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CAPACITY BUILDING TO THE MONGOLIAN VEGETABLE-TANNED YAK LEATHER CLUSTER ON BIO-LEATHER AND BIO-LEATHER PRODUCTS

BEST PRACTICE GUIDE FOR SUSTAINABLE VEGETABLE-TANNED YAK LEATHER MANUFACTURING

Publicity Disclaimer

This publication was produced with the financial support of the European Union. Its contents are the sole responsibility of the SYL consortium and do not necessarily reflect the views of the European Union.

Abbreviations and Acronyms

AOX	Absorbable organic halogens
BAT	Best available technology
BOD_5	Biological oxygen demand, five days
BREF	Best available techniques reference document
COD	Chemical oxygen demand
ECHA	European Chemicals Agency
ETP	Effluent treatment plant
EU	European Union
FAO	Food and Agriculture Organisation
HVLP	High-volume Low-pressure
IPPC	Integrated pollution prevention and control
IUE	Environment Commission of the International Union of Leather Technologists and Chemists Societies (IULTCS)
MRSL	manufacturing restricted substances list
MSDS	Material safety data sheets
OSH	Occupational safety and health
PCU	Preservation-cum-unhairing
PPE	Personal protective equipment
REACH	Registration, Evaluation, Authorisation and Restriction of Chemicals
RSL	Restricted Substances List
SS	Suspended solids
SVHC	Substance of very high concern
SYL	Sustainable Yak Leather project
TDS	Total dissolved solids
TKN	Total Kjeldahl nitrogen
UNIDO	United Nations Industrial Development Organization
VOC	Volatile organic compound

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Foreword

This best practice guide has been prepared by the SYL Project based on previous studies conducted by IUE Commission, United Nations Development Organisation (UNIDO) and the European Commission. The objectives were to:

- revisit the traditional *'standing'* issues about reducing the polluting emissions throughout the entire leather-making process (water saving, deliming, chrome management, etc.), and
- present a fresh, neutral assessment of some cleaner methods based on years of practical experience.

This guide focuses on the manufacture of vegetable-tanned yak leather. The approach was to:

- present information about experiences gathered, and options available to date, and
- point out their advantages and disadvantages; without strong preference and certainly not '*imposing'* a particular method.

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.

1. Major Concerns of Conventional Chrome-Tanned Leather Manufacturing

Today leather is one of the essential commodities and the leather/leather product industry plays an important role in the World's economy.

Leather manufacturing is a series of operations from preservation to finishing, with the aim of converting quickly degradable, highly putrescible raw hides/skins into leather; a stable initial material suitable for use in production of a very wide range of articles: footwear, clothing 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.

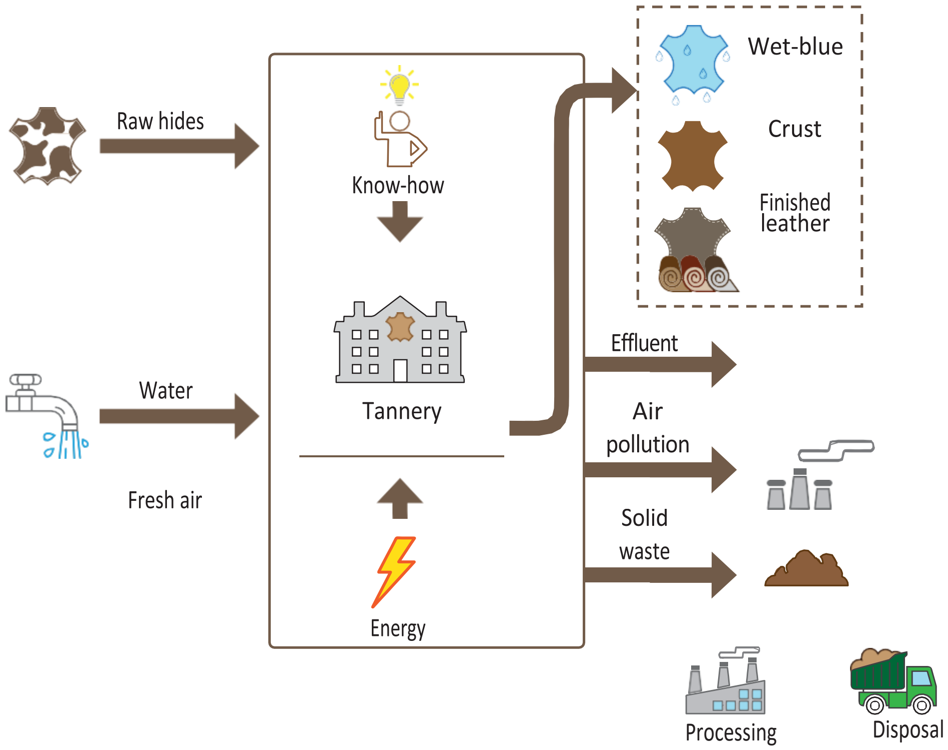

Figure 1. Simplified chart of the tanning industry
Based on the chart prepared by F. Schmel, UNIDO, Sustainable Development Goals

Though the leather sector contributes to social development through a significant amount of employment generation, it is also identified as one of the major polluting industries. The main causative factors for pollution from the tanneries are:

- Waste materials from hides/skins; and
- discharge of residual chemicals in huge volume of wastewater.

The waste generation from the conventional leather manufacturing can be categorized as follows:

- Liquid waste
- Solid waste
- Aerial emissions

1.1 Liquid waste

Water is the largest input in leather manufacturing and its consumption is needed because all the unit operations in leather processing are water mediated. In addition, water is needed for cleaning, energy generation, wastewater treatment and sanitary purposes. Generally, to process one tonne of raw hides/skins into leather, about 30-50 m^3 of water is used. The amount of water used for leather manufacturing is discharged as wastewater with a high pollution load.

1.2 Solid waste

Statistical data from the Food and Agriculture Organization (FAO) revel that globally, 5.84 million tonnes of solid waste is generated by processing 7.3 million tonnes of raw hide/skin. The intrinsic nature of the hide/skin, leather processing steps, wastewater treatment and the nature of chemicals employed, are responsible for the generation of solid wastes. The nature and quantity of solid wastes generated during the processing of one tonne of raw material are given in Table 1.

Solid waste	Quantity (kg/tonne of raw material)
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**

Table 1. Solid waste generation from leather manufacturing
Source: UNIDO. 2019

1.3 Aerial emissions

Odour emanates from leather processing owing to various reasons such as decomposition of incorrectly cured or stored hides/skins, accumulated wastes, beamhouse processes, and wastewater treatment plants that are poorly controlled and maintained. Odour is not necessarily harmful or toxic, but constitutes a nuisance to affected neighbours, which in turn gives rise to complaints. Apart from a natural, distinct smell of raw hides, bacteria degrading the organic matter can cause pungent ammoniacal odours.

Volatile organic compounds (VOCs). Organic solvents are used in leather, predominantly during finishing and sometimes during degreasing. During both the above processes, owing to the low boiling point of the solvents used, they tend to evaporate at ambient temperature, and would result in distinct odour; emitted from finishing and degreasing processes of leather manufacturing.

Ammonia is liberated from improperly cured hides or skins and also from the liming process. However, significant quantities of ammonia - in the form of gaseous emissions, and liquid - emanate from the deliming process, owing to the use of ammonium-based salts for deliming process.

Hydrogen sulphide gas emanates from the use of lime liquor containing sodium sulphide coming in contact with acid.

Dusts and other particulates. Airborne particulate matter can arise during mechanical operations such as milling, buffing and staking. The dust may also emanate from improper handling of powdery process chemicals.

2. Sustainability in the Leather Sector

Sustainable development is defined as '*development that meets the needs of the present without compromising the ability of the future generation to meet their own needs'*. Unless economic growth is driven to meet the needs of the present in an intelligent and equitable manner, the natural resources that are necessary for the future needs of the society cannot be met. Sustainability therefore does not encompass environmental protection alone.

The leather industry utilises co-products of the meat industry: hides and skins. This itself is a perfect model of sustainability in the sense that the waste or co-product of one industrial activity is utilized better to create value and employment.

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.

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.

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 and electrolytes contained therein.

In view of ever increasing legal, local, and global social pressures, no tanner can afford the luxury of being ignorant of 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, remains of paramount importance.

Vegetable tanning and the manufacture of full grain vegetable leather present a number of opportunities for reducing inputs and outputs, and thereby contributing to greener and environmentally friendly production.

3. Concept of Best Available Technologies

Importance of best available technology (BAT). The concept of '*Best Available Technology'* can support industries, decision-makers, and regulators; in addressing environmental and economic concerns in industries, with regard to the application of abatement strategies.

Definition of BAT. According to the Integrated Pollution Prevention and Control (IPPC) directive, BATs are defined as '*the most effective and advanced stage in the development of activities and their methods of operation, which indicates the practical suitability of particular techniques for providing the basis for emission limit values and other permit conditions designed to prevent and where that is not practicable, to reduce emissions and the impact on the environment as whole.'*

- **'*Best'*** means most effective in achieving a high level of production of the environment as a whole.

- ***'Available'*** technologies are those developed on a scale that allows implementation in the relevant industrial sector, under economically and technically viable conditions, taking into consideration their costs and advantages.

- ***'Technologies'*** includes the usage, and the way in which the installation is designed, built, maintained, operated and decommissioned.

Factors to be considered for any BAT.

- Technological advances and changes in scientific knowledge and understanding.
- Economic feasibility of such techniques.
- Time limits for installation, in new and existing plants.
- Nature and volume of the discharge and emissions concerned.

4. Best Available Technologies for Vegetable-Tanned Yak Leather Manufacturing

Consumer awareness and regulations - on waste discharged from the leather industry - call for environmentally sustainable leather manufacturing. In addition, water is the major input of conventional leather manufacturing and today it is a scarce resource. It is projected that by 2025 two-thirds of the World's population could be living under water-stressed conditions (between 500-1,000 m^3 per year per capita). Therefore, water consumption is one of the main criteria to be considered for BAT. The criteria to be considered for the selection of BATs for leather manufacturing are shown in Figure 2.

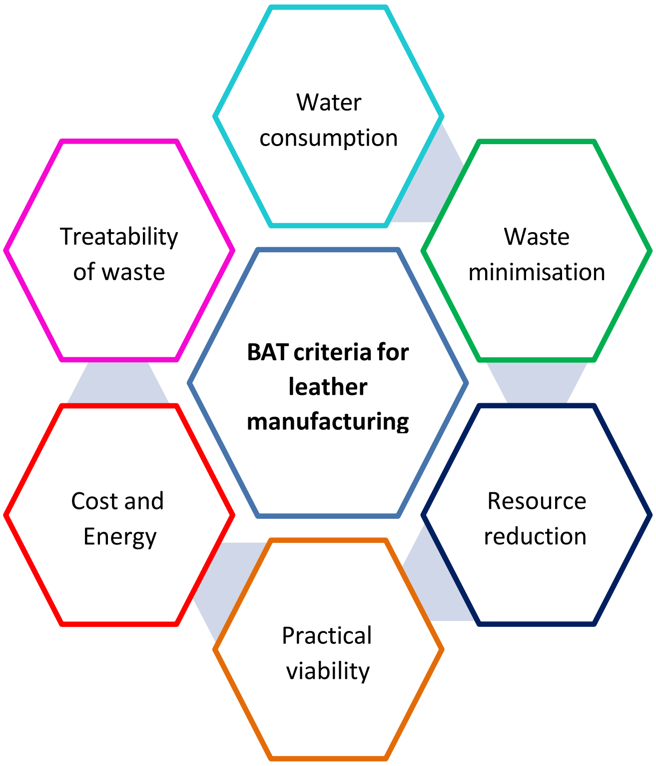

Figure 2. Criteria for selection of BAT in leather manufacturing

Currently available technologies are analysed through the BAT selection criteria. Based on this, some of the technologies are selected as BAT, and their sequence in leather manufacturing is shown in Table 2.

Leather manufacturing step	BAT
Preservation	Chilling. Organic formulation.
Pre-tanning	Hair-save liming and recycling. Enzymatic unhairing and fibre opening. CO_2 deliming.
Tanning	Aldehyde-free mineral-free tanning.
Post-tanning	Restricted-substances-free and high exhaustion. Use of multifunctional auxiliaries.
Finishing	Water-based finishing. Low VOC emissions.
Solid waste	Development of high-added-value products
Liquid waste	Electro-oxidation and reuse of treated water

Table 2. BATs for cleaner leather manufacturing

4.1 Water management

Water consumption consists of two main components:

- water needed for physical-chemical processes (process water), and

- water needed for cleaning, energy generation, wastewater treatment and sanitary purposes (technical water).

The focus here will be on the process water.

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

Values per tonne of raw hide (bovine salted raw hide)	Water (m^3/t), range
Beamhouse (soaking to bating)	7-25
Tanning	1-3
Post tanning	4-8
Finishing	0-1
TOTAL	**12-37**

Table 3. Typical water consumption ranges (IUE)

Water use can be reduced at many points in the leather making process, and good water management should be seen as one of the key components of modern leather technology and 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
- 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 a smaller volume.

There is 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 materials, product range, and technology used, requires 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 flows.
- 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, and 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 and 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 the use of technical water (fleshing, cleaning, etc.)
- Use of high-pressure cleaners for floors, drums, equipment.

Some practical examples of water-saving measures

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 a 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%.

Additional water reduction and more uniform quality is achieved by thorough drainage after each process step, including washes; 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.

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, in terms of quality vs. optimum use of water, chemicals and energy. Short floats mean 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, reproducibility and avoidance of reprocessing are further benefits.

> **Comment**
> It should be appreciated that use of very short floats requires increased attention to avoid problems related to excessive mechanical action (e.g. abrasion, heating, and/or tangling of hair-on hides/skins). It might be useful to mechanically remove (by shearing) some of the excess hair of yak hides, in advance of processing.

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% – 1,000% floats should be replaced with drums.

Recycling and water reuse

Many relatively clean, rinse and wash waters, can be recycled to other processes where the low concentration of residual 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 can be 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 (hydrogen sulphide)!

- Drained pickle float can be used for pH adjustment of deliming liquors.
- Drained pickle float can be reused for building up the new pickle. This process is usually started by adding salt and sodium formate, followed by acidification with formic acid. Only if really needed is 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.
- 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 proposed 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.

Comment
Separation of the pickling and tanning floats (in particular) may be difficult, because tanning is often done in the pickle float. The effort required, the level of control, and the high risk of mistakes may not justify this solution.

Recycling of process liquors - e.g. liming, tanning, etc. - 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 common as one would expect it. The explanation might be that:

- it requires additional space for storage tanks, and/or
- the risk that it may affect the leather quality prevails over possible savings in water and chemicals.

Green fleshing and lime splitting

Green fleshing opens up of the hide structure (allowing for better penetration of chemicals during soaking and liming) and 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 minimises water and chemicals use.

Comment
Fleshing fresh yak hides would facilitate operations but, contaminating dirt and dung (and clumps of hair) might make this difficult, without damaging the hide. Accordingly, the fleshing might be better after preliminary soaking - despite the extra work unloading and loading hides - especially in combination with a shearing (to reduce weight).

Fleshing, vacuum dryers, finishing

In some tanneries, fleshings are collected and transported with the aid of water; equivalent to as much as 1-2 m^3/t of the original, wet salted weight. 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.

Rainwater management

The aim here is twofold:

- To minimise the amount of rainwater that becomes contaminated, and requiring treatment as the main effluent.
- To maximise the amount of rainwater collected separately to be used in the leather process itself, or for cleaning.

The main source of rainwater contamination is paved yards with residues of spills of chemicals. Such areas 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.

4.2 Raw material preservation

Although the preservation of raw hides/skins - be it short-term or long-term - 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.

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

Salt inhibits growth and bacterial activity by making the moisture content in the raw stock physiologically unavailable. After flaying, hides/skins are firstly cooled, spread out (hair side to the floor), uniformly covered with salt, stacked, sandwiched with more salt, and left to drain for about a week, and salt saturates the remaining moisture. 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)

Total dissolved solids (TDS) – mainly chlorides and sulphates (colloquially salinity) – in effluent are the major environmental concern in arid and semi-arid regions of the world. This makes the 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 the 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 sodium chloride, is salt from preservation. Unfortunately, TDS in tannery effluent cannot be removed by conventional treatments (reverse osmosis, which is considered excessively expensive). The environmental damage caused by salting prevails over its positive aspects.

Alternative environmentally friendly short-term preservation methods

Chilling

In addition to the drying mentioned earlier, the only alternatives to salting are the immediate processing of fresh (green) hides/skins, or short-term preservation by:

- cooling (chilling), using crushed ice or refrigerated storage,
- biocides, and
- a combination 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 generously iced, and placed into a storage container.
- By using solid carbon dioxide (CO_2 snow) - which is very convenient where cold storage facilities are already available – combined with good ventilation (so there is virtually no health or safety risk).
- By using refrigerated storage units: the hides must be hanging, without touching.

The cooling chain must not be interrupted during transport and storage. The temperatures to which hides/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/skins can be stored for three weeks without suffering damage.

The main benefit of chilling (avoiding use of salt) is that the amount of (TDS) in the tannery effluent is reduced by 30-40%.

Use of organic formulation as preservation-cum-unhairing (PCU) agent

Recently, Sathish *et al* developed an organic formulation which is capable of preserving hides/skins at ambient conditions without dehydration, and subsequently hair gets loosened during the transport/storage period. A low level of sulphide was used during alkaline fibre opening, for removal of traces of hair. The strength and organoleptic properties were on par with salted skins/hides.

> **Comment**
> This relatively new technology – like some other emerging ones - has yet to be proved commercially, and adopted on a larger scale.

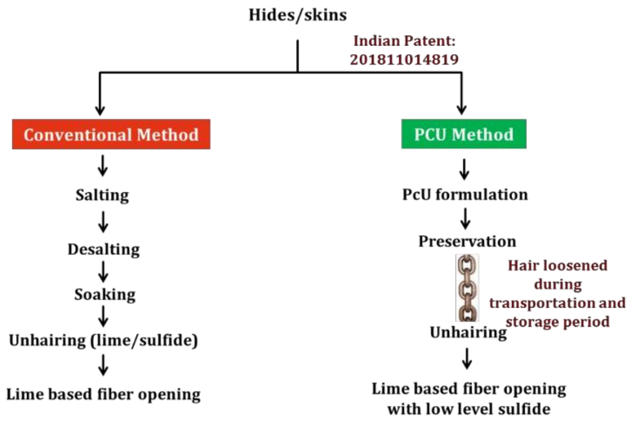

Figure 3. Process flow diagram of conventional and PCU process

The developed process completely eliminates the use of salt and 75% of the sulphide, and also reduces the time and water required for the soaking process. The developed system reduces 85% of the pollution load discharged from soaking and unhairing processes.

4.3 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) 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 there - be it excessive or insufficient liming/opening up, partial or full deliming let alone at the extremely sensitive and risky bating operation - are irreversible.

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.

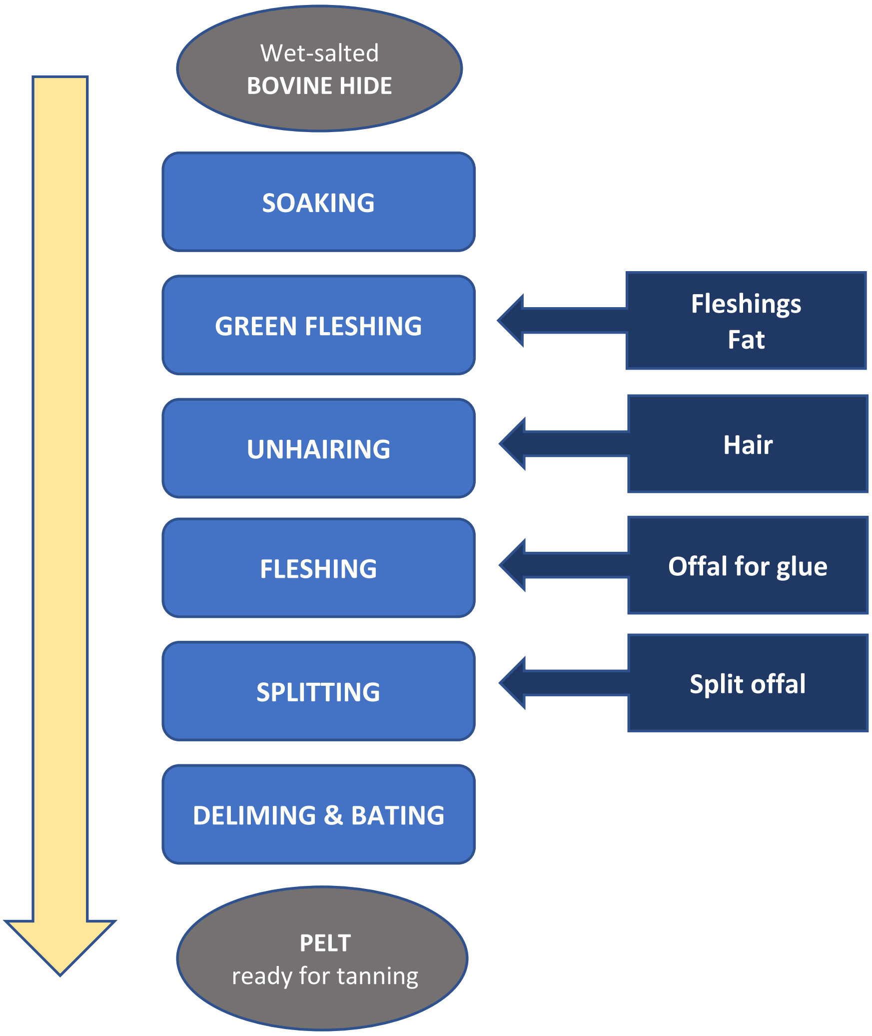

Figure 4. Beamhouse operations
Based on a chart by F. Schmel (UNIDO)

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.

Soaking

The purpose of the soaking process is to return the hides/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).

Waste soak liquors contains soluble proteins, suspended matter (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 Chloride).

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/skins by shaking.
- Use of clean hides or skins only.
- Avoidance or substitution of hazardous, environmentally unfriendly substances.
- Optimisation of water consumption and process control.
- Green fleshing: fleshing after the dirt soak allows a more rapid and uniform penetration of chemicals into the hide.

Figure 5. Drum for desalting of hides
Source: www.rizzi.it

Figure 6. Through-feed fleshing machine
Source: www.rizzi.it

Unhairing, liming

The main aims of the liming process are:

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

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. 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[1], SS, TDS/salinity and nitrogen). Apart from that, the presence of dissolved hair in spent liquor limits the reuse of liming liquor for subsequent batches.

The main reasons for use of **hair-save unhairing** are:

- Significant decrease of organic pollution load, including nitrogen; a quarter of the overall nitrogen released stems from liming and unhairing.
- Significantly lower volume of sludge, for reuse or disposal.
- Lower costs of effluent treatment (chemicals, energy, etc.).

Hair filtration equipment is available, for recirculating the float and separating the hair from the spent liquor before it is sent out for treatment plant. Hair separation is preferably carried

[1] Biological oxygen demand, and chemical oxygen demand.

out at the same time as hair loosening, so as to minimise the degradation of hair. After hair separation, the spent liquor is used again for fibre splitting. The process can be continued up to 20 cycles without affecting the quality of leather. Recycling system also helps to reduce the high level of water consumption in the unhairing/fibre splitting process.

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 0Bé) until about 15°Bé is reached; the final density of the paste of about 20°Bé[2] or more, is achieved by adding kaolin. Very rarely, painting on the grain side is also used for special types of rawstock to produce a particularly smooth and fine grain; but 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 still necessary; so painting is labour intensive, requires more space, and (usually) more time.

Figure 7. Pile of painted sheepskins

In **enzymatic unhairing**, protease and amylase-based enzymes are used, for unhairing and fibre opening respectively. Therefore, usage of lime and sulphide can be completely avoided. However, enzymatic processes are hard to control. Commercial preparations containing proteolytic enzymes attack the collagen of the grain layer to a certain degree, sometimes leading to looseness of grain and '*sueding*'. Moreover, enzymes alone cannot completely eliminate the fine hairs. Thus, it is unlikely that an unhairing process exclusively based on the use of enzymes will ever be practical. Also, enzyme preparations are expensive and, in most cases, the environmental benefits they offer are insufficient to justify their cost.

[2] 9°, 15° and 20° Baume, are equivalent to specific gravities of 1.066, 1.115 and 1.160 respectively.

More recently **oxidative (hair-save) unhairing** has been investigated. The method uses hydrogen peroxide for oxidation and sodium hydroxide as the source of alkali. With calcium hydroxide there would be a risk of hair *'immunization'*. The process is carried out in a propylene drum fitted with two cooling systems, with advanced temperature, pH etc. monitoring and control systems. Depilation is carried out at pH 12.6. It is claimed that the pelts are comparable to those from the traditional unhairing and liming process. Moreover, 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 (SS) and COD, and slightly lower water consumption, whereas the presence of phosphorus is seen as advantage.

Comment
Unlike hides treated with sodium hydroxide – which are very slippery and difficult to handle – those unhaired oxidatively tend to be easier to work with. However, hydrogen peroxide (H_2O_2) is difficult to remove fully by washing, so extra caution is required working with this hazardous material. Furthermore H_2O_2 can corrode concrete in the long term.

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 the 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 present, there are only two areas of wider applications for hair recovered from hair-saving processes:

- Agricultural fertiliser and composting.
- Animal feedstuffs.

Hair-save unhairing must be seen as a partial, but important element in the general optimisation of production, including environmental aspects and better housekeeping. Combining hair-save unhairing, with the partial recycling of lime floats, and the use of second, final washing floats (for the first '*dirty*' soak) is possibly the optimum approach from both practical and environmental aspects. In evaluating a hair-saving method, OSH aspects must also be taken into consideration.

Fleshing

The environmentally preferred green fleshing has been described above. 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.

Deliming

The main aims of deliming are:

- Removal of residual of chemicals used during unhairing and liming.
- 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; usually 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. 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 most commonly used.

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 due to OSH considerations (harmful ammonia gas develops at the initial stage of deliming), and its significant contribution to nitrogen and TDS load in effluents. Reacting with lime, ammonium sulphate forms calcium sulphate $Ca(SO_4)_2$.

Some cleaner technology options to replace ammonium salts are:

- Replacing ammonium salts with weak organic acids (lactic acid, formic acid and acetic acid), esters of organic acids, magnesium lactate, non-swelling aromatic acids, etc. However, replacement of ammonium salts with weak organic acids is not quite satisfactory because:
  - While the ammonium nitrogen 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.

- Deliming with carbon dioxide gas (CO_2). In carbon dioxide deliming, CO_2 gas is passed into a well-equipped vessel or drum (containing water) to produce carbonic acid, which has the ability to neutralize the alkali present in the hides matrix. Solid carbon dioxide (dry ice) can also be used for deliming application, which avoids the risk of pressure valve failures. With CO_2 as a deliming agent, there is a substantial decrease of ammonium nitrogen (NH_4-N), but also of the total Kjeldahl nitrogen (TKN) pollution load in effluents. However, there are also some limitations:
  - 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.

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.

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 associated with the deliming process, and TDS load from non-active components of the commercial bating agent.

4.4 Operations in the tanyard

Tanning is a process that transforms hides/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 its shape, and dries easily.

Vegetable tanning

Vegetable tanning's main traditional use is in the production of sole leather for high quality shoes, leather goods, harnesses, and saddlery; and to a lesser extent for upholstery. These products are still perceived as elite, luxury items; e.g. fashionable leather bags, special upholstery for exclusive automobiles, etc. 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 East India (EI) process mainly used a combination of myrobalan (*Terminalia chebula*) and avaram (*Assia auriculate*) or myrobalan and mimosa (*Acacia mearnsii*).

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.

VEGETABLE TANNING AGENTS	
Hydrolysable tanning materials (Pyrogallol)	**Condensable tanning materials (Catechol)**
(Acid forming)	**(Phlobaphene - forming)**
Acorn galls	Cutch
Chestnut wood	Gambir
Dividivi	Hemlock bark
Galls	Mangrove
Myrobalans	Mimosa bark
Oak wood	Oak bark
Sumac	Quebracho
Tara	Tizera wood
Trillo	Uranday wood
Valonea	

Table 4. Vegetable tanning agents

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. 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 vegetable tannins are now obtained from tree plantations (renewable sources). Though 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. The vast spruce and birch forests in Russia and Scandinavia would ensure a nearly unlimited supply of renewable resources. 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.

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, and
- 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)[3], 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).

Traditional counter-flow pit tanning system

Due to the duration extending from several weeks to even months, the centuries old pit

[3] 18° Baume, equivalent to specific gravities of 1.142.

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).

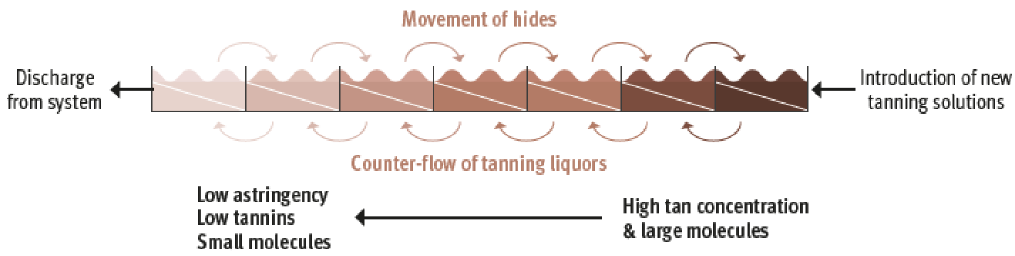

Figure 8. Counter-flow pit tanning system
Derived from WL April 2016

Rapid vegetable tannage

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

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

Pit-drum tannage and semi-rapid vegetable tannage

This was developed to combine the best of both systems. The first processes, deliming and light pre-tannage, are carried out in the drum. The hides are then transferred into a chain of counter-flow pits with steadily increasing concentrations of vegetable extract. Then transferred to a 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 represents a refinement of the well-established pit-drum tanning using a 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.

Wet-Green tannage

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

The Wet-Green concept is based on the utilization of residues from olive harvesting and olive oil production; having (pre) tanning potential. The Wet-Green tanning system uses polyphenols extracted from olive leaves. During olive harvests, leaves account for approximately 10% of the harvest weight and are rich in polyphenols.

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 like 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; and storage for longer than two to three weeks requires application of fungicides.

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. However, to date there are no signs of wider acceptance at the industrial scale.

Emissions and pollution load

The main components of emissions and pollution load in effluents from vegetable tanning are:

- Residues of the tannin extract (not bound to leather).
- Soluble non-tannins present in the readily usable tannin extract.
- Very high COD (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 widespread misconceptions, vegetable tanning agents, syntans, and aldehydes can cause serious damage to surface waters due to their low biodegradability and their toxicity to aquatic life.

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.
- Using short floats and closed loops in drum tanning releasing very little wastewater.
- 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)

Chrome-fee tanning – Tannages with syntans and other synthetic organic compounds

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 preceded 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. These have a well-known positive impact of the usability of solid waste, but the nature of their effluent load might be a disadvantage.

Syntans with a lower impact on the environment (low levels of free phenol) are available commercially. However, normally, syntans have a very high COD, their degradation (in the course of effluent treatment and recipient water bodies) is very slow (aerobically and anaerobically) and even the degradation products are 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.

4.5 Wet finishing

The tanning stage basically converts a putrescible, easily degradable hide into a stable material. However, 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.

The **effluents from all wet finishing operations** are normally collected jointly and that is why there are no specific data for each of the 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 across 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.

POLLUTANT	EMISSIONS kg/tonne RAW HIDE
Total solids	65
SS	7
BOD_5	14
COD	20-30
Nitrogen, total	0.8-1
NH_4	0.6-0.8
Cl	2-5

Table 5. Emissions to wastewater from conventional post tanning operations
Source: EU BREF 2013

Neutralisation

The purpose of neutralisation is to remove free acids present in tanned leather; 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 '*neutralisation*' is '*deacidification*'. For softer leather, and better dye penetration, deacidification is carried fully throughout the cross-section – in contrast to partial deacidification, only to a certain depth - gives firmer leather. 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.

For **cleaner** 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.

Retanning

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

- Make the leather more uniform by filling the looser and empty parts, thus increasing its cutting value.
- Improve buffing properties (important for production of corrected grain leathers).
- Improve resistance to alkali and perspiration.
- Improve the general feel and handle.
- improve light fastness of vegetable tanned leather.

The emphasis of the retanning process will depend upon 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 made accordingly. 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, up to 15% on the shaved weight for shoe uppers.

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 the characteristics it gives to leather, it is important to consider its environmental performance; residues not taken up by leather can contribute to heavy COD effluents. To make it worse, very often the COD load they produce is not biodegradable, and requires specific and costly tertiary treatment. 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.

For optimised retanning, generally, the idea is to achieve a COD optimized and low- or salt-free retanning systems.

Before moving to wet finishing, it is very important to allow sufficient time for proper '*ageing*' (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 melamine) 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.

For retanning agents, the focus is firstly on those that meet the desired leather quality properties, with the best environmental performance (good biodegradability). After all, recalcitrant COD is one of the main evils in wastewater treatment. It is also 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 based mainly fossil fuel-based derivatives - is based on biodegradable polymers (produced from renewable raw materials). Reportedly, this new generation of retanning 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.

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-chambered) dyeing machines. Through-feed machines have met with rather limited acceptance by the industry, while paddle dyeing is in practice is used only for sheep skins.

The typical dyes for leather are either anionic or basic dyes. From the chemical point of view, dyestuffs are predominantly azo dyes or anthraquinone dyes. Triphenylmethane dyes may also be used. Metal complex dyes consist of a central metal ion and one or more azo dyes ligands. The central metal ion can be iron, chromium, nickel, copper, and cobalt.

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.

Emissions from the dyeing process are of comparatively minor importance, and they are mainly discharged as effluent. However, emissions to air, and residues from dyestuffs and auxiliaries (to be disposed of) cannot be disregarded.

Dyes in the effluent are difficult to remove and may result in a colouring of the receiving waters; even the presence of 10 ppm dye is visible to the human eyes. This creates undesirable aesthetic pollution and may have a negative impact on the environment (as it could influence the penetration of light in surface water). Apart from that, the used dyeing auxiliaries are not retained in leather, and discharge into to wastewater. These chemicals not only increase the COD, but also result in the release of absorbable organic halogens (AOX).

By reductive cleavage of one or more azo groups, certain azo dyes can release some of the 22 aromatic amines specified in the restricted substances 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 containing lead and cadmium are no longer used in Europe. Due to its fungicidal and bactericidal properties, high concentrations of copper inhibit degradation.

Obviously, 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 ammonium nitrogen load in effluent; in the range of 0.6 – 1.6 kg per tonne of raw hide.

Apart from avoiding hazardous dyestuffs, the main aim of **optimised 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. The negative environmental impact of dyeing process can be resolved in the following ways:

- Increasing the dye bath temperature (60°C).
- Use of short float (100% on shaved weight).
- Use of amphoteric polymers, which improve the dye intensity thereby reducing the dye consumption.
- Employment of dye fixatives and proper adjustment of dye pH to be around 3.5.
- Use of salt-free dyes.
- Use of liquid dyes.
- Use of natural polyphenol based mordant dyes.
- Use of natural dyes.

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

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, and 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.

Fatliquoring

Fatliquors are produced by emulsification of saturated or unsaturated hydrocarbons, from natural or synthetic sources. Fatliquoring is important because it replaces the natural fat (originally present in the hide/skin) 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.

Fatliquors are a significant cause of wastewater contamination, being the principal source of oil and grease, which also increase the COD and BOD load. In addition, toxic short/medium chain halogenated compounds and ethoxylate-based surfactants, are discharged from the fatliquoring process, raising the AOX values.

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

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 medium chain chlorinated alkanes. For the time being, there is still no adequate replacement for long-chain chlorinated alkanes, needed for special applications.

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. This is why there are many variations in both the type and sequence of dewatering and drying techniques.

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.

The currently prevailing dewatering techniques are sammying and/or setting out. Leather drying is an extremely complex process. A good understanding of theoretical principles and practical experience are needed to achieve the desired properties (e.g. feel, softness, etc.), 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 by immersion of moist saw dust, which was hard to control, and requires a lot of experience. Nowadays it is done in conditioning tunnels with through feed conveyers, synchronized with the pace of staking machines. Staking usually produces some area gain, but milling produces some area loss (though the leather has a very appealing grain appearance).

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

- Natural, air-drying without supply of energy (suspension drying).
- Overhead conveyors, open air.
- Air-drying with or without supply of energy.
- Suspension 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. Due to certain other constraints, the use of high (radio) frequency drying is quite limited.

Each drying method has a very specific impact on leather properties. At one end of the range is natural air drying, which apart from the low cost, lends particular softness ideal for (garment) nappa leather. Unfortunately, natural drying is directly dependent on unpredictable variations in climate and is not quite compatible with high output and tight delivery deadlines. At the other extreme of the range, 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.

Energy saving measures

Conventional energy saving measures include better insulation of pipes and drying equipment, and better monitoring and/control and optimisation 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 (used) continuously, to avoid energy losses due to reheating. 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.

Figure 9. Overhead chain conveyor drier
Source: N. Niedzwiedz

Traditionally leather is taken for staking after the conditioning stage, and with a moisture content of about 30%. More recently, a new approach with staking taking place immediately after sammying/setting (with a water content of about 50%) has been used; or alternatively after vacuum drying (being introduced). The reported advantages of the wet staking concept 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.

4.6 Finishing

The purpose of finishing is to give leather a kind of grain protection (against soiling, staining and water penetration) and 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 resistance to staining by water droplets.

To achieve these aims leather is subject to a series of processes and operations, with many variations adapted to raw material and requirements by individual customers. Also taking into account environmental, occupational safety and health (OSH) aspects and even weather conditions.

The basic components of finishes and the problems associated with finishing system are as follows.

Binders are film forming materials based on protein (e.g. casein) and resin emulsions (like acrylics, butadienes, polyurethane and vinyl acetate). The presence of solvents, toxic catalysts used in binder preparation and usage of harmful cross-linkers for protein finishes are the major environmental concerns.

Colouring agents include dyes and pigments. Both organic and inorganic pigments are used in leather finishing. The inorganic pigments containing lead and chromate are classified as toxic substances.

Crosslinking agents are predominantly based on polyisocyanates, carbodiimides, aziridines, formaldehyde, ethylamine, and formaldehyde. Most of the crosslinking agents are potential carcinogens.

Carriers are used to produce suspensions/dispersions of binders used in finish formulations. Organic solvents are used to dissolve the binders (polyurethanes) and to dilute the binders for desired concentration (e.g. methoxyproponal and isoproponal). Organic solvents are main source for of volatile organic compounds (VOC) or vanadium oxide (VOx).

Other auxiliaries, like dispersing agents, surface active agents, organic solvents, stabilizing agents, thickening agent, stabilizing agents, and plasticizers (phthalates). Some of the phthalates used in leather finishing are potential carcinogens.

The commonly used mechanical operations in the finishing department are:

- Conditioning (optimising the moisture content as described previously).
- Staking (softening and stretching of leather).
- Dry milling.
- Polishing.
- Embossing.
- Plating (flattening).

Some of these operations (e.g. staking) may be carried out: in the wet and dry finishing departments, before and/or after applying a coat, and/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 grain side is to clean and smooth it. An exception is when the product is suede; its fine nap achieved by a series of buffings with abrasive paper of different grit sizes.

Drying, usually in a tunnel with steam, gas or electric (infrared) heating, is obligatory regardless of the method of applying finishes.

Conventional coating by spraying results in considerable losses of coating material. Measured in terms of key pollution parameters (COD, BOD, and SS) and the amount of wastewater discharged at the finishing stage, polluting emissions are quite insignificant in comparison with the beamhouse and tanning department. 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. And the negative impacts of vibrations, dust and noise cannot be ignored either. All these hazards are compounded by the high risk of fire hazards, which 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 impacts of finishing operations.

Approaches for controlling VOC emissions

Water-based finishing

Water-based finishing allows organic solvents – VOC emissions – to be reduced by:

- Full replacement of organic solvents 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-based lacquer is 80-90%, in water-based lacquer emulsions the solvent content is about 40%, and in fully, 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.

For cleaner finishing selection and application of cross-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 VOC emissions, 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 less toxic and less volatile forms. 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 (to make recycling feasible) avoid mixtures.

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. HVLP 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 shoe upper leather and garment leather.

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.

Computer-aided spraying

Computer-aided spraying involves automated systems that sense area, either by a mechanical feeler, electric eye, or ultrasonic system, and controls 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.

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.

Roller coating

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.

Roller coating techniques are nowadays well established but further research and developments are ongoing. More specialised 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/ft^2, 0.09-0.46m^2); reverse coating for heavier impregnation and base coats (3-30g/ft^2, 0.28-2.79m^2).

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.

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.

Figure 10. Roller coater
Source: Gemata

4.7 Restricted Substances

Restricted substances are chemicals 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.

In the globalised 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.

At present, the **REACH (Registration, Evaluation, Authorisation and Restriction of Chemicals) Regulation** is possibly the strictest legislation, valid in the EU, but definitely has global implications. Widely known under its acronym, REACH 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 be familiar with it, and understand its main features.

Restricted substances in Annex XVII of the REACH Regulation, and of interest to tanners, include:

- Pentachlorophenol.
- Cadmium and its compounds.
- Short-chain chlorinated paraffins.
- 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 ethoxylates.
- Dimethyl fumarate
- Organotin compounds
- Azo dyes
- Lead
- Polycyclic aromatic hydrocarbons
- Phthalates

The REACH Regulation also contains a list of SVHCs. These substances are considered extremely harmful for being carcinogenic, mutagenic, toxic for reproduction, persistent, bio-accumulative and toxic, very persistent and very bio-accumulative, having endocrine disrupting properties, and/or having a combination of the mentioned properties. On 17 January 2023, the European Chemicals Agency (ECHA) released the new Candidate List of SVHCs. With the addition of nine new substances, the current list of SVHCs now contains 233 substances.

ECHA additions and lists updates are primarily the 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 the marketing their leather. International leather magazines also publish notices on the latest changes.

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 RSLs have strong impacts; driven by concerns of leading international brands, and major users of leather. Their concerns relate to corporate social responsibility image, and, more specifically, their reputation with environmental public pressure groups (and, ultimately, consumers). Sometimes it appears to be a matter of prestige, to have one's own, more detailed and stricter RSLs than competitors.

The chemicals on these lists originate from government regulations or from various ecolabel agencies, whose desire is to promote '*greener*' and/or *'safer*' products, by restricting chemicals that are perceived to be hazardous. The chemicals included in nearly all lists of restricted substances - RSL, manufacturing restricted substances lists (MRSL), etc. - are:

- Chromium VI.
- Formaldehyde.
- Azo-dyes.
- Nonylphenol and nonylphenol ethoxylates.
- VOC – organic solvents.
- Halogenated organic compounds present in various agents/auxiliaries.
- Ethylenediaminetetraacetate (EDTA) and nitrilotriacetate (NTA) - complexing agents.
- Pesticides.
- Biocides.
- Heavy metals (cadmium, lead, mercury, antimony, and arsenic).

4.8 OSH Aspects

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 the tannery's overall performance. The following 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.

Basic principles of OSH management

While exploring and implementing OSH prioritization measures, it is recommended to adopt the following approach:

- Eliminate the hazard (e.g. by substitution of hazardous agents, putting up protective fences, etc.)
- Minimize the impact of the hazard (e.g. ventilation, general cleanliness, etc.)
- Protect the worker against the hazard's impact (e.g. distribution of personal protective equipment (PPE), personal hygiene, etc.)

Experience has shown that management's commitment to improve OSH standards at work is an essential prerequisite for worker's safety.

Injuries and 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, etc.).
- Injuries caused by fire.
- Impairment of hearing and eyesight.

Main health hazards and safety risks

- Faulty designs and/or poor maintenance of machinery and equipment.
- Chemical substances applied before or during the process can affect the safety and health of personnel exposed to them (e.g. by inhalation, ingestion, skin contact, etc.)
- 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.

Malodour

The traditional perception of tanning is associated with an irritating malodour mainly caused by hydrogen sulphide, ammonia and some other compounds resulting from protein decomposition. This is only a sign of bad practices and, above all, of poor housekeeping.

Hydrogen sulphide gas (H_2S)

Hydrogen sulphide gas is evolved by the mixing of sulphide containing liming liquors/wastewater (alkaline) and tanyard effluents (acidic), especially in deep channels and pits. At higher concentrations 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 usually has a pH of 8.5-9.0).

H_2S is still by far the most frequent killer in tannery accidents, mainly in inadequately ventilated spaces, and especially in pits and channels.

Bad odour problems related to effluent treatment plants

Odours associated with wastewater 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, landscape, 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 and sulphide oxidation.
- Sludge thickening.
- Biological aeration.

- In-plant storage of the dewatered sludge.
- Temporary sludge disposal site.

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; undissociated H_2S is present only at pH below 10. Thus, it is crucial to control the pH, and (if needed) alkalis like sodium hydroxide 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 effluent treatment plant (ETP) is enclosed, and the air purified.

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 mandatory use of appropriate 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 wastewater treatment plants.

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, wastewater, circulating reagents in scrubbers, etc.
- Extraction and aeration fans.
- Air compressors.
- In-plant (forklifts) 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 include:

- Timely preventive maintenance, lubrication.
- Where applicable replacement of metal with hard plastic pinion gears.
- Low-noise spray-guns.
- Better foundations, and noise (and vibration) resilient machine mountings (e.g. for sammying and vibro-staking machines).
- Change of operating speeds, to avoid resonance.
- 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.

Material Safety Data Sheets

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.

The importance of having the key warnings and instructions in a language (and with signs) fully understood even by less skilled workers; cannot be overemphasized.

4.9 Solid waste management

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.

Depending on the emission point and waste properties, local legislation, and availability of facilities for treatment and utilisation (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.

Solid waste 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 raw wastes 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 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, providing more options for 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, such as: packaging material, barrels, paper, etc.

Solid waste utilisation

Preparation of high-grade gelatine and protein hydrolysate is an economically profitable technology for converting waste into valuable products. High grade gelatine is predominantly used in the pharmaceutical industry (to prepare capsules for drugs) and in the food industry to make jelly candies, ice creams, as thickening agent in cakes, etc. The benefits include**:**

- Complete utilisation of raw trimmings.
- High value product from waste.
- Economically profitable.

In addition, some other technologies are available to convert solid waste into valuable materials.

- Preparation of compost from hair.
- Generation of bioenergy from fleshing waste.

Cleaner 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, etc.
	ENERGY	Usual consumption/savings measures combined with the energy from renewable sources, heat pumps, etc.
	RSL	Apply the global strictest Restricted Substances List 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, etc. Noise, vibrations, malodour control; appropriate lighting and ventilation, sanitary facilities, etc. Occupational Safety and Health measures, general and personal protective equipment (PPE), including rigorously implemented and observed training.
BEAMHOUSE	**PRESERVATION/ SOAKING**	Use of green, unsalted 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.
TANYARD	**PICKLING & TANNING**	Low-salt pickling. Consider pre-tanning (wet white tanning). 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 utilisation and safe disposal.
EFFLUENT TREATMENT		On-site pre-treatment and full scale (biological) on- or off-site treatment; compliance with local discharge norms.

Table 6. Cleaner vegetable-tanning technologies at a glance

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