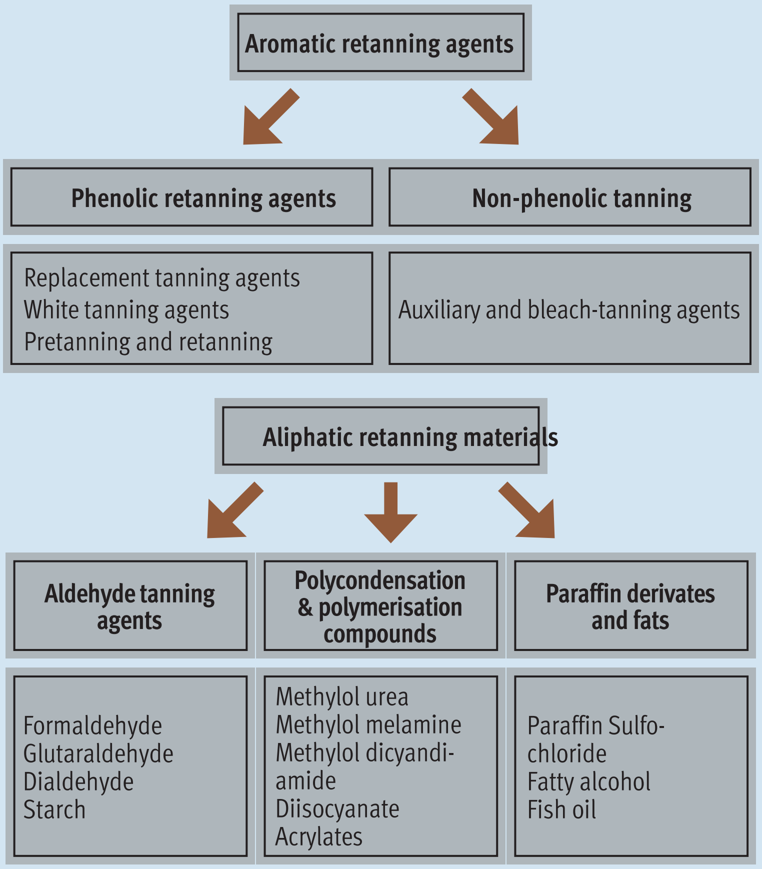
13.3. RETANNING

The retanning process is carried out for several reasons, the main ones being:

- To make the leather more uniform by filling the looser and empty parts, thus increasing its cutting value
- To improve its buffing properties important for production of corrected grain leathers
- To improve the resistance to alkali and perspiration
- To improve the general feel and handle

The emphasis of the retanning process will depend on the type and quality of raw hides, desired leather properties and the customer's specifications. The selection of the retanning agent (or a combination of retanning agents) is also made accordingly.

Figure 63. Structures of aromatic and aliphatic retanning agents


Aromatic retanning agents
Phenolic retanning agents
Non-phenolic tanning
Replacement tanning agents
White tanning agents
Pretanning and retanning
Auxiliary and bleach-tanning agents
Aliphatic retanning materials
Aldehyde tanning agents
Polycondensation & polymerisation compounds
Paraffin derivates and fats
Formaldehyde
Glutaraldehyde
Dialdehyde
Starch
Methylol urea
Methylol melamine
Methylol dicyandiamide
Diisocyanate
Acrylates
Paraffin Sulfochloride
Fatty alcohol
Fish oil

A wide variety of chemicals can be used and they belong to the following categories: vegetable tanning extracts, syntans, aldehydes, mineral tanning agents (not necessarily chromium) and resins. They are used in nearly endless variations of combinations and ratios.

In accordance with what was stated earlier, the dosing also varies a lot, from 3% for clothing leather and up to 15% on the shaved weight for shoe uppers.

In the case of chrome retanning, carboxylic/ di-carboxylic acids and the respective salts as well as phthalates e.g. di-sodium phthalates (DSP) are often used as masking agents; the difficulties they cause with the precipitation of chromium in effluent have to be borne in mind.

Synthetic tanning agents (syntans) used in the retanning process include a wide variety of rather different chemicals which ultimately impart different properties.

When selecting the syntan, in addition to characteristics it gives to leather, it is important to consider its environmental performance: residues not taken by leather can contribute to heavy COD effluent. To make it worse, very often the COD load they produce is not biodegradable and requires specific and costly tertiary treatment.

13.4. DYEING

Obviously, the dyeing process should give leathers a uniform shade of colour corresponding to the customer's specifications, often using a piece of leather as a reference sample. Colour consistency from pack to pack is very important. Dyes are normally used as aqueous solutions and the process is mostly carried out either in wooden drums or in stainless (often three-chambers) dyeing machines; through-feed machines are met with rather limited acceptance by the industry while paddle dyeing is in practice used only for sheep skins.

Dyestuffs in the leather industry are mostly from the anionic group (acid, direct, sulphur, premetallised) and very seldomly from the basic group. From the chemical point of view, the dyestuffs are predominantly azo- or anthraquinone dyes.

Metal complex dyes having metal such as iron, chromium, nickel, copper and cobalt as a central ion and one or two azo dye ligands are quite important in the production of certain types of leather; it is believed that dyes containing lead and cadmium are no longer used in Europe.

Due to a very narrow range of colours, the use of vegetable dyes from the extracts of some trees (logwood, redwood) or leaves (sumac) is limited to some niche articles.

Nearly all leather dyes for drum application bind to leather by the ionic interaction between the anionic sulphonate group of the dye and the cationic amine group of the collagen. The formic, sometimes acetic acid is crucial for good fixing at the end of the dyeing process and they contribute towards improving colour fastness. Depending on the type of finished leather produced (aniline, corrected grain, shade), the quantities of dyestuff vary from 0.05 - 10%. Pigments, especially for white leathers, may also be added.

The dyestuff exhaustion rate depends on many factors: the type of tannage, dye used, auxiliary agents, water hardness, etc. as well as on the process parameters (mechanical action, concentration, pH, time, etc.).

For good results (levelness, shade depth) dyes are added in a dissolved state and in several portions. Long floats and lower temperatures help good distribution while short floats, higher temperatures, longer process time and the dosing of formic acid for fixation in a few portions help better fixing and exhaustion.

In balancing these conflicting effects, the usual approach is to start at a lower temperature (e.g. 30°C) and towards the end of the process bring it to above 50°C.

Due to high costs of dyestuffs, dyeing is a very expensive operation and special efforts are made to achieve the highest bath exhaustion possible. In practice it means exhaustion of at least 90% but nearly complete exhaustion is also possible.

Dyeing auxiliaries

Being a very sensitive and demanding operation dyeing is normally aided by various auxiliary chemicals and agents such as surfactants, levelling agents, shade intensifiers, fixing agents, etc. They are mostly added separately but some can be included in the dyestuff.

Surfactants can be either dispersing agents (e.g. alkyl aryl sulphonates or ethoxylation products, condensates of fatty acids) or wetting agents (auxiliaries) which in turn can be anionic (alkane-sulphonates, alkyl aryl sulphonates), non-ionic (e.g. phosphoric acid esters), or cationic (e.g. alkyl aryl amine polyglycol ethers, amine and urea derivatives, etc.). The surfactants used in wet processes could increase the hydrophilic properties of leather. To rectify this, hydrophobic chemicals (e.g. silicones or organic chlorofluoro-polymers) can be used.

For appropriate use, it is important to understand the character of surfactants and their behaviour, for example, whether emulsifiers make oil-in-water (o/w) or water-in-oil (w/o) emulsion, stability, etc.

Organic acids, buffering salts and mixtures of these chemicals are used as **pH adjustment agents** whereas mixtures of alcohols of higher valence and neutral phosphoric acid esters act as **anti-foaming agents**.

The main sequestering agents used to be nitrilo-tri-acetate (NTA), ethylendiamine tetra acetate (EDTA), polyphosphate (calgon) and carboxylic acids, but, for example in the EU, there are restrictions on their use.

After treatment and fixing agents are surface active substances such as cationic polyquaternary ammonium compounds, cationic formaldehyde poly-condensates and other nitrogen derivatives and some agents based on inorganic complexing agents and metallic salts.

Stripping agents are used generally on vegetable tanned leathers to level out the colour of the substrate prior to the dyeing operation. More rarely this operation is carried out on chrome tanned leathers. The chemicals used for this type of process are: salts releasing sulphur dioxide, oxalic acid, EDTA, bleaching syntans, etc.

Sometimes, usually in reprocessing, it is necessary to remove a certain amount of dye from the already dyed leathers. This is done using alkalis like sodium bicarbonate or ammonium bicarbonate or by bleaching using certain syntans.

13.5. FATLIQUORING

Fatliquoring is important because it replaces the natural fat originally present in the hide and lubricates the leather fibres in a way that gives the product its specific characteristics. Accordingly, the amount added varies from 3-15% on the shaved weight. Some fatliquoring (1-4%) can already be done at the pickling and tanning stages using electrolyte-stable cationic products, but the main fatliquoring takes place after neutralisation and dyeing.

A good fatliquor is expected to have good salt and chromium stability, lightfastness and high resistance to heat yellowing so that is suitable for white and pale leathers.

Traditionally, the oils and fats used for this purpose were of animal (fish oil, neatsfoot oil, tallow) or vegetable (linseed, maize, cotton seed) origin but for some time now commercial synthetic products derived from mineral oils have been in wide use. To make them water soluble, both animal and vegetable oils and aliphatic hydrocarbons are sulphonated. For good characteristics chlorinated hydrocarbons have also been used; however, the use of those stabilized by organic solvents are recently under close scrutiny because of their poor environmental performance: they significantly contribute to higher AOX values and multiple chlorination makes them virtually non-biodegradable.

For good dispersion and penetration fatliquors are prepared as emulsions (mostly oil-in-water) with emulsifiers already incorporated into the fatliquor. To sustain solubility and emulsion the float temperature should be 60-65°C. For good penetration and bonding it can be necessary to adjust pH using formic acid or ammonium. To achieve the silky nap expected from suede leathers, a small amount of cationic fatliquors can be added at the very end of the process.

A special category of fatliquoring is "stuffing", a method applied in the production of heavy vegetable-tanned leather: sammed leather is drummed with a mixture of molten fat, the high temperature often sustained by the blowing of hot air.

Following the set of operations (retanning, dyeing, fatliquoring) leather is usually washed and then piled onto a "wheel-horse" to rest which helps to achieve a more uniform distribution of the chemicals, especially of fatliquors.

13.6. SPECIFIC PERFORMANCE AND RELATED AGENTS

In addition to the auxiliaries mentioned earlier, there is a wide range of various substances, usually readily usable commercial products, applied in wet finishing and that impart some leather type-specific performance:

- Reduce hydrophilic properties
- Waterproof properties
- Better wearing and abrasion resistance
- Oil repellence
- Lower gas permeability
- Anti-electrostatic properties

Substances used to achieve these aims are selected from different natural, mineral or synthetic oils and fats; polymers, poly-condensates and poly-addition products; metallic acid complexing compounds; silicon derivatives; perfluorinated organic compounds, etc. either as a single material, or more often, a combination of them.

More recently flame-retardant properties are also being asked for. While leather cannot be considered a flammable material, leathers for special use (upholstering of aircraft, train, and public building seats, some safety shoes/gloves) can be treated with flame-retardants, usually at the wet finishing stage. The main categories of flame-retardants are:

- Inorganic compounds (e.g. ammonium polyphosphates, ammonium bromide)
- halogenated organic compounds (usually brominated or chlorinated)
- organophosphorous compounds (phosphate esters, e.g. triphenyl phosphate)
- nitrogen-containing compounds (e.g. melamine compounds).

However, due to environmental/health risks flame-retardants from the polybrominated diphenyl ethers (BDE) category such as penta- and octa-BDE are already banned in the EU while others may be added to the list soon.

13.7. EMISSIONS

The effluents from all wet finishing operations are normally collected jointly and that is why there are no specific data for each of its steps. Generally wet finishing contributes about 10 – 20% of the total COD in combined tannery effluent.

In comparison with emissions from the tanning stage that tend to be quite similar, emissions from wet finishing vary within a very wide range both within the same factory (depending on the type of leather produced) and among tanneries producing the same type of leather. This is quite understandable if the great variations in wet finishing technologies are kept in mind. Incidentally, the COD load from wet finishing in the production of upholstery leather is usually higher than that from the production of upper leather. The pollution discharged with effluent from wet finishing mainly emanates from retanning and fatliquoring.

Table 33. Emissions to waste water from conventional post tanning operations

Pollutant	Emissions kg/ton of raw hide
Total Solids	65
Suspended Solids	7
BOD_5	14
COD	20 - 30
Nitrogen, total	0.8 - 1
NH_4	0.6 - 0.8
Cr	1
CL^-	2 - 5

Source: EU-BREF 2013

13.7.1. *Emissions from retanning*

The main pollutant here is the high COD emanating from:

- incomplete exhaustion of retanning agents;
- non-tannins contained in vegetable tanning agents;
- residual monomers contained in syntans and polymeric tanning agents.

Chromium stems from the leaching of chromium from the main tanning process as well as from the chromium from retanning itself; closely linked to that are also emissions of inorganic salts present in chrome tanning agents and syntans. The other source of chromium is the fibres from the shaving operation adhering to the leather surface that eventually end up in neutralisation and washing floats. Using a conventional technique, the amount of chromium in the waste water, derived from the post-tanning operations, is about 1 kg per tonne of raw hide as shown in the following table.

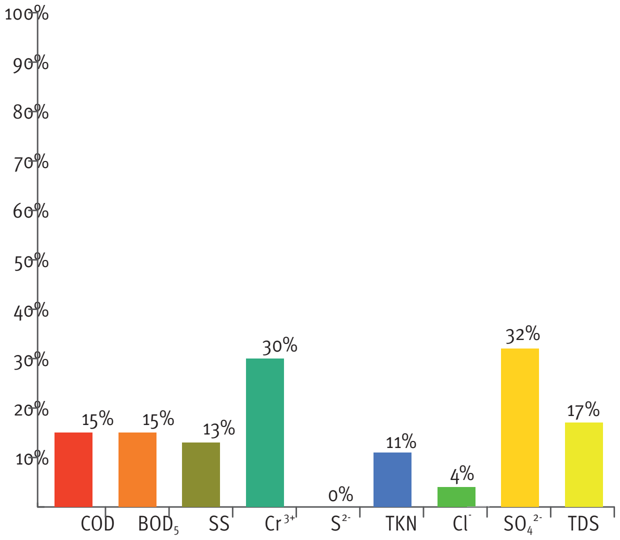
Table 34. Sources of chromium discharges during wet finishing

Source	kg chromium per tonne of raw
Leaching	0.6
In fine leather fibres	0.4
In metal complex dyes	0.03

Source: Frendrup 1999

Retanning agents of the amino-resins type (urea-formaldehyde or melamine-formaldehyde resins) used for their good filling properties contribute to the nitrogen load in the waste water at the level of about 0.2 kg per tonne of raw hide.

Figure 64. The share of post-tanning in total emissions



Based on chart by M. Bosnić

13.7.2. Emissions from dyeing

Emissions from the dyeing process are of comparatively minor importance and they are mainly discharged as effluent; yet emissions to air and residues from dyestuffs and auxiliaries to be disposed of cannot be disregarded. Yet, in the latter case, it is mainly occupational safety and health at the workplace (OSH) that is related to chemical handling and, in particular, with dust control.

Chemicals not retained in leather and released to waste water contribute to the COD load and, if one of those the halogen-containing dyes are used, to the release of the absorbable organic halogens (AOX).

However, dyes in the effluent are difficult to remove and coloured waste water (dye concentration of only 10 ppm is noticeable to the eye) is by the general public a priori considered very polluted. Actually the main negative impact of dyestuffs is that they can reduce the penetration of light; also, most of them have very low biodegradability.

By reductive cleavage of one or more azo groups, certain azo dyes can release some of the 22 aromatic amines specified in the restricted chemicals lists (RSL). The use of such azo dyes has been strictly forbidden worldwide for quite some time and such dyes are no longer produced by reputable suppliers.

Metal complex dyes consist of a central metal ion and one or two azo ligands. The central ion can be iron, chromium, copper, or cobalt for leather dyes; they are needed to achieve good light-fastness as well as special colours. The amount of chromium from this source normally does not exceed 0.3% of chromium in leather or 0.03 – 0.05 kg of chromium per tonne of raw hide in waste water.

Metal complex dyes containing lead and cadmium are no longer used in Europe. Due to its fungicidal and bactericidal properties, high concentrations of copper inhibit degradation.

Obviously, the residues of different auxiliary agents used at various steps of wet finishing end up in effluents (especially if their uptake is poor) and contribute to the pollution load, mainly the COD.

Ammonium used as dye penetrator is an important contributor to the NH_4-N load in effluent: it is in the range of 0.6 – 1.6 kg per tonne of raw hide. However, more recently ammonium is one of the key suspects for the conversion of trivalent (Cr^{3+}) into hexavalent chromium (Cr^{6+}) in finished leather and leather articles.

13.7.3. Fatliquoring emissions

Emissions to the joint wet finishing effluent emanating from the fatliquoring and impregnating agents can be significant: obviously, they are the principal source of oil and grease. Furthermore, in addition to contributing to the COD and BOD loads, chlorinated fatliquors also raise the AOX values.

In the EU the use of preparations containing more than 1% of chlorinated alkanes of chain length C_{10} -C_{13} is banned.

13.8. CLEANER METHODS

13.8.1. Neutralisation

The amount of neutralising salts should be optimised to ensure that the pH of the liquor and the leather by the end of the process are close to each other, ensuring that as little as possible of the unused salt ends up as effluent. Rinsing after neutralisation should also be optimised to ensure good washing without excessive water consumption.

The screening of spent floats to remove chrome containing leather fibres is essential in reducing chrome content in the effluent. A lot of screening equipment, from very simple to rather sophisticated (and suitable for large capacities) is available.

13.8.2. Optimised retanning

Generally, the idea is to achieve COD optimized and low- or salt-free retanning systems.

Before moving to wet finishing it is very important to allow sufficient time for proper “aging” (olification) of the tanned leather as it will significantly reduce the leaching effect.

One of the more pressing environmental issues is the presence of formaldehyde in retanning resins.

A genuine resin retanning agent selectively fills the loose and empty parts of hides or skins thus improving the cutting yield. While they are dicyanamide- or melamin-based, their production requires the use of formaldehyde which means that they cannot be considered absolutely formaldehyde-free. This in turn means that they do not meet the extremely low detectable limits required for automotive leathers.

Reportedly, formaldehyde is not used in the manufacturing of new generation resins and they indeed can be classified as zero formaldehyde resin retanning agents. They also show good buffing properties and resistance to heat yellowing.[24]

Concerning chrome retanning, there are strong voices that chrome retanning is actually a residue from the times when process controls were quite inadequate. Additional chrome tanning was a kind of safety step to avoid the risk of undertanning. With modern equipment (drums, chemicals and water dosing) and control tools this step might be unnecessary.

In any case, a high exhaustion method using appropriate masking agents in appropriate amounts (to avoid difficulties with the precipitation) together with the optimisation of process parameters (chemical inputs, mechanical action, pH, temperature, duration etc.), is considered a must.

A relatively low pH at the end of wet finishing helps the good fixation of dyes and fatliquors (the pH could be brought down to 3.5). However, this is in conflict with retaining chrome because at the pH below 4 chromium could leach out from the leather.

For other retanning agents the focus is firstly on those that meet not only the desired leather quality properties but also with the best environmental performance - good biodegradability; after all, recalcitrant COD is one of the main evils in waste water treatment. Secondly, it is important to ensure the highest exhaustion rates and thus, ultimately, the lowest possible COD load. Finally, water and energy consumption are important parameters for the choice of the retanning process.

One of the leading suppliers of leather specialty chemicals claims that their set of retanning agents (X-Biomer) developed to replace the traditional types (mainly fossil fuel based derivatives), is based on biodegradable polymers produced from renewable raw materials. Reportedly this new generation of retaning agents carries low salt weight, shows good fixation and high exhaustion properties resulting in considerably lower COD load and , to top it all, the residue in effluent is biodegradable.

13.8.3. Optimised dyeing

Apart from avoiding hazardous dyestuffs, the main aim of optimized dyeing is to ensure a firm bonding to leather and thus the highest possible exhaustion of dyes and all dyeing auxiliaries. The target is usually to bring down the concentration of dyestuff in the effluent bellow 10 ppm. To that end short floats (100% on shaved weight) and a high temperature (60oC) are employed; also, to enhance the dye intensity amphoteric polymers are often used. As said earlier, completion of the dyeing process at a relatively low pH value, e.g. 3.5 helps the fixation but too low pH may result in chrome leaching.

To reduce and/or eliminate harmful particulate matter in the air in dye-handling areas (OSH!) after de-dusted powdered dyes (actually mixed with an anti-dusting agent, such as paraffin oil), liquid dyes are also being introduced.

In addition to the dyestuff itself, liquid dyes also contain water, diluents/fillers (chalk, syntans, polymers, etc.), surfactants and anti-foam agents. While dosing automation with liquid dyes is much easier and preferred by OSH, some negative aspects cannot be overlooked: they need more storage space, their shelf-life might be shorter transport and energy costs (heating!) are higher.

Ammonium can be replaced by other acceptable dye penetrators; furthermore, many believe that its use is not really of particular importance.

13.8.4. Optimised fatliquoring

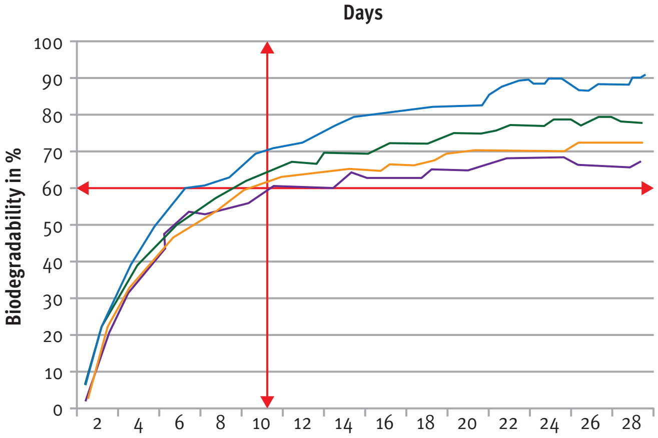
More environmentally friendly fatliquoring in practice is focused on:

- optimisation of process parameters to achieve the highest possible exhaustion level
- use of fatliquors which do not contain halogenated compounds
- biodegradability

By selecting the appropriate fatliquor(s) for a certain type of leather, fine tuning the float length, temperature, pH, etc. and by adding amphoteric polymers, it is quite possible to attain the exhaustion level of 90% and thus significantly reduce the COD load.

Fatliquors that do not need stabilization by organic solvents and do not add to the AOX load are already available. Methacrylates and silicone or modified silicone oils can substitute the hazardous short- and middle-chain chlorinated alkanes; for the time being there is still no adequate replacement for long-chain chlorinated alkanes needed for special applications.

The biodegradability measurement of selected fatliquors



Based on source: J. Guthrie-Strachan, World Leather Oct/Nov 2016

It is important to note that here the biodegradability assessed by the OECD method is quite different from the BOD value, biodegradability of ethylene glycol is the standard.

Readily biodegradable	› 60% within 10 days
Biodegradable	› 60 % within 28 days
Partially biodegradable	20-60% within 28 days
Poorly biodegradable	‹ 20% within 28 days

Parameters	Specific emissions per unit of raw hide from advanced post-tanning processes kg/t
TS	30
COD	13 - 17
Chromium	0.1 - 0.4

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[24] *C. Tysoe, Lanxess, WL*

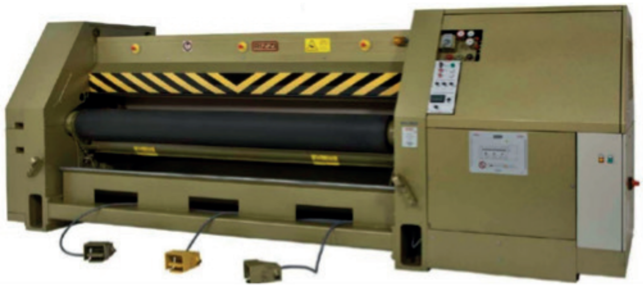
Sequestering agents and wetting agents are problematic substances due to their ability to form stable complexes with heavy metals. Thus, they not only prevent effective precipitation, but also cause the re-mobilisation of heavy metals from sediments. Some of these substances are hardly biodegradable and include nitrilotri-acetate (NTA), ethylene diamine-tetra-acetate (EDTA), polyphosphate (Calgon), carboxylic acids/dicarboxylic acids and their respective salts. Phosphoric acid esters are used as wetting agents and emulsifying agents. For example, tri-butoxy-ethyl phosphate is found in the effluents, which is problematic due to its solubility in water and low biodegradation rates.

13.9. DEWATERING, DRYING, CONDITIONING, STAKING

The purpose of these operations is to prepare leather for dry finishing – the coating that will give it its final appearance and touch. In addition to local climate conditions/season and possible variations in the characteristics of the leather processed, the choice of dewatering and drying methods primarily depends on the type of leather produced because each technique has a specific influence on leather characteristics. Next in importance are area yield and energy consumption considerations and that is why there are many variations in both the type and sequence of dewatering and drying techniques.

Typical moisture content of leather at different stages: 30 – 45% (after dewatering, ready for shaving), 8 – 15% (after drying), 20 – 30% (after conditioning). Dewatering by mechanical means should significantly reduce the water content and thus reduce energy consumption during the drying process. Forced drying is the most energy-intensive processes in leather making and may account for up to 45% of total energy consumption. Good dewatering also shortens the drying time.

Figure 65. Double felts combined sammying and setting out machine



Source: Rizzi

The currently prevailing dewatering techniques are sammying and/or setting out. Leather drying is an extremely complex process and a good understanding of theoretical principles and practical experience are needed to achieve the desired properties (e.g. feel, softness) and to balance other aims and parameters like area yield, energy and labour inputs, duration, etc.

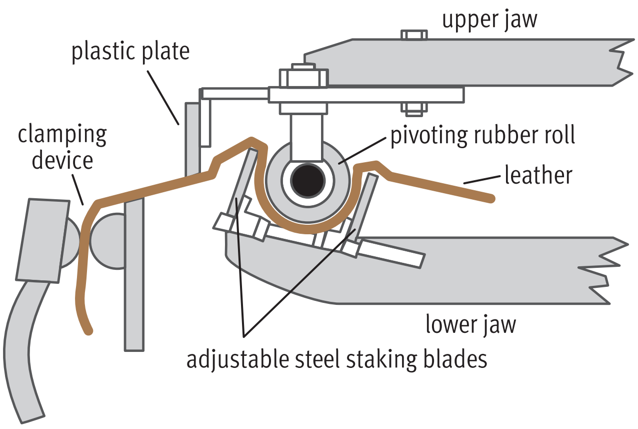
Conditioning is the process of bringing the moisture content of leather to the level suitable for staking: the fibre structure elasticity allows them to freely move against each other. However, too much moisture could lead to leather hardening during subsequent operations.

The traditional method of reintroducing moisture was wooden saw dusting, which is hard to control and requires a lot of experience. Nowadays it is done in conditioning tunnels with throughfeed conveyers synchronized with the pace of stakers. While staking usually produces some area gain, milling produces some area loss but often leather with a very appealing grain appearance.

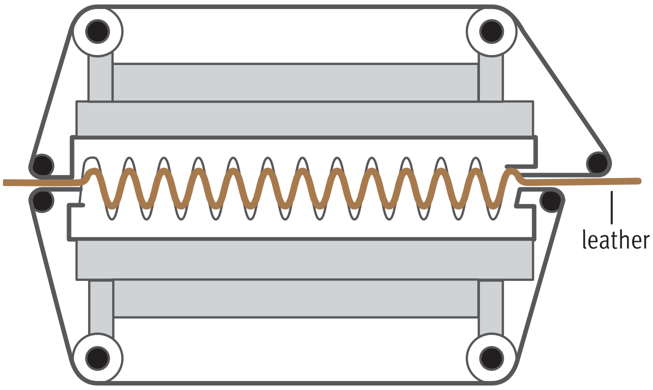
Figure 66. Schematic cross-section view of jaw- and vibro-staking machines

Machines for dry finishing - operating machines

Jaw-type staking machine



Vibration staking machine (Molisa type)



Based on source: BASF Pocket Book for the Leather Technologist, 4th edition

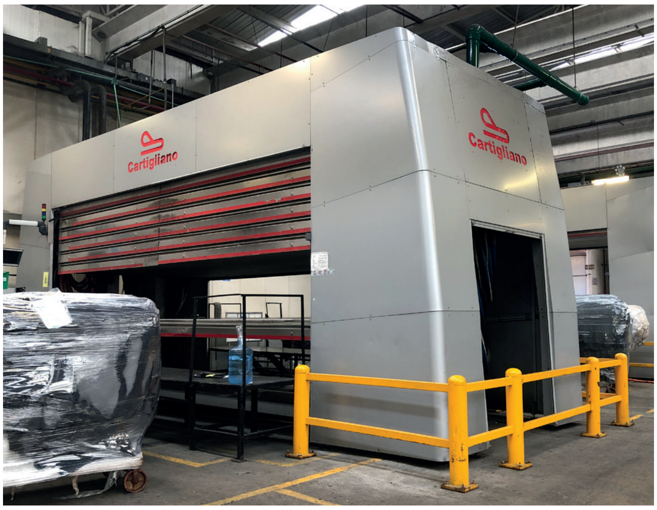
Drying methods could be, somewhat arbitrarily, classified in the following manner:

- Natural, air-drying without supply of energy (hang-drying); overhead conveyers, open air
- Air-drying with or without supply of energy
  - Hang-drying in a channel, tunnel or chamber
  - Toggle drying
- Vacuum drying
- Paste drying

Infrared drying is more used in the drying of coated, finished leather while due to certain constraints, the use of high-frequency drying is quite limited.

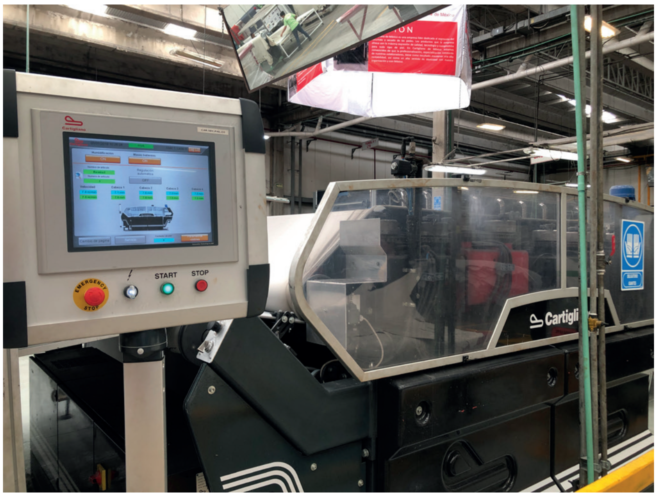
As said earlier, each drying method has a very specific impact on leather properties: on one end is natural air drying which apart from the low cost lends particular softness ideal for (garment) nappa; unfortunately, natural drying is directly dependent on unpredictable variations in climate and is not quite compatible with high output and tight delivery deadlines.

Figure 67. Vacuum dryer



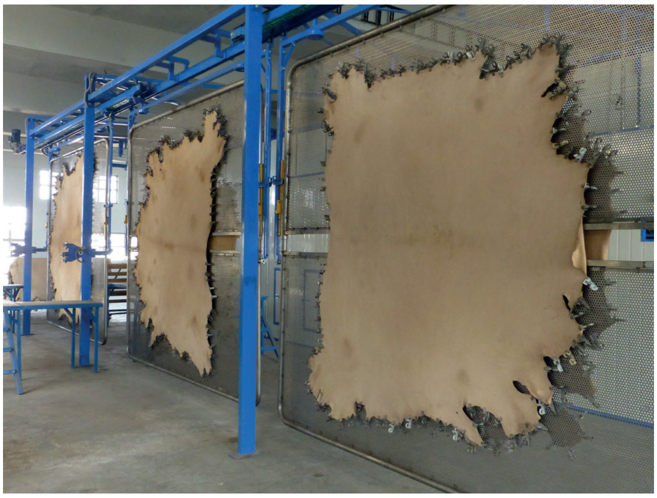
Source: N. Niedzwiedz

Figure 68. Vibro-staking machine



Source: N. Niedzwiedz

Figure 69. Toggle dryer



Source: I.Kral

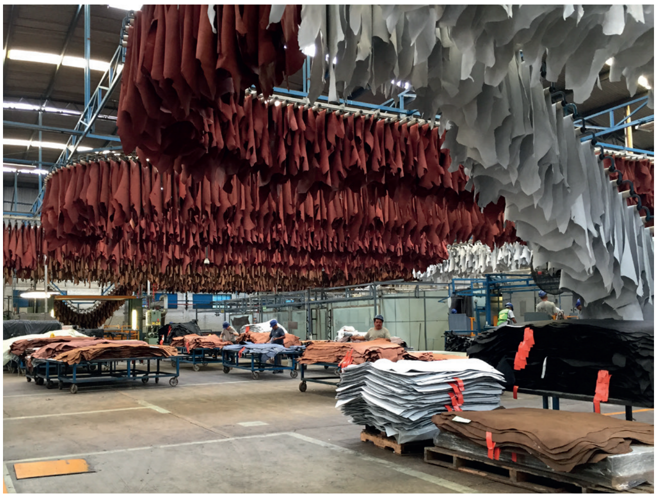
On the other hand, hot air toggling and high temperature vacuum drying give excellent area yield but can easily result in leather with inadequate feel (emptiness).

After drying, the leather is called crust and nowadays it is a tradable intermediate product, almost a commodity like wet blue.

13.9.1. Improved drying methods

The conventional energy saving measures are better insulation of pipes and drying equipment and better monitoring and / control and optimization of the air temperature and humidity. For example, the same leather quality together with considerable energy savings can be achieved by drying at lower air temperatures but with improved ventilation and elimination of poor air flow pockets. Also, drying equipment should ideally be run continuously to avoid energy losses due to reheating.

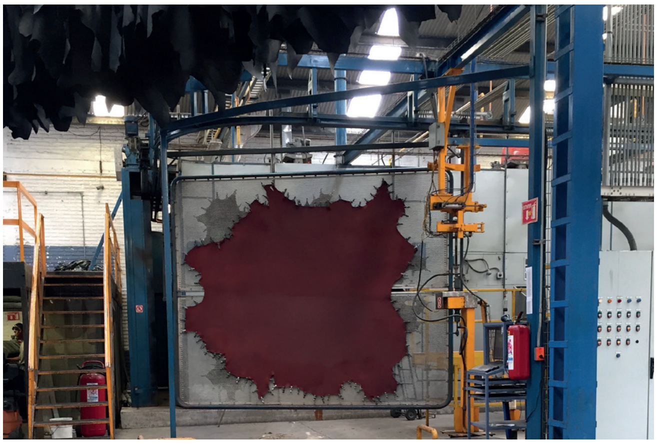
Figure 70. Overhead chain conveyer drying



Source: N. Niedzwiedz

Figure 71. Tension-free drying using overhead conveyer in the tannery Saigon Tan Tec

Figure 72. Toggle dryer, of the Cell Rotaring Conditioning (CRC) System, inside view



Source: N. Niedzwiedz

Other methods to consider are:

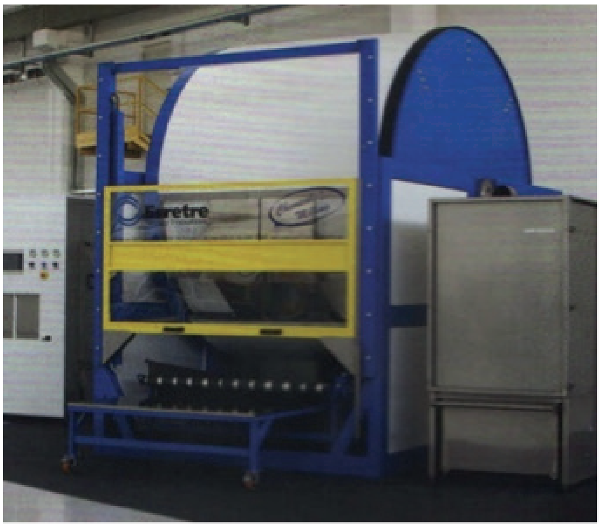
- More efficient dewatering with modern machines; it is estimated that high performance sammying can save about 0.5 – 1.0 GJ/t raw hide.
- One-time investment into larger drying capacities at lower temperatures; it can pay back through lower energy consumption.
- Use of energy from renewable sources (e.g. solar energy) as a supplementary source
- Use of heat pumps

Table 35. Energy consumption with various drying methods

Drying methods	MJ/kg of evaporated water	
	Without heat	With heat
Theoretical	2.48	
Toggling	8.17	
Pasting	6.37	
Chamber drying	5.83	1.62
Vacuum drying	7.20	1.37
Through-feed	5.22	1.12
High-frequency	6.84	

Traditionally leather is taken for staking after the conditioning stage and with a humidity of about 30%. More recently a new approach with staking taking place immediately after sammying/setting (with a water content of about 50%), alternatively after vacuum drying, is being introduced. The reported advantages of the wet staking concept[25] are that the fibre structure remains lubricated, the leather is opened more homogeneously, there is some area gain and less stress, and the subsequent drying process is more uniform.

Figure 73. Milling drum



Source: Erretre, World Leather Dec 2014

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[25] Promoted by the tanning equipment manufacturer Officine di Cartigliano, Italy

14. FINISHING

14.1. GENERAL

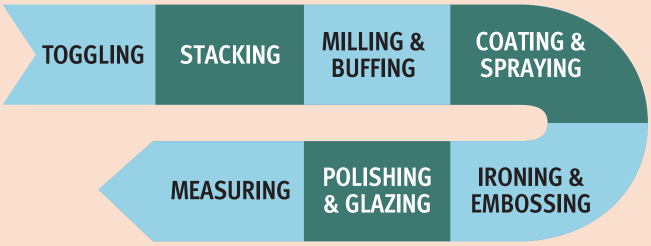
Before focusing on cleaner technology methods, it is useful to recall the main features of leather finishing since nearly each of them calls for specific considerations.

The purpose of finishing is to lend to leather not only a kind of grain protection against soiling, staining and water penetration, but also the desired (uniform) appearance, flexibility, colour, gloss or dullness and handle. Furthermore, depending on the end use, the finish has to meet some specific performance characteristics regarding dry and wet fastness, water vapour and perspiration permeability and high resistance to staining by water droplets.

To achieve that aim leather is subject to a series of processes and operations with many variations adapted to raw material and requirements by individual customers while also taking into account environmental, occupational safety and health (OSH) aspects and even weather conditions. Variations in sequence of operations are so wide that it does not make too much sense to make a typical, representative flow-chart; thus, the following charts provides only a very simplified view of the dry finishing department.

A good example of high performance leather requiring superior finishing is automotive leather. The interior temperatures in the vehicle can vary widely; the leather needs to be able to withstand not only considerable wear and tear but also intense sunlight with very low emissions (fogging).

Figure 74. One of many variations of operations in preparation of wet blue for dry finishing



Based on source: Officine Meccaniche ALPE S.P.a

14.1.1. *Typical mechanical operations*

A very wide range of mechanical operations in very different and varying sequences can be carried out to hide (natural) defects, improve the appearance and lend the desired feel of the leather.

The commonly used mechanical operations in the finishing department are:

- conditioning (optimising the moisture content as described in the previous chapter)
- staking (softening and stretching of leather)
- dry milling
- polishing
- embossing
- plating (flattening)

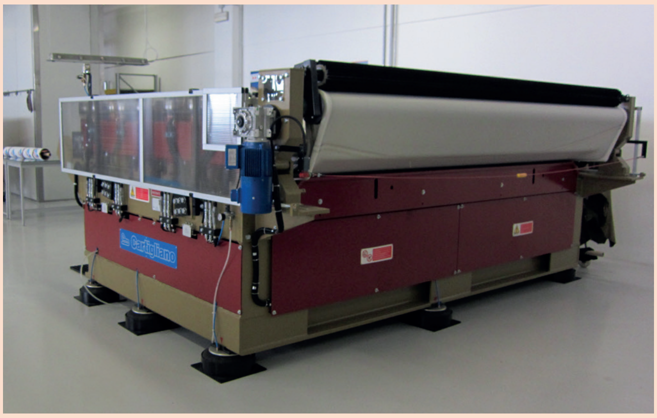
Some of these operations (e.g. staking) may be carried out in both the wet and dry finishing departments, before and/or after applying a coat, or between the applications of coatings.

To achieve specific grain appearance/effects or to hide grain defects, additional operations are needed:

- buffing of the leather surface followed by dedusting
- embossing (a pattern onto leather surface)

The purpose of buffing the flesh side is cleaning and smoothing. An exception is when the product is suede; its fine is nap achieved by a series of buffing with abrasive paper different grit.

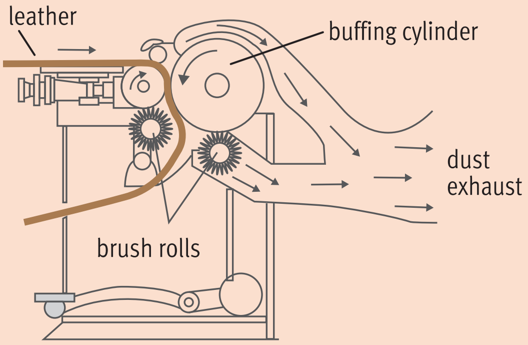
Figure 75. Vibro-staking machine



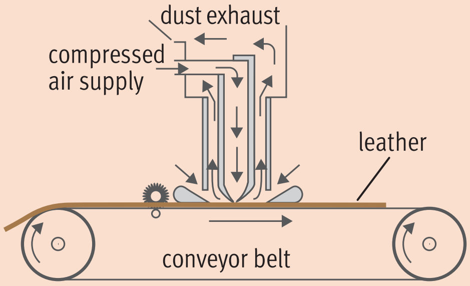
Source: N. Niedzwiedz

Figure 76. Schematic cross-section view of the buffing and dedusting machine

Through-feed buffing machine



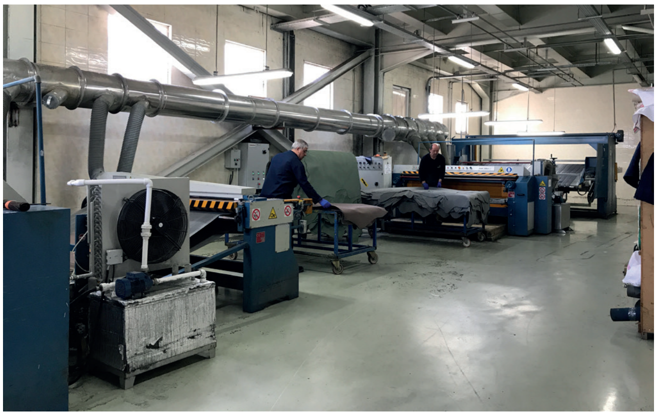
Air-blast dedusting machine



Based on source: BASF Pocket Book for the Leather Technologist, 4th edition

Drying, usually in a tunnel with steam, gas or electric (infrared) heating is obligatory regardless of the method of applying finishes.

Figure 77. Buffing and dedusting machine



Source: I. Kral

14.1.2. Typical coating stages – layers

Impregnation:	**To ensure good adhesion of coating layers, grain smoothness and tightness of the grain. It can be preceded by spray staining (e.g. to level drum dyed shades).**

Base coat:	Responsible for the general appearance and levelness and uniform distribution of pigment(s).
Top coat:	Crucial for final appearance (e.g. gloss/dullness, feel), handle, and, in particular, wet and dry rub fastness of the finish.

Intermediate coats are often applied to improve the adhesiveness and compactness of the coating.

14.1.3. Coatings according to the character of grain

Aniline finish:	**Transparent coats with no pigments except, if needed, very light levelling with aniline dyestuff (spray staining, the depth of penetration regulated by addition of organic solvent or penetrators). Natural appearance of the grain.**

Semianiline:	Small amount of pigments in the base coat but not in the transparent top coat where some dyes can be used
Corrected grain:	The grain with defects (scratches, spots, scars, etc.) snuffed off by buffing, covering finish with heavier coats and pigments, embossed (patterns, grain imitation)
Others, effects:	Brush-off finish (two-tone effect produced by polishing/partial removal of the top layer); antique (two-tone imitation of old leathers); cracked effect, etc.

Other classifications of coating according to effect/appearance (e.g. pull up) or application technique (e.g. foam, film transfer finish), etc. are also possible.

14.1.4. Coatings according to the type of the main finishing materials

According to this criterion coatings can be classified as:

Casein finish:	For elegant glazed finishing (e.g. chevreaux) based on non-thermoplastic protein or protein-like binders.
Nitrocellulose:	Nitrocellulose solution in organic solvent or (water dilutable) emulsion lacquers; alternatively, solvent lacquer based on cellulose aceto-butyrate.
Patent finish:	A specific high gloss finish based on a very thick (nowadays) polyurethane finish
Binder finish:	The most widely used. The thermoplastic binders are based on polyacrylate, polybutadiene or polyurethane polymers.

One somewhat arbitrary, approximate scale of "eco-friendliness" according to the categories of finish coats:

Natural aniline ▸ semi-aniline ▸ nubuck/suede ▸ full grain "eco" finish ▸ full grain conventional finish ▸ corrected grain ▸ coated splits

The basic components of leather finishes are binders, colouring agents (pigments and dyes), carriers (solvents), cross-linking agents, auxiliaries and lacquers.

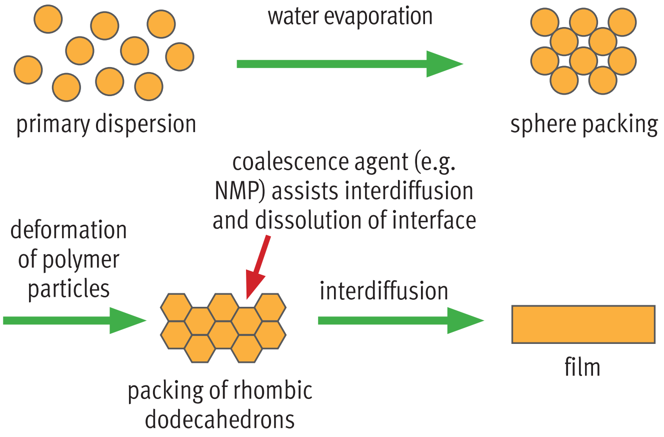
14.1.5. Binders

These agents bind pigment and other materials together; due to their adhesive properties they ensure good adherence of the film to the leather, too.

Protein binders generally consist of preparations based on albumen and casein with some additives like waxes and shellac. Protein binders use plasticisers, such as sulphated castor oil or polyethylene glycol.However, the most commonly used binders are resin emulsions on the basis of poly-acrylics, poly-methacrylic esters, butadienes, polyurethanes, and vinyl acetates. Resins are water-based emulsions.

Polymer films are formed by drying dissolved or dispersed polymers. The presence of organic solvents, especially such as N-Methylpyrrolidone and NMP, should be avoided.[26]

The film formation process


water evaporation
primary dispersion
sphere packing
coalescence agent (e.g. NMP) assists interdiffusion and dissolution of interface
deformation of polymer particles
interdiffusion
packing of rhombic dodecahedrons
film

Based on source: J. Muenter, Clariant Germany, WL June/July 2010

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[26] *The European Chemical Agency (ECHA) issued a restriction on the sale of chemical products*

14.1.6. Colouring agents

Dyes (usually pre-metalised dyes for spray staining or specific applications) are normally supplied in liquid form. Pigments, organic and inorganic, are much more widely used (iron oxides, titanium dioxide and carbon black). The use of inorganic pigments containing lead, cadmium and chromate is harmful and prohibited in most countries.

14.1.7. Cross-linking agents

These are used to bind joint polymer chains in the finishing material. They can be polyisocyanates and carbodiimides (for both base- and top-coats), applied for polyurethane finishes, epoxies (top-coats only) and metal oxides (butadiene finishes for splits). Ideally, cross-linkers should be VOC-free.

While their acute toxicity is rather low, isocyanates[27] are potentially dangerous irritants to the eyes and respiratory tract; it is also believed that they might contain carcinogenic components.[28]

Higly toxic aziridines have been replaced by polyaziridines which are less toxic and can be used for base-coats and top-coats. The use of formaldehyde, traditionally for casein finishes, has been abandoned (carcinogenic). Ethyleneimine-based cross-linking agents used for top-finishes are also not acceptable (toxic and carcinogenic).

14.1.8. Lacquers, lacquer emulsions, auxiliaries, carriers

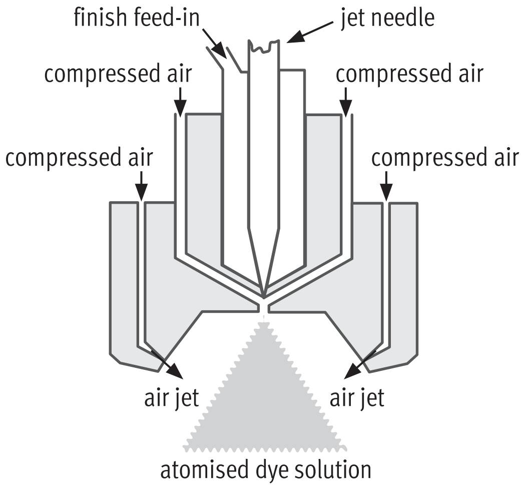
These are used for the top or to fix the coat of a finish. They are made by dissolving nitrocellulose in solvents (e.g. ethyl acetate, methoxypropanol, methyl isobutyl ketone) subsequently emulsified with water and surfactant to give lacquer emulsions. Polyurethane lacquers are also used.

A very wide range of auxilliary agents is used for specific purposes such as better film forming or better dispersion of pigments, improved penetration, thickening, dulling, fixing or sticking prevention. They can contain waxes, plant mucilages, phtalate-free plasticisers, cellulose products or polymers as protective colloids or natural or synthetic oils as softening agents.

Carriers is another name for water and organic solvents needed to make suspensions/dispersions of binders used in finish formulations. There are organic solvents that actually dissolve the binders (e.g. ethyl acetate) and diluents, i.e. those that enable the ready-made solution to be diluted to spraying viscosity or the desired concentration (e.g. methoxypropanol, isopropanol).

These products can be used instead of toluene or xylene as solvents for lacquers.

Figure 78. Operating principle of compressed air spraying machine and spray gun



Based on source: BASF Pocket Book for the Leather Technologist, 4th edition

Table 36. Solvents and diluents used in finishing (aqueous systems)

Solubilizers for aqueous systems							
Product	Abbreviation	Boiling range °C	Flash point °C	Ignition temperature °C	Density at 20/4 °C g/ cm^2	Risk class
1-Methoxypropanol-2*	PM	119 - 122	32	270	0.962	A II
Butylglycol (2-Butoxy ethanol) *	BG	168 - 172	67	230	0.8995 - 0.902	A III
Butyldiglycol (2-(2-Butoxyethoxy)- ethanol) *	BDG	228 - 232	105	210	0.952 - 0.956	-
Dipropyleneglycol-methylether (tech.mixture) *	DPM	185 - 195	80	205	0.957	A III
Propylenecarbonate**	PC	240 - 243	123	455	1.204	-
N-Methylpyrrolidone dist.	NMP	204	91	245	1.028	A III

Based on source: BASF Pocket Book for the Leather Technologist, 4th edition
**Recommended as substitutes for Ethylglycol*

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[27] *Isocyanate: R-N=C=O; Carbodiimide: RN=C=NR*
[28] *See, for example https://www.osha.gov/SLTC/isocyanates/*

Table 37. Solvents and diluents used in finishing (lacquers)

Solvents for lacquers						
Product	**Abbreviation**	**Boiling range °C**	**Flash point °C**	**Ignition temperature °C**	**Density at 20/4 °C g/cm²**	**Risk class**
Ethyl acetate (Acetic acid ethylester)		74 - 78	-6	460	0.898-0.902	A I
iso-Butylacetate (Acetic acid iso-butylester)	i-BuAc	115 - 118	19.5	425	0.866-0.871	A II
n-Butylacetate ((Acetic acid n-butylester)	n-BuAc	124 - 128	26.5	415	0.880-0.881	A II
2-Ethyl-hexylacetate		192 - 205	77	270	0.870-0.875	A III
Butylglycolacetate		185 - 188	76	300	0.940	A III

Source: BASF Pocket Book for the Leather Technologist, 4th edition

Figure 79. Spraying equipment

Head of the rotary spraying machine Reciprocating spraying machine with 8-12 gun holding arms

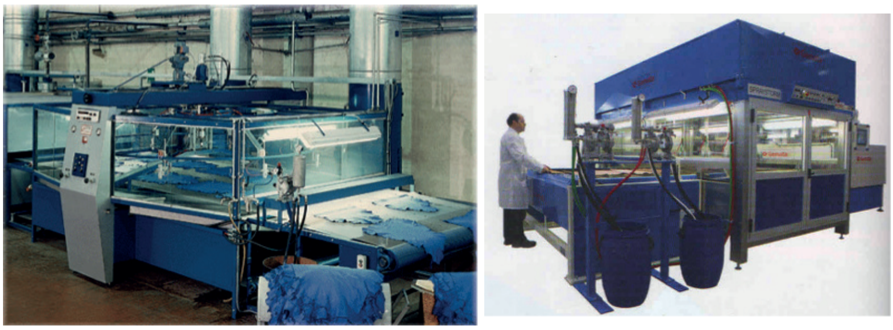
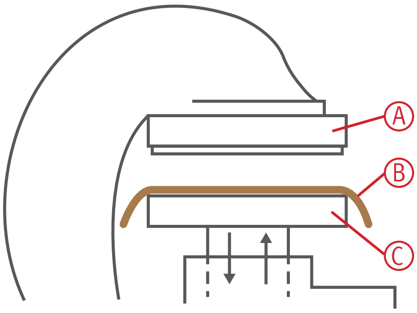


Table 38. Finishing products – Approximate amounts required in grams/m² of leather

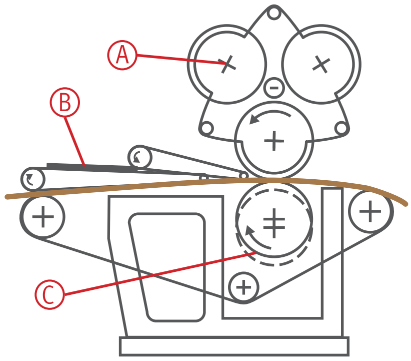
Products	**Full grain leather**			**Corrected grain**	**Splits**
	Aniline	**Semi aniline**	**Pigmented**		
Pigments	0-3	5 - 20	20 - 40	20 - 50	30 - 60
Aniline dyes	20 - 40	10 - 20	5 - 10	0 - 10	0 - 5
Binders	5 - 30	10 - 50	40 - 80	80 - 120	140 - 240
Auxiliaries	5 - 20	10 - 30	10 - 40	20 - 40	20 - 40
Top coating emulsions	20 - 60	20 - 60	20 - 60	30 -60	30 - 60
Water-based top coats	20 - 60	20 - 60	20 - 60	30 - 60	30 - 60
Organic solvents	0 - 10	0 - 30	0 - 30	0 - 80	0 -40
Total	**70 - 223**	**75 - 270**	**115 - 320**	**180 - 420**	**250 - 505**

Derived from the BASF Pocket Book for the Leather Technologist, 4th edition

Figure 80. A simplified cross-section and the working principles of the hydraulic press and throughfeed rotary press



A: Heated Plate B: Leather C: Work Table



A: Work Cylinders B: Leather
C: Pressure Roller

Based on source: World Leather, June/July 2009

Although the solvents listed in the tables are less hazardous than previously used solvents, necessary precautions when handling organic solvents must be observed.

Quantities of surface coat materials applied range from only a few grams per square metre to 400 g/m2 for corrected grain, pigmented splits and oily leathers.

Application of the surface coat

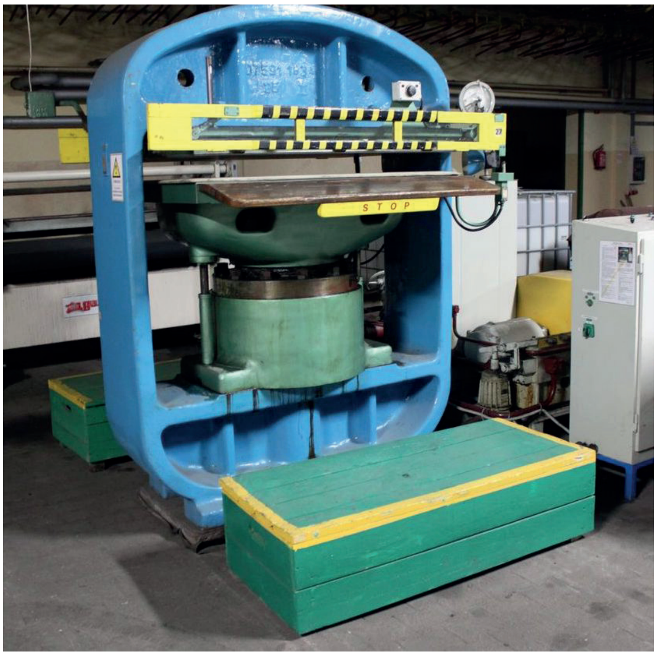
- Padding (manually or by machine)
- Curtain coating
- Roller coating (forward and reverse)
- Spray coating - manual and (usually) by rotary spraying machine;

All of these finishing applications are followed by drying.

A very special category are anti-soiling (dirt remains on the surface) and anti-staining (dye penetrates onto and into leather surface) properties expected from automotive and furniture leathers. As a rule, the performance criteria (standards) are defined by individual manufacturers and brands.

Heat and light ageing, flammability and resistance to scuffing and abrasion are further parameters regularly defined and tested by the automotive industry.

Figure 81. Hydraulic plating and embossing press

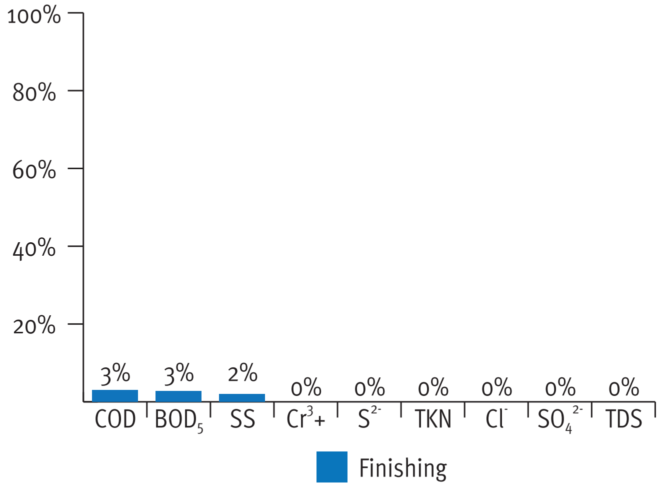


Source: N. Niedzwiedz

14.2. POLLUTING EMISSIONS FROM FINISHING

Conventional coating by spraying results in considerable losses of coating material. Measured in terms of key pollution parameters (COD, BOD, SS) and the amount of waste water discharged at the finishing stage, polluting emissions are quite insignificant in comparison with the beamhouse and tanning department (See the diagram below).

Figure 82. The share of finishing in total emissions – usual parameters



Based on chart by M. Bosnić

However, environmental threats due to use and emissions of pigments, organic solvents (VOCs), airborne particles and malodours in old poorly ventilated areas are quite serious; the negative impact of vibrations, dust and noise cannot be ignored either. All these risks compounded by high fire hazards make old finishing departments possibly the most potentially harmful to workers' health.

Evidently, good housekeeping and monitoring finish usage, equipment optimisation (especially spraying), avoidance of re-work, etc. are also important in reducing the negative environmental impact of finishing operations.

14.2.1. Airborne particulate matter

While a certain amount results from milling (softening due to mechanical action in drums), the main emissions of airborne particles in finishing emanates from buffing where leather surface is abraded; the particles are wet or dry and with a high organic content. In addition to irritation of the respiratory tract, the health risk depends on the particle size and its chemical composition.

Buffing dust concentrations vary widely (0.1 to 30 mg/m^3) depending on the space and equipment in place. An efficient extraction ventilation system fitted with bag filters or wet scrubbers is a must; in the EU the efficiency norm to meet is 3 to 6 mg/Nm^3 of exhausted air expressed as a 30-minute mean. It is also necessary to reduce the noise pollution from the exhaust system itself, which can be considerable; the design, selection and positioning of fans is thus very important.

A disposal route for the dust collected is not easy to find; in some cases it is taken away, compacted and briquetted.

14.2.2. Solid waste and waste water

Solid wastes in finishing are mainly residues from finishing mixtures and sludges from air pollution abatement systems. Waste water comes from the finishing kitchen and equipment cleaning; while the volume of waste water is insignificant, the water can be heavily polluted by the presence of organic solvents, pigments containing some metals as well as hazardous chemicals present in other finishing materials such as cross-linkers and auxiliaries.

In some tanneries, particulate matter is compacted and briquetted after being collected by various systems. These residues are wastes for which a use or disposal route must be found. If a wet scrubbing system is used, the slurry produced is a waste for disposal. Recycling the washing water can reduce the water consumption.

14.2.3. Organic solvents - Volatile organic compounds (VOC)

As said earlier, organic solvents are used as carriers in the formulation of the finish. However, as a rule they are also already contained in commercial finishing products (e.g. lacquers) very often without indication about the type and quantity of organic solvent used.

The main problem with organic solvent-based coating agents is the emission of volatile organic compounds (VOCs) released during and after the coating process and there are considerable variations

Table 39. Solvent emission limits for leather coating

Annex VII of Directive 2010/75/EU Activity No. 13	Annual solvent consumption in tonnes	ELV g of solvent emitted per m2 of product produced
For leather-coating activities in furnishing and particular leather goods used as small consumer goods like bags, belts, wallets, etc.	> 10	150
Other coating of leather (medium use)	10 - 25	85
Other coating of leather (high use)	> 25	75

Source: BREF 2013

in the use of solvents not only for different types of leather but also between individual producers.

The issue of VOC emissions in the leather industry were largely triggered by the so-called fogging problem related to the automotive industry but subsequently issues like smell and toxicity were also raised. Particular challenges were acetaldehyde and propylene glycol ether to be followed by other substances not quite anticipated.

According to EU legislation, organic compounds are classified as VOC if their vapour pressure at 20 $^{\circ}$C or at application temperature respectively is more than 0.1 hPa[29]. In the USA it is the compounds that take part in photochemical reactions in the atmosphere.

A number of organic compounds are directly harmful to human health or to the environment. Moreover, many organic solvents undergo chemical reactions in the atmosphere that cause a number of indirect effects, in particular the formation of photochemical oxidants and their main constituent, ozone. Pollution by tropospheric ozone is a widespread and chronic problem.

Due to their persistency and accumulation in the biosphere, halogenated hydrocarbons and, in particular, highly volatile halogenated hydrocarbons, are subject to special attention and relevant legislation.

Certain halogenated organic compounds are ozone-depleting substances and in compliance with the Montreal Protocol have to be phased-out.

Table 40. Comparison of VOC emissions from different types of finishes

Coating material	Organic solvent	Emission (kg/h)	Emission concentration (g/m^3)
Solvent-based finish	> 75 %	50	3
Water-based finish	10 - 75 %	5	0.3
Solvent-free finish	< 10 %	< 1	

Source: BREF 2013

Either the pure solvent is used or products like biocides and auxiliaries used in the finishing process may contain halogenated organic compounds.

Untreated organic solvent emissions from the finishing process can vary between 100 and 3500 mg per m3 in conventional processes. About 50% of measurable emissions arise from spray-finishing machines, 50% from dryers. Fugitive emissions to the air and solvents in wastes account for the rest of solvent consumption.

The leather industry as a whole has considerably reduced its solvent use. For example, in some parts of Europe the consumption of organic solvents in finishing in the last 15 years has more than halved.

The VOC emission levels considered to be in conformity with Best Available Technologies (BAT) in the EU are given in the next Table.

Table 41. BAT-associated solvent use levels and BAT-associated emission levels for VOC

Parameter	Type of production		BAT-associated levels g/m^2 (annual avg. values)
Solvent use levels	Where water-borne coatings are used in combination with an efficient application system	Upholstery and automotive leather	10 - 25
		Footwear, garment, and leather goods leathers	40 - 85
		Coated leathers (coating thickness > 0,15 mm)	115 - 150
VOC Emissions	Where an extraction ventilation and abatement system are used as an alternative to the use of water-borne finishing materials		9 - 23 (1)

The main parameters for an assessment of organic solvent-based finishing agents are:

- the type of organic solvent used with regard to toxicity and the recycling options;
- the efficiency of abatement in all processes where organic solvents can be released consequently, i.e. also in drying and storage;
- the ratio of recycling or reuse of the organic solvent.

The minimum requirement for organic solvent-based coatings is the recording of solvent consumption, to include not only the solvents bought as solvents but also the solvents contained in the finishing chemicals. This is the only acceptable way to calculate the overall emissions of VOC, as it is not possible in practice to monitor fugitive emissions. VOC releases from leather during storage are estimated as 10% of the applied organic solvents that remain in the leather and about 60% of the amount emitted in the drying tunnel. The rest is emitted during storage. Ideally, VOC free finishing systems should be based on renewable resources.

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[29] *Official definition: Any organic compound having at 293.15 $^{\circ}$K a vapour pressure of 0.01 kP (0.1 mbar resp. 0.075 mm Hg) or more or having a corresponding volatility under the particular condition of use.*

14.3. POLLUTION PREVENTION AND/OR REDUCING MEASURES

14.3 1. Water based finishing – avoidance of VOCs

Reducing organic solvents – VOC emissions is in principle possible by:

- Full replacement of organic solvents based with water-borne coatings (e.g. by replacing lacquers with hard resin topcoats)
- Partial replacement (e.g. replacing lacquers with lacquer emulsions)
- Use of advanced extraction ventilation and abatement systems (wet scrubbing, adsorption, bio-filtration and/or incineration)
- A combination of the above methods with particular attention to the coating techniques themselves

Completely organic solvent-free finishing is still not available; however, while the organic solvent content in organic solvent thinnable lacquer is 80-90%, in water thinnable lacquer emulsions the solvent content is about 40%, in water-based systems it is only 5-8%. Provisions for organic solvent recycling include a careful selection of organic solvents; otherwise recycling can be impossible.

Furthermore, for cleaner finishing selection and application of X-linkers, careful consideration and control are needed; similarly, water-based spray dyes should be used to the greatest possible extent.

The release of VOCs requires special abatement techniques. Organic solvent-based processes in closed spray cabinets and closed drying systems, which offer an acceptable environmental performance, require cost- intensive abatement techniques.

Scrubbers create an effluent containing finish mixes and water-miscible organic solvents. Organic solvents that are not water-soluble will be emitted into the air. Equipment for wet scrubbing of the exhaust air has become a standard installation in most spraying units in order to eliminate dust particulate and aerosols.

In assessing the VOC emissions, a distinction has to be made between the applied solvents according to their toxicity.

The spray booth must be closed during processing in order to minimise emissions from the over-spray (aerosols, organic solvents) into the working environment. Extracted air requires treatment to reduce particulate and organic solvent emissions.

In the finishing process, water-based systems are increasingly favoured because of environmental concerns about organic solvents and in order to comply with regulations.

In order to achieve equal characteristics with low organic solvent and water-based systems, cross-linking agents for the finishing polymers often have to be used. The toxicity of these agents is problematic, but commercial products offer the agents in a less toxic and less volatile form. Nevertheless, appropriate safety precautions are required when handling and applying these agents.

For any organic solvent applied in the process that cannot be substituted by aqueous systems, the alternative is to use organic solvents with the lowest impact on workplace safety and the environment and, in order to make recycling feasible, to avoid mixtures.

The main advantage of water-soluble lacquers is the considerable reduction of organic solvent consumption and releases. Most water-based finishing products still contain a low amount of organic solvents. The suitability of water-based coatings is still dependent on the final product that is produced. The coatings are being improved, and the range of uses is being expanded.

The storage and use of organic solvents require special measures to reduce releases into the air and avoid spillage onto the ground; it is not quite known, for example, whether or not chlorinated organic compounds can even easily pass through concrete floors. On the other hand, their substitution i.e. non-halogenated compounds may require additional safety fire and explosion precautions.

Energy consumption for drying water-based top-coats is higher, yet the solvent-based finishing is higher in CF than water-based finishing.[30]

There may also be an increase in the organic content of waste water from finishing.

Base coats are generally water-based. If very high standards of top-coat resistance to wet-rubbing, wet-flexing and perspiration are required, then solvent-based systems cannot always be substituted by aqueous-based systems. In general, solvent- and water-based systems have similar costs.

14.3.2. Improved coating techniques

Padding, curtain coating, roller coating, and spraying of leather are substantially different coating techniques suited to different types of leather articles produced and coating materials applied.

14.3.3. High-volume low-pressure (HVLP) spray guns

The air column from the conventional spraying gun (pressure about 2.0 bar) carrying finishing articles bounces back from the leather surface resulting in a loss of 55-65% of finishing material.

High-volume low-pressure spray guns spray with a large volume of air at low pressure (only about 0.7 bar) can be used so that the "bounce-back" is considerably reduced in comparison with conventional spraying. The HVLP technique does not give completely satisfactory results for some articles, such as upper leather and garment leather.

Table 42. Comparison of conventional and HVLP spray guns

	Advantages	Disadvantages
Conventional	• No special pipework needed • Cheaper than HVLP	• Poor transfer efficiency (40-60%) • Considerable risk of high emissions from the extraction system • Rapid build-up of solids in the spray cabin and transport lines
HVLP	• Material wastage less than 30% • Reduced emissions/pollution • Shorter cleaning times	• More expensive • Air supply lines have to be changed • Fan stability quite sensitive

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[30] *Reducing the carbon footprint of leather, B. Wegner, World Leather Dec 2014*

14.3.4. Airless spray guns

When using airless spray guns the coating material itself is pressurised. It is then atomised at a spray nozzle without the use of air. Airless spraying is more suited for high application rates.

Compared to a spraying efficiency of as low as 30 % for conventional spraying operations, HVLP and airless spraying improve spraying efficiency up to 75%. HVLP or airless spraying may not be suitable for all coating materials. This situation is likely to change as low solvent coatings are improved.

14.3.5. Computer-aided spraying

Computer-aided spraying means that automated systems sense the area, either by a mechanical feeler, electric eye or ultrasonic system, and control the opening of the guns so that they only spray when the leather is passing directly beneath them. The technique is widely available in more or less sophisticated versions. Care must be taken that the detection equipment is properly adjusted.

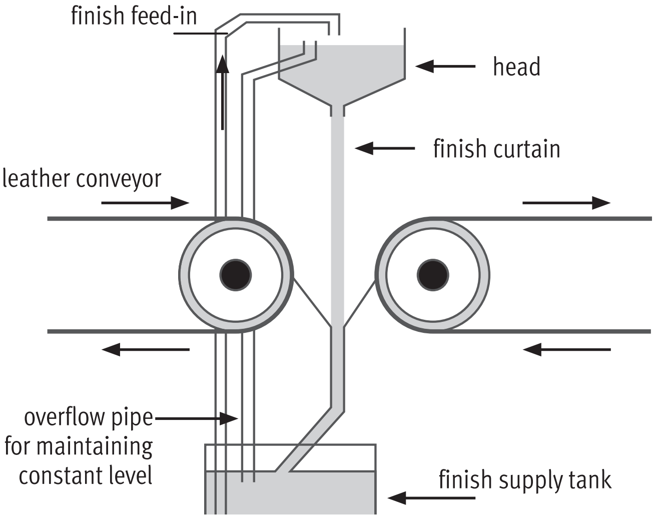
Computer-aided spraying can prevent up to 75% of the finish being lost as overspray. The emissions of spray mists are reduced, and because coating efficiency is improved, solvent emissions are reduced too.

Existing equipment can be retrofitted for HVLP, airless and computer-aided spraying, but the costs and effort involved will depend on the type of systems already in place. Proper design and operation of the spraying exhaust is important for reducing pollution and fire risks.

14.3.6. Curtain coating

Curtain coating can be compared to roller coating but cannot be used as a substitute for spray coating. This technique may be used to apply finishes that have a high organic-solvent content.

Figure 83. Operating principle of the curtain coater



Based on source: BASF Pocket Book for the Leather Technologist, 4th edition

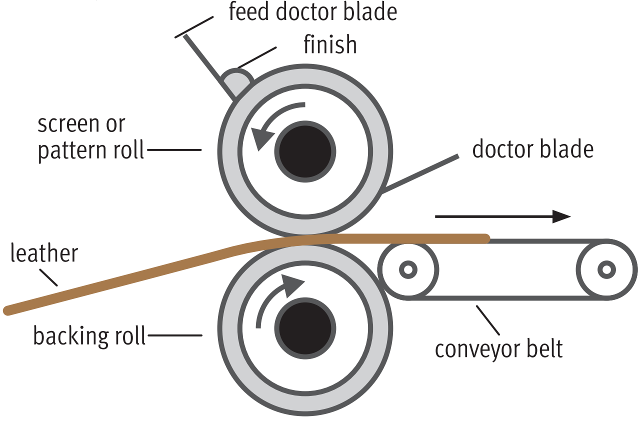
14.3.7. Roller coating - roller coating vs. spraying

In roller coating the finish is applied by grit rollers to the surface of the leather, similar to the process used in printing. Differences exist concerning the grit size of the roller, the direction of application and the speed of the conveyor and the rollers.

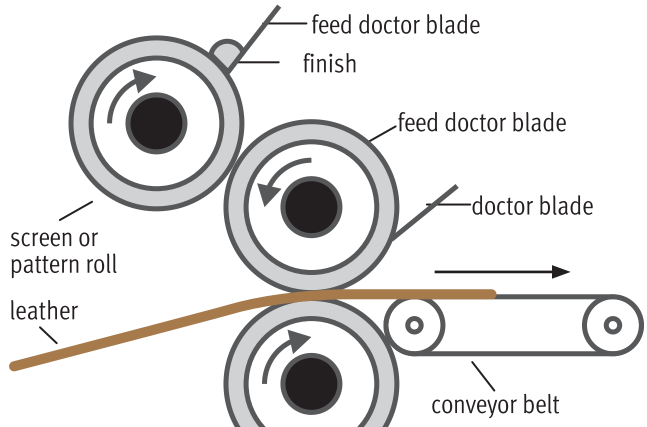
This process is used especially, but not exclusively, to treat large pieces of leather, but the stability, softness, and thickness of the leather are important parameters. The operation needs careful adjustment with respect to speed, viscosity, and the cleaning of rollers to produce the desired quality. It might not be applicable to very thin leathers.

Figure 84. Operating principle of the roller coater

a. Direct process



a. Indirect process

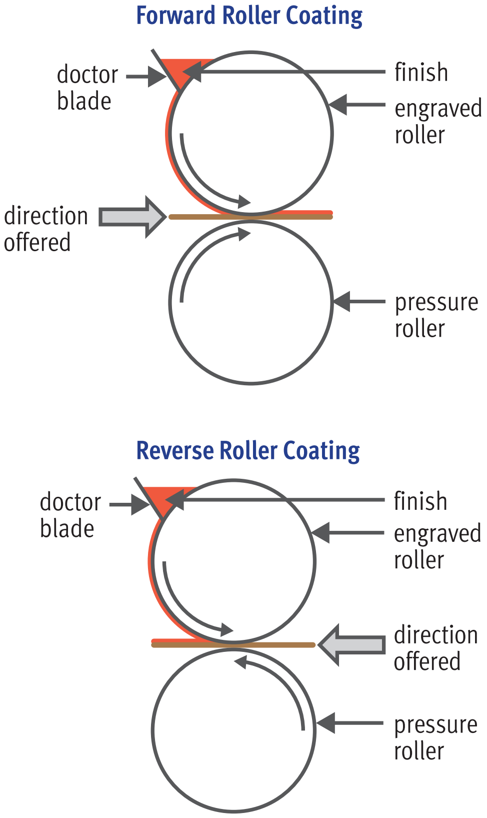


Based on source: BASF Pocket Book for the Leather Technologist, 4th edition

Roller coating techniques are nowadays well established but further research and developments are ongoing. More specialist models allowing for hot and cold applications of oils, waxes and microfoam products are also available on the market and are used in several tanneries in Europe. The same conveyor/drying unit as for the spraying booth can be used.

Forward coating is suitable for lighter top and contrast coats (typically 1-5g/sqft); reverse coating for heavier impregnation and base coats (3-30g/sqft).

Figure 85. Reverse and forward roller coaters: schematic view



Based on source: BASF Pocket Book for the Leather Technologist, 4th edition

The more efficient application of coating materials leads to less waste and less solvent emission for the coating of a given area, to the benefit of the environment. Avoidance of the mist and solid particulate emissions associated with spraying is also beneficial.

The operational data will entirely depend on the product that is being produced. Coating wastage rates of 3 – 5% are reported as opposed to 40% for conventional spraying.

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

Recycling of the cleaned air might save energy for workplace heating.

Attempts with through-feed and water transfer systems finishing via coat paper have not gained much ground.

Finally, it should be remembered that while the leather character is basically defined in the beamhouse, tanyard and during post-tanning, it can nevertheless be significantly affected by the finishing process. For example, high temperatures, especially during convection drying together with moisture loss can lead to leather hardening and area loss.

Comparison of consumption of chemical product in a 3400 mm water curtain spray cabin with those of roll coater

	Consumption of chemical product g/sq ft	**Quantity applied g/ sq ft**	**Quantity lost g/sq ft**
1st sprayed base coat	20	13	7
2nd sprayed base coat	6.7	4	2.7
Sprayed intermediate (before embossing)	5	2	3
Sprayed colour coat	7.5	3	4.5
1st sprayed top coat	6.2	2.5	3.7
2nd sprayed top coat	6.2	2.5	3.7
Total	**46.6 + (5 intermediate)**	**25 + (2 i ntermediate)**	**21.6 + (3 intermediate)**

	Consumption of chemical product g/sq ft	**Quantity applied g/sq ft**	**Quantity lost g/sq ft**
1st Jumbostar pre-coating (stucco)	3	3	0
2nd Jumbostar coating	12	12	0
Topstar Colour coating	3	3	0
1st Topstar Top coating	2.5	2.5	0
1st Topstar Top coating	2.5	2.5	0
Total	**23**	**23**	**0**

Comparison of the water, compressed air and electric power consumption of a 3400 mm water curtain spray cabin with those of roll coater

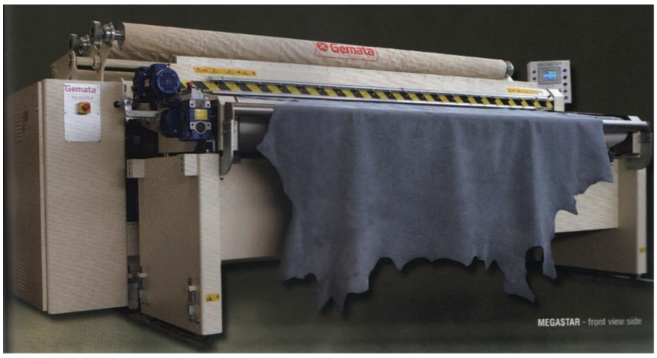
3400 WATER CURTAIN SPRAY CABIN		
Water consumption:		
Water consumption at every 12 article charge		20-35 Lt
Cabin water consumption in maintenance every 40 working hours (1700 Lt)		42.50 Lt/h
Water consumption per scrubber while working		22.00 Lt/h
Total consumption per scrubber per 40 working hours For cleaning and sludge disposal (750 Lt)		18.75 Lt/h
TOTAL consumption		**83.25 Lt/h**
Electric power:		
Carousel gearbox	1.1 kw (installed)	absorbed 0.77 kw
Water recirculating pump	4 kw (installed)	absorbed 2.8 kw
Scrubber motor	22 kw (installed)	absorbed 15.4 kw
Scrubber pump	0.75 kw (installed)	absorbed 0.52 kw
TOTAL	**27.85 kw (installed)**	**absorbed 19.49 kw**
TOTAL electrical power consumption		**19.49 kWh**
Compressed air consumption:		
Consumption for the guns' changeover		144,000 Lt/h
Air nozzle pipe to remove dust from leathers		1,500 Lt/h
TOTAL compressed air consumption		**145,500 Lt/h**
TOPSTAR		
Water consumption:		
Water consumption at each article charge		20-35 Lt
Water consumption for the washing of the rubber roller		2 Lt/h
TOTAL water consumption		**2 Lt/h**
Electric power:		
TOTAL	**7.85 kw (installed)**	**absorbed 5.2 kw**
TOTAL energy consumption		**5.2 kWh**
Compressed air consumption:		
Machine		400 Lt/h
Product pump		1,500 Lt/h
Air nozzle pipe to remove dust from leathers		1,500 Lt/h
TOTAL compressed air consumption		**3,400 Lt/h**
JUMBOSTAR		
Water consumption:		
Water consumption at each article charge		20-35 Lt
Water consumption for the washing of the conveyor		3 Lt/h
TOTAL water consumption		**3 Lt/h**
Electric power:		
TOTAL	**5.4 kw (installed)**	**absorbed 3.5 kw**
TOTAL energy consumption		**3.5 kWh**
Compressed air consumption:		
Machine		400 Lt/h
Product pump		1,500 Lt/h
Compressed air nozzles to remove dust from leathers		1,500 Lt/h
TOTAL compressed air consumption		**3,400 Lt/h**

Based on source: World Leather, Gemata (Topstar-Jumbostar)

Table 43. Overview of leather coating methods

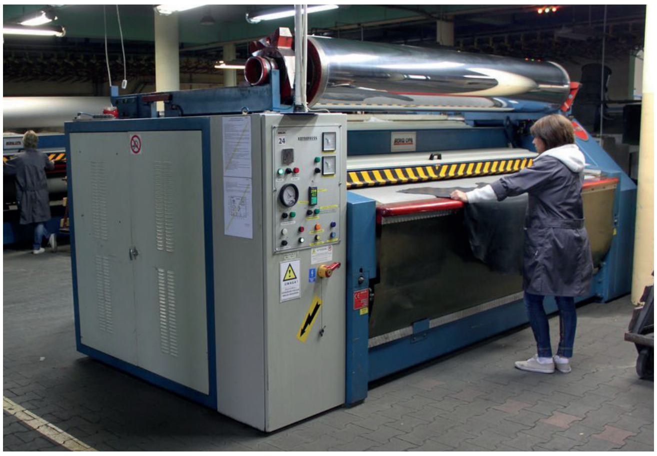
	Advantages	Disadvantages
Padding	• Good adhesion • Compensation of uneven wetting	• Labour intensive • Not good for top coats • Additional spray coats needed • Machine padding not quite satisfactory
Spraying	• Uniform application • Wide range of applications • High output • Possible various angle spraying effects • Easy to make minor colour adjustments	• High percentage of material wastage (40-60% normal, 25% with HVLP guns) • Sometimes adhesion and inter-coat problems • Air pollution • High energy consumption
Curtain coating	• Suitable for impregnations corrected grain • Waste is only about 10% • Lowest investment	• Not suitable for grain/quality leathers • Rather low output
Roller coating	• Better adhesion than with spray coating • Suitable for large hides, hot applications of oils and microfoam finishes • Possible wide variations in amount of material applied (1- 30g/sqft) • Waste is only about 10% • Higher solids, the same dryer but less energy for drying • Environmentally friendly	• Viscosity adjustment required • Thin areas missed • Pleating of soft leathers • Turkey tracks due to system imbalance • Lower output in comparison with spray coating

Figure 86. Roller coater



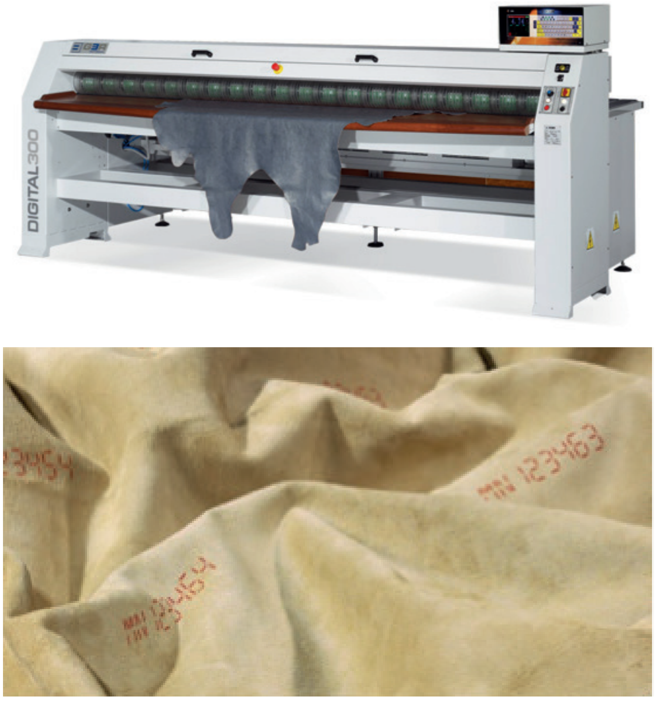
Source: Gemata, World Leather, Dec 2014

Figure 87. Rotary ironing machine, adjustable pressure



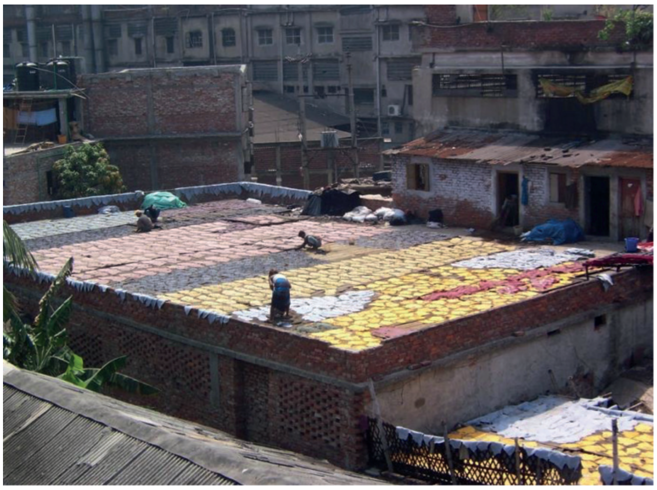
Source: N. Niedzwiedz

Figure 88. Electronic measuring machines with multiple integrated stamping system



http://www.gerelettronica.com

Figure 89. Low cost drying in a developing country



15. RESTRICTED SUBSTANCES

15.1. GENERAL

Restricted substances are chemical substances controlled by national or regional legislation, (multinational) brands and/or ecolabels due to their proven negative impact on human health (of both workers and consumers) and ecosystems.

The normal transfer routes of such substances are by absorption through skin, inhalation or ingestion; although typically present in very small quantities, their impact can be significant.

Too often there is a lot of misunderstanding and unscientific interpretations of hazards associated with exposure to directly or potentially harmful substances. Too often the gist of the statement by the medieval chemist Paracelsus is forgotten: *Everything is cure everything is poison, it depends on dose* (and the transfer route). Even a perfectly innocent chemical like distilled water injected into our bloodstream in larger amounts can be fatal!

Below are some considerations that might be useful in this regard:

- Hazardous products **are not a priori harmful**; handled properly with adherence to the prescribed/recommended safety precautions, they are quite safe. In other words, the potential hazard and the real risk are not the same.
- The potential hazard posed by a certain chemical is a constant factor; it is the level of exposure (i.e. quantity/concentration, the transfer route, length of time, frequency, etc.) that determines the overall risk.
- In this context it is useful to understand the categories of the Threshold Limit Value - Time Weighted Average (TLV-TWA$_8$) and the Short Term Exposure Limit (TLV-STEL).
- Of particular importance is the maximal workplace concentration (MAK) value i.e. the maximum allowable concentration in the workplace in the form of gas, vapour, or air-suspended matter which, according to our present state of knowledge, generally does not impair the health of the workers and does not inconvenience them unduly, not even on repeated and prolonged daily (8 hours) exposure under the condition of a weekly working time of up to 45 hours.
- It is also useful to understand the significance of measured or prescribed amounts of a substance such as D$_{tox}$ (toxic dose), DE (efficient dose) DL/LD (lethal dose), ID (individual dose), IMD (individual maximum dose), MD (maximum dose), MDD (maximum daily dose), ND (normal dose), DD (daily dose), LD$_{100}$ (the absolutely lethal dose), LD$_{50}$ (the average lethal dose, at which 50% of animals in an experiment are killed) and LD$_0$ (the maximum non-lethal dose).
- Exposure assessment is needed for both intended and foreseeable unintended use of material such as inhalation, exposure (physical evaporation and chemical decomposition), dermal exposure (skin contact) and oral exposure (mouthing and swallowing).
- Use of “greener” chemicals (e.g. biocides) is not necessarily better if they are weaker and higher amounts have to be applied.
- Here it is important to distinguish the risk of *acute toxicity* (poisoning produced by a single dose), *subchronical* (poisoning produced by toxicity of repeated dosage within) a relatively short time) and chronical toxicity (poisoning produced by repeated dosage over a relatively long time).
- All chemicals have to be evaluated according to their acute oral toxicity, irritation to the skin and mucous membranes, mutagenic, teratogenic and carcinogenic effects and the effects of repeated or prolonged exposure.
- The worker in production (much less the ultimate user of leather product) can be protected from the actual or potential hazard posed by a chemical in various ways, for example by wearing personal protection equipment (gloves, goggles, mask) or by limiting the extent to which he is exposed to it.
- It is vital that all important data and risks are communicated to all involved in a readily understandable form. In addition to Safety Data Sheets this also includes symbols, drawings as well as warnings in the local language.
- Regrettably, there are no widely accepted standardised analytical tests for all chemicals found on RSLs; in principle, all limits should be realistic and accurately measurable.

In the globalized world economy and certainly for any export oriented leather and/or leather products manufacturer, it is prudent to go beyond national legislation and adhere to the strictest norms concerning the presence of some proven or potentially harmful substances.[31]

15.2. REGISTRATION, EVALUATION, AUTHORISATION AND RESTRICTION OF CHEMICALS (REACH)

At the moment it is possibly the strictest legislation, valid in the European Union (EU), but definitely having global implications. Widely known under its acronym, REACH[32] entered into force on 1 June 2007. It is the leading chemicals management scheme – complex, sophisticated, expensive and bureaucratic, but it is likely to bring about much better information and control on potentially harmful substances than any system to date. Also, it can be safely assumed that the use of substances limited or banned under REACH is very likely to be similarly restricted under other national or international legislations. Thus, it is very useful to familiarize with and understand its main features.

- Its proclaimed aim is to ensure a high level of protection of human health and the environment as well as the free movement of substances, on their own, in preparations and in articles while enhancing competitiveness and innovation.
- Its key operational body for implementation is the European Chemicals Agency, ECHA.
- REACH terminology:
    - **substance** is a chemical element and its compounds in the

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[31] *Of particular interest to tanners could be the Global Automotive Declarable Substance List (GADSL), http://www.americanchemistry.com/s_plastics/blank*

[32] *According to ECHA, REACH is a regulation of the EU, adopted to improve the protection of human health and the environment from the risks that can be posed by chemicals, while enhancing the competitiveness of the EU chemicals industry. It also promotes alternative methods for the hazard assessment of substances in order to reduce the number of tests on animals.*

Source: http://echa.europa.eu/en/regulations

natural state or obtained by any manufacturing process (including any additive, but excluding any separable solvent) whereas
  - **mixture** is composed of two or more substances; leather is an "article" which does not intentionally release chemicals like a pen or an ink jet printer which means that leather per se is exempt from REACH registration
  - Tanneries fall into category of **downstream users (DU)** - unless they manufacture some substances by themselves. The same applies to leather footwear, apparel and leather goods companies. In turn, all of them, including tanneries, are producers of articles.
- Only registered substances and preparations (chemicals) i.e. only those which properties, including possible risks in application and use that have been thoroughly investigated and made widely known, can be used in manufacturing
- Obligatory and extensive exchange of information along the entire supply line is essential
- A particular emphasis is on monitoring, control and avoidance of substances considered carcinogenic, mutagenic, toxic for reproduction, persistent, bioaccumulative and toxic or having endocrine disrupting properties.[33]

15.2.1. *Restricted substances (Regulations, Annex XVII)*

Restricted substances in Annex XVII of interest to tanners:

- Pentachlorophenol
- Cadmium and its compounds
- Short-chain chlorinated paraffin
- Cement and cement-containing preparations: the limit is less than 2 mg/kg (0,0002%) soluble chromium VI of the total dry-weight of the cement and cement-mixtures (some exemptions apply).
- Leather articles and leather parts coming into contact with the skin shall not be placed on the market where they contain chromium VI in concentrations equal to or greater than 3 mg/kg (0,0003 % by weight) of the total dry weight of the leather.
- Nonylphenol
- Nonylphenol ethoxylate

As of 22 January 2018, this Annex contained 66 substances/entries.

15.2.2. *Substances of very high concern, SVHC (Regulations, Annex XIII)*

- On this list are classified substances which are considered extremely harmful for being *carcinogenic, mutagenic, toxic for reproduction, persistent, bioaccumulative and toxic, very persistent and very bioaccumulative, as having endocrine disrupting properties or having a combination of the mentioned properties*.
- The list is expected to be expanded/updated with other substances for which there will be sufficient scientific evidence for falling into some of the listed categories.
- The threshold value for their content in articles is 0.1% weight per weight (w/w).
- Towards the end of 2009 there were only 15 substances and 15 more were added in January 2010. Some believe that ultimately the list might include more than a thousand substances.
- The list does not include inorganic substances

15.2.3. *SVHCs requiring special authorisation (Regulations, Annex XIV)*

Some substances must not be used without specific authorization as they are classified as toxic to reproduction, carcinogenic and/or persistent, bioaccumulative and toxic *(PBT)* or very persistent and very bioaccumulative *(vPvB)*

Tanners as well as also footwear, apparel and leather goods manufacturers should make sure that their suppliers are aware of REACH and comply with its requirements. Tanners' main obligations are to:

- Follow the instructions in the Safety Data Sheets
- Contact the suppliers if they have new information on the hazard of the substance or preparation

Provide their customers with information if the content of certain very dangerous substances, which are candidates for authorisation, exceeds the prescribed concentration limit, for example, 0.1 % weight per weight (w/w) in the articles they produce. Follow the ECHA Candidate List of substances of very high concern for authorisation; as of March 2018, it contained 181 substances.

15.3. PRACTICAL CONSIDERATIONS

The chemicals included in nearly all lists of restricted substances (RSL, MRSL) are:

15.3.1. *Hexavalent chromium (chromium VI)*

Carcinogenic if inhaled, a very low intensity allergen. However, exposure via inhalation is absolutely irrelevant to the leather industry while the allergic reaction is rare and usually very mild. Concerns about carcinogenicity of CrVI actually do not apply to leather consumer articles since such effects require inhalation exposure.

Quite a different situation is with incineration of chrome tanned leather. Ash from combustion is very hazardous and has to be perceived as having a high CrVI content. Gasification can produce an ash that is CrVI free and is in principle a good system.

Yet, the EC regulation stipulates that leather articles or articles containing leather parts coming into contact with skin may not contain chromium VI in concentrations equal to or greater than 3mg/kg at the test method detection level.

Tanners argue that it is a chemical that is not used and/or intentionally added in leather manufacturing as it has no tanning effect at all. Its presence cannot be excluded in rare cases of very low quality chrome powders. Incidentally, determination of CrVI in tanning agents requires a special procedure such as developed by the Leather Institute FILK, Germany.

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[33] *The EC/ECHA SVHC Roadmap to 2020 speaks of 1. CMRs (carcinogenic, mutagenic or toxic for reproduction) 2. PBTs (Persistent, bioaccumulative or toxic for environment) 3. vPvBs (very persistent and very bioccumulative) and 4. Substances of equivalent concern (such as endocrine disruptors, respiratory and dermal sensitisers)*

However, it has been established that a synergistic effect of some factors can support oxidation of chrome III to chrome VI during manufacturing and subsequently transportation and storage of leather and leather articles:

- Certain conditions during wet-finishing (neutralisation)
- Drying, especially at higher temperatures for a prolonged time, heat exposure to (UV) light
- The presence of fatty acids in fatliquors may be a very important influence as unsaturated fats may promote chromium oxidation[34] and generation of VOCs.

The risk of the formation of chrome VI can be virtually eliminated by applying the following measures:

- Use of a reducing auxiliary agent for the neutralisation of wet blue leathers,
- Replacing ammonia as a wetting back agent for crust leather
- Obligatory use of at least a small amount of a vegetable agent (preferably tara, up to 4%) in retanning
- Avoidance of fatliquors containing unsaturated fatty acids[35]; fatliquors containing unsaturated fats and oils must be formulated with antioxidants
- Use of fatliquors with antioxidants
- Degreasing skins with a high content of natural grease (sheep and pig skins) before tanning.

The limit of CrVI in leather and leather articles is 3ppm.

The analysis on the presence of CrVI in leather is very sensitive; moreover, it has been argued that the official ISO/IUC 18 analysis systematically gives false-positives because the method itself is a source of a small amount of CrVI. Actually, it appears that at the moment there is no reliable method to accurately detect CrVI in leather; all of them relate to extracts from a leather sample.

The current ISO 17075 test using a phosphate buffered solution at pH 8 can be affected by traces of oxidising substances in addition to chromium and produce false readings.

Conversely, if the extraction were to be carried out using an artificial sweat solution at pH 5.5 the reduction of CrVI cannot be excluded.

Contrary to some perceptions and in accordance with current EU legislation (Annex X, the Water Framework Directive 2000/60/EC amended in 2008), neither chrome III nor tannery wastes containing chrome III are included in the European Hazardous Waste List. In the USA, the limit for chromium in biosolids for application to land was deleted as there was not enough evidence for regulation. Chrome containing solid wastes from the leather industry are also excluded from the USA EPA hazardous list.

The prevailing view in the leather industry is that chrome has been unduly vilified, the potential health hazards grossly exaggerated.

It is interesting to read the Danish EPA Submission Report of 2012 to the EU for restriction of chromium (VI) and recommending the enforcing of the 3ppm limit. In the only clinical study listed (page 44 of the report) patients with known chromium allergy were exposed to chrome leather that had various amounts of chromium VI. Some allergic reactions were noticed with leather that had less than 3ppm and no allergic reactions were noticed on leather that had 15ppm or more chromium VI. None of the leather samples used for the allergy testing were tested for the presence of other possible allergens. (Source: J. Christner, TFL)

Loud, competent voices already object to inflated concerns about the presence of chrome VI in leather and leather articles.

Regrettably, the same sector has not been quite unified in resisting pressures based on misperceptions and/or old biases. Actually, even some advertisements in leather magazines implicitly suggest that chrome-free leather is somehow superior and not just a different product.

Chromium VI: acute toxicity

- Consumer or worker safety is not only the issue of an individual chemical but of exposure to it
- Only risk assessment can lead to reliable data on
  - ▸ Lethal Dose (LD) thresholds and No Observed Adverse Effect Level (NOAEL)
- There is a reasonably good database on toxicokinetics of CrVI for animals
- Only a few data are available for humans but there is potential that they are generally likely to behave in a similar manner

Example: 1 pair of shoes ▸ 2 sq.ft of leather
2 sq.ft of leather ▸ 200 g weight
Worst case scenario:
10 ppm CrVI in leather ▸ 2 mg CrVI/pair of shoes

LD 50, oral: 26 mg CrVI/kg ▸ 1.8 g/70 kg ▸ 900 pairs of shoes
NOAEL: 1.0 mg CrVI/kg ▸ 70 mg/70 kg ▸ 35 pairs of shoes
LD 50, dermal: 410 mg CrVI/kg ▸ 28 mg/70 kg ▸ 14000 pairs of shoes

Source: D. Tegtmeyer, IULTCS, Istanbul 2013

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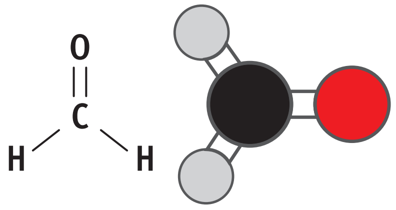
[34] The mechanism seems to be very complex. Some researchers suggest that highly reactive free radicals initiate the primary oxidation of unsaturated fatty acids and cleavage of double bonds resulting in a lipid radical (L) which reacts with atmosphere oxygen to form a peroxy radical (LOO) which in turn reacts with another fatty molecule to form a lipid hydroperoxide molecule and which, in the course of secondary oxidisation, breaks down to form an alkoxy radical (LO) and hydroxyl radical, the so-called heavy metals acting as catalysts or starters. However, the ultimate products of the reaction, VOCs (alcohols, ketones, and aldehydes) gradually reduce CrVI formed earlier back to CrIII.

[35] There is currently no official test method for measuring the Iodine Value of commercial fatliquors, which would make comparisons between products from different suppliers unreliable. The Iodine Value of a properly formulated commercial fatliquor has therefore limited value in terms of predicting CrVI development and should not be employed to compare fatliquors from different suppliers.

15.3.2. Formaldehyde

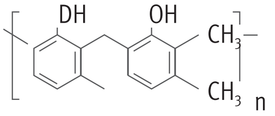
Traditionally formaldehyde is mainly used as a crosslinking agent in finishing but also as a tanning agent.



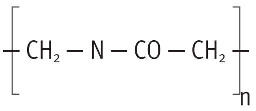
The most common source of formaldehyde or free formaldehyde in leather are tanning and retanning agents. Formaldehyde is typically used in the manufacturing of syntans and resins where it joins together smaller molecules in condensation and polymerization reactions.

Examples of products that may contain formaldehyde:

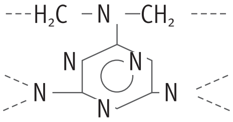
Phenol formaldehyde condensation syntans



Melamine and dicyandiamide resins



Urea-formaldehyde condensation products



Inadeqaute production methods can leave residual, unreacted formaldehyde in the product and ultimately in leather and leather products. It is believed that it is safer to use high quality chemicals with very low residual formaldehyde rather than rely on the use of scavangers.

Analytical methods developed for the leather industry are HPLC based and colorimetric.

Even in low concentrations free formaldehyde can be irritating to the eyes and mucous membranes. Skin irritiation or allergic reaction might occur if higher amounts of free formaldehyde come in contact with skin. Formaldehyde is also variously classified as a “probable” and by some authorities as a “known” human carcinogen. The demand in today’s global market is for leathers without formaldehyde.

However, low formaldehyde retanning products and auxiliaries are available to meet the levels set for formaldehyde in some automotive leathers (10ppm – emission into air) and childrens’ shoe leathers (20ppm – extraction by water). There are various methods to keep the free formaldehyde within acceptable limits. One rather recent method proposes use of 2% of Origanum onites essential oil in fatliquoring to prevent release of free formaldehyde from tetrakis (hydroxymethyl) phosphonium salts and various synthan products.

A new concern is about reported traces of emitted acetaldehyde from automotive leather, which could originate from certain surfactants and polymer products. The allowed acetaldehyde levels in leather are unduly extremely low and often can be achieved only by using aldehyde scavenger products. At the same time, it is commonly present in the environment, including, for example, in the metabolism of ethanol.

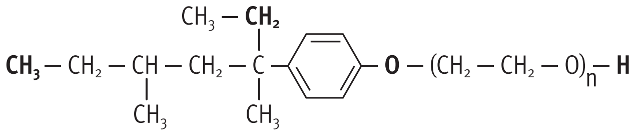
15.3.3. Azo-dyes

Certain azo dyestuffs have the potential of cleavage to form hazardous (carcinogenic) aromatic amines, especially in prolonged contact with skin; such dyestuffs are actually not manufactured by reputable suppliers anymore. Restrictions have been set worldwide (USA, India, Turkey etc.). The limit throughout the EU is 30 ppm.

15.3.4. Nonylphenol and nonylphenol ethoxylates (NPE)

Surfactants (non-ionic, anionic, cationic, or amphoteric) are mainly used as emulsifiers but sometimes also serve as anti-electrostatic, slipping and water-repellent agents.

Nonylphenol ethoxylate (NPE)



$$\mathbf{CH_3}-CH_2-\underset{\displaystyle CH_3}{CH}-CH_2-\overset{\displaystyle CH_3-\mathbf{CH_2}}{\underset{\displaystyle CH_3}{C}}-C_6H_4-\mathbf{O}-(CH_2-CH_2-O)_n-\mathbf{H}$$

n = 1 to 100

The use of nonylphenol and nonylphenol ethoxylates (NPE) based surfactants is now being restricted and/or entirely banned; they have been replaced by aliphatic polyethoxylates that do not break down to phenols.

15.3.5. Volatile organic carbon, VOC – organic solvents

These are volatile components of chemicals mainly used in finishing such as toluene and trichlorbenzene. Of primary concern is workers’ exposure.

The pertinent legislations and/or norms are quite complicated and vary a lot. That is why it is essential to closely follow the latest developments on the global scale; also, it is prudent to adopt the lowest, i.e. the strictest limits. Similarly, chemicals should be obtained from reliable suppliers with proven record of adherence to the highest safety standards.

More recently a new HS-SPME-GC-MS method applying a solid phase micro extraction (SPME) on-site procedure is claimed to be appropriate for the detection and identification of VOCs emitted by leather and for simple and rapid determination of the qualitative and semi-quantitative composition of organic compounds in the sample.

However, a dramatic progress in water-based finishing combined with more efficient coating techniques and air purification is such that nowadays VOC legal limits for most leather are not a serious constraint anymore. Nevertheless, monitoring and reporting is mandatory in Europe and it is also requested globally by the voluntary LWG audit protocol.[36]

However, testing methods represent another challenge, especially since the detection range of volatile substances emitted per kg of leather have been refined from grams to micrograms. That in turn makes it hard to establish what can be called VOC-free!

Incidentally, long-chain aliphatic aldehydes, together with oxidised phenols are responsible for the pleasant smell traditionally associated with leather.

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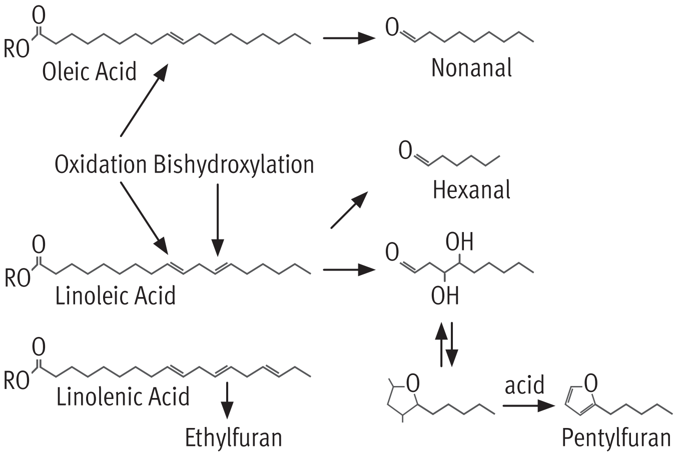
[36] *According to J. Fennen, TFL, China has the toughest VOC (volatile organic compound) regulations in the world having effectively taken the strictest limits from both the EU and North America. In particular, it concerns emissions of acetaldehyde.*

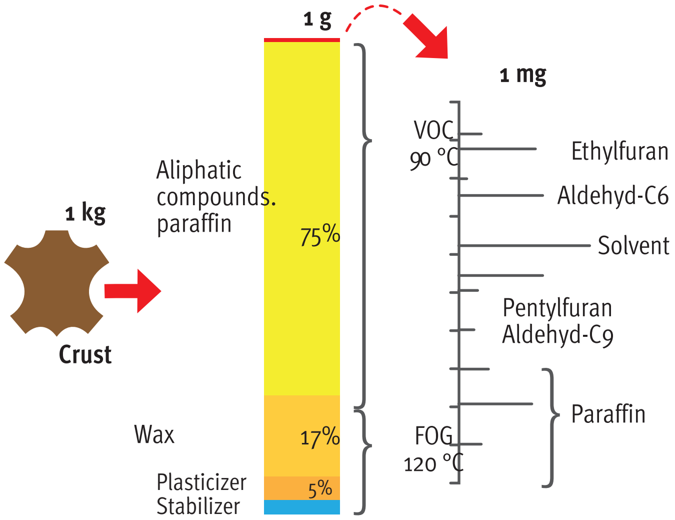
Note: *Europe classifies organic compounds as a VOC if their vapour pressure at 20°C or at application temperature is more than 0.1 hPa.*[37]

In the USA VOC are classified as chemical compounds that take part in photochemical reaction in the atmosphere.

Panel 4: Degradation mechanism of unsaturated fatty acids from natural fat or fatliquors to form long-chain aliphatic aldehydes



Panel 5: Relation of emission quantity from a typical furniture leather analysed by VDA 278



Source: M. Kleban, Lanxess, WL June/July 2014

15.3.6. Halogenated organic compounds present in various agents/auxiliaries

Fatliquors containing more than 1% of chlorinated alkanes of chain length C10-C13 are banned in the EU (REACH Annex XVII). They can be replaced by fatliquoring polymers based on methacrylates or (modified) silicone oils; for the time being there is still no adequate replacement for long-chain chlorinated alkanes required for special leathers.

In water- soil- and oil-repellent agents

Like fatliquors, these agents can also contain organic solvents and organic halogenated compounds and they should be abandoned and replaced. When a complete substitution is not possible, optimised fluorocarbon resins in combined finishes for water-, soil- and oil-repellent leather can reduce the release of halogenated organic compounds.

To meet the very high performance requirements expected from combined water-, soil- and oil-repellent leather finishes, aqueous fluorocarbon resins containing up to 30% of active polymer compound with 20 – 50 % fluorine in the polymer are still used. However, there is a wide range of products (paraffin formulations, polysiloxanes, modified melamine resins, polyurethanes) that could be used if only water repellence is required.

Considerable progress has been made in this area in avoiding perfluorooctane sulphonates (PFOS) and perfluorooctanoic acid (PFOA), considered potentially carcinogenic and banned by Stockholm Convention on Persistent Organic Pollutants (POPs) and which are actually the undesirable by-products in the production of fluorocarbon resins. The recently introduced optimised fluorocarbon resins are not based on raw materials with a chain length of eight (C8) but with a chain length of four (C4) or six (C6); yet, further monitoring and control of releases into the environment are still needed.

In addition to elimination of such substances in the effluent, avoidance of halogenated agents also brings about a decrease in COD.

The EU 2006 limit for presence of PFOS is 0.005%; further restrictions cannot be excluded.

Inflame retardants

Widely used brominated flame-retardants also fall into the category of POPs forbidden by the Stockholm Convention.

There are already ways and means to deal with this problem. Firstly, it is known that appropriate wet-end finishing (strong retanning with selected syntans and melamine resins, suitable fatliquoring) produces firm, more flame resistant leathers. Ammonium bromide and inorganic phosphorus compounds (e.g. ammonium polyphosphate) can also lend to the flame resistance of the level satisfactory for some end-uses. Silicon polymer products applied in finishing provide some fire resistance on quite a different principle: they burn leaving a residue of silica (SiO_2) and protect the leather beneath. Unfortunately, some high performance waterproof leather may still require the use of halogenated chemicals.

15.3.7. EDTA (ethylenediaminetetraacetate) and NTA (nitrilotri-acetate) - complexing agents

EDTA (ethylenediaminetetraacetate) and NTA (nitrilotri-acetate) are used as sequestering agents. Apart from affecting waste water treatment (EDTA can even "re-activate" some chrome contained in sludge), they also have an adverse impact on the environment especially in view of their poor degradability, EDTA in particular.

In dyeing and pretanning to wet white they can be replaced by polyphosphate-based and phosphonate-based products but not quite in wet finishing, mainly in avoidance of iron stains.

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[37] EC Directive 1999/13/EC, VOC definition: Any organic compound having at 293.15 °K a vapour pressure of 0.01 kP (0.1 mbar resp. 0.075 mmHg) or more or having a corresponding volatility under the particular condition of use.

15.3.8. Pesticides

Many pesticides are classified as POPs. Pesticides are normally used neither in preservation nor in the course of leather manufacturing; their presence is due to the application of pesticides to protect animals from ectoparasites. Many pesticides are harmful and, to make it worse, some like synthetic pyrethroids and organophosphates, are not destroyed during leather processing or even during effluent treatment. Some pesticides, such as 'drins' and lindane can be found in imported skins, while arsenic is by now a real exception.

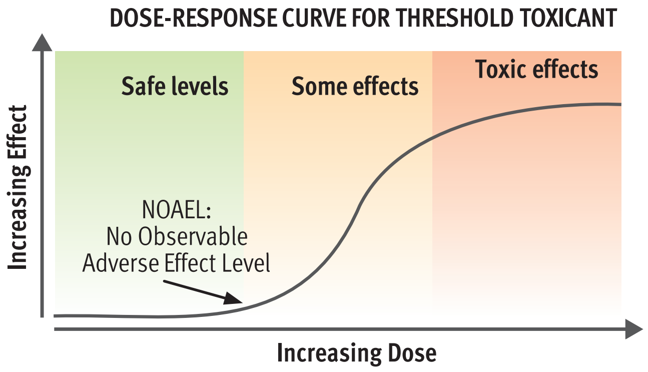
The use and presence of pesticides is regulated by national legislation. For example, the use of HCH, DDT and naphthalene is prohibited in Europe but they might end up in waste waters of tanneries processing raw material from countries where legislation and/or enforcement are not so strict.

15.3.9. Biocides

The EU/ECHA Biocidal Product Regulation (BPR, Regulation (EU) 528/2012) defines that biocidal products are products used to protect humans, animals, materials or articles against harmful organisms, like pests or bacteria, by the action of the active substances contained in the biocidal product.

The efficient commercial production of leather would not be possible without biocides, especially fungicides. Small amounts of the active substances remain within the leather product, and that is why their presence has to be controlled and regulated. In leather processing biocides can be used at several stages, actually from preservation of raw hides and skins, soaking, pickling to tanning and wet finishing; they are also present in some chemicals used in liquid forms such as dyes, fatliquors and casein finishes.

Since they are developed to destroy certain life forms (microorganisms), there is no perfectly innocent fungicide - all biocides are potentially toxic; there is always some risk. There is also a level below which chemical substances have no adverse effect on living things or the environment. This is known as the No Observable Adverse Effect Level (NOAEL) which needs careful calibration.



Based on Source: E. Hurlow, ILM

"If we consider the three pillars of sustainability – people, planet, and profits – it is readily apparent that less is better may not be the sustainable approach for biocides. Insufficient use of appropriate biocides will result in damaged leather and economic loss; and it may also result in an unhealthy working environment."[38]

In broad terms, the biocides used in tanneries fall into two main categories: **bactericides** (predominantly used in raw material preservation and soaking) **and fungicides** (mainly used in pickling to drying phases, typically for the suppression of mould growth on wet blue and wet white hides and skins but also on finished leather during storage and transport in humid conditions).

Some commonly used bactericides are:

- Sodium dimethyldithiocarbamate
- Didecyldimethylammonium chloride
- N-hydroxymethyl-N-methyldithiocarbamate
- Tetrahydro-3,5-dimethyl-2H-1,3,5-thiadiazine-2-thione
- 2-Thiocyanomethylthiobenzothiazole (TCMTB).

These materials are added at rates of between 0.02 and 0.1% by weight. In the course of leather processing their concentration is rapidly decreased and the residues destroyed in the reducing conditions of combined tannery effluents before treatment.

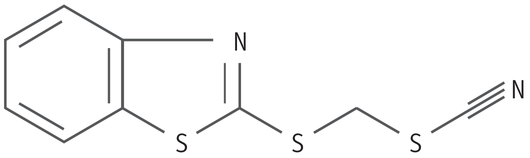
Some commonly used fungicides are:

- o-phenylphenol (OPP)
- p-chloro-m-cresole (CMK)*
- n-octylisothiazolinone (OIT)
- 2-Thiocyanomethylthiobenzothiazole (TCMTB)

* *belongs to the category of organic halogen compounds*

The molecular structures of these compounds are actually simpler than it might appear at the first glance.

Figure 90. The molecular structure of TCMTB



The widely used pentachlorophenol, PCP was banned long ago due to harmfulness and persistence in the environment, its use discontinued; the limit was 5 ppm. A mould inhibitor DMF (dimethyl fumarate) is banned in the EU; buyers of leather upholstered furniture check fungicide levels.

In practice the choice of approved biocides is very limited and the pertaining legislation is likely to become even more restrictive, especially in the EU. The main reasons are the growing concerns about the effects of biocides on aquatic environments because some of them (notably organochlorine compounds) can "survive" the usual treatment of tannery waste waters.

For better effect some commercial products are actually mixtures of different active ingredients.[39] The amounts applied vary considerably: e.g. OIT 80 mg/kg, CMK or OPP not less than 580/280 mg/kg for wet blue and considerably more for wet white.

More recently, in addition to synthetic organic biocides largely used by the industry there are attempts to test and promote some non-synthetic products (essential oils, chitosan) as well as inorganic nano-compounds (e.g. nano-Ag, nano-TiO_2, nano-SiO_2).

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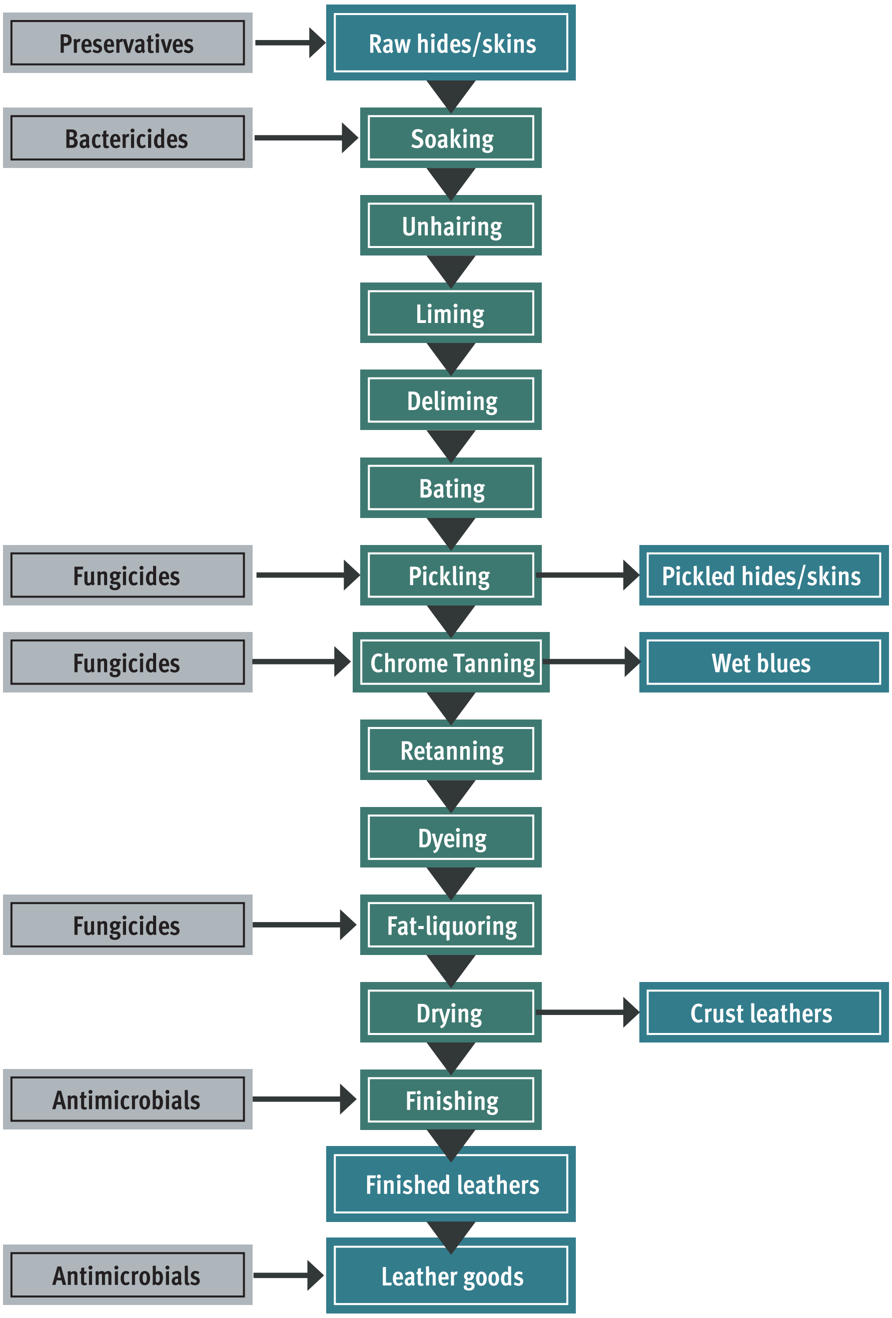
[38] *According to E. Hurlow, Buckman, ILM*

[39] *For example Preventol U-Tec G from Lanxess is a mixture of o-phenylphenol (OPP, 2-hydroxybiphenyl), p-chloro-m-cresol (PCMC) and octylisothiazolinone (OIT) Source: http://lanxess.com/en/corporate/media/press-releases/2013-00058e/5/*

Biocides in the EU are subject to special regulation, the latest introduced on 1 September 2013[40].

The Blue Angel ecolabel has three standards for leather products (upholstery leathers, upholstered furniture and shoes). The threshold values are 1000 ppm for OPP, 600 ppm PCMC, 500 ppm for TCMTB and 250 ppm for OIT.

Figure 91. Typical points of adding biocides in the course of leather processing



Based on source: Haibin Gu et al. JALCA, March 2016

15.3.10. Heavy metals

Apart from chromium in this (scientifically not clearly defined, ambiguous) category of main concern are cadmium, lead, mercury, antimony and arsenic. Cadmium, for example, is often used in finishing pigments (orange, yellow, red, green); it is believed to be carcinogenic, the limit being 75-100 ppm.

In metal complex dyes, which are known for their good lightfastness, chromium (III), copper (II) and cobalt (II) are used as the metal ions and are bound strongly to the organic molecule matrix. During use the metal complex dyes are fixed in the leather and are not accessible; it is believed that there is no health risk associated with their use. It is possible to substitute them, provided some compromises are acceptable regarding lightfastness and matching some particular shades.

Arsenic, which is very rare but still found as a biocide used in raw hide/skins preservation, is both toxic and carcinogenic.

Some brands' requests for metal-free leather should actually be 'free of toxic metals' to avoid limiting the available options for environmentally sound tanning.[41]

In 2017 ECHA reclassified titanium dioxide as a Category 2 carcinogen.

The tanning industry makes use of titanium dioxide pigment pastes, which do not dust, but the substance might be inhaled (in the form of aerosol) if a face mask is not worn. Of more concern to the tanner should be the use of dust formulations in the wet-end. Tanners may use titanium dioxide powders in the preparation of white or pastel coloured leathers, or for upgrading purposes. Titanium dioxide pigment pastes are extensively used in the finishing areas as an opaque colourant that covers defects, changes the lightness value (L*), and provides uniformity to the colour coats.

Titanium dioxide does not currently appear on Annex XVII (the list covering restriction of use); Annex XIV (the list covering authorisation for use); or the candidate list of substances of very high concern. The conclusion of this committee may escalate the restriction or authorisation of this substance.

15.4 ECHA ADDITIONS AND UPDATES

ECHA additions and lists updates are primarily concerns of suppliers of specialty chemicals to the leather industry. However, it is prudent for tanners to be properly informed too to avoid unpleasant surprises in marketing their leather. International leather magazines also publish notices on latest changes, here are some examples.

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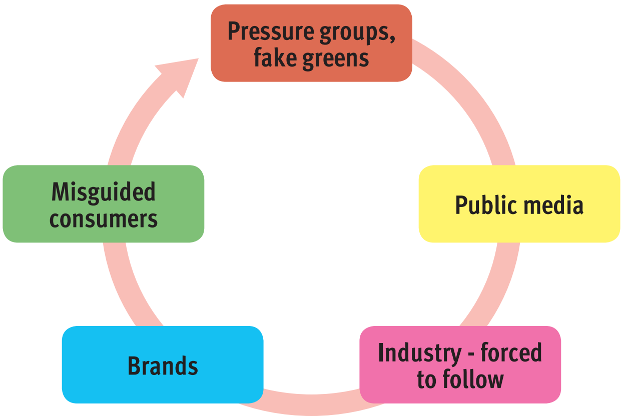
[40] *From 1 September 2015, a biocidal product consisting of, containing, or generating a relevant substance, cannot be placed on the EU market if the substance supplier or product supplier is not included in the Article 95 list for the product type(s) to which the product belongs. Source: http://echa.europa.eu/en/biocides-2015*

[41] *Metal-free leather, CEN definition: ≤ 0.1 % of Fe, Al, Cr, Zr, Ti*

- In July 2015 ECHA put forward a proposal to the European Commission for the inclusion of 15 Substances of very High Concern (SVHC) in Annex XIV of REACH. The listed substances include boron compounds and phthalates. The restriction is irrespective of tonnage.Didecyldimethylammonium chloride
- In November 2016 ECHA called for the final registrations of substances for its REACH 2018 Roadmap with May 31, 2018 as deadline. In December 2016 it offered toolkits in 23 EU languages.
- In cooperation with the Commission on the European Union Observatory (EU-ON) for Nanomaterials, ECHA intends to provide better access to relevant and understandable information about nanomaterials. It will include data generated by various pieces of EU legislation regulating the safe use of nanomaterials (such as biocides used in leather making), from national inventories, research projects, and market studies.
- On 17 January, 2018 ECHA listed seven new chemicals on the REACH Candidate List of Substances of Very High Concern (SVHC).The seven chemicals include Bisphenol A (BpA), a plasticiser sometimes found in PVC for laminates and foils and in polycarbonate finishing resins; two polycyclic aromatic hydrocarbons (PAH), three cadmium compounds, a fire retardant (commonly referred to as Dechlorane Plus), and a reaction product of Bismuthiol I/formaldehyde/heptyl phenol.
- On 23 January, 2018 three further areas of changes directly affecting the tanning industry were introduced:
  - Formaldehyde (HCHO) and substances that release HCHO over time are under consultation and member states are asked to feed comments and points of consideration back to the ECHA for consultation.
  - The presence of two siloxanes found as building blocks, breakdown products, or standalone siloxane products must be declared.
  - The biggest impact is to come from the restriction intentions and call for evidence for substances that can cause skin sensitivity and skin irritation. Sensitivity is a level of skin reaction well below irritation and could cause enormous difficulties for tanneries, manufacturers, and brands and retailers
- On February 5, 2018, ECHA announced that 1(N)-methyl-2-pyrrolidone (NMP) was forwarded to the European Commission for inclusion onto Annex XIV. NMP was widely used in the leather industry as a co-solvent in the manufacturing of polyurethanes in the past. While NMP was often recovered for further polymerisations, trace quantities were often found in polyurethane products. Most large leather chemical manufacturers have discontinued manufacturing NMP, it seems that some still use it in the manufacture of polyurethane.

Caveat lector !



15.5. RESTRICTED SUBSTANCES LISTS (RSL)

> **The norms pertaining to the use of chemicals in the tanning industry in the last few years are in a kind of permanent evolution. In addition to formal national and regional legislation, various Restricted Substances Lists (RSL) have the strongest impact driven by concerns of leading international brands, major users of leather, about their corporate social responsibility image, and, more specifically their reputation with environmental public pressure groups and, ultimately, consumers. Sometimes it appears a matter of prestige to have an own, more detailed and stricter RSL than the competitors.**

The chemicals on these lists originate from government regulations or from various ecolabel agencies whose desire is to promote “greener” or “safer” products by restricting chemicals that are perceived to be hazardous.

15.5.1. Zero Discharge Hazardous Chemicals (ZDHC) Group and its programme

> **In 2011, a group of major apparel and footwear brands and retailers made a shared commitment to help lead the industry towards zero discharge of hazardous chemicals (ZDHC) by 2020. The current signatory members committed to ZDHC include many leading global brands.**

The ZDHC Group claims to take a holistic approach to tackling the issue of hazardous chemicals in the global textile, leather and footwear value chain, the goal being to eliminate the use of priority chemicals by focussing on the following areas: Manufacturing Restricted Substances List (MRSL) & Conformity Guidance; Wastewater Quality; Audit Protocol; Research, Data and Disclosure; and Training. They see the need to evaluate chemicals used in the apparel and footwear industry and to establish a sector-wide list of hazardous chemicals and strive to achieve the zero-discharge goal. The main steps are Hazard Assessment and Prioritisation, Phase Out Actions and Research Actions.

In March 2013, the ZDHC Group launched a programme to develop a chemical hazard assessment approach specific to the apparel and footwear industry. It started with creating and publishing a database of chemicals (at the CAS number level) used in the apparel and footwear industry in 2012 followed by a paired down list of restricted chemicals. The list was a subset to chemicals appearing on restricted or watch lists, such as the bluesign® system substance list (BSSL), brand restricted substance lists (RSLs), the Substitute it Now (SIN) list etc.

While many would argue that legislation and pressure-driven initiatives are potentially forcing a compromise in product performance or an increase in costs, there is also significant argument that legislation and NGO pressure is indeed the best driver for innovation and advancements within the chemical industry and collaboration with the supply chain.

15.5.2 Leather Working Group, LWG[42]

Following the ZDHC (Zero Discharge of Hazardous Chemicals) initiative the Leather Working Group (LWG) is reportedly also working on a Manufacturers Restricted Substance List (MRSL). It is hoped that such a list would help to start to harmonise the different RSL requirements and list all products that should not be intentionally used in leather production.

15.6. OEKO-TEX

Oeko-tex is an EU organization offering a kind of environmental certificate to tanners. Apparently, their certificate covers not only the key statutory regulations but also chemicals considered harmful to health; it also corresponds to the requirements from the U.S. Consumer Product Safety Improvement Act (CPSIA) regarding lead. Leather products are tested with regard to formaldehyde, heavy metals such as chromium (VI), arsenic (!?), lead and cadmium, pesticides, chlorinated phenols, phthalates, processing agents and preservatives, PFOS, PFOA, as well as banned azo colourants and other colourants.

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[42] *See more about LWG in the sustainability chapter.*

16. SOLID WASTE

> *Note: It is expected that in the near future UNIDO will prepare a detailed study specifically dealing with solid wastes in the tanning industry.*

16.1. SOURCES, QUANTITIES

> **Since only about 50-55% of corium collagen actually ends up as finished leather it is not surprising that a tannery generates large amounts of solid wastes. As a matter of fact, utilization and/or disposal of solid waste is nowadays one of the most difficult challenges especially in countries with stricter legislation and enforcement pertaining to waste handling; moreover, it is very likely that the pressures will escalate further.**

Table 44. An example of the amounts of solid waste, from 1 tonne of wet salted, light European hides (25.6 kg per hide), processed to shoe uppers, conventional technology

Type of waste	Kg
Fleshings	300
Trimmings	100
Unusable chrome splits	107
Chrome shavings	99
Chrome off-cuts	20
Crust leather waste	5
Buffing dust	1
Finished leather trimmings	5
Total	**637**

Source: Mass balance, J. Buljan et al. UNIDO

At the same time, the goal of a sustainable strategy should be to produce no waste and turn any potential waste into an effective and valuable product. Therefore, it is important that waste does not contain chemicals of concern as they would only limit its further use.

Depending on the emission point and waste properties, local legislation and availability of facilities for treatment and utilization (read: market!), solid wastes can be categorized as tradable by-products, non-hazardous waste or hazardous waste. Whatever the case, the best practices for waste management should be adhered to in the widely known order of priority:

- prevention
- reduction
- re-use / recycling / recovery
- disposal

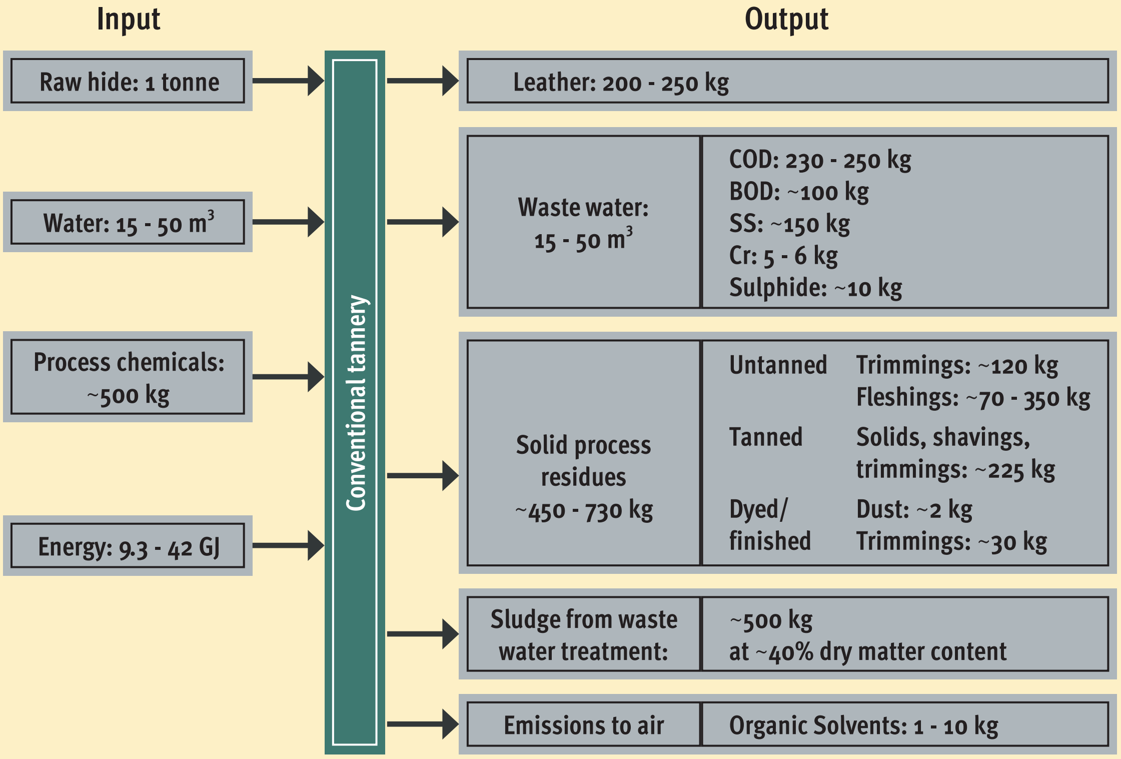
In the technical literature the figures about the amount of solid waste differ widely and are sometimes are not comparable at all. The reasons are:

- Considerable differences in the type of raw material processed, e.g. heavy, very fat from Europe, USA vs. light hides from developing countries
- differences in the tanning process
- substantial variations in water content in the waste

There are also emissions of about 40 kg of organic solvents and sludge from waste water treatment (approx. 420 kg at 30% of dry substance).

The EU BREF 2013 input/output overview for the conventional process suggests the following figures[43]:

Figure 92. Typical solid waste ranges according to EU BREF 2013


Input
Output
Raw hide: 1 tonne
Water: 15 - 50 m³
Process chemicals: ~500 kg
Energy: 9.3 - 42 GJ
Conventional tannery
Leather: 200 - 250 kg
Waste water: 15 - 50 m³
COD: 230 - 250 kg
BOD: ~100 kg
SS: ~150 kg
Cr: 5 - 6 kg
Sulphide: ~10 kg
Solid process residues ~450 - 730 kg
Untanned
Trimmings: ~120 kg
Fleshings: ~70 - 350 kg
Tanned
Solids, shavings, trimmings: ~225 kg
Dyed/ finished
Dust: ~2 kg
Trimmings: ~30 kg
Sludge from waste water treatment:
~500 kg at ~40% dry matter content
Emissions to air
Organic Solvents: 1 - 10 kg

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[43] *The EU BREF 2013 input/output overview for an advanced tannery (including much higher share of by-products, i.e. usable solid wastes is not quite convincing).*

F. Langmaier et al. Journal of SLTC, Vol 83 :

Estimated amount of solid (protein, tanned and untanned) waste during the processing of 1 tone of salted hides according to various authors

	Püntener	Alexander	Buljan et al.*
Untanned waste			
shavings		120	100
subepidermal tissue	530	70 - 230	300
trimmings	135		
Tanned waste			
shavings	145	100	99
split		115	107
Dyed and finished waste			
shavings	10	32	10
fluff		2	1
Total	**870**	**439 - 599**	**637**

** The values pertain to European hides, weight class 25 - 29.5 kg green weight.*

16.2. WASTE MANAGEMENT

16.2.1. Prevention/mitigation

The only component of raw hides ultimately converted into leather is corium collagen; other components are a "surplus" and have to be removed. Therefore, while the volume of solid waste per se cannot be reduced, there are ways and means to facilitate its handling:

- Increase the share of native and reduce the share of chemically treated solid wastes, especially those that are tanned; for example, by green fleshing and lime splitting. Obviously this also significantly improves the uptake, and reduces both the consumption and discharge of chemicals.
- Reduce the amount of (non)usable waste by improving the efficiency and accuracy of some mechanical operations such as splitting and shaving or coating.
- Avoid unnecessary contamination of solid waste, thus leaving a wider range of options for their utilization.
- Good housekeeping implying very strict segregation and prompt handling of all categories of solid wastes
- Proper classification, segregation and handling of wastes not directly related to the tanning process: packaging material, barrels, paper, etc.

16.2.2. Utilisation and safe disposal

In conformity with what was said earlier about their inherent properties, local legislation and availability of facilities for treatment, the scope for utilization of solid wastes varies a lot. A good, workable method and/or purpose in one country or region can be simply impractical elsewhere.

It is also necessary to emphasise that in papers presented in conferences or appearing in technical publications quite often are proposed solutions for utilization of solid wastes tested only at the bench scale and without any serious attempt to explore their commercial viability. Another aspect is that most conversion methods to be commercially feasible require a considerable concentration of tanneries producing sizable quantities of solid waste. Tannery clusters (or leather cities) often offer such advantages of scale.

In any case, as a rule some of the wastes need to be treated on site before being sold or disposed of. Such treatments could include dewatering and/or drying and compacting.

Regrettably, it has to be admitted that for certain waste fractions, a landfill is still often the only option available.

> A large amount of waste, in particular of organic waste, is inherent to production in tanneries. Both organic waste fractions and other residues can be prevented and considerably reduced by using Best Available Techniques (BAT) in the process units. Recycling options are numerous and can be carried out on site or off site. The potential for recycling should be exploited by ensuring segregation of waste. Of equal importance is the commercialisation of wastes as by-products and co-operation between tanners to make recycling and re-use options economically feasible.
> Source: UNIDO, D. Nemec

The next table provides a simplified overview of re-use/recycling/recovery and/or disposal of individual waste fractions, partially based on EU BREF 2013.

Table 45. Overview of re-use/recycling/recovery and/or disposal of individual waste fractions

Type of waste	Contents	Further treatment/ disposal/recycling
Raw hide trimmings	Collagen, hair, fat, connective tissue, blood	Production of hide glue Animal feed stuff Biogas Thermal treatment Landfill
Solid salt Brine	NaCl and possibly biocides	Reuse (problems with infectious material on salt) Landfill
Green fleshings	Fat, blood, meaty scraps	Production of hide glue Recovery of fat Composting Biogas Thermal energy

Type of waste	Contents	Further treatment/ disposal/recycling
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
Fleshings	Fat, meaty scraps Liming and unhairing chemicals	Production of hide glue/gelatine protein hydrolysate Recovery of fat (fleshings only) Composting Biogas Landfill
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
Tanned split	Leather material of inconsistent thickness and no 'grain' surface	Split leather Leather fibreboard production Protein hydrolysate Composting Agriculture
Shavings, metal-free shavings, trimmings	Organic matter with tanning chemicals	Leather fibreboard production Protein hydrolysate Composting Filler in tanning and retanning Agriculture Thermal treatment
Obsolete chemicals	For chemical composition of agents	Disposal of chemicals according to their characteristics
Particulate matter	Organic matter with contents according to tanning	Landfill Thermal treatment Filler for plastics
Residues from finishes, Sludges from finishing agents (over-spray, etc.)	For chemical composition of agents Solvents Heavy metals	Landfill hermal treatment
Trimmings with or without finish	Leather with contents according to tanning and finishing	Leather fibreboard production Other reuse: patchwork, small leather goods, etc. Landfill Thermal treatment
Activated carbon, sludges from wet-scrubbers, filter	Depending on the off-gas stream	Recovery of organic compounds (e.g. solvents) Thermal treatment Landfill
Sludge from waste water treatment	Depending on the separation of waste water streams	Use in agriculture Composting Biogas Landfill Thermal treatment
Residues from on-site waste treatment	Greaves from rendering, residues from anaerobic or aerobic digestion	Use in agriculture Landfill Thermal treatment
Pallets, paper Plastics Containers for chemicals		Recycling Landfill Thermal treatment
Obsolete chemicals Scrap metal and defunct equipment		Recycling Landfill Thermal treatment

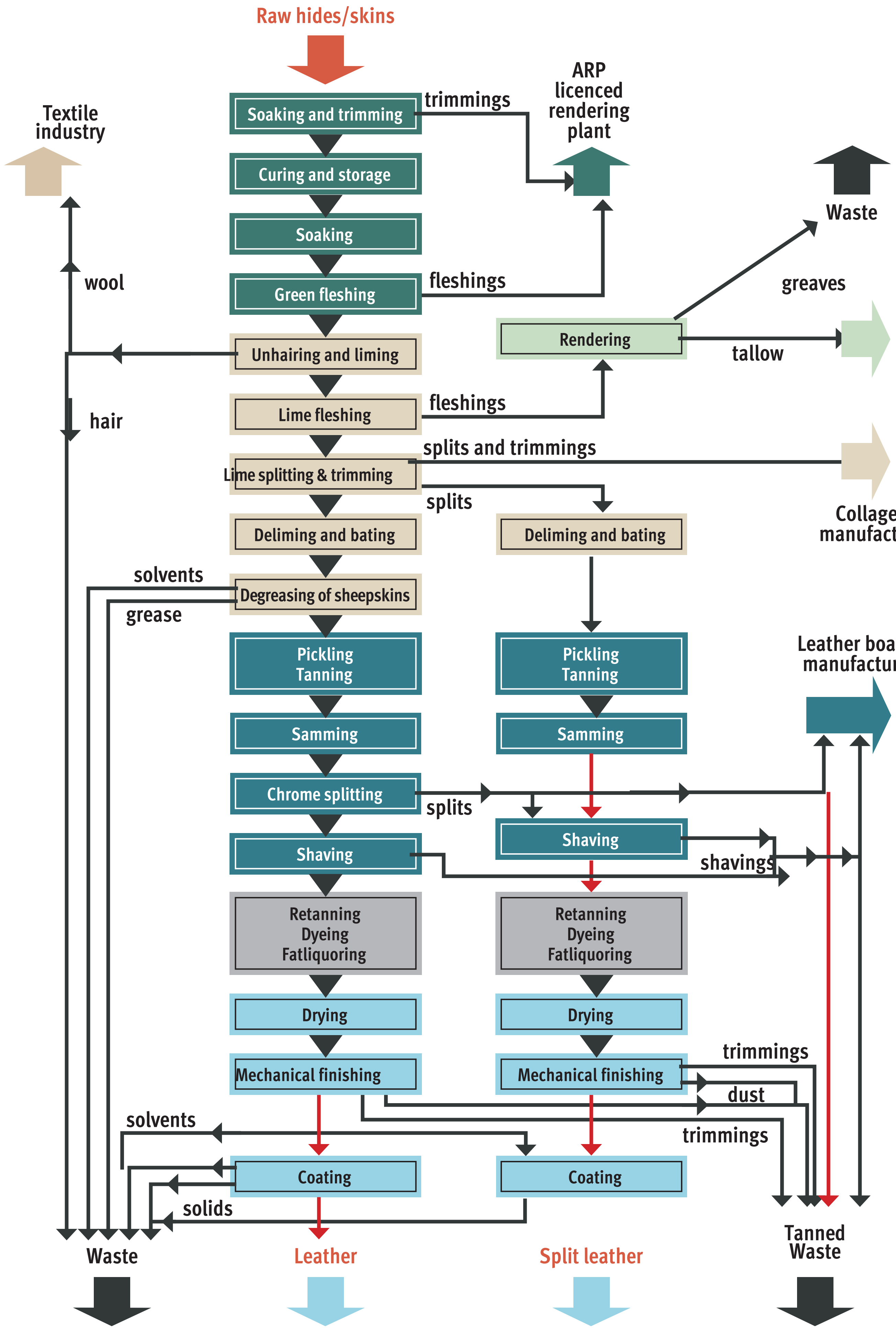
Management and good housekeeping

Commitment of the tannery management is a prerequisite for good environmental performance. Technology by itself is not sufficient; it needs to go together with good housekeeping measures. A key to good performance is awareness of the inputs to and outputs of the process with regard to the characteristics of the materials, the quantities, and their potential environmental impacts. Criteria that ensure a better environmental performance can then be taken into account as well as technological criteria that focus on the properties of the end product. Furthermore, contamination should be kept at a bearable level with a reduction of spills, accidents, water wastage and chemical usage. This can be achieved by the choice of appropriate techniques, good maintenance and operation control – by monitoring and adjusting process parameters – and good staff training.

Source: UNIDO, D. Nemec

16.3. CONCLUSION

Figure 93. Overview of the tanning operations and linkages


Raw hides/skins
Soaking and trimming
trimmings
ARP licenced rendering plant
Textile industry
Curing and storage
Soaking
Waste
Green fleshing
fleshings
wool
greaves
Rendering
tallow
Unhairing and liming
Lime fleshing
fleshings
hair
splits and trimmings
Lime splitting & trimming
splits
Deliming and bating
Deliming and bating
Collagen manufacture
solvents
Degreasing of sheepskins
grease
Pickling Tanning
Pickling Tanning
Leather board manufacture
Samming
Samming
Chrome splitting
splits
Shaving
Shaving
shavings
Retanning Dyeing Fatliquoring
Retanning Dyeing Fatliquoring
Drying
Drying
trimmings
Mechanical finishing
Mechanical finishing
dust
solvents
trimmings
Coating
Coating
solids
Waste
Leather
Split leather
Tanned Waste

The only component of the raw hide required for and ultimately converted into leather is corium collagen; other components have to be removed. As a corollary, the amount of solid waste per se cannot be reduced.

With stricter regulations governing the utilization of by-products and disposal in landfills, costs in industrialized countries are expected to rise even further and this trend is likely to spread to developing countries too.

Thus, efforts need to be focused on:

- Increasing the share of native and reducing the share of chemically treated solid wastes, especially of those that are tanned
- Avoiding unnecessary contamination of solid waste and opening a wider range of options for their utilization
- Very strict segregation and prompt handling of all categories of solid wastes
- Proper classification, segregation and handling of wastes not directly related to the tanning process: packaging material, barrels, paper, etc.

Management of solid waste is presently one of the most difficult tasks in environmental management: a well-established reutilization and/or disposal method can almost overnight become unviable anymore either on account of changes in regulations or for commercial reasons.

As a rule, the picture of solid waste handling in a tannery is a good reflection of the overall competence and commitment of the tannery management. Simply said, it is a true picture of the company.

17. ENERGY CONSIDERATIONS IN LEATHER PROCESSING

17.1. GENERAL

Energy consumption in tanneries mainly depends on the following factors:

- production method, capacity, equipment
- performance of electric motors, controls sophistication level
- the ratio of manual vs. mechanical/automated handling (e.g. in moving the hides)
- tannery location – geographic zone, ambient temperature
- drying methods
- heat losses from process vessels and from buildings
- air exchange rates to meet workplace safety conditions
- type of waste water treatment on site
- types of waste treatment and recovery of energy from waste on site.

17.2. ENERGY CONSUMPTION

The data in literature concerning the consumption of thermal and electric energy differ considerably, which is quite understandable because of significantly different conditions of production. There are also wide variations in both methodologies in computing and the presentation of data. In practice, the figures on electricity and fuel consumption over longer periods and different seasons are the most reliable.

The category of the energy source is also very relevant - fossil fuel (natural gas, coal, Diesel), renewable (wood, biomass) or self-generated renewable (solar energy, wind).

It is important that comparisons between tanneries be made on the same basis. For example, 'effluent treatment' may or may not include biological treatment which can account for more than 50% of the energy consumption in the treatment of tannery effluent and also make a significant part of the tannery's total energy consumption. Following are some selected data drawn from more recent publications.

17.2.1. The share of energy consumption for the main components in a European tannery

Table 46. The share of energy consumption for the main components in a European tannery

	Use	% of overall consumption
Energy type	Drying	33
	Hot water	33
	Space heating	19
Electric	Machinery and process vessels	10
	Compressed air	2.5
	Light	2.5

Source: Andres and Frendrup[44] (figures rounded up)

The table gives an indication of energy consumption by type of energy input. The proportions can vary greatly between tanneries. For example, mechanical handling can be from largely manual to transfer by forklift trucks powered by internal combustion engines or by electric powered conveyors. Ideally, energy use should be monitored and reported separately for each process stage, and it is known that some of the most energy-efficient tanneries do so.

In such cases, comparisons of the energy inputs for the same stages and of the total energy input for the entire leather making process are more informative and reliable.

17.2.2. The LWG Protocol

In the LWG's document[45] the reference figures on energy consumption, including waste water treatment (ETP) are conveniently given for processing stages e.g. from "raw to tanned" or "tanned hide to finished leather". While in the first case it is expressed in MJ/t of raw hides for all other stages the energy consumption is expressed in MJ/m^2 of produced leather, using the conversion factor of 160 m^2/t of raw hides.

Not surprisingly, the energy consumption ranges are very wide: based on reference figures given it can be derived that, for example, for tanneries processing from raw hide to finished leather the energy consumption is 26.8 - 160.6 MJ/m^2 of finished leather or from 4288 - 25696 MJ/t of raw hides.

17.2.3. EU BREF 2013

The EU BREF 2013 indicates the following consumption to correspond to the Best Available Technology (BAT)

Table 47. Specific energy consumption associated with BAT

Activity stages	Specific energy consumption per unit of raw material (1)
	GJ/t
Processing bovine hides from raw to wet blue or wet white	< 3
Processing bovine hides from raw to finished leather	< 14
Processing sheep skins from raw to finished leather	< 6

(1) The energy consumption values (expressed as an annual average not corrected to primary energy) cover the energy use in the production process including electricity and the total heating for indoor spaces, but excluding the energy use for waste water treatment.

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[44] *Andres 1995, Frendrup 1999*

[45] *LWG Environmental Protocol Audit Responses Report, Issue 6.0*

17.2.4. A French sheep tannery

The estimation by for the consumption of thermal energy for sheep skins tanning and the values derived from these data presented in the IULTCS paper[46] are given in the following table.

Table 48. Estimates of energy consumption in a French sheep tannery

	KWh/m^2	MJ/m^2	MJ/t	%
Heating of the buildings	3.20	11.5	1840	33%
Dryers in the dyeing department	1.06	3.8	608	11%
Dryers in the finishing department	2.78	10	1600	28%
Hot water for the process	2.78	10	1600	28%
Total	**9.8**	**35.3**	**5648**	**100%**

It is not clear whether these data are calculated as the net thermal energy consumption (not corrected to primary energy) or from the fuel used. Estimates of the consumption of electric energy are given in the next table.

Table 49. Estimates of the consumption of electric energy for various purposes in a French sheep tannery

Tannery steps	Electricity KWh/m^2	KWh/t	MJ/m^2	MJ/t	%
Main processes (pumps, motors, cooling systems)	0.99	158	3.6	576	45
Drums	0.34	54	1.22	197	16
Lighting	0.31	50	1.11	178	14
Ventilation and air heater	0.14	22	0.5	80	7
Compressed air	0.22	35	0.79	126	10
Finishing	0.12	19	0.43	67	6
Fleshing machine	0.03	5	0.11	18	1
Offices	0.01	2	0.04	6	1
Total	**2.16**	**345**	**7.8**	**5648**	**100**

Obviously the electric energy for the effluent treatment is not included. Also, the values for sheep skin tanneries are not directly comparable with those for bovine hides; nevertheless, they are quite interesting.[47]

17.2.5. EU BREF 2003

Energy consumption in the company Elmo Calf AB processing from raw hide to finished product (automotive and furniture use) for the year 1999 provides the following values:

Annual production	**11,700 t raw hides** 2.4 million m2 finished products (automotive and furniture use)
Energy Electric energy Thermal energy	11.3 GJ /t raw hide 3.0 GJ 8.3 GJ

Source: BREF, February 2003.

17.2.6. Estimate of energy consumption for a virtual tannery of 10 t of w.s. hides/day (UNIDO)

Drawing on figures from the sources mentioned earlier and in-house computations, it is estimated that for a tannery processing 10 t of raw hides/day from raw to fully finished leather (shoe uppers), with the yield of 160 m^2/t of raw hides (the same as applied in LWG document![48]), the order of magnitude of energy consumption would be as shown below:

Processing	GJ/t	kWh/t	MJ/m^2	GJ/d for a 10 t/d tannery	TJ/y for a 10 t/day tannery
Thermal energy	8.3	2306	52	83	30.3
Electric energy	3.0	833	18	30	11
Total energy	**11.3**	**3139**	**70**	**113**	**41.3**

Calculation using a calorific value of approx. 10 kWh/l = 36 MJ/l the amount of liquid fuel required to produce this amount of thermal energy is:

Processing	GJ/t	Liquid fuel l/t	Liquid fuel l/d	Liquid fuel l/y
Thermal energy	8.3	230	2300	84000

17.3. ENERGY LOSSES, COSTS

There are many sources of losses of thermal energy:

- heat lost from hot surfaces (vessels, tubes) and from buildings
- the use of inadequate equipment (combustion equipment and

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[46] *Eco-Design: Life Cycle analyses show that energy is a key factor for the environmental impact of leather and might save money, T. Poncet et al. IULTCS Congress, 2011*

[47] *The energy prices provided (0.081 EUR/ kWh for electric energy, and 0.054 EUR/kWh for thermal energy) are comparably too low and do not seem realistic.*

[48] *LWG Environmental Protocol Audit Responses Report, Issue 6.0*

boilers) for production of hot water necessary for processing
- the use of inadequate equipment for drying

Heat losses may be mitigated by thermal insulation but may be exacerbated by a low external temperature. High moisture content in the air may increase the energy consumed in drying.

Energy use data from one climatic zone may not be an accurate guide to what may be achieved in another.

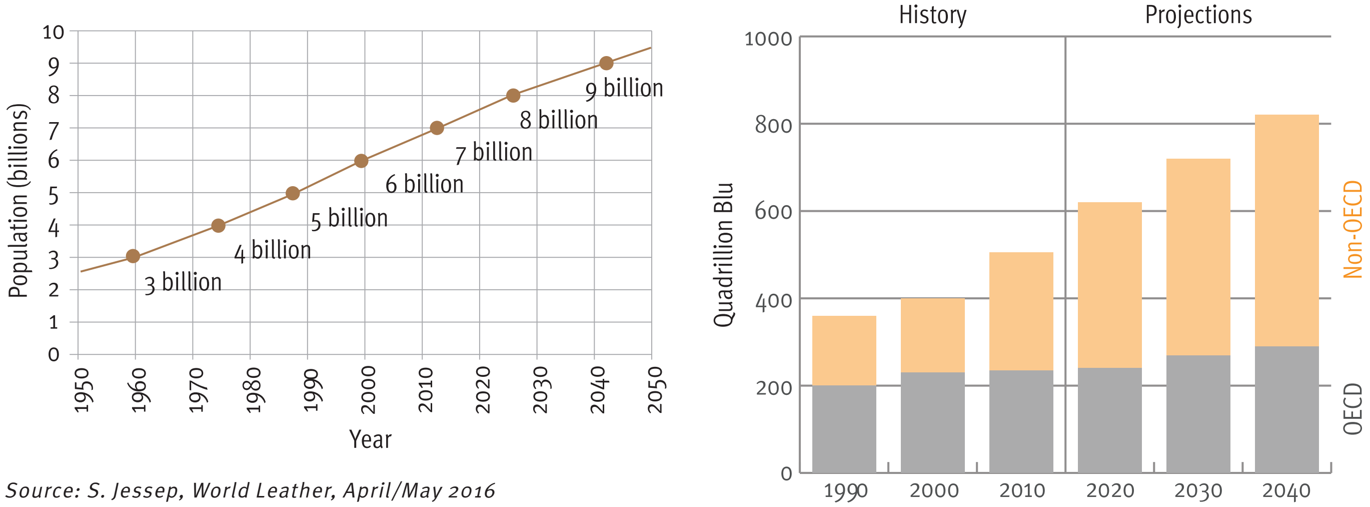
Modern combustion equipment and boilers (especially boilers that utilize the energy from the condensation of water steam from the fumes) can have an efficiency rate of above 90%. A larger central boiler may be more efficient, but if operations are dispersed over a large area, heat losses from pipework may eliminate the gains.

The cost for thermal energy can also be reduced by the correct choice of fuel, depending on its local accessibility and prices. The most practical way of reducing the cost of thermal energy is the use of solar and/or ambient renewable energy.

17.4. USE OF NON-TRADITIONAL AND/OR RENEWABLE ENERGY SOURCES

Before turning to this specific subject, it is enlightening to see estimates of historical and predictions about future energy consumption related to the explosion in human population.

Figure 94. World population 1960-2040 and world energy consumption 1990 – 2040



Source: S. Jessep, World Leather, April/May 2016

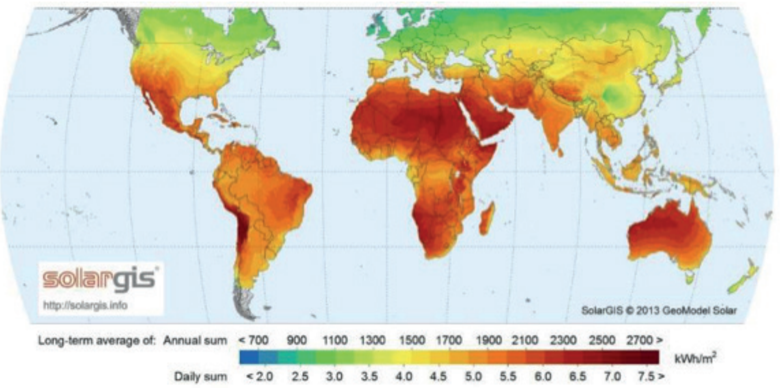
17.4.1. Solar energy

The furnishing of the sun's energy depends firstly on location (climate zone). The next figure shows the yearly average furnishing of energy (insolation) in kW/m²/y and kW/m²/d, related to geographic location.

The most simple, effective and cheapest method for the use of the sun's energy is its conversion to thermal energy. Solar thermal energy can be used by the direct heating of the process fluid (water) or special fluids, which transmits the heat to the process water via a heat exchanger.

The inconvenience of this type of energy is that its production completely depends on daylight hours (no production during the night) and seasons of the year (especially so in a temperate zone).

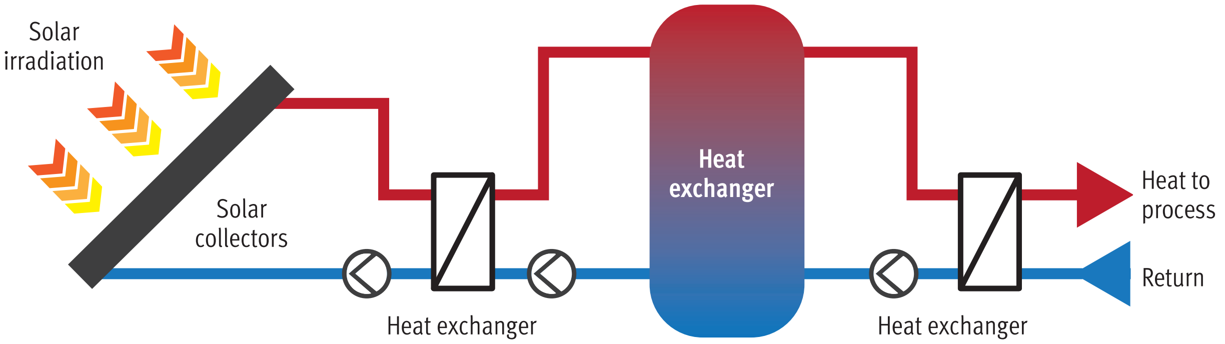
Figure 95. The world insolation map



Source: http://www.city-data.com

Although it is possible to heat the water and use it immediately, it is seldom viable in practice due to the different dynamics in the hot water production and consumption. The installations containing the storage vessel are used more than the direct use of the heated fluid. The principle of the installation of solar thermal collectors with a storage vessel is presented in the next figure.

Figure 96. A simplified scheme of solar supported water heating with storage



Based on source: J. Salem, M. Matteini, UNIDO, 2007

Solar thermal energy production and the efficiency of the transformation of insolation energy to thermal energy depend on many factors such as location, type of solar collectors and their installation and, most importantly, on the desired temperature of the heated fluid.

The maximal efficiency of solar thermal collectors is 50 – 80%, and the efficiency of the whole installation is 30 – 50%.

In practice, even in hot climate zones it is not possible to rely on solar heating only and a fuel-fired boiler is necessary; electric energy needed for the fluid/water circulation and transfer pumps should not be overlooked either.

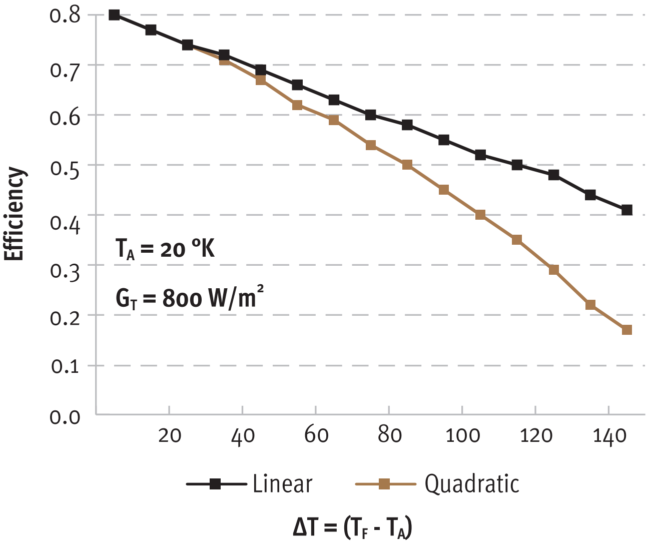
In any case, it is important to conduct a proper study to design the optimum installation taking into account the desired temperature of the hot water, work out the efficiency and, ultimately the type and cost of a solar collector and of the complete installation.

The main parameters concerning the solar thermal collectors for water heating in a tannery in Spain[49] are given as follows:

- Mean need of hot water at 52°C: approx. 47 m^3/d
- Mean supplied water temperature: approx. 12°C
- Mean daily energy consumption for water heating: 9400 MJ/d
- Mean insolation accepted on collector: 16.42 MJ/m^2/d
- Mean thermal energy production: 8.6 MJ/m^2/d
- The measured efficiency, depending of the type and collector producer and the actual local and seasonal conditions, was 20 – 60%
- The best efficiency was the Atesa collector (40 – 60%)
- The optimum surface with optimum inclination (40°C) was calculated as 583.74 m^2

Figure 98. Solar collectors installed in a tannery under a UNIDO project in Bangladesh

Figure 97. Solar collector efficiency curve



Where: T_F = heated fluid temperature
T_A = atmospheric temperature

- The area meets approx. 78% of the total necessary thermal energy for hot water, and this value presents the possible thermal energy saving for hot water preparation.

The second important thermal energy consumer is leather drying.

Solar thermal energy can be used for direct heating of the air; alternatively, special fluids can be used so that the heat is transferred to the air by a heat exchanger, similarly as for hot water preparation.

Practically all that was said regarding the use of solar thermal energy for the water heating also applies to air heating, except for the limitation to store the hot air. It means that if hot air is used directly for drying, the working hours of the air heating should be synchronised with working hours of the leather drying.

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[49] *Diseño de una instalación de energía solar térmica para la producción de agua caliente de proceso de una tenería, Luisa F. Cabeza, Miquel Nogués, Joan Roca.*

UNIDO assisted Leather Development Project in Kanpur, India

1.Solar energy supported air heating

Solar energy potential in Kanpur

The solar insolation data for aknpur (Latitude 26.45 Longitute 80.332) obtained from *NASA Surface meteorology and Solar Energy - Available Tables* is provided below in Table 1.

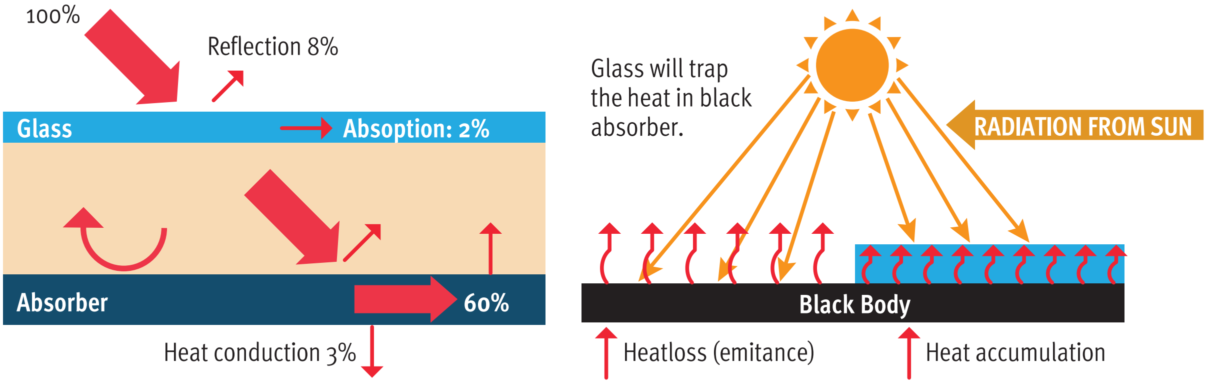
MONTH	JAN	FEB	MAR	APR	MAY	JUN	JUL	AUG	SEP	OCT	NOV	DEC	ANNUAL AVERAGE
22 year average	3.72	4.67	5.75	6.32	6.57	5.91	4.8	4.48	4.51	4.87	4.26	3.6	4.95

Based on source: https://eosweb.larc.nasa.gov

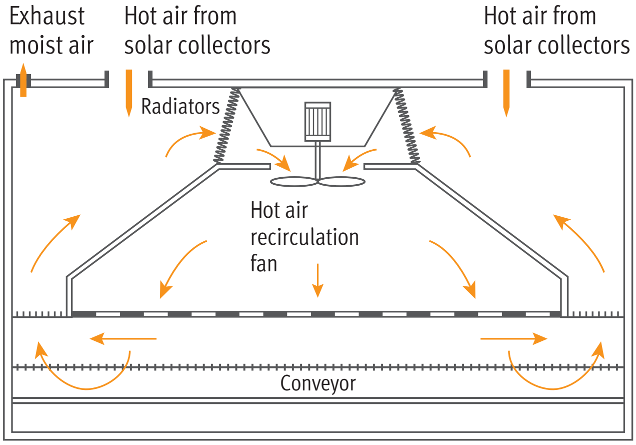
Brief description of the system

A black surface absorbs solar heat. Air is passed through the space between the glass and the corrugated black surface, thus allowing the air to be heated by the direct solar rays as well as the reflection from black surface. The heat convection from the black surface adds to the increased temperature of air. The heat loss below the black surface is prevented by insulation.

Let us see about how to use the acculumulated heat?


100%
Reflection 8%
Glass
Absoption: 2%
Absorber
60%
Heat conduction 3%
Glass will trap the heat in black absorber.
RADIATION FROM SUN
Black Body
Heatloss (emitance)
Heat accumulation

Conceptual diagram of solar hot air generation Cross section view of an autospray drier with the introduction of solar hot air


Exhaust moist air
Hot air from solar collectors
Hot air from solar collectors
Radiators
Hot air recirculation fan
Conveyor

Distribution hot air into drying tunnels

Solar air heating solar panels

Technical description an process flow

The solar collector is made using aluminium extrusions, highly sensitive special absorbers, 4 mm thick toughened glass (partial double), mineral wool insulation, polyurethane sealant and an EPDM rubber. Almost all (92 percent) of the short wavelength radiation emitted by the sun is transmitted through the glass. When it falls on the black absorber, radiant energy is converted into thermal energy. Since glass blocks re-radiation (long wavelengths) from the absorber, the temperature rises in the absorber. Fresh air meanders below the absorber sheet so that the collector delivers hot air in the range of 70-100°C, depending upon the solar radiation. After passing through three segments of solar collectors, the air finally exits through the insulated outlets, which are connected to an insulated metal boy. A blower with specifications of 2.2 kW, 7000 m^3/h, and 1420 rpm draws the hot air from the panel and pushes it into the auto sprayer through the insulated duct.

In this pilot demonstration unit, the solar hot air is provided to one autospray drier and one roller coater drier. It is also possible to use only one of these driers at a time.

The steam flow meter measures the cumulative flow of steam to the autospray drier, which is used to calculate the energy savings. In addition, the control panel includes an energy recorder device which provides the energy supplied by the solar air heating in kWh units.

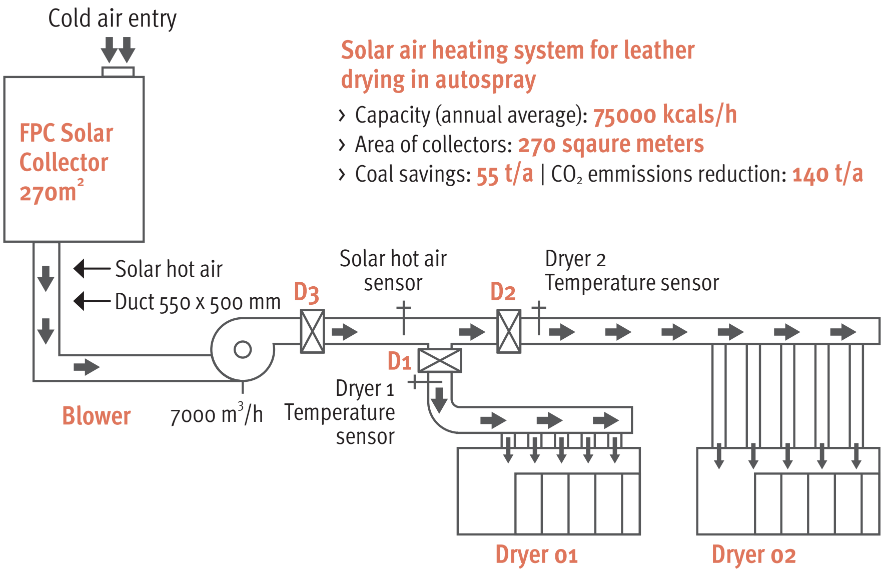
Energy and environmental savings

The use of hot air in leather drying during the autospray process reduces dependency on fossil fuel and increases the renewable energy footprint.

Specific energy consumption in leather production	**54 MJ/m² of finished leather**
Energy savings from solar hot water	**7.47 MJ/m² of finished leather**
Savings in energy by using solar water heating system	**14%**
Reduction in CO_2 emissions	**1 kg of CO_2/m² of finished leather**

Cost benefit analysis

Investment cost	**Rs. 2,200,000**
Operating cost (electricity for blower) @ Rs.7 per kWh	**Rs. 26,000 per annum**
Cost of coal saved	**Rs. 642,000 per annum**
Annual net savings	**Rs. 616,000 per annum**
Payback period	**3.6 years**


Cold air entry
FPC Solar Collector 270m²
Solar hot air
Duct 550 x 500 mm
D3
Solar hot air sensor
D2
Dryer 2 Temperature sensor
D1
Dryer 1 Temperature sensor
Blower
7000 m³/h
Dryer 01
Dryer 02

Solar air heating system for leather drying in autospray

- Capacity (annual average): **75000 kcals/h**
- Area of collectors: **270 sqaure meters**
- Coal savings: **55 t/a** | CO_2 emmissions reduction: **140 t/a**

Operational data

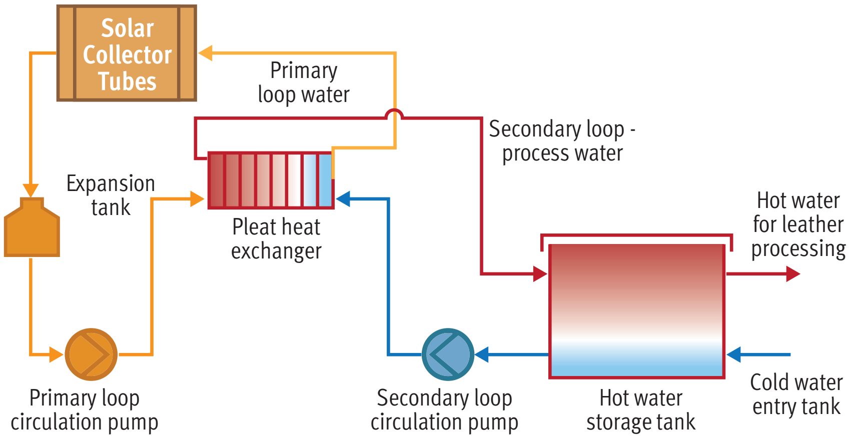
The steam consumption without solar air heating in autospray drier is 210 kg/h @ 5 bar pressure.

DESCRIPTION / PARAMETER	FEBRUARY 2017	MARCH 2017	APRIL 2017
Savings in steam saved using solar hot air (9 AM to 5 PM)	1127 kg/d	1586 kg/d	1656 kg/d
Steam consumption along with solar	553 KG/D	94 kg/d	24 kg/d
Average maximum temparature obtained from solar collectors	83° C	92° C	95° C
Savings in coal (annualized)	71 tonnes		
Reduction in CO_2 emission	181 tonnes		

2. Solar energy supported water heating

Brief description of the system

In the primary loop, pure water is sent to the solar collectors for heating. After heating by solar irradiation, it flows to the expansion tank. This primary loop water is pumped to the plate heat exchanger where heat is transferred to the process water. The primary loop water is then sent to the solar collector tubes for further heating, thus the primary loop is a closed loop. The process water, which is kept in the hot water storage tank, is pumped to the plate heat exchanger to gain heat from closed loop water. The hot water is then circulated between plate heat exchanger and storage tank until the desired temperature is reached. This forms the secondary loop.


Solar Collector Tubes
Primary loop water
Secondary loop - process water
Expansion tank
Pleat heat exchanger
Hot water for leather processing
Primary loop circulation pump
Secondary loop circulation pump
Hot water storage tank
Cold water entry tank

Solar cells on the roof

Operational data

DESCRIPTION / PARAMETER	DECEMBER 2016	MARCH 2017	APRIL 2017
Volume of hot water from the system	2,000 - 3,000 litres	6,000 - 7,000 litres	8,000 - 9,000 litres
Average temparature of the hot water from the system	48° C	52° C	61° C
Average time taken to heat 2,000 litres from ambient to desired temperature	300 minutes	230 minutes	115 minutes

To save on energy consumtion and costs the tannery, wherever possible, worked with floats at room temperature. Using hot floats significantly improved the uptake of chemicals and reduced the COD and, to some extent, TDS load. The qulity of finished leather also improved.

Obviously, the main savings are in the consumption of coal and CO_2 emissions. However, for more accurate estimates of all benefits, including pay-back period, the system has to be monitored for a longer period.

Water hardness is a serious constraint

Water hardness

If the hardness of the water is high, scaling inside the plate heat exchanger or hot water pipelines occur frequently, which needs frequent cleaning. It is necessary to operate the system at following conditions: (a) temperature of primary loop water should not go beyond 80°C and (b) the temperature difference (Δt) in secondary loop before and after heating should not be › 30°C.

Scaling in plate heat exchanger

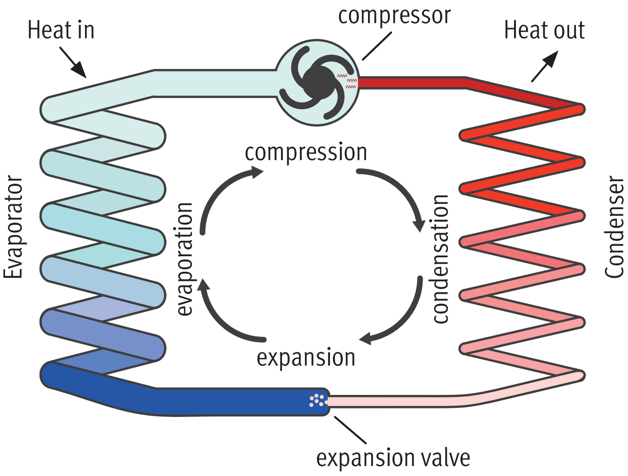
17.4.2. Use of heat pumps

Energy saving is also possible using a heat pump.

According to one of the key laws of thermodynamics, the spontaneous transfer of the heat is possible only from the hotter fluid to the cooler fluid. Nevertheless, according to the laws of thermodynamics it is possible to transfer the heat from cooler fluid to hotter fluid applying special processes and devices. This system is called a heat pump.

The heat pump uses special fluids, “refrigerants” (because they are used in refrigeration and known as freons). Many freons are prohibited today because if released they destroy the ozone layer in the atmosphere.

Figure 99. A simplified scheme of the heat pump



Based on source: http://www.diracdelta.co.uk

As shown in the figure, the heat pump operating cycle consists of evaporation, compression, condensation and expansion.

For the evaporation of the “refrigerant” it is necessary to take the heat from the fluid. The compression is mostly performed by a compressor driven by an electric motor. Due to the compression the refrigerant is heated. During condensation the heat (with the temperature higher than the temperature of the fluid used for evaporation) is transferred to the fluid which should be heated. The expansion is performed by an expansion valve.

The sources of heat from which the heat is taken can be ambient (air or water), soil, underground water, thermal water, (warm) waste water, (warm) waste air and any other (warm) fluid. Preferable sources of heat are those with the most possible constant temperature during the day and during different years’ seasons (e.g. underground water, thermal water, seawater).

The media to absorb the heat with elevated temperatures are mostly water or air.

The heat pump can be economically used in a tannery for the (supplementary) heating of water needed in the process and of the air needed for leather drying.

The use of the combination of direct solar heating with a heat pump is also a viable option e.g. for heating the fluid to the higher temperature required to heat the process water.

Apart from the construction characteristics of the heat pump, the most important value is the “coefficient of performance” (COP), i.e. the ratio of the thermal energy transferred to the fluid during condensation and the consumed electric energy of the electric motor for the compressor. The COP depends on the difference of the temperature of the source fluid and the temperature of the heated fluid. A rough estimation of COP can also be made using the following formula:

$$COP \leq \frac{T_{hot}}{T_{hot} - T_{cool}}$$

Where:

- T_{hot} is the temperature of the heated fluid, in K
- T_{cool} is temperature of source fluid, in K

The viability of heat pumps as an energy source depends on the ratio of the thermal *energy prices vs. the fuel and the electric energy prices*. Generally, it is considered that recovery of thermal energy by means of heat pumps is normally only economical at a price relation of:

$$\frac{\text{GJ (electric)}}{\text{GJ (thermal)}} < 2 - 2.5$$

The economic use of the heat pump is limited to the relatively low temperature difference.

The thermal energy consumption for building ventilation depends on the difference of the temperature in the building and the ambient temperature and the air exchange rate necessary to keep the demanded air quality in the buildings. The temperature difference is higher in the winter seasons, especially in temperate zones.

It is reported that building heating (temperate zone, France) consumes about 33% of total thermal energy consumption.[50]

To save thermal energy for building ventilation, heat exchange between the warm exhausted air and fresh air is usable. A simple air-to-air heat exchanger has the exchange factor of up to 80%. The use of solar air heating is also viable due to the relatively low temperature of the air for ventilation air and can bring considerable savings in the thermal energy obtained from the combustion of (fossil) fuel.

17.5. OPTIMISATION OF ELECTRIC MOTORS

Electric energy can be saved by using modern electric motors with higher efficiency.

In the EU the new Directive defines 3 classes of electric motors according to their efficiency:

- IE2 (replaces earlier EFF1) > 94%
- IE3 (premium class); from 1. Jan 2017, all motors between 0,75 375kW must fulfil the IE3 requirements
- IE4 (super premium class) > 97%

Usually the electric power for industrial use (tannery) is purchased on the higher voltage (10000 V or higher) and transformed to 400 V locally, in the tannery; in such cases the price is lower. Generally, the price consists of more components, such as:

- installed electric power
- peak consumed power
- consumed real or active electric energy
- production of reactive energy, connected with the power factor (cos φ)

A tannery can influence power consumption peaks by planning the dynamic variance in equipment use.

The most important saving of electric power is achieved by reducing reactive energy. All inductive electric power devices produce reactive electric energy. Real or active electric energy is the energy consumed by electric driven devices expressed in Watts (W). The *apparent electric energy* is the electric energy calculated as volts (V) multiplied with current (A), and expressed as volt-amperes (VA).

The relation of real or active electric energy and apparent electric energy is the power factor (cos φ):

$$\frac{\text{real or active electric energy}}{\text{apparent electric energy}} = \text{power factor} (\cos \varphi)$$

Usually if the power factor (cos φ) is > 0.95 reactive power is not paid.

To achieve a higher power factor it is necessary to compensate the reactive energy installing devices containing the capacitors. Such devices can be installed at the main electric distribution station and/or on individual equipment having a power factor (cos φ) < 0.95.

17.6. OWN GENERATION OF ELECTRIC POWER (DG, PHOTOVOLTAIC, WIND)

17.6.1. Diesel generator(s), DGs

Unfortunately, in many developing countries the supply from the mains is not very reliable; "power shedding" patterns are unpredictable and tanners have no choice but to install supplementary sources such as their own Diesel generators sets (D.G.s). It was reported that in one African country the cost of D.G. produced energy was about USD 0.35 - 0.8/KWh.

17.6.2. Photovoltaic cells, wind

It is also possible to produce one's own electric energy by using photovoltaic cells (renewable energy), which directly converts solar rays into electric energy. Unfortunately, this kind of production of electrical energy is still very expensive, due to very high equipment cost, but once installed the energy is practically gratis. Today's price of this energy is 4 – 5 (and more) times the price of energy from local electrical energy suppliers. In many countries the state financially supports this kind of production if the photovoltaic installation is connected to the mains.

The inconvenience with this type of energy is that its production entirely depends on daylight hours (no production during the night) and on the seasons (especially in a temperate zone). The electric energy storage is not applicable (with the exception of special cases), and for this reason the connection to the local supplier is advisable.

Solar electric energy production depends on location, type of photovoltaic cells and type of installation (with fixed or regulated position and inclination).

The efficiency of the direct transformation of solar into electrical energy depends on the material and construction of the photovoltaic cells and today it is from 6 – 18% for industrial products. This efficiency increases constantly with the introduction of new materials and constructions. There are already some experimental materials and constructions with an efficiency of more than 30 %. Normally, the cells with higher efficiency are more expensive.

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[50] *Eco-Design, T. Poncet et al.*

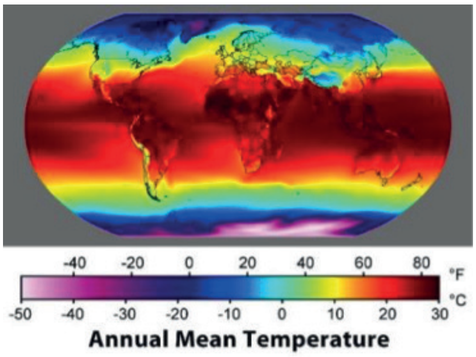
The best use of photovoltaic cells is when the installation is vertically to sunlight. Because the sun "moves" over the horizon, the angle of the sunlight to fixed surface changes; ideally, the position of the installation can be regulated in such a manner that the sunlight is always vertical to the surface.

Equipment harnessing wind can also be installed as a supplementary source of renewable energy; many factors determine its efficiency but, of course, the very first precondition being frequent and rather steady winds.

17.7. COMPARISON OF THERMAL ENERGY CONSUMPTION IN A TEMPERATE VERSUS A TROPICAL ZONE

> **Due to different ambient temperatures many would expect that the overall thermal energy consumption in a tannery in a hot climate zone is considerably lower than in a temperate zone. In reality it is somewhat more complex and worth comparing.**

Figure 100. World climate zones – mean temperatures



Source: http://www.wattsupwiththat.com

A simple computation based on average yearly water and air (ambient) temperatures shows that the amount of net thermal energy needed for heating the float in (sub)tropic zones (South India) is from 20% (dyeing) to about 50 % (bating) of that in temperate zones (Middle Europe).

Chamber drying in (sub)tropic zones benefit from the higher ambient (air) temperature but at the same time it is negatively affected by high relative humidity and consequently much higher volume of fresh air is required: a rough estimation is that on average it is about 20% less than in the temperate zone. However, this advantage almost entirely disappears during the peak of the monsoon season.

However, if solar energy is used to support water heating, the conditions in the tropic zones are more favourable primarily due to higher insolation.

The insolation in the temperate zone (Europe) is approx. 1500 kWh/m^2/y (4.1 kWh/m^2/d), and in the tropical zone (South India) approx. 2200 kWh/m^2/y (6.0 kWh/m^2/d). Thus, the ratio is:

$$2200/1500 \approx 1.5$$

It means that the solar-based production of thermal energy in a hot climate country is about 1.5 times more favourable than in temperate climate.

If heat pumps using ambient air or water as the medium are installed, a higher temperature of the heated water or air can be achieved; alternatively, a smaller system can be installed or the best COP can be reached in the same installation.

Obviously, there is no need to heat the building spaces in the tropic zone but there is some consumption for the air-conditioning of offices.

Figure 101. Solar panels at Packer Leather, Australia

Source: C. Money

17.8. ENERGY AND WATER AND WASTE WATER

17.8.1. Treatment

> **Leather production needs a very high quantity of water and produces practically the same quantity of the waste water. Typical water consumption is 12 – 37 m^3/t of raw hide for the tannery processing from raw wet salted hides to finished leather (shoe uppers)[51]. Here the value of 25 m^3/t will be taken as representative.**

Regrettably, the reduction of water consumption does not reduce the investment much and the operation costs of waste water treatment because the total pollution remains practically the same; only the concentration of pollutants increases, which can require more extensive and/or sophisticated treatment.

The tannery waste water temperature is usually higher than the temperature of the fresh water and the ambient air temperature due to the use of warm floats in the process; however, due to transportation and relatively long time of the treatment, the temperature during the treatment almost entirely depends on the ambient air temperature. As a reminder, the typical effluent characteristics and treatment effects by the activated sludge process are given in the next table.

The excess sludge, typically 125 kg dry solids/t of raw hides results from the treatment; anaerobic digestion of sludge, separately or together with other tannery wastes (e.g. fleshings) can be applied to produce biogas (methane), which can be used in a tannery. This approach is viable for larger tanneries and/or tannery clusters.[52]

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[51] *IUE Table – Typical pollution values in conventional tannery processes*

[52] *Biomethanation of fleshings and sludge from tannery, UNIDO*

Table 50. Typical effluent characteristics and treatment effects[53]
Primary & biological treatment, including nitrification/denitrification, final $BOD_5 < 20$ mg/l

Parameter	Pollution load in the raw effluent	Raw, composite effluent	Pollution load after biological treatment	Fully treated effluent	Total treatment efficiency
	kg/t of raw hide	*mg/l*	*kg/t of raw hide*	*mg/l*	*%*
COD	150.0	6,000	6.00	240	96.00
BOD_5	62.5	2,500	0.50	20	99.20
SS	100.0	4,000	0.75	30	99.25
Cr^{3+}	4.0	160	0.025	1	99.3
S^{2-}	5.0	200	0.025	1	99.5
TKN	12.5	500	1.25	50	90.00
Cl^-	150.0	6,000	No change	No change	No change
SO_4^{2-}	62.5	2,500	No change	No change	No change
TDS	375.0	15,000	No change	No change	No change
Sludge - DS	100		125.00		

17.8.2. Energy consumption related to waste water treatment

A (C)ETP uses only electric power.

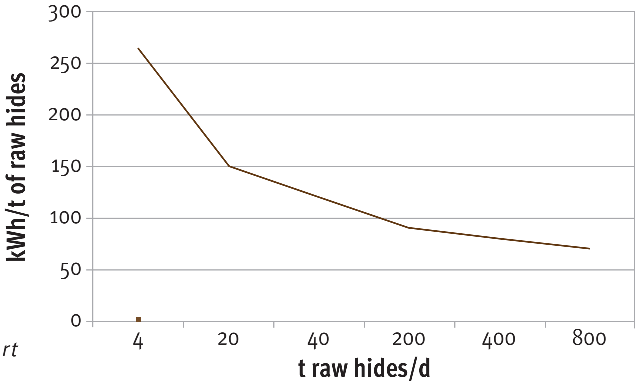
The LWG document[54] estimates the consumption of electric energy for effluent treatment at 10 kWh/m^3 of effluent. For the accepted value of 25 m^3/t of raw hides it is 250 kWh/t of raw hides, or 900 MJ/t of raw hides. In reality the electric energy consumption in the (C)ETP very much depends on its capacity as shown in a UNIDO study[55].

Table 51. Some indicative effluent treatment plant parameters

Parameter	Unit	Tannery/cluster capacity, *tons of wet-salted hides/day*					
		4	20	40	200	400	800
		Treatment capacity, *m^3 of effluents/day*					
		100	500	1000	5000	10000	20000
Power consumption	*kWh/day*	1060	3000	4850	18400	32500	54000
Power consumption vs. input	*kWh/t raw hide*	265	150	120	90	80	70

Power consumption vs. tannery and (C)ETP capacity is presented in the next diagram.

Figure 102. (C)ETP energy consumption vs. capacity



Based on chart by M. Bosnić

One theoretical calculation made for a (virtual) tannery of 10 t/d of the raw hides and 25 m^3 of the effluent/t of raw hide, gives the value of 1850 kWh/d (6660 MJ/d), or 675250 kWh/y (2431000 MJ/y), or 185 kWh/t (666 MJ/t), or 7,4 kWh/m^3 (26.6 MJ/m^3) of effluent.

All general suggestions pertaining to the consumption and cost of electric energy for leather processing are also valid for effluent treatment.

17.8.3. Comparison of energy consumption in (C)ETPs installed in temperate and tropical zones

Waste water temperature significantly influences the parameters of waste water treatment; thus, it might be of interest to compare energy consumption needed for effluent treatment (the largest consumer being the biological step).

In some regions in temperate zones, the temperature during the winter period can be very low and sometimes it is necessary to have a (C)ETP in a closed building, which considerably increases not only the

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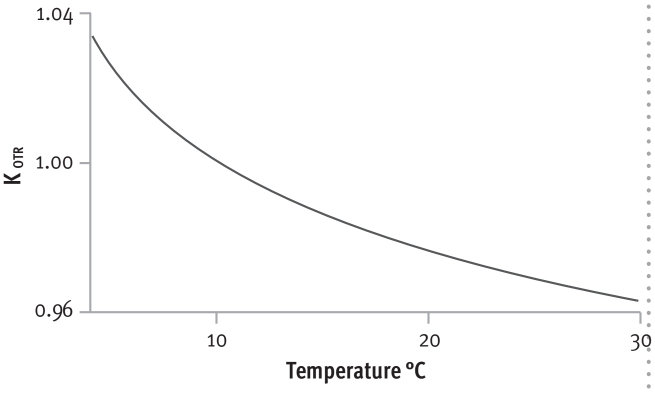
[53] As said earlier, all based on consumption/discharge of 25 m^3/t of raw hide.
[54] LWG Environmental Protocol Audit Responses Report, Issue 6.0
[55] Benchmarking in the tanning industry, J. Buljan, I. Král, UNIDO

investment, but also the operation costs (ventilation, air treatment).

At a temperature of < 10°C the biological aerobic activated sludge effluent treatment is slowed down and the nitrification practically ceases.

While higher ambient temperatures are good for construction costs, they have a negative impact on electric energy consumption: the negative difference between the elevated coefficient of the velocity of the oxygen solution in the water and reduced solubility of the oxygen in the water results in a lower Oxygen Transfer Rate (OTR).

The values of the factor for the correction of OTR in function of the temperature are shown in the following diagram[56].



Because of the lower OTR, it is necessary to introduce more air for aeration in the biological activated sludge treatment for the same configuration of the (C)ETP, and thus uses proportionally more electric energy.

Thus, while the consumption of the biological treatment under given conditions in a temperate zone is approx. 63.3 kWh/ton of raw hide, in hot climate zones with the corresponding (lower) Oxygen Transfer Rate (OTR), the electric energy consumption is slightly higher:

$$\frac{63.3}{0.98} = 64.6 \text{ kWh / t of raw hide}$$

In summary it can be said that while the biological treatment in hot climate zones is positively influenced by higher effluent temperature, lower solubility of oxygen and lower oxygen transfer rate (OTR) have a negative effect and result in a slightly higher consumption of electric energy.

17.9. ENERGY SAVINGS MEASURES

Considerable savings can be made by the careful selection of methods and equipment as well as close control of thermal efficiency. Wherever possible, the principle "no production, no consumption" should be strictly followed.

The UNIDO paper *Benchmarking in the Tanning Industry* provides a brief overview of the main energy saving measures in a tannery.

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[56] *W. v. d. Emde: Suvremena primjena procesa sa aktivnim muljem u kondicioniranju otpadnih voda naselja i industrije (Contemporary practice of the activated sludge in the conditioning of the communal and industrial wastewater), Sarajevo 1973.*

18. OCCUPATIONAL SAFETY AND HEALTH IN THE WORKPLACE (OSH)

18.1. INTRODUCTION

The OSH issues in tanning operations are extensively addressed in the paper *Occupational safety and health aspects of leather manufacture* prepared by UNIDO and jointly published with the Council for Leather Exports, Chennai, India in 1999. The paper is still quite relevant especially regarding conditions prevailing in developing countries. There is also a small "dedicated" brochure titled *How to deal with hydrogen sulphide gas*.

The OSH general principles are covered by ISO: 18000.

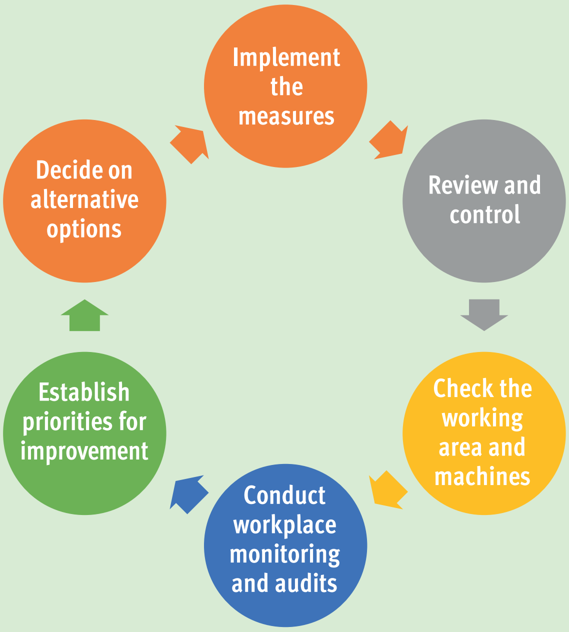
Accordingly, here are only a few highlights, including some considerations about the OSH impact of cleaner technologies: the fact that on the whole they are environmentally friendlier does not mean that they are necessarily quite innocent and/or without bringing some (new?) risks, possibly not even fully recognized yet.

18.2. BASIC PRINCIPLES OF OSH MANAGEMENT

While exploring and implementing OSH prioritization measures it is recommended to adopt the following approach:

1. Eliminate the hazard (e.g. by substitution of hazardous agents; putting up a protective fence)
2. Minimize the impact of the hazard (e.g. ventilation, general cleanliness)
3. Protect the worker against the hazard's impact (e.g. distribution of PPE; personal hygiene)

Figure 103. Basic principles of OSH management


Implement the measures
Review and control
Check the working area and machines
Conduct workplace monitoring and audits
Establish priorities for improvement
Decide on alternative options

Experience has shown that management's commitment to improve OSH standards at work is an essential prerequisite for worker's safety.

18.3. TYPICAL INJURIES AND NEGATIVE HEALTH IMPACTS IN TANNERIES AND TANNERY EFFLUENT TREATMENT PLANTS

- Injuries caused by falls due to slippery floors, unguarded door openings and pits
- Injuries on fingers, hands, legs and head from contact with moving machinery parts
- Skin burns and allergic reactions, respiratory problems either due to dust or chemical agents/gases either in course of (inappropriate) handling or due to poor ventilation
- Shocks and burns caused by contact with live electrical installations (inadequate protection/poor practice, corrosion)
- Injuries caused by fire
- Impairment of hearing and eye sight

18.4. THE MAIN CAUSES OF SAFETY RISKS AND HEALTH HAZARDS

Faulty designs and/or poor maintenance of machinery and equipment

A series of events can ultimately result in an accident.

Chemical substances

Applied before or during the process they can affect the safety and health of personnel exposed to them (e.g. by inhalation, ingestion, skin contact)

Working conditions

Influence staff behaviour and thus indirectly contribute to accidents and health hazards.

Employees' job experience, training and attitude

General education and, in particular, understanding of and specific training in the containment of safety risks and hazards are of paramount importance; this applies not only to operators but possibly even more to managers and supervisors.

18.5. MALODOUR

The traditional perception of tanning is associated with an irritating malodour mainly caused by hydrogen sulphide and ammonia and some other compounds resulting from protein decomposition; in reality it is only a sign of bad practices and, above all, of poor housekeeping.

Table 52. The main categories of air-transmitted hazardous or irritating substances

Substance/cause	Mitigation/elimination	Limitations, warnings
Malodours in stores	Proper raw material preservation; good housekeeping and ventilation	Higher preservation and energy costs
Ammonia	Replacement of ammonium compounds in deliming (e.g. by CO2); Scrubbing and/or bio-filtration of extracted air	Not applicable to pelts with thickness over 1.5 mm; old drums
H_2S tannery	Good segregation of liming (alkaline) and tanning (acid) streams; the pH of effluents containing sulphide kept above 9.5 until treatment (oxidation)	Oxidation reversible!
H_2S, ETP	Continuous aeration, immediate (catalytic) oxidation	Long collecting channels, power shedding
Glutaraldehyde	Modified glutaraldehyde with lower vapour pressure; automated dosing system	Cost
Volatile (halogenated) organic compounds, VOCs (mainly finishing)	Water based finishing; replacement by acceptable solvents; efficient extraction and wet scrubbing/adsorption systems	"Pure" water based coating inadequate for some articles; treatment cost

18.6. HYDROGEN SULPHIDE GAS, H2S

Nearly all fatal accidents in tanneries are caused by hydrogen sulphide gas which is why it is addressed separately here.

Hydrogen sulphide gas is evolved by the mixing of sulphide containing liming liquors/waste water (alkaline) and tanyard effluents (acidic), especially in deep channels and pits and at higher concentrations when the typical (warning!) smell is not pronounced. Strict segregation of alkaline and acidic streams to ensure that the pH will not fall below 9.5 is essential.

Hydrogen sulphide gas is quite easily eliminated by catalytic oxidation using manganese sulphate as a catalyst before being mixed with acid effluent or being discharged to the general mixing tank, which generally has a pH of 8.5-9.

It is useful to recall once again the properties of hydrogen sulphide gas, H_2S, still by far the most frequent killer in tannery accidents, mainly in inadequately ventilated spaces and especially in pits and channels.

However, in view of new toxicological data, authorities in some countries have started reducing the recommended chronic exposure limits to hydrogen sulphide; the 8 hour time weighted average Threshold Limit Value (TLV-TWA_8) for H_2S is brought down from 10 ppm to 1 ppm, and the Short Term Exposure Limit (TLV-STEL) from 15 ppm to 5 ppm so that even confirming compliance with the new standards will be a challenge for health and safety practitioners.

Instruments needed to detect and

Figure 104. The main tannery streams, segregation

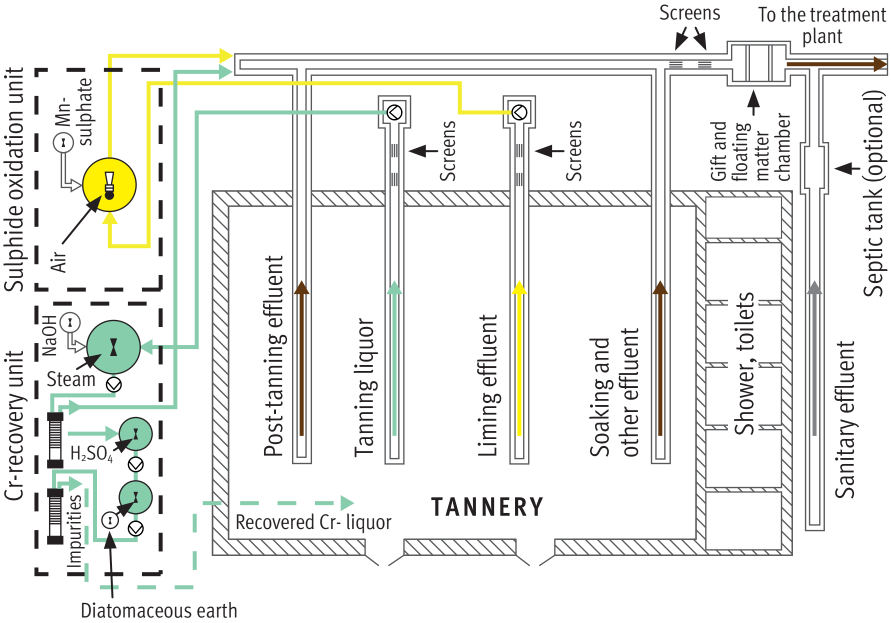
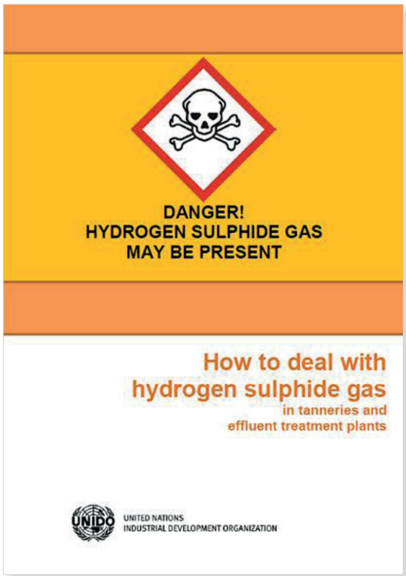

Screens
To the treatment plant
Sulphide oxidation unit
Mn-sulphate
Air
Screens
Screens
Gift and floating matter chamber
Septic tank (optional)
Cr-recovery unit
NaOH
Steam
H_2SO_4
Impurities
Post-tanning effluent
Tanning liquor
Liming effluent
Soaking and other effluent
Shower, toilets
Sanitary effluent
Recovered Cr- liquor
TANNERY
Diatomaceous earth

Table 53. Poisoning effects of hydrogen sulphide gas (H_2S)

Exposure Ppm	Time	Impact on unprotected person
0.03	No time limit	No effect
0.08 - 2.0	No time limit	(Mal)odour threshold
10	Up to 8 hours	No effect
15	Up to 15 minutes	Threshold limit value
15 - 200	Up to 15 minutes	Headache, nausea, general weakness, pain in legs
200 - 500	**1 minute**	**Irritation of nose & throat, vertigo, blurring of vision, loss of consciousness lasting a few minutes**
500 - 900	**1 minute**	**Profound coma, convulsions, disorientation after recovery**
› 900	**1 minute**	**Instant coma and death**

ppm = parts per million

Figure 105. Cover page of UNIDO H_2S manual

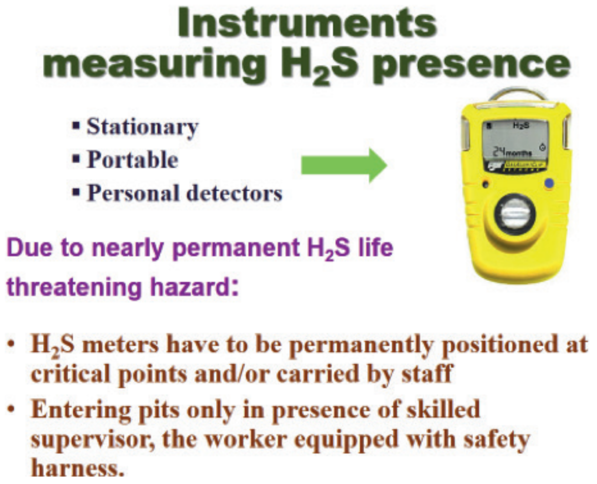


DANGER!
HYDROGEN SULPHIDE GAS
MAY BE PRESENT

How to deal with
hydrogen sulphide gas
in tanneries and
effluent treatment plants

UNITED NATIONS
INDUSTRIAL DEVELOPMENT ORGANIZATION

monitor H_2S exposures can either be fixed or portable whereas personal detectors are worn by employees and typically sound an alarm at levels of 10-15 ppm. Due to nearly permanent life-threatening hazards, H_2S meters are always positioned at critical points and/or carried by staff. Also, certain activities such as entering pits can only be carried out in the presence of a skilled supervisor and the worker must be equipped with a safety harness.



Instruments measuring H_2S presence

- Stationary
- Portable
- Personal detectors

Due to nearly permanent H_2S life threatening hazard:

- H_2S meters have to be permanently positioned at critical points and/or carried by staff
- Entering pits only in presence of skilled supervisor, the worker equipped with safety harness.

H2S
24 months

18.7. BAD ODOUR PROBLEMS RELATED TO EFFLUENT TREATMENT PLANTS

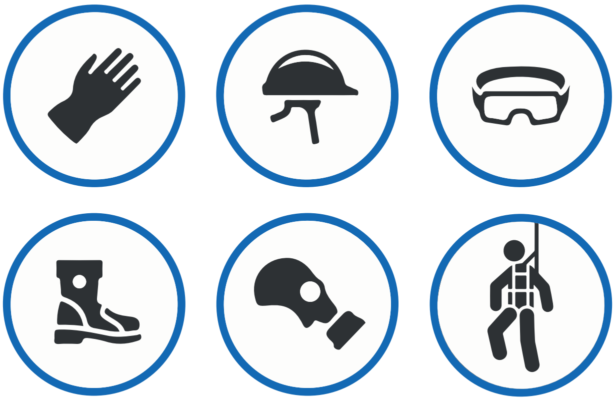
Odours associated with waste water are difficult to quantify because they are caused by a wide variety of compounds. It is a nuisance that is more qualitative than quantitative: sensitive persons easily detect very low concentration of odoriferous substances in the air (sulphides/other sulphur compounds, ammonia, amines, etc.). Local geographic and climatic conditions such as wind direction, land shape, air humidity, ground and air temperature, etc. greatly influence the level of the problem. Along the treatment line the main sources of bad odour are:

- Equalisation & sulphide oxidation
- Sludge thickening
- Biological aeration
- In-plant storage of the dewatered sludge
- (Temporary) sludge disposal site

Yet, the main source of bad odour remains to be the stripping of hydrogen sulphide; however, it is not the concentration of sulphide per se but the lowering of pH: the not disassociated H_2S is present only at pH below 10. Thus, it is crucial to control the pH and if needed alkalis like NaOH or lime are added to ensure a pH of > 9.5-10. More extensive, uninterrupted aeration may help but sometimes rigorous (and expensive) methods like adding hydrogen peroxide or pure oxygen are necessary. Nowadays, in some places nearly the entire ETP is covered and the air purified.

(C)ETPs & OSH

General and specific OSH measures, including use of Personnel Protection Equipment (PPE) about handling equipment and chemicals like fencing, protection from moving parts, storing & handling of chemicals etc.



also apply to (C)ETPs!!

18.8. AIRBORNE PARTICULATE MATTER (DUST)

Shaving, milling (softening in rotating drums) and, in particular, buffing are the main sources of airborne particulate matter (dust).

Higher accuracy of both splitting and shaving can drastically reduce the amount of particles carried by air. Mitigation measures primarily include correctly designed and maintained low noise extraction ventilation systems fitted with bag filters or wet scrubbers; the target is 3 - 6 mg /Nm^3 of particulate matter in exhausted air expressed as a 30-minute mean.

The mandatory use of appropriate Personal Protection Equipment (PPE) such as masks, goggles and ear protective equipment (mufflers) is now a widely accepted standard.

A specific category are solid aerosols with a particle size smaller than 200 x 10^{-3} mm; in a tannery they can be generated by (surface) aerators in waste water treatment plants.

18.9. NOISE AND VIBRATION

There is a long list of potential culprits, i.e. machines, equipment and operations responsible for pollution by noise and vibrations:

- Drum driving gears
- Chemicals mixers
- Various pumps for water, float collection/recirculation, waste water, circulating reagents in scrubbers, etc.
- Extraction and aeration fans
- Air compressors
- In-plant (fork lifts) external transportation
- Diesel power-generating sets

Some further contributors include:

- Sammying and setting out
- Shaving, especially dry shaving
- Staking, especially vibro-stakers
- Buffing and dedusting, together with dust collection systems
- Finishing (coating), especially by rotary spraying machines together with air extraction and scrubbing systems.

The main noise and vibration preventative and/or mitigation measures:

- Timely preventive maintenance, lubrication
- Where applicable replacement of metal with hard plastic pinion gears
- Low-noise spray-guns
- Better foundation and noise & vibration resilient machine mountings (e.g. for sammying and vibro-staking machines)
- Change of operating speeds, avoid resonances
- Placing equipment such as exhaust fans on the outside of the (main) building
- Modify the building layout
- Silencing exhaust outlets
- Using purpose designed, properly balanced fans; ducts designed to ensure smooth airflow

18.10. CRITICAL REVIEW OF ANY NEW (CLEANER) LEATHER PROCESSING METHOD

Traditionally, chemicals suppliers tend to reveal as little as possible about the composition of specialty agents they promote; normally, apart from mandatory data for safety data sheets, they are silent about their environmental performance for example about the COD load and biodegradability.

Also, as said earlier, the fact that on the whole a new process or agent is environmentally friendlier does not mean that it is necessarily quite innocent and/or without bringing some (new?) risks, possibly even not fully recognized yet. A good example is carbon dioxide deliming.

Replacement of ammonium sulphate with carbon dioxide in deliming

Purpose: ***Reduction of nitrogen load in effluent***

Positive impact:
- Reduced nitrogen load in effluent
- Elimination of potential hazards due to workers' exposure to ammonia gas (respiratory problems, eye irritation)

Potentially negative impact:

- Dizziness, headache, hyperventilation due to excessive inhalation of carbon dioxide (e.g. by leakage) even, in the worst and unlikely case, asphyxiation.
- Poisoning due to inhalation of the hydrogen sulphide gas due to reaction of carbon dioxide and the residual sulphide in pelt.

18.11. MATERIAL SAFETY DATA SHEETS, MSDS

There are many different categories of safety and health hazards related to substances and specialty chemicals used in the tanning process. They are classified according to their acute oral toxicity, irritation to the skin and mucous membranes as well as according to their potential mutagenic, teratogenic and carcinogenic effects and the effects of repeated or prolonged exposure. This must be clearly stated in Material Safety Data Sheets, MSDS and appropriately marked on packaging to make it possible to classify the product at one glance.

Potential hazards by the product are not identical with the real risk. A product handled by observing safety precautions and properly used is not (necessarily) harmful; it is harmful only if the user is exposed to it in a particular way. Furthermore, the route (inhalation, ingestion, skin contact), the quantity/concentration, duration and similar factors determine the level of exposure and thus the overall risk.

In that context it is useful to be familiar with some basic terms and common abbreviations concerning the safe handling of chemicals:

Dose (D):	Measured or prescribed amount of a substance.
Dtox	toxic dose
DE	efficient dose
DL(LD)	lethal dose
ID	individual dose
IMD	individual maximum dose
MD	maximum dose
MDD	maximum daily dose
ND	normal dose
DD	daily dose

The lethal dose is subdivided into:

LD_{100}	The absolutely lethal dose
LD_{50}	The average lethal dose, at which 50% of the

	animals in the test are killed
LD_0	The maximum non-lethal dose.

Toxicity, defined as the degree of being poisonous, is subdivided into:

- acute toxicity = poisoning produced by a single dose
- subchronical = poisoning produced by toxicity repeated dosage within a relatively short time
- chronical toxicity = poisoning produced by repeated dosage over a relatively long time.

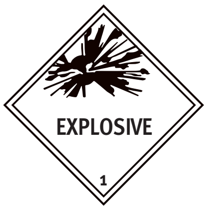
Flash Point: The lowest temperature, at a pressure of 1013.25 mbar, at which vapours are developed and with air over the liquid level form a mixture that can be inflamed by foreign ignition.

The importance of having the key warnings and instructions in language and signs fully understood even by less skilled workers cannot be overemphasized.

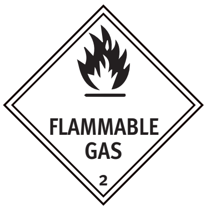
Without going into details here, all involved should, for example, understand signs established by international regulations concerning the transportation of materials classified as Compressed, liquefied or dissolved gases under pressure; Inflammable, liquid materials (combustible liquids)/Inflammable materials; Spontaneously combustible materials; Oxidizing materials; Toxic materials, etc.

Danger labels prescribed by IMDG Code

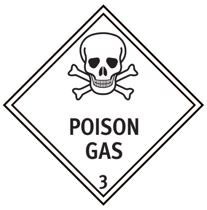
(International maritime dangerous goods code)
Marking according to the Regulation on Dangerous Goods.



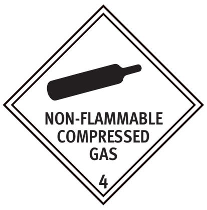
Explosive
Orange

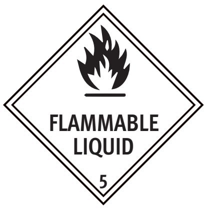


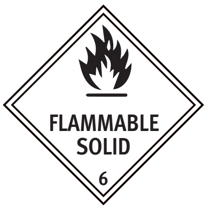
Flammable Gas
Red



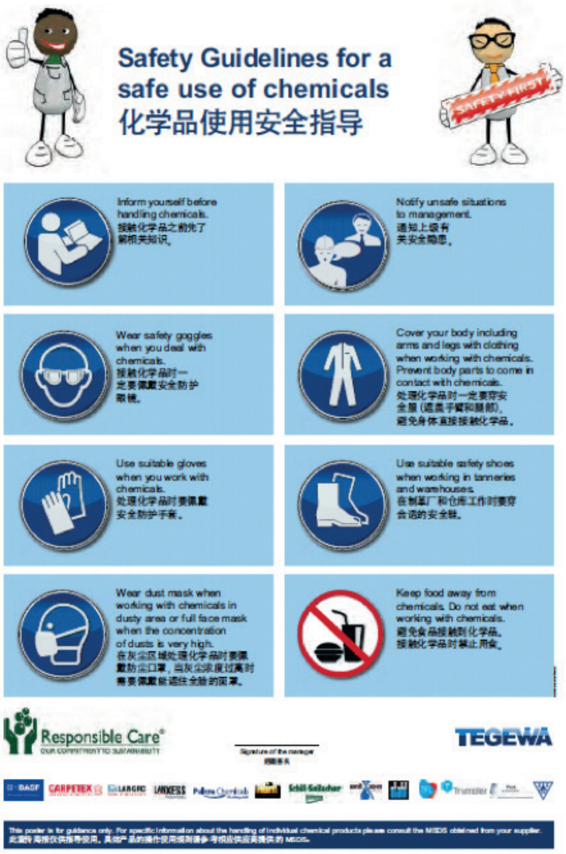
Poison Gas
White







A good example of safety posters are posters developed by the German industrial association TEGEWA; they are freely available in several languages such as English, Chinese, Bangla, Urdu, Thai, Hindi etc.



Safety Guidelines for a safe use of chemicals
化学品使用安全指导

Inform yourself before handling chemicals.
接触化学品之前先了解相关知识。

Notify unsafe situations to management.
通知上级有关安全隐患。

Wear safety goggles when you deal with chemicals.
接触化学品时一定要佩戴安全防护眼镜。

Cover your body including arms and legs with clothing when working with chemicals. Prevent body parts to come in contact with chemicals.
处理化学品时一定要穿安全服（遮盖手臂和腿部），避免身体直接接触化学品。

Use suitable gloves when you work with chemicals.
处理化学品时要佩戴安全防护手套。

Use suitable safety shoes when working in tanneries and warehouses.
在制革厂和仓库工作时要穿合适的安全鞋。

Wear dust mask when working with chemicals in dusty area or full face mask when the concentration of dusts is very high.
在灰尘区域处理化学品时要佩戴防尘口罩，当灰尘浓度过高时需要佩戴能遮住全脸的面罩。

Keep food away from chemicals. Do not eat when working with chemicals.
避免食品接触到化学品。接触化学品时禁止用食。

Signature of the manager

This poster is for guidance only. For specific information about the handling of individual chemical products please consult the MSDS obtained from your supplier.

The content of the Material Safety Data Sheet, MSDS in the EU (EC-MSDS) has to include:

1. Substance/preparation name, company name, intended use
2. Composition/information on hazard ingredients
3. Possible hazards
4. First aid measures
5. Fire-fighting measures
6. Accidental release measures
7. Handling and storage
8. Exposure controls and personal protection
9. Physical and chemical properties
10. Stability and reactivity
11. Toxicological information
12. Ecological information
13. Disposal considerations
14. Transport information
15. Regulatory information (labelling)

18.12. BENCHMARKING IN THE AREA OF OCCUPATIONAL SAFETY AND HEALTH (OSH)

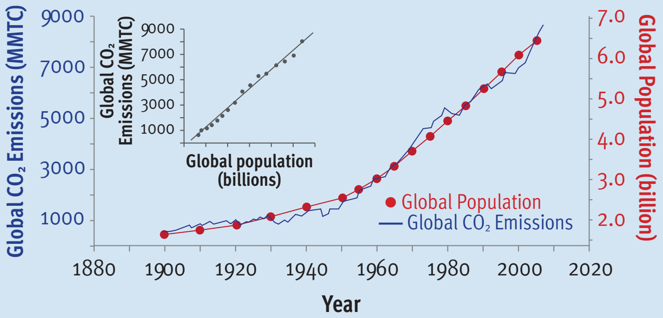
The main factors relevant for health hazards and safety at work are machines and equipment, chemicals, working environment and conditions and people. As a rule, OSH standards in a tannery are among the best visual indicators of its overall performance. For full overview, including a very detailed list of items to be monitored, refer to the study *"Occupational Safety and Health Aspects of Leather Manufacture" by J. Buljan, A. Sahasranaman and J. Hannak, jointly published by UNIDO and Council for Leather Exports (CLE), India, 1999*. Also, please refer to the UNIDO paper *Benchmarking in the tanning industry*.

19. CARBON FOOTPRINT – LEATHER LIFE CYCLE ANALYSIS (LCA)[57]

19.1. GENERAL

> **Climate change(s), greenhouse effect, carbon footprint and related topics are very present on the global media scene; there is no shortage of reports, statements, debates and opposing claims. Political decisions with strong financial implications are already being implemented.**

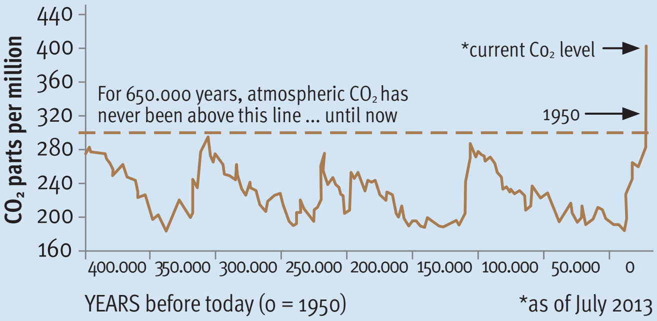
Figure 106. Evolution of global population (red) and global carbon dioxide emissions (blue) since 1900



The inset shows the tight relationship between population and CO_2 emissions[58].

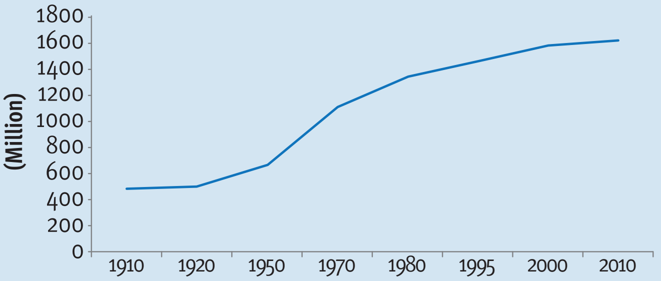
Another source:

Figure 107. Atmospheric CO_2 levels



Based on source: US National Oceanographic and Atmospheric Administration (NOAA), via S. Jessep and World Leather, April/May 2016

Figure 108. Cattle stock population



Based on source: Reich, FAO

An important part of CO_2 emissions emanates from livestock (cattle) population and this is certainly of interest to the leather sector. For illustration, Figure 109 shows cattle stock population since 1910; it can be assumed that a leather production increase over the last 100 years has followed a similar pattern.

Since GHG emissions are one of the main environmental challenges, it is very likely that figures about GHG or CO_2 emissions will be part of mandatory information on any product and will be "taxed" to encourage the use of more sustainable products. For some products (e.g. cars) such information (g CO_2/km) and corresponding taxes are already introduced in some regions.

Apart from a brief "refresher" about the rather specific terminology related to these topics, this chapter will only deal with issues closely related to the tanning industry; and although the leather industry is not a major contributor to CO_2 emissions, it cannot afford to ignore this issue. Therefore, the leather industry needs to not only develop suitable tools and reduce CO_2 emissions but also globally agree on the methodology to measure and to report on CO_2 emissions. The European Standard EN 16887:2017 already provides a good framework for that purpose.

Actually, UNIDO was among the very first international organization that turned its attention to this particular area and its relevance to the leather sector in belief that in view of the consequences already felt by the trade tanners simply could not afford to ignore the challenge. Particular pressures come from companies eager to demonstrate green credentials of their suppliers.

The study *Life Cycle Assessment, Carbon Footprint in Leather Processing* prepared by F. Brugnoli for the XVIII Session of UNIDO Leather and Leather Products Industry Panel, Shanghai, 2012[59] was not only extensively discussed by eminent international leather specialists but it has triggered a series of activities involving different regional and global establishments and it very likely strongly influenced the content of the European Standard EN 16887:2017, Leather – Environmental footprint – Product Category Rules (PCR).

19.2. GLOSSARY AND BASIC CONCEPTS

CF	**Carbon Footprint**
CF-PCR	Carbon footprint product category rules
CO2e	Carbon dioxide equivalent
GHG	**Green House Gases**
GWP	Global Warming Potential
ILCD	International Reference Life Cycle Data System
IPCC	Intergovernmental Panel on Climate Change
IPP	INTEGRATED POLLUTION PREVENTION
IPP	Integrated Product Policy
ISO	International Standard Organisation
LCA	**Life Cycle Analysis or Assessment**
LCI	**Life Cycle Inventory Analysis**
LCIA	**Life Cycle Impact Assessment**

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[57] A separate UNIDO paper, Leather Carbon Footprint, Review of the European Standard EN 16887:2017, Leather – Environmental footprint – Product Category Rules (PCR) prepared in 2017 provides a rather detailed overview of this subject, including historical positions of important stakeholders and experts in this subject. Accordingly, this chapter is a compressed version of that study with certain amendments and supplements to meet the "need to know" of most tanners.

[58] Population data are from the U.S. Census Bureau, and CO_2 emissions data are from the Carbon Dioxide Information Analysis Center (CDIAC).

[59] Later on in the text referred as FB-UNIDO

PCF	**Product Carbon Footprint**
PCR	Product Category Rules
TOE	Tonnes of Oil Equivalent
WBCSD	World Business Council for Sustainable Development

19.2.1. Terms and Definitions

(from ISO DIS 14067)

For easy understanding, the most important terms and definitions are reported here. For additional ones please refer to ISO DIS 14067 (1 & 2), from which the following definitions have been taken:

- **Carbon Footprint (CF)**
  Weighted sum of greenhouse gas emissions and greenhouse gas removals of a process, a system of processes or a product system, expressed in CO_2 equivalents.[60]
- **Product Carbon Footprint (PCF)**
  Carbon footprint of a product system.
- **Product Category Rules (PCR)**
  A set of specific rules, requirements and guidelines for developing environmental declarations for one or more product categories.
- **Carbon Footprint Product Category Rules (CF-PCR)**
  A set of specific rules requirements and guidelines for developing carbon footprint declarations for one or more product categories.
- **Product System**
  Collection of unit processes with elementary and product flows, performing one or more defined functions and which models the life cycle of a product.
- **Life Cycle Assessment (LCA)**
  Compilation and evaluation of the inputs, outputs and the potential environmental impacts of a product system throughout its life cycle.
- **Life Cycle Inventory Analysis (LCI)**
  A phase of life cycle assessment involving the compilation and quantification of inputs and outputs for a product throughout its life cycle
- **Functional Unit**
  Quantified performance of a product system for use as a reference unit.
- **Products**
  Any goods and services
- **Primary Data**
  Quantified value originating from a direct measurement or a calculation based on direct measurements of a unit process of the product system at its original source.
- **Secondary Data**
  Quantified value of an activity or life cycle process obtained from sources other than the direct measurement or calculation from direct measurements.
- **Greenhouse Gas (GHG)**[61]
  Gaseous constituent of the atmosphere, both natural and anthropogenic, that absorbs and emits radiation at specific wavelengths within the spectrum of infrared radiation emitted by the Earth's surface, the atmosphere, and clouds.
- **Global Warming Potential (GWP)**
  Factor describing the radiative forcing impact of one mass- based unit of a given GHG relative to an equivalent unit of carbon dioxide over a given period.
- **Carbon Dioxide Equivalent (CO_2e)**
  Unit for comparing the radiative forcing of a GHG to carbon dioxide.

19.2.2. Environmental Footprint

Several different standards are available today to footprint product and companies' activities; here are their main approaches and characteristics to provide a general overview and to identify potential commonalities for harmonization purposes.

The analysis is based on the EUROPEAN COMMISSION JOINT RESEARCH CENTRE, Institute for Environment and Sustainability (Ispra, Italy, November 2011) Analysis of Existing Environmental Footprint Methodologies for Products and Organizations: Recommendations, Rationale, and Alignment.

ISO 14040:2006 Environmental management - Life Cycle Assessment - Principles and framework

This ISO framework describes the principles and framework for Life Cycle Assessment, including: definition of the goal and scope of the LCA, the life cycle inventory analysis (LCI) phase, the life cycle impact assessment (LCIA) phase, the life cycle interpretation phase, reporting and critical review of the LCA, limitations of the LCA, the relationship between the LCA phases, and conditions for the use of value choices and optional elements. It also covers life cycle assessment (LCA) studies and life cycle inventory (LCI) studies. It does not describe the LCA technique in detail, nor does it specify methodologies for the individual phases of the LCA.

ISO 14044: Environmental management - Life Cycle assessment – Requirements

ISO 14044 specifies requirements and provides guidelines for life cycle assessment (LCA) including: definition of the goal and scope, the life cycle inventory analysis (LCI) phase, the life cycle impact assessment (LCIA) phase, the life cycle interpretation phase, reporting and critical review, limitations, the relationship between the LCA phases, and conditions for use of value choices and optional elements.

ISO 14025: Environmental labels and declarations - Type III environmental declarations - Principles and procedures

ISO 14025 establishes the principles and specifies the procedures for developing Type III environmental declaration programmes and Type III environmental declarations. Type III environmental declarations as described in ISO 14025:2006 are primarily intended for use in business-to-business communication, but their use in business-to-consumer communication under certain conditions is not precluded.

Ecological Footprint

The Ecological footprint (EF) standard was developed by Global

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[60] *Another good definition of CF: A carbon footprint is the total amount of CO_2 and other greenhouse gases, emitted over the full life cycle of a process or a product. It is expressed in grams of CO_2 equivalents.*

[61] *GHGs include among others carbon dioxide (CO_2), methane (CH_4), nitrous oxide (N2O), hydrofluorocarbons (HFCs), perfluorocarbons (PFCs) and sulphur hexafluoride (SF6).*

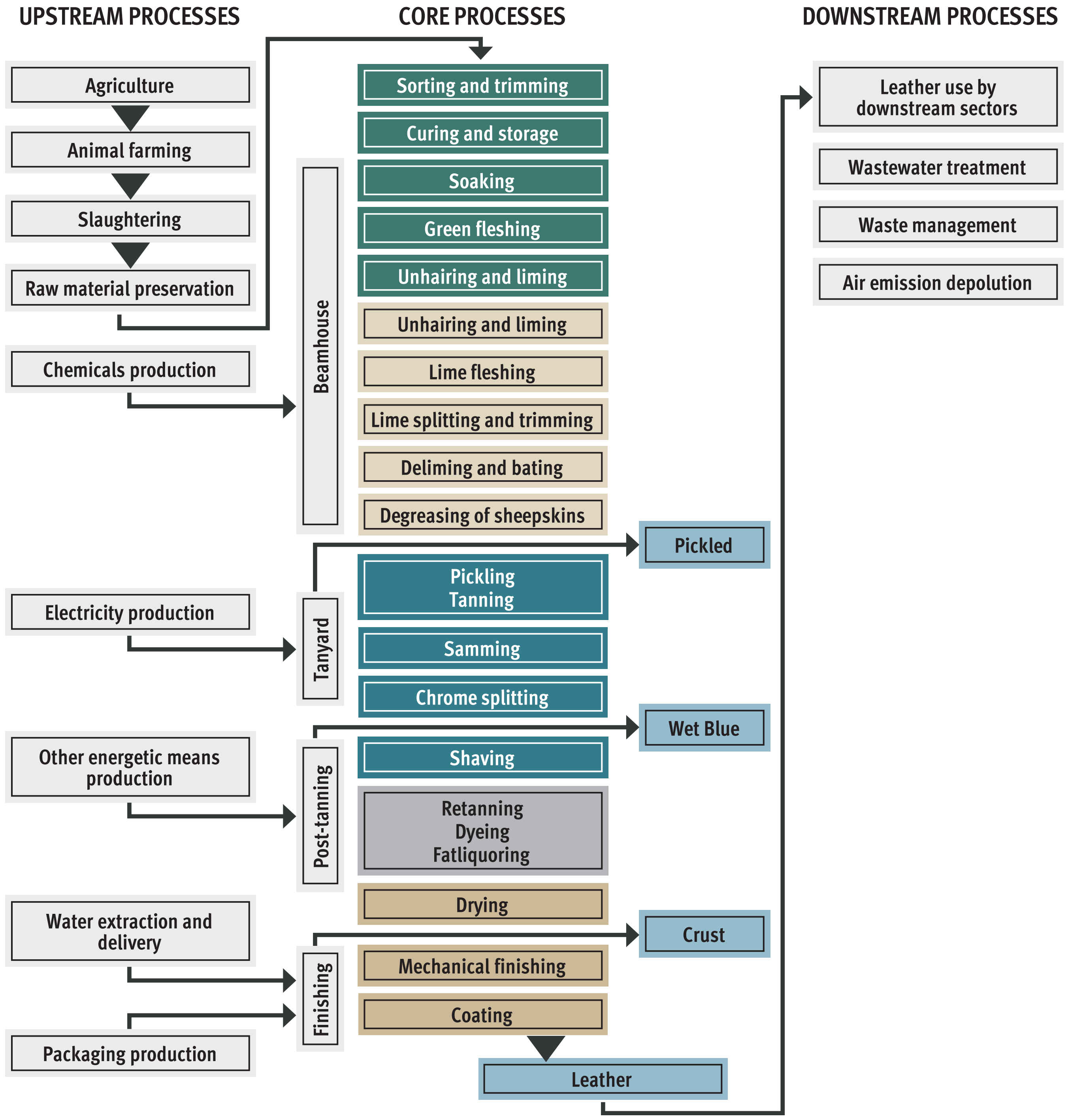
Footprint Network. The EF provides measure of the extent to which human activities exceed biocapacity. Specifically, the EF integrates the area required for the production of crops, forest products and animal products, the area required to sequester atmospheric CO_2 emissions dominantly caused by fossil fuel combustion, and the equivalent area estimated to be required by nuclear energy demand.

Product and Supply Chain Standards Greenhouse Gas Protocol (WRI/ WBCSD)

The World Resources Institute (WRI) and the World Business Council on Sustainable Development (WBCSD) started to develop their Product and Supply Value Chain GHG Accounting and Reporting Standard in September 2008. The GHG Protocol Corporate Standard provides standards and guidance for companies and other types of organizations preparing a GHG emissions inventory. It covers the accounting and reporting of the six greenhouse gases covered by the Kyoto Protocol—carbon dioxide (CO_2), methane (CH_4), nitrous oxide (N_2O), hydrofluorocarbons (HFCs), perfluorocarbons (PFCs), and sulphur hexafluoride (SF_6). The Product Standard builds upon the ISO 14040 series of standards.

19.3. CARBON FOOTPRINT, LIFE CYCLE ANALYSIS (LCA) FOR LEATHER

Figure 109. Overview of leather processing – UNIDO/LCA Brugnoli


UPSTREAM PROCESSES
CORE PROCESSES
DOWNSTREAM PROCESSES
Agriculture
Animal farming
Slaughtering
Raw material preservation
Chemicals production
Electricity production
Other energetic means production
Water extraction and delivery
Packaging production
Beamhouse
Tanyard
Post-tanning
Finishing
Sorting and trimming
Curing and storage
Soaking
Green fleshing
Unhairing and liming
Unhairing and liming
Lime fleshing
Lime splitting and trimming
Deliming and bating
Degreasing of sheepskins
Pickling
Tanning
Samming
Chrome splitting
Shaving
Retanning
Dyeing
Fatliquoring
Drying
Mechanical finishing
Coating
Leather
Pickled
Wet Blue
Crust
Leather use by downstream sectors
Wastewater treatment
Waste management
Air emission depolution

Carbon Footprint definition:

A carbon footprint is the total amount of CO_2 and other greenhouse gases, emitted over the full life cycle of a process or a product (e.g. leather); it is expressed in grams of CO_2 equivalents.

The CF for leather includes material and operations from the raw material starting from the slaughterhouse to the end of leather product life cycle. The issue of boundaries is crucial.

In principle, cleaner and more efficient technologies are very important for the reduction of CO_2 emissions; however, there are also other factors which significantly influence the total leather CF, among them being mainly the following:

i. Transport
ii. Water consumption
iii. Efficiency in use
iv. Energy footprint
v. Nature of raw material
vi. Biodegradability
vii. Use/recyclability

At the moment there is still no **globally agreed** methodology for a CF calculation and it is far beyond the scope of this paper to discuss the difference of various methods proposed. It might suffice to give two examples that directly affect the leather industry.

Until recently two methods of Life Cycle Analysis (LCA) computation prevailed.

Attributional LCAs (ALCA) use predefined allocation factors to allocate the burdens between the different co-products. These allocation factors are based on definable relations between the co-products – commonly economic values or mass weight, although other relationships are used.

Consequential LCAs (CLCA) use a process known as system expansion to avoid the need for allocation. System expansion considers what alternative production system is displaced when the co-product from the system is produced, and then credits the avoided burdens to the system.[62]

It is claimed that ALCA typically create an account of the environmental impacts of co-products as a static result. CLCA, on the other hand, is typically change-oriented and studies the marginal effects on the whole life cycle of a specific change.

Similarly, it can be said that while attributional LCAs seek to establish the burdens associated with the production and use of a product, or with a specific service or process, at a particular point in time (typically the recent past), consequential LCAs seek to identify the environmental consequences of a decision or a proposed change in a system under study (oriented towards the future).

The system boundaries are determined in different ways for different types of LCA.

F. Brugnoli in a UNIDO paper from 2012 proposes a new and rather innovative concept believed to be optimal for the leather sector. It applies the model of system expansion to the process from which the raw material of the sector is derived – the meat industry. The premise is that LCA results should be a means for practical improvement for those tanneries that wish to contribute to the design and development of leather products with levels of environmental performance that can be improved at the industry level. For this reason, the studies need to be based not on theoretical data or literature but increasingly on analyses based on surveys on the ground, which can be integrated at the international level.

The methodological support proposed by the UNIDO report aims to provide a set of verifiable data, which can be used to promote policies to mitigate the effects on the environment of the production processes, adopting strategies and technologies that the tanneries themselves can control and develop.

The innovative definition of system boundaries (starting from the slaughterhouse) makes it possible for the leather industry to focus on processes that it can control, to draft policies to ensure a real reduction of impact, and to avoid systematic uncertainties brought about by a lack of reliable and comparable data at the international level.

The other main contentious and obviously related issue is whether raw hides and skins should be categorized as a co-product, by-product or waste, which again substantially affects the CF level.

The document European Standard EN 16887:2017 Leather – Environmental footprint – Product Category Rules (PCR) – Carbon footprints approved in November 2016, published in March 2017 and applicable since Sept 2017 represents a dramatic step in defining the PCR rules and, in particular, in setting the system boundaries for leather. For more details see item European Standard EN 16887:2017.

19.4. OVERVIEW OF SOME CONTRIBUTORS TO CO_2 EMISSIONS IN LEATHER PROCESSING

19.4.1. CO_2 emissions from raw material transport

The two main factors here are the means of transportation and distance. Globalization makes it easy to send goods around the world. The cost for shipping goods has never been as low as now. However, the choice of the means of transportation and distance severely influences the amount of CO_2 emitted due to the transportation of goods.

The means of transport chosen largely depends on the country of origin, destination and the infrastructure available. From that point of view, ideally, tanneries should be near the source of raw material whenever possible; obviously, this would also help avoid the negative impact of (long-term) preservation.

Table 54. The amount of CO_2 (in grams) emitted per metric ton of freight & km of transportation

Air plane (air cargo), average Cargo B747	500 g
Modern lorry or truck	60 - 150 g
Modern train	30 - 100 g
Modern ship (sea freight)	10 - 40 g
Airship (Zeppelin, Cargolifter) as planned	55 g

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[62] *C. Clarke in ILM*

19.4.2. Energy and CO_2 emissions

In cases where liquid fuel is used for the preparation of hot water, the emission is approx. 3 kg CO_2/l of combusted fuel. Thus, for example, the CO_2 emissions for a tannery with a daily input of 10 tons of w.s. hides are as follows:

Liquid fuel emission kg CO_2/l	Liquid fuel l/t of raw hide	CO_2 emission		
		kg CO_2/t of raw hide	kg CO_2/d	kg CO_2/y
3	230	690	6900	2518000

The CO_2 emissions related to electric energy consumption depend on the primary source (or the source mix) of the electric energy, which is very different for different countries.

According to Poncet[63], for example, for the source mix in France consisting of 80% nuclear energy, 10% fossil energy and of 10% from renewable resources (mainly hydroelectric) the emission is 0.059 kg CO_2/kWh.

If some thermal energy saving, using solar energy instead of the fuel is installed, the CO_2 emission decreases proportionally. Using self-produced electric energy from photovoltaic cells and wind, the direct CO_2 emission would be practically zero. CO_2 emissions for different energy sources are presented in the next table.

Table 55. Carbon dioxide emissions for energy from different sources

Source	CO_2 emission, Kg/m^2
Coal	2.14
Liquid fuel	1.51
Gas	1.28
Photovoltaic	0.14
Wind	0.11
Nuclear	0.01
Hydro	0.007

The ways and means to reduce energy consumption are described in more detail in the chapter on energy; below are only a few important points:

i. Use of efficient equipment (e.g. low speed drums)
ii. Green fleshing
iii. Splitting in lime
iv. Use of natural light

As CO_2 emissions depend on the source of electrical energy (fossil, renewable etc.), this should be taken into consideration. In some regions a customer/tannery can choose the supplier and the source of energy. However in many countries, especially in developing ones, a tannery has no influence whatsoever on this important factor, although, for example, emissions from fossil fuels can be 40 times higher than from a hydroelectric source.

Table 56. Summary of Lifecycle of GHG emissions intensity for various electricity generation sources

Technology	Mean	Low	High
	grams CO_2e/kWh		
Lignite	**1,054**	790	1,372
Coal	**888**	756	1,310
Oil	**733**	547	935
Natural Gas	**499**	362	891
Solar PV	**85**	13	731
Biomass	**45**	10	101
Nuclear	**29**	2	130
Hydroelectric	**26**	2	237
Wind	**26**	6	124

Source: WNA, Comparison of Lifecycle Greenhouse Gas Emissions of Various Electricity Sources, 2011

19.4.3. Thermal energy

Most of the thermal energy in a tannery is needed for water heating and, in temperate climates, for the heating of the premises. Usually it is provided by a central boiler; the fuel used to have a significant impact on the level of CO_2 emissions.

As in the case of electricity, CO_2 emissions depend not only on the type of source of fuel but also on the efficiency of the heating system and heat exchanger. In countries with sufficient insolation, a very attractive (supplementary) source of energy can be a Solar Water Heating System (SWHS), which not only reduces CO_2 emissions but also the operational costs. That is why it is very attractive from both an economic and an environmental point of view.

Table 57. The amount of CO_2 emitted per GJ of energy for various fuels

Source	kg of CO_2/GJ
Coal (anthracite)	109.3
Coal (bituminous)	98.3
Coal (lignite)	102.9
Coal (subbituminous)	102.4
Diesel fuel & heating oil	77.1
Gasoline	75.1
Propane	66.4
Natural gas	55.9

19.4.4. Waste Water Treatment [64]

Effluent treatment with aerobic biological activated sludge treatment directly emits CO_2 in the atmosphere through the

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[63] *Poncet*

[64] *Contribution by M. Bosnić*

conversion of carbon contained in the organic matter in the waste water. This organic matter does not have a defined formula and differs from case to case. The content of the organic matter in the effluent is expressed as COD, or BOD_5.

The content of organic carbon in effluent is expressed as Total Organic Carbon (TOC). The relation of the TOC to COD is approx. 1 : 3, and BOD_5 approx. 1 : 1.4, and the TOC calculated from the accepted value before biological treatment for COD (60 kg COD/t of raw hides) is:

$$\frac{COD}{3} = \frac{60}{3} = 20\ \text{kgC / t of raw hide,}$$

or calculated from accepted value for BOD_5 (25 kg BOD_5/ t of raw hide) is

$$\frac{BOD_5}{1.4} = \frac{25}{1.4} = 18\ \text{kgC / t of raw hide.}$$

The mean value is 19 kg of the organic C/t of raw hide. The equivalent value of the CO_2 to C is 3.67. According to these values, the quantity of the CO_2 emitted from the biological treatment due to conversion/oxidation of the organic matter is approx. 19 x 3.67 = 70 kg CO_2/t of raw hides (or, about 700 kg CO_2/d, or 255.5 t CO_2/y for a tannery with a daily input of 10 tons of w.s. hides).

The anaerobic waste water treatment produces biogas (methane, not CO_2), but due to later combustion of methane, ultimately CO_2 will be emitted.

Evidently, the consumption of electric energy in the course of effluent treatment is (indirectly) a cause of CO_2 emissions.

Under the same conditions valid for the tannery, the CO_2 emissions from the (C)ETP operations are:

185 x 0.059 = **11 kg CO_2/t of w.s. hide**

The total CO_2 emissions, direct and indirect, are:

70 + 11 = 81 kg CO_2/ton of w.s. hide

It means that, for example, operations of a tannery with a daily input of 10 tons of w.s. hides is responsible for 700 + 110 = 810 kg CO_2/day or 255.5 + 40 = 295.4 t/year.

Table 58. Estimated CO_2 emissions from solid wastes in a well-managed solid waste disposal site

Waste	CO_2 kg/t
Putrefied hides / skins	624
Raw trimmings	624
Salt	624
Hair (pasting)	373
Lime sludge	455
Lime splits	624
Fleshing	624
Wet blue trimmings	221
Chrome splitting (bovine)	221
Chrome shavings	221
El/crust shavings*	221
Buffing dust*	221
Dyed trimmings*	221
Sludge (35% dry matter)	455

The direct CO_2 emission from production of electric energy from photovoltaic cells and wind is practically zero.

Solid waste

Disposal of solid wastes also contributes to CO_2 emissions allocated to leather and that is why it is important that all fractions of solid wastes are re-utilized whenever possible.

It is estimated that yearly CO_2 emissions from solid wastes decay can be 10-20 times higher than those from a properly designed and managed landfill disposal sites.

19.5. CASE STUDY, BANGLADESH: SOLAR WATER HEATING SYSTEM IN A TANNERY

The results of the operations and impact of the Solar Water Heating System, SWHS in Dhaka, Bangladesh):

Performance/energy produced per day: 18 – 30 MJ/m^2.

One square metre of the solar panel reduces carbon footprint by 5 – 8.3 kg CO_2/ day.

19.6. ANALYSIS AND RECOMMENDATIONS (BRUGNOLI, UNIDO 2012)[65]

- **The ten hottest years on record have all occurred since 1998. Eighteen out of the last 21 years are among the 20 warmest years since 1880. The common conclusion is that the long-term trend is one of global warming.**
- The increase in global average temperature since the mid-20th century is very likely due to the rise in anthropogenic greenhouse gas concentrations, specifically Carbon Dioxide, CO_2.
- It is estimated that industry and manufacturing contribute for 19% of all GHG emissions.
- The total amount of GHG produced during various stages in the life cycles of products is referred to as Product Carbon Footprints (PCFs).
- In the case of finished leather, the carbon footprint should obviously be expressed as: **Kg of CO_{2e}/m^2 of finished leather and Kg of CO_{2e}/kg of sole leather.**
- Similarly, to ensure a common approach to be followed in future activities the following aspects are of particular importance:
  - **Functional unit**
    Used in LCA and CFP analyses to provide a reference to which environmental impacts are related; it should be consistently measurable and correspond to the basic unit used in the trade. The recommendation is to use 1 m2 of finished leather, including an indication of the thickness of the material (1 kg for sole leather).

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[65] *Although in the meantime general consensus has been achieved on most points listed here, it might be of interest to recall dilemmas confronted at that time.*

- **System boundaries:**
  It is important to recognize the implications of the different conceptual approaches to raw hides and skins as raw materials for the tanning industry: in particular, whether they are to be considered as a **waste**, as a **by-product** or as a **co-product** of the milk and meat industry. If the raw hides and skins are considered as **waste** of the milk and meat industry, the whole environmental impact (and therefore of the CO_2 equivalent content) has to be allocated to the main product of the economic value chain (i.e. milk and meat). This implies that agriculture and animal farming, as processes of the upstream module, shall be excluded from the System Boundaries of LCA studies on leather. In the case that raw hides are considered as a by-product or co-product of the milk and meat industry, some may argue that part of the environmental impacts (and therefore of the CO2 equivalent content) have to be allocated to the co-product itself, on the basis of different allocation criteria. Accordingly, for raw hides and skins coming from animals raised mainly for human feeding purposes, such as milk and meat production (and therefore, bovines, sheep, goats and some other), the system boundaries are to start in the slaughterhouse.
- **Quantification**
  The different approaches reviewed show a certain similarity, converging in the subdivision of leather production in individual processes and quantifying the emissions from each process. The harmonized methodology proposed, in order to obtain Kg of CO_{2e}/m^2 of finished leather, lies in the quantification of CO_{2e} content of all the different products and material entering the tannery (UPSTREAM PROCESSES), adding CO_{2e} produced in the tannery itself (CORE PROCESES), as well as CO_{2e} emanating from water and air purification and waste recycling/disposal (DOWNSTREAM PROCESSES).
- **Allocation**
  Choosing an allocation rule conditions the environmental impact distribution between economic actors from the same value chain. Economic allocation seems to be rather vague due to factors contributing to it (market price of raw hides, value of the animals during their lifespan) and it should be avoided whenever possible; if unavoidable, the allocation should be made according to the physical relationship within the single process under consideration.

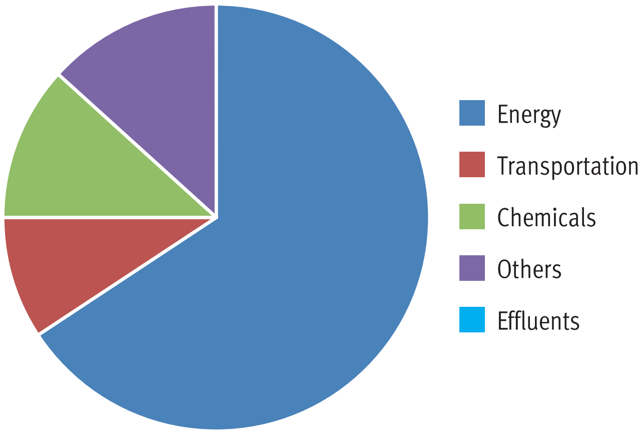
It is recognized that at the moment the LCA – Carbon Footprint topic is primarily of interest to tanners in industrialized, especially EU countries; however, it is felt that also those in BRIC and even Least Developed Countries should be aware of the current environmental impact assessment and protection trends and be ready to apply them at the appropriate time as needed. It is hoped that in the meantime better standardized methodologies and hopefully some blueprints will also be made available.

19.7. SUPPLEMENTARY INFORMATION FROM VARIOUS SOURCES

- **The impact/reduction of leather weight/thickness on CO_2 emissions from car upholstery is insignificant**
- Corporate Carbon Footprint, CCF (Knoedler) of finished leather in cars is estimated at 1.4 – 6.4 kg of CO_2/m^2 of finished leather (without chemicals, breeding and ultimate leather disposal after use)
- The higher the complexity of the chemical, the higher the CO_2 emission
- Accordingly, the main impact is from retannage, minor from the beamhouse and finishing
- Powdered products are higher in CO_2 emissions than liquid
- Energy (source and consumption) is the key factor for the environmental impact of leather due to abiotic depletion, greenhouse effect, acidification and photochemical pollution.
- Some 9 billion people will live on this planet by 2050, 67 % of population will live in cities by 2025, 50 % or more primary energy will be needed in 2030, 1.2 billion cars will be in use by 2020 (B. Wegner et al).

The chart below shows the relative part of CO_2 emissions due to energy for the production of leather through a life cycle analysis. It considers energy of the tannery, the production of chemicals used in the tannery and transportation.

Relative green house effect emissions of leather



Based on source : T. Poncet et al., XXXI IULTCS, Valencia

It is often overlooked that in addition to carbon dioxide, CO_2 there are other greenhouse gases as well as ozone depleting substances.

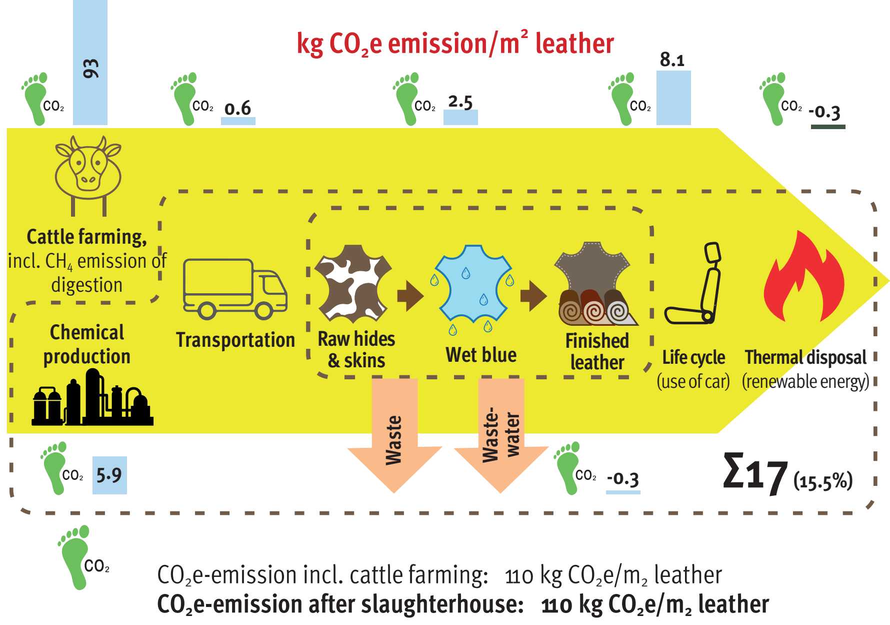
Table 59. Some greenhouse gases and their Global Warming Potential, GWP

	Greenhouse gas	Chemical formula	100 year GWP
	Carbon dioxide	CO_2	1
	Sulphur hexafluoride	SF_6	22800
	Methane	CH_4	25
	Nitrous oxide	N_2O	298
Some HFCs	HFC-23	CHF_3	14800
	HFC-32	CH_2F_2	675
	HFC-236a	$CF_3CH_2CF_3$	9810
Some PFCs	PFC-14	CF_4	7390
	PFC-116	C_2F_6	12200

Source: IPCC

Methane production: 550 – 700 litres/cow/day. Methane is about 25 times worse than CO_2!

Estimate of leather Carbon Footprint (CF)
Figure 110. Carbon dioxide emissions, CO_2e/m^2 of leather
(Before European Standard EN 16887:2017)


kg CO_2e emission/m^2 leather
CO_2 93
CO_2 0.6
CO_2 2.5
CO_2 8.1
CO_2 -0.3
Cattle farming, incl. CH_4 emission of digestion
Chemical production
Transportation
Raw hides & skins
Wet blue
Finished leather
Life cycle (use of car)
Thermal disposal (renewable energy)
Waste
Waste-water
CO_2 5.9
CO_2 -0.3
Σ17 (15.5%)
CO_2
CO_2e-emission incl. cattle farming: 110 kg CO_2e/m_2 leather
CO_2e-emission after slaughterhouse: 110 kg CO_2e/m_2 leather

Based on chart by F. Schmel, derived from the presentation by J. Knoedler

- CO_2e emissions including cattle farming: 110 kg CO_2e/m^2 of leather
- CO_2e emissions after slaughterhouse: 17 kg CO_2e/m^2 of leather

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19.8. EUROPEAN STANDARD EN 16887:2017

The document European Standard EN 16887:2017 Leather – Environmental footprint – Product Category Rules (PCR) – Carbon footprints was approved in November 2016, published in March 2017 and applicable since Sept 2017.

The normative references (linkages) are:

EN 15987:2015, Leather – Terminology – Key definitions for the leather trade
EN ISO 2589, Leather – Physical and mechanical tests – Determination of thickness (ISO 2589)
EN ISO 14021:2016, Environmental labels and declarations – Self-declared environmental claims (Type II environmental labelling), (ISO 14021:2016)
EN ISO 14025, Environmental labels and declarations – Type III environmental declarations, Principles and procedures (ISO 14025)

CEN ISO/TS 14067, Greenhouse gases – Carbon footprint of products – Requirements and guidelines for quantification and communication (ISO/TS 14067)

In the general part the document provides the list of terms and definitions used (leather, split leather, sole leather, crust, semi-processed leather, primary/site-specific/secondary data etc.).

The main part is the Product Category Rules (PCR), defined as documents that stipulate mandatory requirements for environmental declarations of a certain category of products ensuring transparency and comparability among different environmental footprints of products of the same category.

The key PCR elements are:

- Specification of the product - leather type (e.g. bovine, full grain, flesh split etc.), thickness, process stage (wet blue, crust, finished), type of tanning (vegetable, synthetic, other), intended use (footwear, leather goods)
- Functional unit: 1 m^2 of leather, 1 kg for sole leather
- Bill of materials (BoM)

Here it is specified that finished leather is composed of stabilized collagen and chemical residuals; that the weight of collagen may vary from 50% (vegetable sole leather) to 85% (chrome tanned); and that chemicals used fall into a category intended to treat the substrate but are not retained in the finished leather (e.g. acids, surfactants, bases) and those that remain in the leather.

While all chemicals used should be included in the calculation of the leather carbon footprint, the bill of materials, expressed in percentage ranges (e.g. 0.2 - 0.5%) should include only chemicals from the second category (retained):

- tannins
- dyes
- pigments
- fatliquors
- resins
- salts

Tanners and the whole leather industry can be satisfied with the norm set by the European Standard EN 16887:2017 concerning the critical issue, **system boundaries for PCF calculation: they start at the slaughterhouse floor and end at the tannery exit gate**. They include waste water treatment, waste and by-products management, but, most importantly, exclude all operations up to and including flaying because they are considered as integral parts of meat production.

Accordingly, raw material collection and preservation, production of chemicals, production of electricity and other types of energy, water extraction and supply, packaging as well as the impact of transportation of supplies are classified as upstream processes.

Core processes are: beamhouse and tanning, post tanning, finishing, internal mechanical operations, transportation within the tannery (only energy and fuel consumption), factory outlet.

Downstream processes are: treatment of effluent and air emissions, by-products, and (solid?) waste management, including relevant transportation impact.

Wastes and possible by-products should be clearly identified; only splits leaving the leather value chain are considered by-products, otherwise they are considered products.

Data quality rules are elaborated in great detail, the following are the most important points:

- All data used for calculation have to be verifiable and auditable
- A correlation of the weight changes along the tanning process should be

presented and related to the final unit measure (**m**^{2} or **kg** for sole leather)

- Whenever possible primary site specific data should be used
- In absence of primary site specific data primary data from commonly available sources can be used
- Similarly, if primary data sources are not available, secondary data can be used and documented; the environmental impact of the processes for which secondary data are used should not exceed 10% of the total environmental impact of the product system.

Allocation rules, geographical & time boundaries, boundaries to other products life cycles, some features:

- Allocation between different products and by-products (e.g. fleshings) are weight based and in proportion to the different products and co-products.
- Allocation between different products and co-products (e.g. splits) are surface based and in proportion to the different products and co-products.
- A minimum of 99% of the total weight of declared product (1% cut off rule), including packaging, should be included.
- Maintenance activities (proportionally allocated) are included in the impact calculation of the general management; the recycling process and transportation of an inflow of the recycled material should be included whereas for an outflow recycling material only transportation is included; business travel and staff travel to and from works are not included.
- The data should be representative for the site/region and the year for which the PCF is valid (maximum 3 years).

The Product declaration is expected to contain:

- Reference to European Standard EN 16887:2017, Leather and CEN ISO/TS 14067, Greenhouse gases
- Reference to certification (any); if a self-declaration then the reference to EN ISO 14021:2016, Environmental labels and declarations
- As mentioned earlier, the results are to be expressed in kg of CO_{2e} per m^2 or per kg for sole leather
- The name of the product, the manufacturer and the year of reference

Note:

Annexes to the document provide the guidance on how to calculate the impact together with the list of chemicals used by the tanning industry (Annex A), classification codes for leather and leather products (Annex B) and emissions profile formulae/allocation rules for waste and by-product treatment (Annex C).

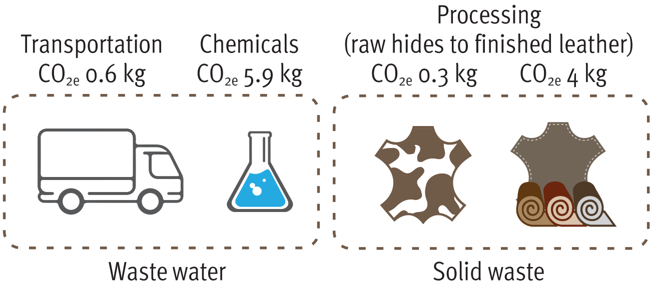
It is worth noting that Annex C specifies that a tannery is credited for the difference between the CO_{2e} emissions for waste/by-products vs. new materials; it is also credited for CO_{2e} from the heating value of the net produced bio-gas and the heating value of the incinerated material in case of incineration in co-generation plants.

Conversely, the CO_{2e} produced by the thermal plant as well from landfilling are allocated to the tannery.

Despite the European Standard EN 16887:2017 the issue of borders for the computation of leather CF may not be fully resolved.

Figure 111. Tentative estimate of leather CF according to European Standard EN 16887:2017*

Kg CO_{2e} emissions/m^2 of leather



Total, from the slaughterhouse floor to the tannery exit gate: approx. 11 kg CO_{2e}/m^2

(Life cycle, automotive leather, would add some 3.1 kg CO_{2e}/m^2)
*Partially derived from data provided by J. Knoedler, Germany, advanced tannery

19.9. PRODUCT USE, PRODUCER'S RESPONSIBILITY ISSUES, END OF LIFE (EOL)

> **Leather is nowadays mainly used for footwear production, automotive & furniture upholstery, garments, gloves and other leather goods production. The useful life of shoes is relatively short and progressively decreasing as a result of rapid market changes and consumer fashion trends. This creates a large waste stream of worn and discarded shoes at the time their functional life has ended most of them are being disposed of in landfills. Producers' responsibility issues and forthcoming environmental legislations, as well as increasingly environmental consumer demands, are expected to challenge the way the footwear industry deals with the EoL of its products.**

Possible re-use of leather and/or incineration can be considered. In most cases it is disposed.

Product life span should be taken into consideration when leather is compared with other materials.

Over the last few years the footwear industry has placed significant effort in improving energy and material efficiency, as well as eliminating the use of hazardous materials during the production phase. However, the environmental gains and energy efficiency made in production are being overtaken by the considerable increase in the demand for footwear products, the so called rebound effect.

In most countries, managing EoL[66] waste has long been and, in most cases, still is the responsibility of governmental agencies and local authorities. Once products reach the end of their functional lives, producers play no role in collection, recycling and/or disposal of EoL products.

This approach has started to change with the emergence of a producer's responsibility concept. This concept was first introduced in Germany with the 1991 Packaging Ordinance which required manufacturers and distributors to take back packaging from consumers and ensured that a specified percentage is recycled. In 2000, the European Commission passed a Directive requiring its Member

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[66] *See the UNIDO paper End of life (EoL), 2014*

States to institute a producer responsibility program for end-of-life vehicles (ELV) which also includes leather used in cars and vehicles.

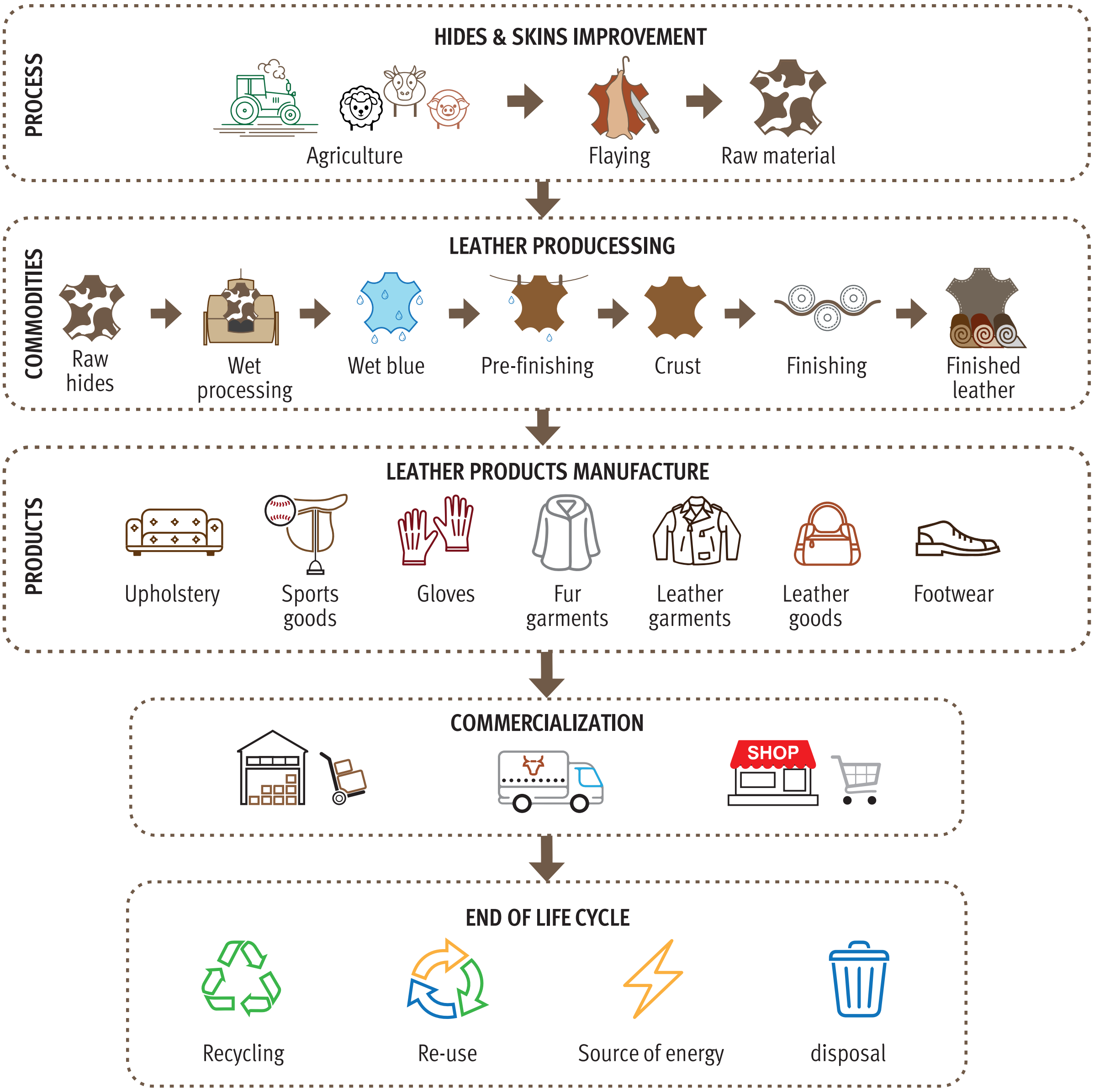
This concept of broadening a manufacturer's responsibility for products beyond their useful life and into the post-consumer phase includes closing the loop concerning materials used and waste management. This approach should provide a source of financing to offset the cost disadvantage of recycling versus disposal and energy recovery.

In this context, take-back and producer responsibility legislation is expected to affect the footwear sector including leather, similarly to what has happened in the case of cars (ELV).

In any case, CO_2 emissions during product life (shoes, leather goods, upholstery, etc.) are beyond the tanners' control.

Currently around 19 billion pairs of leather shoes are produced worldwide every year, and this figure continues to rise. This creates an enormous amount of post-consumer (end-of-life) shoe waste that is currently being disposed of in landfill sites around the world. Over the last few years the footwear industry has placed significant effort in improving energy and material efficiency. Producers' responsibility issues and forthcoming legislation as well as increasing environmental consumer demands are expected to challenge the way the global footwear industry deals with its end-of-life waste.

Figure 112. Leather supply chain


PROCESS
HIDES & SKINS IMPROVEMENT
Agriculture
Flaying
Raw material
COMMODITIES
LEATHER PRODUCESSING
Raw hides
Wet processing
Wet blue
Pre-finishing
Crust
Finishing
Finished leather
PRODUCTS
LEATHER PRODUCTS MANUFACTURE
Upholstery
Sports goods
Gloves
Fur garments
Leather garments
Leather goods
Footwear
COMMERCIALIZATION
SHOP
END OF LIFE CYCLE
Recycling
Re-use
Source of energy
disposal

19.10. CARBON FOOTPRINT CERTIFICATION

There are already companies offering certification of the actual Corporate Carbon Footprints (CCF). During expert auditing specific energy consumption of individual production steps is compared with the benchmark so that a tannery can easily identify the potential for improvement. This process should ultimately result in substantial reduction of energy consumption and costs as well as ensure a competitive edge due to image enhancement. It is believed that demand for such services will expand be it due to legislative pressures to have CF declared for all products, be it due to buyers' preferences for low CF materials or both.

20. EMERGING TECHNOLOGIES

20.1. CONTEXT

> **It is very likely that the trend of small- and medium-scale tanneries disappearing (unless operating in special niches) will continue despite strong lobbies in some countries (mis) using the myths of traditional, small scale family units actually unable to cope with up-to-date technologies and, in particuar, with environmental requirements. At the same time, processing capacities of individual tanneries and/or systems will expand with substantial investments in modern equipment. Attempts to replicate Italian-type clusters with highly specialized small units elsewhere, vigorously promoted for quite some time, do not appear successful.**

However, leather cities, encompassing a wide range of tanning, footwear, leather goods operations with appropriate infrastructure and allied activities benefiting from the concentration and scale (e.g. utilization of by-products and treatment of wastes, but also qulity control, training etc.) seem to gain in importance in developing countries.

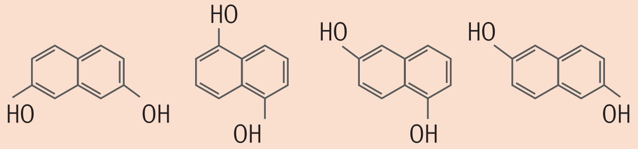
As a corollary of such developments it is certain that there will be further significant improvements and innovations in the automation of tanning processes and operations such as in-plant transfer of materials, weighing, mixing, dosing, heating, drying, etc. There is no doubt that new generations of machines will be more accurate, safer and easier to operate; noise and vibrations will probably be considerably reduced, etc.

However, without a crystal ball it is very hard to make any predictions about possible changes in the basic physical-chemical principles of leather tanning that have been with us for quite some time. In any case, at the moment nothing of that kind is clearly on the horizon and the theorethical explanation of why it is so is largely provided in research work of A.D. Covington and his team.

The underpinning problem of the leather industry is that it does not understand how its technology works. Whilst it is clear that some of the fundamentals are understood at a level at which the technology is practicable, there is not enough scientific understanding to allow significant changes to be made with confidence about the outcome(s).

According to Link-Lock[67] theory no single tanning agent is capable of conferring high thermal stability, i.e. shrinkage temperature above 100 °C. High thermal stability is only possible by combining two reagents with no chemical affinity, the linking agent and locking agent, which react with collagen independently via different mechanisms.

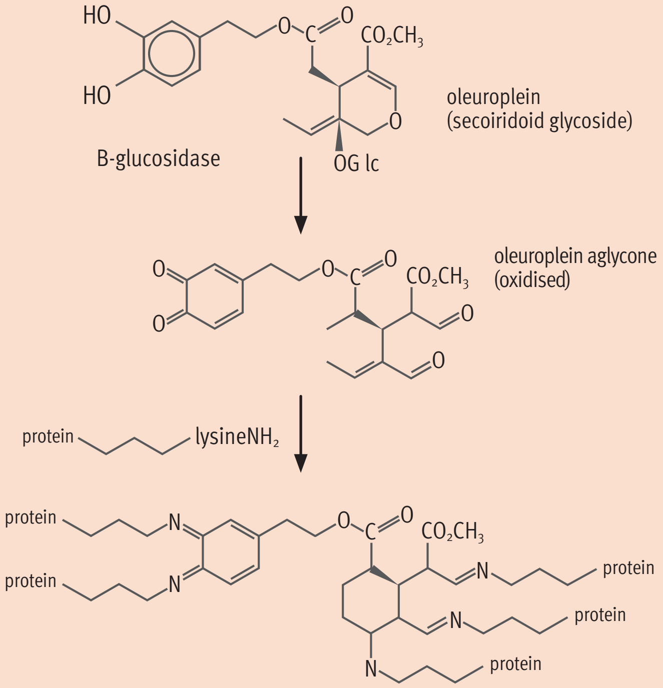
The structures of some naphthalene diols and the shrinkage temperature achieved in tannage with the polyphenol crosslinked with oxazolidine.



The same thinking can be extended to considering third or fourth reagents or more.

Nordihydroguaiaretic acid (NDGA), a naturally occurring polyphenol in stabilizing reagent collagen exhibits the unusual phenomenon of increasing the strength of the fibre. The mechanism is oxidative polymerization of NDGA. **Genepin**, an iridoid derivative from the fruits of Gardenia jasminoides is an effective tanning agent although conferring only low shrinkage temperature and making the leather bright blue. An alternative to genepin is oleuropein, a secoiridoid glycoside found in olive vegetation (see the section on Wet-green).

Figure 113. Schematic representation of the oleuropein reaction with protein



These biomimetic approaches are the beginning of a new, potentially promising application of biotechnology in leather making. However, it is equally clear that they do not offer the opportunity for a single step high hydrothermal stability tannage.

Tanners have a rough idea of how the isoelectric point (IEP) varies in their process but there is no current model of how to predict the charge on leather as a function of pH.

Overview of some combination processes

Combination	Technology
Enzymatic opening up with bating	Alkali stable enzymes in unhairing and deliming
Non swelling acid (NSA) pickling with retanning	NSAs function al low astringency syntans
Retanning with colouring	Biomimetic use of melanin chemistry
Retanning with dyeing	Reactive dyes Dyes fixed to tanning agent e.g. polyphenols
Retanning with lubrication	E.g. Lubritan, hydrophobic polyacrylate ester
Colouring with lubrication	Not attempted but not difficult to envisage
Retanning with colouring and lubrication	Can be achieved by matching the solution of the reagents Not attempted as a single agent

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[67] *Subsequently evolved into lock-lock theory, neither confirmed, but very probable!*

The concept of **"compact processing"** is the condensing or shortening of processing by combining two or more reactions into a single process step applicable in some (future) tannages. **Processing in non-aqueous solutions** avoids water as a solvent: the tanning of wet pelt in a tumbling medium of the water-immiscible solvent, paraffin.

Ideally, leather should be made in such a way that it can be broken down by some simple treatment. Actually, the need and potential for change and improvement is often overlooked.

Any single component stabilizing reaction has the effect of linking part of the collagen structure into the surrounding matrix of water conferring moderate hydrothermal stability, up to 85 °C and no single component can exceed this moderate level. A second reaction component may have the ability to lock the linked structure together creating a macromolecular structure around the triple helices and thereby raise the hydrothermal stability to much higher values.

Table 60. Typical effects of chemical modifications on denaturation temperature ranges of collagen

Chemical modification	**Denaturation temperature (oC)**
None	65
Metal salts: eg Al(III), Ti(IV), Zr(IV) etc.	70 - 85
Plant polyphenol: gallotannin or ellagitannin	75 - 80
Plant polyphenol: flavonoid	80 - 85
Synthetic tanning agent: polymerised phenols	75 - 85
Aldehyde: formaldehyde or glutaraldehyde	80 - 85
Aldehydic: phosphonium salt or oxazolidine	80 - 85
Basic chromium (III) sulphate	105 - 115
Combination: gallotannin + Al (III)	105 - 115
Combination: flavonoid polyphenol + oxazolidine	105 - 115

X-ray absorption shows that the dominating species of chrome bound to collagen are linear tetrachromium compounds with sulphate as counterion, acting as a structure maker in water, not directly bound to collagen.

All attempts to date to find a straight substitute for chromium (III) turned out futile because "...the periodic table holds little hope of discovery of new commercially useful tanning agents, based on elements not previously considered." (Nursten). It means that chromium is here to stay as by far the most superior and environmentally friendly tannage.

However, the use of masking agents of more complex structure than the conventional reagents could lead to a better matching of the required reaction rate and a diminishing chrome concentration.

20.2. SOME POTENTIAL INNOVATIONS

Against the backdrop described earlier, the folowing is an almost random selection of some more recent ideas and methods at various stages of research and development.

- **Application of ultrasound in chrome tanning and retanning**
  A combination of wringing and ultrasound in a two-step process (penetration and basification tank) is used to accelerate the chrome tanning process based on the mechanical extrusion formation of the micro-vacuum and ultrasonic cavitation effect. Similarly, the effect of ultrasound (US) has been investigated in improving the penetration and uptake rate of different syntans (phenolic based, melamin resin, acrylic compound) in leather retanning and compared with magnetic stirring (MS). Favourable influence of pre-sonification of both the substrate (leather) and the syntan solution result in a considerable improvement of the diffusion rate, a shorter processing time and better leather quality.
- **Inverse chrome tanning with wet-white pretanning**
  The proposed process sequence is: bating, washing, white pretanning, sammying, shaving, weighing, re-wetting with acidification with formic acid, retanning (synthetic fatliquor/dispersing syntan/acrylic resin/mimosa, phenolic syntan, melamine resin/formic acid), fatliquoring (synthetic fatliquor, formic acid), drain, followed by the usual chrome tanning with basification (100% fresh float, 14% chrome powder). The main gains should be chrome emissions limited to one process only and reduced by about 50% plus chrome-free shavings. There is no information about other pollutants (BOD,COD, salts etc.).
- **Collagen modification and nano technologies**
  Some R&D establishments, in particular in Xian, China, have been searching for ways to depart from using traditional, chemical-based leather making methods. Instead, they are looking into various options for modifying collagen fibers by nano-size emulsions, clay minerals, nano silicon dioxide or nano silver and nano technologies in general.
- **A fresh attempt with Fe tannage**[68]
  One among many attempts in searching for alternatives to the prevailing tanning methods is tanning with Fe2+-gluconic acid compound, apparently still at the laboratory scale.
- **Elimination of free formaldehyde with essential oil**
  The conclusion of one study is that the release of free formalaldehyde from tetrakis (hydroxymethyl) phosphonium (THP) salts and various syntan leather products can be supressed by using Origanum onites essential oil.
- **Bioresistance by application of nanosilver**
  A combination of the colloidal silver solution (CSS) and polyhydroxiurethanes is used to interact with collagen or keratin from medical leather and sheepskins to induce bioresistance properties against fungi as well as a good antibacterial action.
- **The ISO 17075 method for Cr^{6+} detection**
  The ISO 17075 method for Cr^{6+} detection (at pH 8) systematically gives false positive values. Moreover, Solid Phase Extraction (SPE) cartridges absorb about 10% of chromate; thus the calibration curves should be obtained after filtering each standard with the SPE employed.
- **Chromogenic leather**
  There are already reports on tests with chromogenic leather, i.e. leather that changes colour in response to optical/thermal changes.
- **Biochemical degradation and closed cycle dechroming of chrome shavings**
  There are new investigations into the scope of combined chemical and enzymatic degradation of chrome shavings and protein

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[68] *As said earlier, this attempt runs against the view that the search for a straight substitute for chromium (III) is futile because "...the periodic table holds little hope of discovery of new commercially useful tanning agents, based on elements not previously considered." (Nursten)*

By the turn of the century several eminent leather scientists offered their predictions about key issues and likely developments in the leather sector in the UNIDO paper titled "What is the future of (chrome) tanning? Leather manufacture in the new millennium". It might be interesting to briefly recall some of the points made.

Shorter delivery time will favour the trade between a tanner and product manufacturer in crust and product components, finishing may be carried out by the product manufacturer.

Cost effective and clean recovery of proteoglycans and glyco- and lipo-proteins, amino acids from fleshings and hair as well as other proteins are likely to gain significance.

While, strictly speaking, chromium is not a renewable resource, the commercially extractable reserves suffice for several centuries; Cr will remain the main tanning agent.

Reversal to vegetable tanning for soft leather (even significantly improved), is unlikely. Vegetable tannins can be qualified as a renewable resource if obtained either within eco-compatible plantation programmes or as by-products from natural species (fruits, leaves).

The likely directions for new, high stability organic tannages might be: i) natural polyphenol derivatives, with reagent-like specificity, crosslinkable in situ with oxazolidine type reagents and ii) synthetic polymers based on melamine and phenols, crosslinked with formaldehyde or other simple compounds, to produce specified low molecular weight resins, crosslinkable in situ with phosphonium salt or other aldehydic compounds.

Spray finishing, roller or curtain coating equipment will be developed to automatically adjust the colour of the finish. Finishing equipment could use ink-jet technology.

Finishing equipment will be designed to finish pre-cut pieces, panels and patterns of leather rather than whole hides or sides.

New automated "instant" methods, including non-destructive physical property tests, to determine the quality of leather (such as the already existing mass-spectroscopy method to determine the amount of chrome in leather) will be developed.

Splitting accuracy, and, in particular, uniformity will further improve; it is quite possible that splitting of raw hides will be introduced, ideally combined with shaving using a high-pressure water jet instead of a metal blade.

A pH electrode and other sensors will also be developed that will be able to sense the uptake of chemicals; end-point of a process step is not time- but concentration-related.

Colour matching using a calibrated spectrophotometer assisted by a computer to accurately colour match leather will be introduced.

There is a good possibility of a mechanical assist to accelerate some processes; ultrasound had been shown to speed up the penetration of fatliquors and dyes.

Life cycle assessments (LCAs) are certainly going to be important. However, ultimately, an LCA is a subjective evaluation, as selection and weighing of the various parameters forming parts of a LCA are subjective, depending on the prevailing scientific opinions, a priori assumptions, practical circumstances, and "political correctness" at the time the LCA is carried out.

Sooner or later, at least before 2050, the leather industry will have to provide for removal of discarded leather.

extraction. Also, Ethylen Diamine Tetraacetic Acid (EDTA) is used for dechroming chrome shavings during extended processes involving heating, UV light (photocatalysis), chrome precipitation with NaOH and acidification with sulphuric acid. High chrome removal efficiency and preservation of the collagen triple helix are claimed in these mini-lab scale tests.

- **Highly biodegradable leather**
  A success is claimed in developing an aldehyde based tanning system resulting in leather showing biodegradability four times higher than chrome tanned and two times higher than wet-white based leather. Full desintegration of leather under composting conditions according to ISO 20200:2004 was reportedly achieved within 11-14 days as well as of footwear made of biodegradable components and with uppers and linings of leather tanned by the new system within 21 days.
- **Composting**
  A new attempt in composting tannery waste at the industrial scale is underway: dewatered sludge with dry matter content of 20-25%, fleshing and grease residues are mixed with shavings from vegetable tanning, grass and green farm residues. From time to time some quantities of cow and horse dung are added. Composting takes place in two-months cycles in windrows in a roofed area. It is reported that the Cr content is about 1500 mg/kg calculated on dry weight, which is, after mixing with other organics, reduced to about 1000 mg/kg to be used as a nutrient and soil conditioning agent.[69]
- **Probiotics**
  Some biotech products, marketed as fully biodegradable and non-hazardous probiotics, claim to offer a viable alternative to and ability of replacing some conventional chemicals for most leather manufacturing stages. At the moment it does not appear to be widely implemented.
- **Application of nanotechnology**
  There is apparently no confirmation of successful industrial scale application of nanotechnology that can strengthen sheep skins to be converted into leather for use in shoes and other products reported in 2014 with the potential of applying the same process with deerskins and cattle hides.
- **Ionic Liquids as chemicals for leather processing**
  Ionic liquids (ILs) such as imidazolium, choline and some others have been found to have both stabilising and destabilising effects on collagen - at the molecular level, thermal and dimensional stability at the interfibrillar level and at the fibre structure level. Their properties can be garnered and fine-tuned for various applications in leather processing. ILs, the greener solvent media, are seen as potential advanced "designer" chemicals for making leather processing cleaner and greener.[70]
- **Analysis of odour compounds in leather by GC-MS and GC-Olfactometry**
  The volatile compounds in leather are extracted using a solid-phase microextractionfiber and subsequently identified using a gas chromatography-mass spectrometry (GC-MS) and gas chromatography olfactometry (GC-O), i.e. human assessors. More than 20 volatile compounds have been identified by GC-MS, the main among them being hexanal, heptanal, octanal, nonanal, heptanol, octanol, 2-ethoxyethanol, and 2-buthoxyethanol. Aldehyde such as octanal and alcohol such as octanol were characterized by GC-O.

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[69] *According to regulations in some EU countries, it is necessary to maintain a temperature of 60°C (in a closed system) or 65°C (inside the piles) and fleshings must have come from healthy animals.*

[70] *Ionic Liquids: New age "designer" chemicals for leather processing, N Nishad Fathima et al, IULTCS Chennai, 2017*

- **Bio-based polyurethanes for leather finishing**
  Until recently, coating technology for the finishing step of the leather process has largely been based on petroleum feedstock chemicals, like ethylene and propylene. Recent advances in biotechnology have made it possible to develop an entirely new class of aqueous polyurethanes. This class of polyurethanes are bio-based, derived from renewable raw materials and reportedly show superior film performance. Certain polyols (bio-based polyols) , the main building blocks in making polyurethane finishes, can be made using different plant oils such as canola (rapeseed), soy, palm or linseed. The bio-content level achieved so far can range from 10-35%.

20.3. A LEATHER-LIKE MATERIAL PRODUCED USING BIOTECHNOLOGY

Leather is a business worth $100bn a year and it is small wonder that there is another attempt to use genetic engineering to make leather without animals. It seems that research on creating artificial collagen mentioned in the first edition of this paper has made a significant step forward.

A biotech company claims to have developed a new biofabrication process that can produce a protein identical to bovine collagen, including triple-helices ultimately wound together to make fibres, at a competitive cost and on an industrial scale. The new concept has departed from the tissue engineering. Instead, it relies on DNA editing tools to engineer specialised collagen-producing yeast cells. The cells are optimized to manufacture the type and quantity of collagen required.

Reportedly, the material has a good looking grain with a good simulation of a complete hair follicle. The material can be made in convenient sheets with straight edges, rather than being constrained by the irregular shapes that animals come in. Its properties are consistent and, of course, it is devoid of the scars, marks and other defects.

Reportedly, the process can be scaled up easily and carried out in existing industrial plants and the cost of the material competitive with that of natural leather. However, there is no intention either to ape or to call it leather but rather a biofabricated material. Moreover, it appears that the plan is to work with tanners to whom the material would be supplied as a raw material in a crudely tanned state to make and market the final product.[71]

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[71] *Apparently, it is recognized that genuine leather comes only from an essentially intact animal skin.*

21. THE FUTURE OF LEATHER

21.1. HISTORY LESSONS

> **The uses of leather have changed and continue to change. In some cases leather has lost its prime position as it could not compete with new materials developed during recent decades. At the same time the use of alternative materials was called for in many areas due to limited availability of leather.**

One of the main threats for leather are new materials and substitutes with superior properties. Ski boots offer a good example. The variety of requirements and combination of properties such as waterproofness, stability (softer or harder skeleton), warmth, support (foams hold the foot firmly in the boot without compromising on comfort) is impossible to achieve with leather, and that it is why it is no longer used in ski boots. Other examples are leather (protective) headgears, used in contact sports, by pilots, and in the mining industry.

The case of sport shoes is also quite illuminating. In the 1970's-80's white leather was used almost exclusively for sport shoes. However, with the increase in the production of athletic shoes there was a shortage of leather for this growing market. At the same time, it became quite difficult to achieve some high performance parameters required for sport shoes. Furthermore, the price comparison was in favour of synthetic materials. Now athletic shoes are mostly fully synthetic.

The following are some examples illustrating dramatic changes that took place in the last few decades.

Some entirely new uses of collagen:

COLLIN
GEL COLLAGENE REGENERANT

However, the reversal to leather in the automotive industry seems more than to balance it off:

1 set of car upholstery = 40 – 70 pairs of shoe uppers

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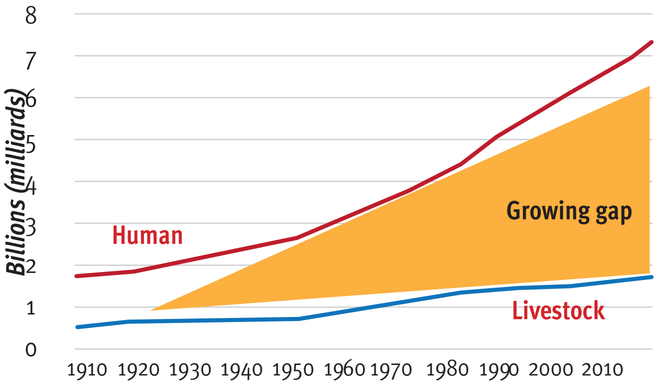
[67] *Subsequently evolved into lock-lock theory, neither confirmed, but very probable!*

21.2. KEY CONSIDERATIONS FOR THE FUTURE OF LEATHER

Any strength, weakness, opportunities and threats (SWOT) analysis of leather, especially in comparison with alternative materials, should include a very wide range of factors such as the role of hides as waste from the meat and dairy industries, the impact of possible development of artificial collagen and new materials, biodegradability, recyclability and disposal of leather products, effects of globalization and increasing demand, leather apparel as a luxury and status symbol but also malpractice, unfounded claims and agendas and, in particular, the role of fashion and designers. Some of these aspects are briefly elaborated here.

- An important advantage of leather is its ability to "breathe". The parameters for measuring this property are *water vapour permeability* (WVP), *water vapour absorption* (WVA) and *water vapour coefficient* (WVC). These parameters are not always easy to achieve and depend on the technology of chemicals and products used and their methods of application. Furthermore, these values also depend on the structure of the raw material: this is different from piece to piece as well as from which part of a skin/hide a sample is taken.
- These cross-hide and inter-pack variations apply to other physical properties. It should be appreciated that the properties of various textile materials, both natural and synthetic, are uniform both across the piece and from batch to batch.
- Heavily coated leather is a threat to this concept. In particular, automotive manufacturers have very strict requirements and the majority of leather required is heavily coated to achieve durability and light-fastness making it hard even for an expert to determine if the material used is leather.
- It seems that there is considerable progress in upgrading lower grades hides. A new generation of polymer fillers used along with other selected products in tanning and retanning operations are able to fill loose structured areas of the hide very effectively. In finishing, the stucco and pre-bottom products, which are using microsphere technology, cover defects very well, keep leathers light and give a more uniform grain break. The subsequent finishing coat add-on is reduced, thus allowing more natural and elegant finishes. Oil and wax-based finishing products are able to cover small to medium defects nicely while also accentuating the natural character of leather, especially if the leathers have a vegetable retannage.[72]
- In automotive leather the emphasis is rightly on durability and performance. It will be interesting to see the success of the latest efforts of marketing more natural leather with lower (but still good) fastness properties to the high-end automotive sector.
- Hides as waste from the meat and dairy industries: If the approximately 10 million tons of raw hides and skins as by-products of the meat industry (generated irrespective of the needs of the leather industry) is not processed into leather and subsequently into consumer goods, then it would remain as organic waste. This would be a significant problem – rotting, odour, volume/mass – to be handled or disposed of somehow. It is even claimed that the carbon footprint of the disposal footpath would be greater than processing (for the short and long term) into leather.
- In case of serious food shortages in the future, the dilemma *hide for leather vs. hide for food* might tip in favour of the latter. Many of the essential amino acids are absent in collagen, but it is still a protein, although of lower value. It may be that hide utilisation in the future becomes similar to the prevailing use of pig skins.
- A futuristic technical avenue of development is the conversion of collagen emanating from raw hides and skins into a sheet material. In this event the focus would be to retain the advantageous features of leather but as a uniform and predictable material for applications already being served by various types of leather today. This might be viewed as a product with handling advantages of say leather board but created using intelligent/smart material processing technology. In this situation, the leather products industry will benefit rather than lose, whereas the leather processing industry will change into a higher-tech form of biotechnology.
- In the event where hides/skins were widely converted into other kinds of material - food, cosmetics or other collagen products - jobs in tanning and leather products industries would be lost. Regardless, automotive interiors, furniture, clothing, shoes and accessories will always be required - be it with leather or some substitute. Employment and opportunity would change to other industrial sectors - most likely chemical and textile industries.
- The limited availability of hides would offer advantages for specialised leathers in the higher value sectors. There would never be a surplus of these types of leathers, so they would become more valuable. For those willing to provide for these status sectors, there will be opportunities.

Figure 114. The projected growing gap between human population (demand) and cattle livestock (availability of raw hides)



Based on chart by F. F. Schmël, UNIDO

- If growing artificial collagen in the sheet form is to eventually succeed, and a natural uniform material with all of the desirable properties is produced, then very specific and improved properties might be developed. This would side-step all of the unwanted components that tanners receive and address as part of raw hides and skins from meat production.
- Ever improving living standards - in both industrialised and developing countries – generates wealth and purchasing power. This stimulates demand in fashion, personal preference, prestige and luxury for materials and products made from natural materials and genuine origin, and this includes leather. Increasing demand generates higher trade values, which in turn enables better revenues within in the leather value/supply chain. This is instrumental to provide employment and income to all those associated with this industry - manufacturing and commerce, management and workforce, equipment and materials suppliers, logistics and general services.
- It is very important to understand and appreciate the value of

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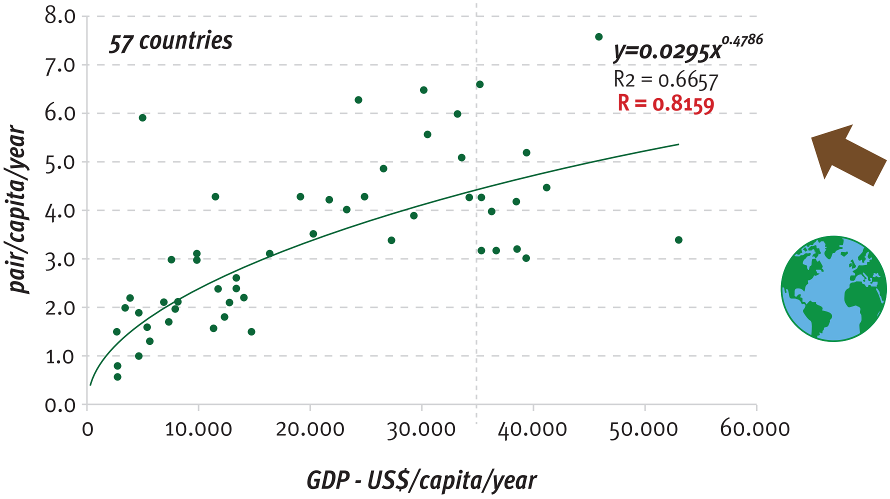
[72] *J. Christner, TFL*

designers as they significantly influence fashion and product demand. It is also important to recognise that designers do not want to be restricted to synthetics materials, or heavily coated leathers of limited scope. Leather can always offer designers - and in turn consumers - an attractive and flexible alternative to mass production and materials.

Figure 115. Footwear consumption vs. GDP-US$/capita/year

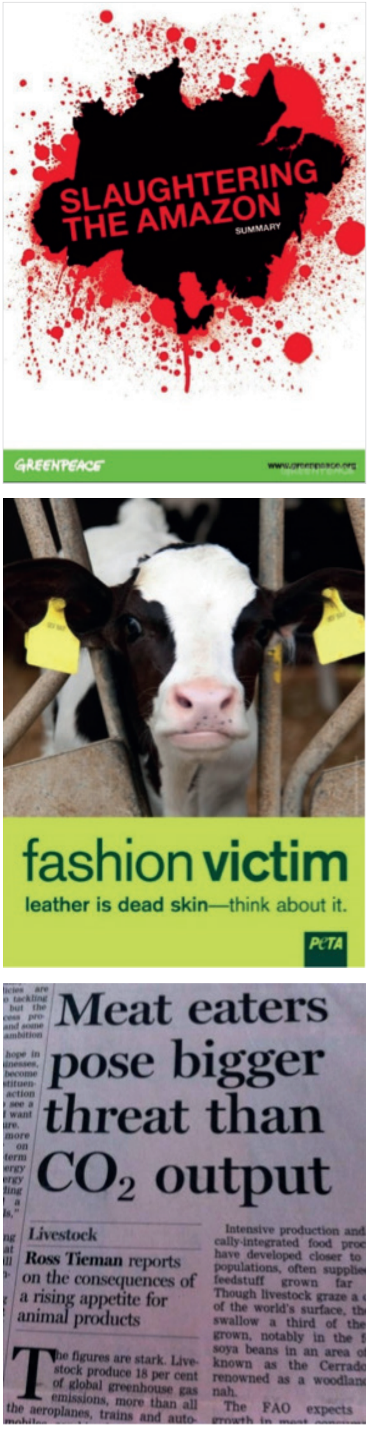


Sources:
1. **World Foorwear Markets 2007**
   Satra Technology Development Centre, Kettering, 2007
2. **CBI Market Survey**
   The Footwear Market in the EU
3. **World Economic Outlook Database**
   International Monetary Fund - April 2008

Based on chart by F. F. Schmél, UNIDO

- Globalization is irreversible and stimulated by demand. This creates conditions for different manufacturing bases depending on ever changing social, economic and environmental conditions. Related capacities are subject to *(more-and-more frequent)* relocations that create additional business and employment opportunities, including the leather sector. These opportunities include construction, equipment, evolving technologies, improved manufacturing efficiencies, education and training, and logistics.
- If it were not for fashion, durability would be of great advantage to leather made items. In reality fashion changes shorten the actual use-span of clothing apparel, including footwear, leather goods and garments. It does not seem likely that a rational and environmentally friendly approach will prevail over this short-term consumer culture that results in an excessive production of wastes of all kinds. Finally, the key element that determines the shoe lifetime is not the leather upper but the sole, normally worn out sooner than the upper part.
- Supporters of rapid fashion changes argue that changes in design greatly improves the turnover rates of the industrial and trade sectors concerned. In this case, the key participants within these drivers are textiles including leather, apparel including footwear and accessories, and associated sectors. As a corollary, and as many economists believe, these changes are a highly effective accelerator towards higher employment and ultimately overall social and economic growth.
- To date, fashion has stimulated a high consumption of footwear and other leather products. It has been instrumental in improving leather processing technology, manufacturing capacities and productivity, without compromising any essential leather properties such as durability, form stability, comfort and breathability.
- However, designers drive change that can readily shift the way that products and materials are used and perceived. The force of marketing is also very powerful, and both advertisements and promotions can be used very effectively to highlight advantages of substitutes.
- One/A threat is that in the future the consumer vision of leather might change so that it is not necessarily associated with luxury. Designers and marketing have a crucial role in the long-term success of the leather industry.
- Very aggressive campaigns based on false claims and agendas and disregard for science are damaging to the leather industry. Compounded with excessive legislation and the exaggeration of risks associated with presence of Substances of Very High Concern (SVHC) may in the long-run seriously undermine the future of the leather sector.

Figure 116. Examples of pressure groups' attempts to discredit leather and its products



Meat eaters pose bigger threat than CO_2 output

Livestock

Ross Tieman reports on the consequences of a rising appetite for animal products

The figures are stark. Livestock produce 18 per cent of global greenhouse gas emissions, more than all the aeroplanes, trains and auto-

- The majority of the leather processing industry is responsible and complies with social and environmental requirements. However, there are still some producers that disregard their social and environmental obligations. These people do serious damage to the credibility of the industry: they perpetuate the image of a dirty, exploitive and irresponsible industry, and provide fuel to support distorted beliefs, opinions and agendas.

21.3. LEATHER VS. SYNTHETIC MATERIALS, MISLEADING LABELLING

The substrate for making leather is collagen, a high molecular weight bio-polymer with a unique structure. Depending on how the collagen is being tanned, very different and unique properties can be achieved.

Leather has a unique and characteristic surface (grain) pattern. This becomes even more evident in combination with specific finishing technologies, which can be oil/wax based, natural proteins, modified cellulose or synthetic resins.

Leather behaves quite differently from synthetic materials under high wear or mechanical stress. The wearing (ageing) process happens gradually since the finishing layer (if done correctly) and collagen form a strong coherent matrix, which does not tear or rupture abruptly, as opposed to substitute materials, which often look shabby after heavy use.[73]

Synthetic products imply product uniformity and similarity. However, consumers like to express their individuality, hence the appeal of natural materials and products. Leather offers special appeal in this aspect, as each piece is unique and therefore offers opportunity.

For all practical purposes synthetic materials are not biodegradable. The ultimate disposal of footwear and garment made of synthetic materials may pose a bigger problem than the disposal of leather products. However, increasing legislative pressure for recycling synthetic materials (already present in EU) may diminish this advantage especially given the fact that leather is not easily recyclable.

Some synthetic materials can imitate some of the properties of leather, but none can emulate all of its properties.[74] Furthermore, since leather has to be a product that appeals to the consumer's senses, the right balance between fastness properties (pigmentation) and natural appearance and touch needs to be found. This could also mean accepting a higher visibility of natural defects (a kind of unique product-selling approach).

Leather will not be the preferred choice for people where price is a primary buying argument. This includes the fast fashion and volume markets. Red meat is still regarded by many as the "caviar" of meats. The growing demand for meat, or protein, is mainly satisfied by pork, chicken, fish, vegetable proteins, etc. and thus the growing demand for shoes, bags and sofas cannot be satisfied by leather alone.[75]

Yet, what too often escapes not only many consumers but also to poorly informed greens is the fact that leather is a good example of a sustainable material whereas synthetics are essentially petroleum-based products.

When the performance properties of leather are combined with the appeal of the way the material looks, feels and smells, it is truly deserving of its reputation as something special. It is unfortunate that influential voices in fashion and animal rights campaign against the use of leather.[76]

The issue is not only whether faux leather products are better but rather which product uses the fewest non-renewable resources in terms of oil- and petroleum- based inputs!

However, it is not really the common plastics widely used and suitable for many purposes that is of concern to the leather sector. The real issue is intentional misuse of the term leather. Various materials (e.g. reconstituted leather waste) are misnamed and mispresented as genuine leather to increase profits.

21.4. NEGATIVE PUBLICITY ABOUT LEATHER

Incorrect and obsolete information about the leather industry continues to be published or broadcasted on television and radio, in newspapers and magazines, even in reports from reputable organisations such as World Bank or FAO. Such opinions fail to recognize that tanners take a waste product from the meat industry and convert it into a highly versatile and beautiful material.

The negative publicity about leather can be classified into five main categories.

- Accusations linking raw hides and skins supplies with cruelty toward animals
- Accusations linking raw hides and skins supplies with deforestation (in particular rain forests)
- Following that logic, raw hides and skins production and ultimately the tanning industry is held responsible for a substantial share of carbon footprint due to greenhouse gases (GHG), especially methane generated by livestock. The recent EU decision of attributing carbon footprint load only from the slaughterhouse floor to the tannery exit gate might settle that issue.
- Applying the principle pars pro toto, a few remaining ugly spots in developing countries (those in North Africa, which in terms of production are actually irrelevant and kept mainly as tourist attractions) are constantly presented as representative of the whole industry and confirming its prevailing polluting and harmful character.
- Disregarding the fact that tanners all over the world use only "instant" powders containing harmless trivalent chromium (Cr^{3+}) salts, chrome tanned leather and leather goods made of it are drummed as being carcinogenic due to presence of hexavalent (Cr^{6+}) and, in the best case, only chrome-free leathers should be used.

The Naked Truth:
LAMBS SUFFER AND DIE IN LIVE EXPORT.
SEE MORE
SaveTheSheep.com
PETA

»As a designer, I like to work with fabrics that don't bleed; that's why ***I avoid all animal skins.***«"
(Stella McCartney)

A typical case of negative publicity is the campaign group The Friends of Earth, which, using data compiled by the consultancy group Trucost claim:

- 50.2m^2 of land and 14.5m^3 of water (or even 25m^3 if untreated) needed for one pair of boots
- The largest factor in the land footprint for a pair of boots is from cattle farming (86%)
- Workers in tanneries there are exposed to dangerous chemicals (true), including hexavalent chromium (untrue), a known

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[73] *J. Christner, TFL*
[74] *E. Hurlow, Nothing to hide, WL*
[75] *J. Christner, TFL, ILM, 2014*
[76] *S. Jessep, ICG, Nothing to hide*

carcinogen (only if inhaled).[77]

A particular contradiction (contradicio in adjecto) is the term “vegan leather”. Since vegans do not eat or use animal products so how can the word leather (“a material made from the skin of an animal by tanning”) be associated with veganism![78]

Due to their (in old days) noxious nature, tanning activities and tanners in virtually all cultures all over the globe were assigned to a very low social status, very often entirely outside “normal” society. In the worst case scenario, such deeply rooted biases compounded by very aggressive campaigns based on false claims and agendas and possibly excessive legislation might jeopardize the future of the tanning industry as we know it.

Admittedly, it (unnecessarily) took some time for tanners to accept that under some circumstances (long storage, high temperatures, use of low quality fatliquors etc.) small amounts of Cr^{3+} can be oxidised to Cr^{6+} form. Again, the real risk from the Cr^{6+} is regularly grossly exaggerated. Furthermore, nowadays this can be easily prevented by using appropriate retanning agents (e.g. tara vegetable tannin) and appropriate fatliquors.

It is a paradox that contemporary tanners only in very old books can read about long forgotten times when the two-baths tanning method was used (e.g. for chevreaux leather) or when tanning liquors were made by converting (reducing) chromium dichromate (Cr^{6+}) into trivalent chromium (Cr^{3+}) with molasses within a tannery’s own premises.

The problem of the testing method itself, detection level etc. only contributed to the cacophony and confusion stemming from a lack of understanding of elementary chemistry and unfounded myths.

21. 5. SOME INITIATIVES AGAINST MISLEADING TERMINOLOGY AND FOR THE PROTECTION OF GENUINE LEATHER

In this respect some initiatives and specific actions deserve special mention.

21.5.1. GLCC

The Global Leather Coordinating Committee (GLCC), comprising of the International Council of Tanners (ICT) and the International Union of Leather Technologists and Chemists Society (IULTCS) interacting with the International Council of Hides, Skins, and Leather Traders Association (ICHSLTA), sees itself as the primary international policy-making body for the industry.

The GLCC is concerned by the practice of applying the term “leather” to materials that are either synthetic substitutes made of fossil fuel derivatives or developed from a variety of natural substrates. They warn that “With such practices the good reputation of leather is increasingly diminished by unscrupulous traders; affecting public perception of leather and causing significant damage in the market, both to legitimate producers and consumers of leather products around the world. The latter have the right to transparent and truthful information on the goods sold or bought to facilitate informed purchasing decisions in the market and avoiding unfair competition”.

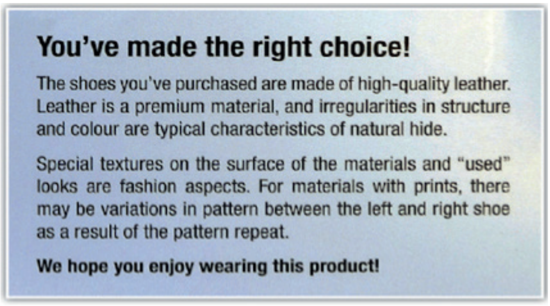
Accordingly, in 2017 the GLCC called upon national Governments around the world to counter the spread of false and misleading descriptions that deceive and confuse consumers.

The GLCC reaffirms its position that the term “leather” must be exclusively reserved for the hide or skin of an animal that has been tanned in order to become imputrescible, and where the natural fibrous collagen structure can be clearly identified.

It also supports UNIDO’s efforts to improve the environmental performance of the tanning industry in some countries.

The GLCC reportedly intends to engage many of the negative claims the firms developing various (bio-fabricated) materials tend to make in the promotion of their products.

The GLCC continues to monitor initiatives that seek to ascribe an environmental footprint of leather, such as the European modelling of the Product Environmental Footprint for Leather and the FAO facilitated LEAP (Livestock Environmental Assessment and Performance) Partnership as well as of certification organizations whose activities affect the leather trade, such as the Leather Working Group (LWG), Zero Discharge of Hazardous Chemicals (ZDHC), and the Responsible Leather initiative. The aim is to ensure that guidelines are fair, not duplicative, and take into full account the specific requirements of the hides, skins and leather industry.



You’ve made the right choice!

The shoes you’ve purchased are made of high-quality leather. Leather is a premium material, and irregularities in structure and colour are typical characteristics of natural hide.

Special textures on the surface of the materials and “used” looks are fashion aspects. For materials with prints, there may be variations in pattern between the left and right shoe as a result of the pattern repeat.

We hope you enjoy wearing this product!

A note found in a shoe box of an Austrian footwear manufacturer.

21.5.2. COTANCE

The European Confederation of Tanners’ Associations of the European Community (COTANCE) and trade union Industri-All issued a statement in December 2017 that “The use of the term leather for materials that are not leather jeopardises the competitiveness of companies in the sector and puts at risk jobs, skills and know-how of the leather industry, while misleading consumers by creating confusion over what is leather.” They claim that there is “..the proliferation of abusive denominations on the market through digital communication” Misleading terms such as mushroom leather, apple leather and Nike’s Flyleather are just some of the examples of the terms used that trade off of the back of genuine leather’s reputation.

COTANCE strongly feel that disregard for correct labelling constitutes a challenge not only to EU labelling and fair-trade rules, but also to the EU Environmental Footprinting initiative.

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[77] *The unfortunate (and by now already exceptional) situation at Hazaribagh, Dhaka is taken as a representative for the whole tanning industry.*

[78] *The Toggler, ILM, January, 2014*

Based on the recent examples of the EU dairy industry, whereby purely plant-based products such as soya or tofu cannot, in principle, be marketed with dairy related descriptions such as ‘milk’, ‘cream’, ‘butter’, ‘cheese’ or ‘yoghurt’, COTANCE demands that the leather sector also benefits from such legal protection and called for EU rules to protect the term ‘leather’.

COTANCE also submitted a paper to the European Commission requesting regulatory action for uniform leather authenticity rules in the EU; a legitimate right of protection against the misuse of the term “leather”, and protection against deceptive commercial practices that avoid disclosing the true composition of the products purchased by consumers.

It is very encouraging that upon objection by COTANCE, a reputable European footwear company reportedly no longer uses the term ‘vegan’ or ‘synthetic leather’ in any of its ranges, has introduced new brand logos stated that only genuine leather would be labelled as such.[79]

21.5.3. Leather naturally!

Striving to manage the industry’s image, Leather naturally[80] is an initiative from within the leather industry promoting the use of globally-manufactured sustainable leather. It also wants to inspire and inform designers, creators and consumers about its beauty, quality and versatility.

The initiative reacts to false claims and misrepresentations and promotes the cause of leather in columns in a leather magazine, lectures and communications in a very competent and articulated way. The following excerpt from a letter by M. Redwood, the spokesperson of Leather naturally!, to the editor of a widely read magazine is a good illustration of their activities.

“Modern leather, properly made, is one of the most sustainable materials available. No one has ever or will ever keep livestock like cattle in order to make leather. The hides and skins used to produce leather come entirely from the meat and dairy industry. While population growth and an increasing middle class have grown volumes, the equation is such that for some centuries leather supply has not been able to expand with demand. We believe that this long-term trend will continue and leather, the prime and best use for the hides and skins, will continue in those roles where it’s natural beauty and performance work best.

We do not accept that modern tanning, using chromium or not, is as difficult as you say. Chromium tanning was introduced at the end of the 19th century and its development since means that today it is one of the best methods, although others such as traditional vegetable tanning, titanium and other materials are increasingly being used. The conspiracy to condemn chromium is unfortunate. It is only a problem in the hexavalent form, which tanners do not use, and even then only when ingested.

Of course, as with any industry the leather industry does have problems in certain areas where weak enforcement of the laws and misbehaving management do not manage waste streams correctly but it is not wise to leverage these tiny groups against a whole industry who make an excellent product in first rate tanneries.

New materials will continue to be needed alongside leather, and the industry fully accepts that life will become more competitive. We believe that all materials should be objectively evaluated and presented with full transparency. Many “new” materials are presented as being sustainable and “green” that are essentially petroleum based products wrapped around some form of natural substrate. We accept that we will not convince a committed vegan that leather is a good option. The rest of the consumer base as well as the supply chain however, should hear a much louder, consistent, and objective message.”

And reaction to Nike’s reconstituted ‘leather’:

“The claim that the material made by binding around 50% reclaimed leather shavings together with synthetic materials, is more sustainable is simply untrue. It is also of various types have been produced and used in the footwear industry for many years and usually work well alongside leather, but it is wrong to call reconstituted materials leather and thus mislead the consumers. To be called leather the material must be made of the hide and skin of an animal, largely intact.”

21.6. THE UNIQUE BEAUTY OF LEATHER

The value of an article may be defined as a function of its performance during use and perceptions of its uniqueness or desirability. Performance is determined as a combination of material properties and engineered design whereas perceptions are subjective and malleable. The leather manufacturing industry has significant interest in maintaining a strong identity and favourable image for leather.

Important properties of leather: mouldability, moisture and temperature management, durability and dimensional stability, elegance in ageing. The leather is a feature of an article and promoted and selling point; thus, it fits all the definitions of a brand.[81]

It is important to appropriately store leather and leather articles: ideally, the temperature should be from 15 – 20 °C and relative humidity 50 – 70 %. Sudden temperature and humidity changes as well as direct exposure to sun light, strong lighting and, in particular storing in humid basements and in folded plastic wrapping should be avoided.

The recent ruling of the European High Court effectively prohibits the use of misleading terms such as soya, almond and rice ‘milk’; only diary based products can use the term.

This could hopefully open the door further for the leather industry to push its claim to have the word ‘leather’ legally protected in a similar way to milk and avoid some of the misleading marketing of textiles, synthetics and vegetable based products using the term ‘leather’ when describing their own products and trading off the back of the genuine leather brand.

Traceability in the leather supply chain from the farm through to the finished product is very important as it can help to demonstrate best practices and clean supply chain (hide origin, appropriate animal welfare issues, avoidance of suppliers with poor environmental and social performance, prevention of counterfeiting, etc.) and be an advantageous marketing tool.

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[79] *The Leather Industries of America (LIA) with the support of the International Council of Tanners (ICT), point out that leather is an environmentally sustainable material as opposed to many petroleum-based non-leather options.*

[80] *See www.leathernaturally.org*

[81] *Source: Nothing to hide, World Leather, February/March 2016*

22. CONCLUSION

22.1. GENERAL CONSIDERATIONS

It is important, at the global scale, to accelerate the implementation of the best technologies currently available combined with efficient waste handling and treatment of tannery effluent. The forthcoming table gives a condensed overview of cleaner leather technology methods.

Equally important is a better worldwide coordination of efforts to oppose the perception of leather manufacturing as a dirty, polluting industry. Emphasis on its sustainable character and comparisons with some other sectors/products (blue jeans!) can be very helpful. Recent activities of several international and regional organizations are indeed on the right track.

Figure 117. The projected growing gap between human population (demand) and cattle livestock (availability of raw hides)

(The mezzanine in the wet finishing department in Dani Tannery, Italy)

Source: World Leather, June/July 2012

However, research and development centres, institutes, education and training centres and, in particular, public media in the leather sector should contribute to achieving this objective. A good example could be a better balanced approach and more careful wording when it comes to chrome vs. chrome-free tanning; poor science should not prevail over facts.

Practical experience to date shows that no metal tanning agent matches the versatility of chrome (III). Total chrome replacement is possible if reduced hydro-thermal stability and lower handling qualities are acceptable. However, most end-uses of leather require high hydro-thermal stability. For example, shoe upper leather must withstand hot lasting and heat setting, while garment leather must withstand steam pressing.

22.2. CLEANER TECHNOLOGIES AT A GLANCE

In setting and presenting its cleaner technology targets, the tanning industry should be realistic and bear in mind that a tanner's genuine raw material is actually collagen and that the rest is, if not waste, a kind of undesirable burden.

Similarly, while it is essential to strive for the better uptake of chemicals used in the process, it has to be accepted that we deal with organic, protein substrate and chemical reactions of specific types.

Ideally, preservation by salting of raw hides & skins should be discontinued all over the world as soon as possible. They are to be processed locally at least to semi-processed stage (wet blue, whet white, wet green, crust, ready to finish).

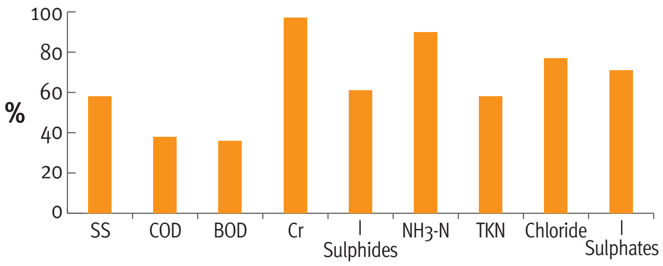
Table 61. Cleaner leather technologies at a glance

Category/Process stage		Cleaner methods
EMS		A licensed or own Environmental Management System, incorporating OSH and Corporate Social Responsibility (CSR) in place
General	*Water*	Strict water monitoring/control and savings measures at process, department and company level; batch washing, recycling
	Energy	Usual consumption/savings measures combined with the energy from renewable sources, heat pumps, etc.
	RSL	Apply the global strictest Restricted Substances and SVHC lists and avoid any limitations and risks in exports of leather and leather products
	OSH	Strict segregation of acidic and sulphide containing streams, H_2S monitors in place, staff trained
		Noise, vibrations, malodour control; appropriate lighting and ventilation, sanitary facilities
		Occupational Safety and Health measures, general and personal (Personal Protection Equipment, PPE), including rigorously implemented and observed training
Beamhouse	*Preservation/ Soaking*	Use of green, non-salted hides Green fleshing Biodegradable surfactants Watch for harmful pesticides
	Liming	Hair-save liming Consider reuse of liming liquors Ex-lime splitting
	Deliming	Low- or ammonium-free deliming (CO_2) deliming
	Bating	Low- or ammonium-free bating agents

Category/Process stage		**Cleaner methods**
Tanyard	***Pickling and (chrome) tanning***	Low-salt pickling Consider pre-tanning (wet white tanning) One or a combination of better chrome management systems • optimization of process parameters • high exhaustion • direct recycling of spent bath • reuse after chrome recovery Use of acceptable fungicides
Wet finishing	***Retanning***	Use of acceptable retanning agents (phenol- and formaldehyde-free) Use of low salt retanning agents High exhaustion rate Careful selection of auxiliary agents
	Dyeing	Avoidance of banned dyes Use of dedusted dyes High exhaustion rate Careful selection of auxiliary agents
	Fatliquoring	Strict avoidance of halogenated (AOX) products High exhaustion rate Careful selection of auxiliary agents
Finishing	***Coating***	Control of airborne particles/dust Use of water-based finishing systems Avoidance of harmful cross-linkers Avoidance of pigments containing banned/restricted metals Coating by advanced spraying equipment (airless, HVLP guns, scrubbers); curtain and roller coating
Solid Waste		Consequent segregation of different waste categories, innovative approach in utilization and safe disposal
Effluent treatment		On-site pre-treatment and full scale (biological) on- or off-site treatment; compliance with local discharge norms.

The next figure derived from practical experience and some educated projections indicates the presently achievable targets of reducing the pollution load (measured in terms of the traditional parameters such as BOD, COD, SS, Cr etc.) typical for conventional technology.

Figure 118. Decrease of pollution loads in waste water after introducing advanced technologies



Based on chart by M. Bosnić, derived from UNIDO paper The scope for decreasing pollution load in leather processing, Ludvik J, 2000

Obviously, given such a variety of raw material, types of leather(s) produced, specific local conditions, including climate, legislation, etc. each tannery and/or tannery cluster has to define their own strategies and ways and means of achieving them in close interaction with national and international R&D establishments and trade organizations.

22.3. NEW CHALLENGES

In advanced industrialized countries, primarily in Europe, where traditional pollution is well under control,[82] some other issues are coming more into focus.[83] The first is the question of use and presence of substances with proven and/or perceived long-term negative impact and thus placed on Restrictive Substances Lists (RSL). No tanner operating in the globalized market can afford not to be familiar with them and act accordingly.

The second issue is about Life Cycle Analysis (LCA) in practice appearing as the question of GHG or simply carbon dioxide and greenhouse effect.

> ***It is actually regrettable that the focus of RSL and LCA pressures shadows more critical environmental issues of the leather industry. A good example is the scientifically unjustified and inflated problem of hexavalent chromium in leather is of far less importance and effect than salinity of tannery effluents!***

The leather industry should persist in its view that leather manufacturing is actually a recycling industry using as its initial substrate waste generated by the food (meat) industry; more than 85% of the dry weight of leather consists of collagen, which is a renewable biopolymer with extraordinary properties. In essence, leather making converts a renewable resource into a highly valuable, durable and safe material and thus provides employment of a significant scale in several downstream industries. Transformation of raw hides and skins into leather applying the Best Available Technologies (BAT) and following the highest environmental standards should ensure the position of leather as the preferred, sustainable material.

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[82] *Except hard to degrade, recalcitrant COD mainly emanating from retanning.*

[83] *In short, the bottom line of current trends is that obnoxious beamhouse (for centuries associated with tanning activities) being cleaned up, it is chemicals in wet and dry finishing and LCA coming into the limelight of green pressure groups.*

Consumerism, short-termism vs. quality and durability

Is it not about time to consider a paradigm shift, a very different strategy - superior quality and durability, coinciding with the old principle waste not want not i.e. towards responsible and rational utilization of resources and sustainable development? Or will a suggestion that the same leather bag or briefcase be used for several years, a pair of shoes proudly worn for a few seasons in the best case bring nothing but a benign smile...

J. Buljan, JALCA, J.A. Wilson Memorial Lecture 2014

The mood in the tanning sector (and not in the tanning sector only) in developing countries about the whole LCA/CF concept is quite different.

Indeed, it seems that the view that human activities are responsible for the rapid increase of the GHG related climate change gradually prevails. At the same time, it is hard to oppose the argument that the carbon footprint of a cluster of small- and medium-sized tanneries in a developing country is almost negligible in comparison with some other activities. Many feel that, for example, city and home lighting for celebrations, not to mention (unnecessary?) war operations, make hair splitting about CF from some stages of leather processing irrelevant and irritating.

From that point of view, by now the already widely known concept of the UN Brundtland's Commission Report that there is a unity of environment and development and that they cannot and should not be distinguished as separate entities is still valid; the two are inseparable and as relevant as ever.

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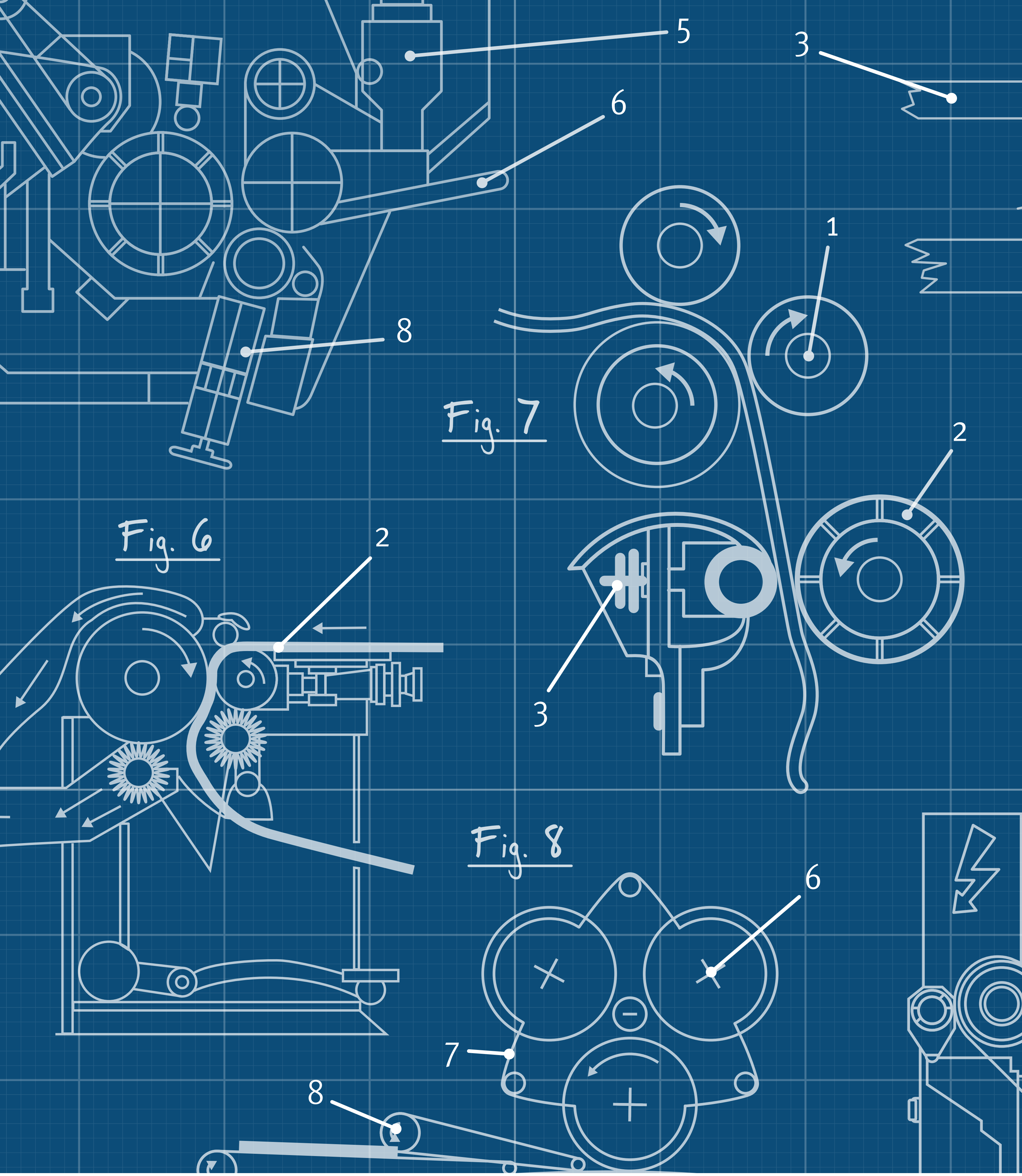
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