EUROPEAN COMMISSION

Integrated Pollution Prevention and Control (IPPC)

**Reference Document on Best Available Techniques
for the Tanning of Hides and Skins**

February 2003

EXECUTIVE SUMMARY

This reference document on best available techniques in the tannery industry reflects an information exchange carried out according to Article 16(2) of Council Directive 96/61/EC. The document has to be seen in the light of the preface, which describes the objectives of the document and its use.

Scope

The scope of the BREF for the tanning industry is based on Section 6.3 of Annex I of the IPPC Directive 96/61/EC as 'Plants for tanning hides and skins where the treatment capacity exceeds 12 tonnes of finished products per day'. The types of hides and skins are restricted to those of ovine and bovine origin, because the production capacities for any other type of raw material for the production of leather and furs are far below the threshold value in the Directive.

Structure of the industry (Chapter 1)

The tannery operation consists of converting the raw hide or skin, a highly putrescible material, into leather, a stable material, which can be used in the manufacture of a wide range of products. The whole process involves a sequence of complex chemical reactions and mechanical processes. Amongst these, tanning is the fundamental stage, which gives leather its stability and essential character. The production of raw hides and skins depends on animal population and slaughter rate and is related mainly to meat consumption.

On the world scale, significant cattle populations are to be found in the US, Argentina, the former USSR and the EU. Sheepskins originate predominantly in New Zealand, Australia, the Near East and the EU. For both bovine hides and sheepskins, the EU is a net importer, indicating the necessity of proper storage and means of transport for the typically salted raw materials.

The EU is the world's largest supplier of leather in the international marketplace. Italy is the major country in Europe in terms of establishments, employment, production and turnover. It accounts for 15 % of the world's cattle and calf leather production and 65 % of EC production. Spain ranks second and – with France, Germany and UK – accounts for most of the balance in the European leather industry. The EU's share of world markets is tending to shrink with the development of the leather industry in other regions of the world such as Asia and the Americas.

Tanneries in Europe are SMEs; only 10 of them are reckoned to employ more than 200 people. Only 1 % employ between 101 and 200 people and 8.5 % employ between 21 and 100 people. Companies are generally family businesses with a long tradition. The most important outlet for EU tanneries' production is footwear, with a share of 50 %. The clothing industry takes approximately 20 % of all finished leather produced in the EU. Leather for furniture and automotive upholstery represents some 17 % and the leather goods sector 13 % of EU tanners' output.

Leather tanning is a raw materials and labour intensive industry. Raw materials account for 50 to 70 % of production costs, labour 7 to 15 %, chemicals about 10 %, energy 3 %. EU tanners' environmental costs are estimated at about 5 % of their turnover.

The tanning industry is a potentially pollution-intensive industry. The environmental effects that have to be taken into account comprise not merely the load and concentration of the classic pollutants, but also the use of certain chemicals: e.g., biocides, surfactants and organic solvents. Tanneries in Europe usually discharge their waste water effluents to large waste water treatment plants, which are either municipal treatment plants or plants operated for large tanning

complexes. Few tanneries discharge directly to surface water. Most tanneries discharging to sewer have some form of on-site effluent treatment installed, ranging from pre-treatment to biological treatment. Of world tanneries, 80 – 90 % use chromium (III) salts in their tanning processes. The degree of toxicity of chrome is perhaps one of the most debated issues between the tanning industry and authorities.

Applied processes and techniques (Chapter 2)

The production processes in a tannery can be split into four main categories: hide and skin storage and beamhouse operations, tanyard operations, post-tanning operations and finishing operations. After the hides and skins are flayed from the carcass at the abattoirs, they are delivered to the hide and skin market, directly to the tannery or to the fellmongery. Where necessary, hides and skins are cured before transport to the tannery in order to prevent the hides and skins from putrefying. Upon delivery to the site, hides and skins can be sorted, trimmed, cured and stored pending operations in the beamhouse.

The following processes are typically carried out in the beamhouse of a tannery (see the glossary): soaking, unhairing, liming, fleshing and splitting. Typically, the following processes are carried out in the tanyard: deliming, bating, pickling, and tanning. Sheepskin tanneries may degrease the skins prior to, or after, pickling or after tanning. The tanned hides and skins are tradable intermediate products (wet-blue) as they have been converted to a non-putrescible material called leather. Processes typically carried out in post-tanning operations are: samming, setting, splitting, shaving, retanning, dyeing, fatliquoring and drying. At this stage the leather is called 'crust'. Crust is also a tradable intermediate product. Finishing operations include several mechanical treatments as well as the application of a surface coat. The selection of finishing processes depends on the specifications of the final product. Tanneries generally use a combination of the following processes: conditioning, staking, buffing, applying a finish, milling, plating and embossing.
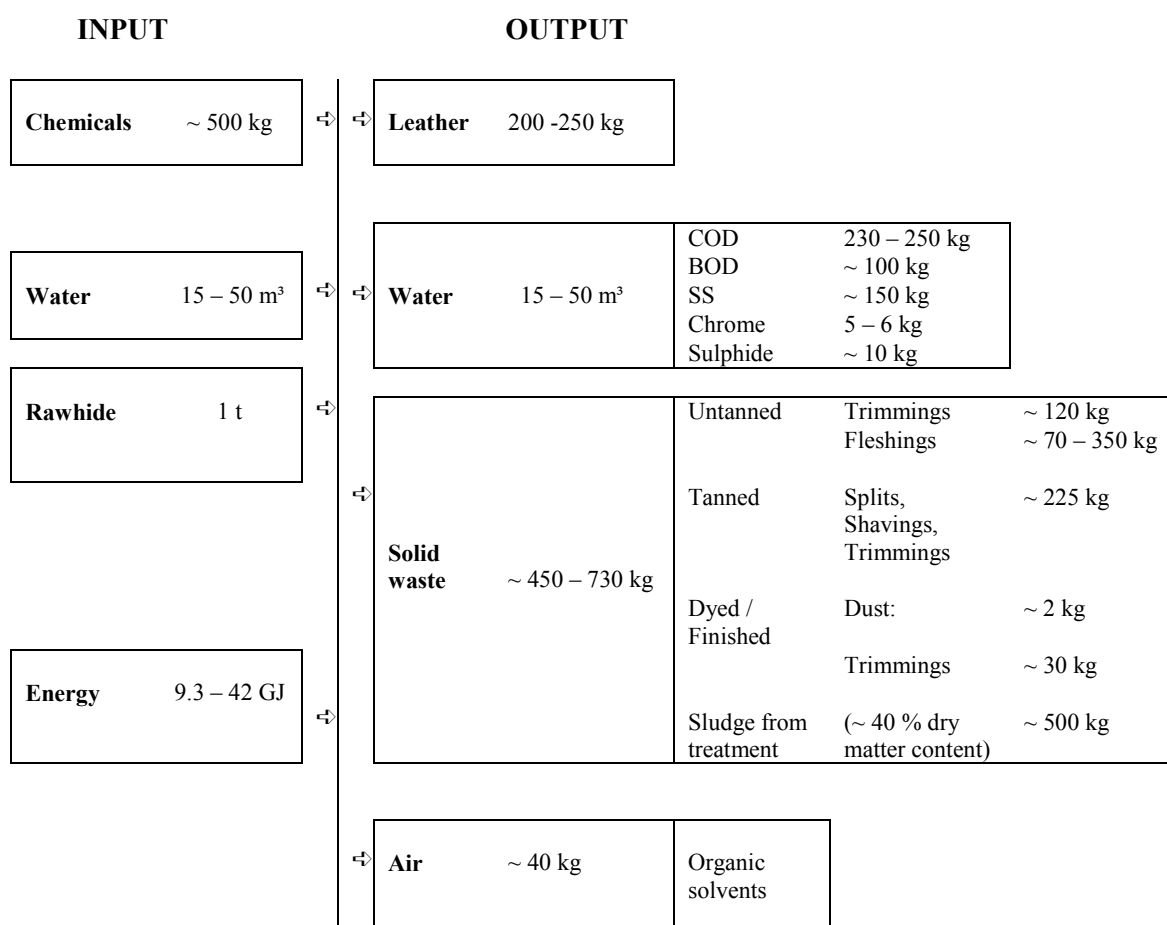
Current emission and consumption levels (Chapter 3)

Due to the wide versatility of tanneries, both in terms of the types of hides and skins used and the range of products manufactured, the reported emission and consumption levels are generally indicative. They serve to indicate the ranges of emission and consumption levels that can be seen in a wide range of tanneries. Where possible, a range for consumption and emission levels for particular processes is given. The figures strongly depend on the raw material processed, the quality and specifications of the final product, the processes chosen and local requirements.

The environmental impacts of tanneries originate from liquid, solid and gaseous waste streams and from the consumption of raw materials such as raw hides, energy, chemicals and water.

The main releases to waste water originate from wet processing in the beamhouse, the tanyard, and the post-tanning operations. The main releases to air are due to the dry-finishing processes, although gaseous emissions may also arise in all other parts of the tannery. The main sources of solid wastes originate from fleshing, splitting and shaving. A further potential source of solid waste is the sludge from the effluent treatment plant (but this is not an on-site activity in all tanneries). However, many of these wastes may be classified as by-products as they may be sold as raw materials to other industry sectors.

The following figure gives an input / output overview for a conventional (chrome-tanning) process for bovine salted hides per tonne of raw hide treated.

INPUT		OUTPUT

Chemicals ~ 500 kg ⇨ ⇨ **Leather** 200 -250 kg

Water 15 – 50 m³ ⇨ ⇨ **Water** 15 – 50 m³

COD	230 – 250 kg
BOD	~ 100 kg
SS	~ 150 kg
Chrome	5 – 6 kg
Sulphide	~ 10 kg

Rawhide 1 t ⇨

Solid waste ~ 450 – 730 kg

Untanned	Trimmings	~ 120 kg
	Fleshings	~ 70 – 350 kg
Tanned	Splits, Shavings, Trimmings	~ 225 kg
Dyed / Finished	Dust:	~ 2 kg
	Trimmings	~ 30 kg
Sludge from treatment	(~ 40 % dry matter content)	~ 500 kg

Energy 9.3 – 42 GJ ⇨

Air ~ 40 kg | Organic solvents

The following table shows the consumption level of the main process chemicals, tannage agents and auxiliary chemicals for a conventional tanning process for salted, bovine hides.

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

The most environmentally significant and most used tanning agents (with their auxiliaries) are:

Type of tannage	Tanning agents used	Auxiliaries used
Chrome tannage	Basic sulphate complex of trivalent chrome	Salt, basifying agents (magnesium oxide, sodium carbonate, or sodium bicarbonate), fungicides, masking agents (e.g. formic acid, sodium diphthalate, oxalic acid, sodium sulphite), fatliquors, syntans, resins
Other mineral tannages	Aluminium, zirconium, and titanium salts	Masking agents, basifying agents, fatliquors, salts, syntans, resins etc.
Vegetable tannage	Polyphenolic compounds leached from vegetable material (e.g. quebracho, mimosa, oak)	Pre-tanning agents, bleaching and sequestering agents, fatliquors, formic acid, syntans, resins etc.

Techniques to consider in the determination of BAT (Chapter 4)

Efficient raw material and energy usage, optimum process chemical utilisation, recovering and recycling of waste and substitution of harmful substances are important principles of the IPPC Directive. For tanneries the focal points are water consumption, efficient use and substitution of potentially harmful process agents and waste reduction within the process in conjunction with the recycling and re-use options.

Substitution of substances
Biocides may be used in the curing, soaking, pickling, tanning and post-tanning processes. Halogenated organic compounds have been used for a long time in tanneries and halogenated biocides are still sold. Sodium- or Potassium-di-methyl-di-thiocarbamate is considered to be a less environmentally significant bactericide, due to its lower persistency and toxicity levels.

Halogenated organic compounds can be substituted in almost every case, but there are exceptions. One of the exceptions addressed is the dry-degreasing of Merino sheepskins. The degreasing is carried out in closed machines with abatement for air and waste water releases; the solvent is automatically distilled and re-used. Other exceptions addressed are HOC-containing fatliquors and water-repellent agents used for waterproof leathers.

In order to reduce VOC emissions in the finishing process, water-based systems are increasingly favoured over systems based on organic solvents. Another option to reduce VOC emissions is the use of low-organic solvent finishing systems. Base coats are generally water-based. If very high topcoat standards of wet-rubbing, wet-flexing and perspiration are required, then solvent-based systems cannot always be substituted by water-based systems. In some situations, upholstery leathers for automotive and furniture use are examples of such applications. 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. Binders based on polymeric emulsions with low monomer content are used in finishings to replace the conventional polymeric products. The use of cadmium and lead in pigments is not common in European tanneries; it should be stressed, however, that any use should be discouraged.

Surfactants are used in many different processes throughout the tannery, e.g., soaking, liming, degreasing, tanning and dyeing. The most commonly used surfactant is NPE, because of its emulsifying property. The main alternatives in the leather industry are alcohol ethoxylates but, when very fatty sheepskins have to be degreased – to date – only NPE can achieve the desired result.

Complexing agents such as EDTA and NTA are brought into the water as sequestering agents. Because of their biodegradability, EDDS and MGDA are possible substitutes, but no information has been submitted about the use of those substances in the tanning process.

Ammonium deliming agents can be wholly or partially substituted by carbon dioxide deliming. The technique is easy to handle and can be automated. It requires the installation of a pressurised storage tank for CO_2, diffusers and a warming chamber that has to be checked regularly by trained personnel. With the use of CO_2 deliming, a 20 – 30 % decrease in total Kjeldahl nitrogen emissions and a 30 – 50 % reduction in BOD in the effluent from the tanning process can be achieved. A complete substitution is possible for bovine hides, but the process can be very slow with thicker hides. In deliming ovine skins, the problem with the use of CO_2 is the amount of sulphide that is released and has to be abated. The payback time of the investment costs is estimated to be 1 - 2 years.

Ammonium deliming agents can also be substituted by weak organic acids, such as lactic acid, formic acid and acetic acids. The ammonia levels in the waste water are reduced, but these agents increase the COD load. The organic agents are about 5 - 7 times more expensive than ammonium salts. Because of the increase of the COD load and because organic agents are more expensive, the viability has to be analysed carefully for each specific case.

Concerning the dyeing process, achievable techniques and technologies to reduce the impact on the environment are:

- to substitute powder dyestuffs with liquid ones, to reduce dust emissions
- to select dyestuffs and auxiliaries with lower environmental impact, e.g. substitute poor-exhausting dyestuffs with high-exhausting ones, substitute dyestuffs containing high levels of salts with dyestuffs containing a limited amount of salts, etc
- to avoid the use of ammonia as penetrating agent, as ammonia can be substituted completely in most cases
- to substitute halogenic dyes by vinyl sulphone reactive dyes to reduce the AOX load.

The use of high-exhaustion fatliquor systems will result in lower COD levels. An exhaustion of fatliquor equivalent to 90 % of the original offer can be considered achievable. Applying solvent-free or low-solvent content mixtures will result in less solvent emissions. This also applies to water-repellent agents which are preferably also free of metal salts, although the substitution of metal salts (chrome, aluminium, zirconium, calcium) as fixing agents is not applicable for very high standards of water resistance.

There is already movement away from the use of brominated and antimony-containing fire retardants. This is due to their potentially toxic combustion products. The natural successors will almost certainly be phosphate-based.

Process-integrated measures
For curing and soaking the processing of fresh (unsalted) hides will result in a significant reduction of the level of salt in the effluent. An emission load of 5 kg/t chloride when salt-free hides are processed, compared with an emission load of 65 kg/t chloride from an average soaking process using salted hides, is reported. When the hides can be processed within 8 - 12 hours after slaughter, the hides do not need to be chilled. Chilled hides have to be processed within 5 - 8 days. When longer transport times are necessary, e.g. because the hides have to be transported overseas, the energy consumption can become prohibitive because of transporting extra weight (ice) or the use of refrigerated units. In those situations the only alternative is to use salt. Fresh hides may not always be available, e.g. where a significant proportion of hides are imported or exported. The decision whether to process cooled or salted hides also depends very much on the end-product. Where salt is used in conserving the hides, various options exist to achieve a reduction of the salt input. They are mainly a question of optimising the management of the process and the input of chemicals rather than applying particular techniques.

In the unhairing and liming process for bovine hides, the use of hair-save technologies can reduce the emission levels of several parameters. Reported reduction data are:

Parameter	Reduction in waste water from the liming/unhairing section
COD	- 60 %
TKN	- 35 %
Sulphide	- 50 %

Hair-save processes for bovine hides are well known but they demand precise operating conditions and control. The technique involves manipulating the conditions of alkalinity and reducing the agent in such a way that the hair comes out of the follicle without being pulped and without destroying the hair shaft. A recirculation system with a screen is used to separate the intact hair. The hair is usually landfilled or, where possible, used as new raw material (e.g. fertiliser) elsewhere. The technique requires high capital investment for existing tanneries and may not be viable where, on the one hand, landfill is the only disposal option for the saved hair and, on the other, the waste water treatment plant can handle the high organic load of burned hair and high sludge production is not a problem because the sludge is treated and therefore suitable for re-use as, e.g. fertiliser. A careful balance has to be struck, taking each case on its merits.

A total substitution of the sulphides used as an unhairing agent for bovine hides is currently not possible in practice, but the use of enzyme preparations can reduce the consumption of sulphides. It is reported that COD and sulphide are reduced by 40 – 70 % each. This technique is not suitable for sheepskins, because the upgrading of the wool as a saleable by-product hinders the reduction in the sulphide consumption. When processing sheepskins that are already dewoolled by painting, the recycling of the spent sulphide liquor is common practice.

In most cases, lime splitting is an environmentally better option than splitting after tanning (blue splitting). Lime splitting allows the grain layer and the flesh layer to take different routes – e.g. different tannages or different end uses – and the split may be used for the manufacture of gelatine or collagen casings for foodstuffs. Following lime splitting the consumption of all chemicals and water in the subsequent processes is reduced, because only the parts of the hides processed into leather are treated. The structure and chemical nature of the liming process for a lime splitting operation involves a higher degree of penetration and swelling of the hide fibres. This is not suitable for making firmer leathers, such as shoe upper leather. Limed pelts are more difficult to handle than either tanned or crust leathers and therefore lime splitting is less accurate than blue splitting and is not suitable if a more uniform and accurate thickness is needed in the final product.

Not enough information is available about sheepskin degreasing to enable a conclusion to be drawn on whether the substitution of solvent degreasing systems by aqueous degreasing systems will result in a better environmental performance. This is because it is difficult without further information to compare the environmental impact of the use of organic solvent with that of the use of surfactants.

Spent pickle liquors from the pickling process can be recycled into the pickling process or re-used in the tanning process in order to reduce the amount of salt and effluent discharged to sewer. Another technique to reduce the amount of salt and effluent is the use of a short pickle float. Some processes use an average pickling float of about 100 %; this can be reduced to 50 - 60 %, which means that the use of 0.5 - 0.6 m^3 water per tonne fleshed pelt is achievable.

Although <u>tanning</u> can be performed with different tanning agents, about 90 % of leathers are tanned with chromium salts. Another well-known process is vegetable tanning. The vegetable tanning process is not seen as an alternative to the chrome tanning process, because first of all they are two completely different processes to produce different products. Another reason is that research has shown that selection of a certain tanning agent (chromium or a vegetable agent) will not in itself reduce the environmental consequences of the process. A comparison of chromium with other mineral tanning agents is not possible because the environmental impact of the latter tanning agents has not been assessed in enough detail. In chrome tanning, amongst others, the following techniques are discussed:

1. Increasing the efficiency of chrome-tanning. The conventional chrome tanning carried out in long floats is characterised by poor exhaustion; 30 – 50 % of the chrome applied being lost with the waste water. The chrome uptake can be increased up to 80 % through careful control of pH, float, temperature, time and drumspeed.

2. High-exhaustion chrome tanning methods. In this technique the tanning agents used are modified to enhance uptake up to 90 %. In conventional tanning (without chrome recovery) 2 - 5 kg/t raw bovine hides of chrome salts are released via the spent liquors; with high-exhaustion chrome tanning this quantity can be reduced to 0.05 - 0.1 kg/t raw bovine hides. Because of the low concentration, the remaining chrome in the effluent is not recovered.

3. For the conventional chrome tanning process, chrome recovery through precipitation and separation; as mentioned above, chromium from high-exhaustion chromium processes is not recovered. Chrome recovery is from the chemical point of view a simple process with excellent environmental results, but it needs careful analytical control and it requires special equipment. Chrome recovery is applied by individual tanneries (e.g. in Germany), whereas Portugal and Italy each have one common chrome-recycling unit, although the Italian one is available only for the tanneries situated in the Santa Croce tanning area. The recovered chrome sulphate can be recycled into the tanning process by replacing 20 – 35 % of the "fresh" added chrome tanning salt. Certain types of leathers (e.g. split) can be tanned with 100 % recovered chromium. Efficiencies of 95 to 99.9 % of chrome precipitation are reported; concentrations, measured as total chrome in a daily composite sample, after sedimentation or flotation of the separate chrome-containing effluent (before mixing) of 1 - 2 mg/l and even < 1 mg/l can be achieved. A survey in Italy of the economic costs has revealed that for a single medium-to-large tannery, the installation of a chrome recovery unit can cost about EUR 520000 (estimated value). Based on Greek conditions (year 1990 - 1991), the maximum payback period for installing a chrome recovery unit is 1.6 years. In India two different examples of running a chrome recovery unit show payback periods of 1 and about 1.6 years (reference years 1994 and 1995).

Vegetable tanning systems with a high degree of tanning exhaustion (~95 %) are available. Common systems are the counter-current (pit-system) and drum tanning with recycling of the tanning material. When (in combination with vegetable tanning) syntans and resins are used, products with low-phenol, low-formaldehyde and low acrylic acid monomer content are the best alternatives.

In the post-tanning operations of <u>retanning, chrome fixation and neutralisation,</u> careful control of processing parameters such as the levels of chemical inputs, the reaction time, the pH and the temperatures can enhance the exhaustion of the post-tanning treatment agents. Chrome fixation of the tanning agents can be improved by allowing the necessary ageing time for the tanned leather prior to the post-tanning processes. An optimum input of the neutralising salts ensure that the pH of the liquor and the leathers by the end of the process are close, ensuring either no or low unused salt discharged to waste water.

Forced <u>drying</u> of leather is among the most energy intensive processes in the tannery. Natural air-drying does not consume energy but is not applicable under all circumstances, as it requires time and favourable climate conditions. Considerable reductions in energy consumption can be achieved by optimising the mechanical dewatering processes prior to drying.

<u>Applying a surface coat</u> on the leather is an important source of VOC emissions. The use of roller coating, curtain coating, HVLP spray guns and air-less spray guns result in less VOC emissions compared to conventional operations (with an efficiency as low as 30 %). HVLP, or airless spraying raises the efficiency to 75 %. But conventional spraying techniques have to be applied to achieve very thin finishes on, e.g. aniline and aniline-type leather. Suitable abatement techniques for VOC emissions are wet scrubbing, absorption, bio-filters, cryogenic removal or incineration.

Water management and treatment
For bovine hides it is reported that a water consumption of 40 - 50 m^3/t raw hide can be cut to 12 - 30 m^3/t, if the tannery operates efficient technical control and good housekeeping. For the processing of calf skins, about 40 m^3/t and sometimes more is needed. There are several techniques or technologies to improve the efficiency of water use. The first step involves optimisation of water consumption and lowering the consumption of chemicals used in the process and in the waste water treatment. It is found that in tanneries with poor water management only 50 % of the water consumed is actually used in the process. Running water washes is one of the major sources of water wastage. In those cases it is important to <u>improve the matching of water flow to the requirements of the process and to use 'batch' versus 'running water' washes.</u> The use of <u>short-float techniques</u> can be achieved either by modifying the equipment to utilise short floats, or by installing modern tannery machines. With a combination of batch washing and short floats, savings of water consumption up to 70 % can be achieved, compared with a conventional process. <u>The re-use of waste water</u> can decrease water consumption considerably, but tanners are reluctant to re-use it because of the risk that residual chemicals or other contents in the water will damage the hides.

In order to carry out <u>effluent treatment</u> in the most effective manner, flow segregation is useful to allow preliminary treatment of concentrated waste water streams, in particular for sulphide- and chrome-containing liquors. And although a reduction of water consumption does not reduce the load of many pollutants, concentrated effluents are often easier and more efficient to treat. Where segregation of flows is not possible, thorough mixing of chrome-bearing effluents and other effluent streams improves the efficiency of the effluent treatment plant because the chromium tends to precipitate out with the protein during pretreatment. The treatment of chrome-containing liquors has already been discussed, so only the treatment of sulphide-containing effluent will be discussed here. It is common practice to keep sulphide-containing effluent from the beamhouse separate and at a high pH until the sulphide is treated, because at a pH lower than 9.0 the formation of toxic hydrogen sulphide gas can occur. The sulphides in the deliming and pickle liquors can easily be oxidised in the drum by adding hydrogen peroxide, sodium metabisulphite or sodium bisulphite. The associated emission level after treatment of sulphide is 2 mg/l in a random sample in the separate effluent. Where segregation of sulphide-bearing liquors is not possible, the sulphides are generally removed by means of precipitation with iron (II) salts and aeration. A disadvantage of this precipitation is the generation of high volumes of sludge. The levels that can be achieved in treating the mixed effluent are - depending on the mixing rate – 2 mg S^{2-}/l and 1 mg Cr_{total} /l (e.g. if 50 % of the mixed effluent consist of the chrome-bearing effluent and 50 % of the mixed effluent consist of the sulphide-bearing effluent, emission levels for the total effluent will be 1 mg S^{2-}/l and 0.5 mg Cr_{total} /l).

Usually the first treatment of the raw effluent is the <u>mechanical treatment</u> that includes screening to remove coarse material. Up to 30 – 40 % of gross suspended solids in the raw waste stream can be removed by properly designed screens. Mechanical treatment may also include skimming of fats, grease, oils and gravity settling. After mechanical treatment, physico-chemical treatment is usually carried out, which involves the chrome precipitation and sulphide

treatment described above. Coagulation and flocculation are also part of this treatment to remove a substantial percentage of the COD and suspended solids.

Effluent from tanneries after mechanical and physico-chemical treatment is generally easily biodegradable in standard aerobic biological treatment plants. The data in the table below represent typical values for tannery waste water treatment efficiency for conventional process liquors for production of finished leather from raw material.

Parameter	COD		BOD$_5$		SS		Chrome	S^{2-}	TKN	
% or mg/l	%	mg/l	%	mg/l	%	mg/l	mg/l	mg/l	%	mg/l
PRETREATMENT										
Grease removal (dissolved air flotation)	20 - 40									
Sulphide oxidation (liming and rinsing liquors)	10							10		
Chromium precipitation							1 - 10			
PRIMARY TREATMENT										
Mixing + Sedimentation	25 - 35		25 - 35		50 - 70		20 - 30		25 - 35	
Mixing + Chemical treatment + sedimentation	50 - 65		50 - 65		80 - 90		2 - 5	2 - 10	40 - 50	
Mixing + Chemical treatment + flotation	55 - 75		55 - 75		80 - 95		2 - 5	2 - 5	40 - 50	
BIOLOGICAL TREATMENT										
Primary or chemical + Extended aeration	85 - 95	200 - 400	90 - 97	20 - 60	90 - 98	20 - 50	<1	<1	50	150
Primary or chemical + Extended aeration with nitrification and denitrification	85 - 95	200 - 400	90 - 97	20 - 60	90 - 98	20 - 50	<1	<1	80 - 90	30 - 60

Post-purification- sedimentation and sludge handling are the last step in waste water treatment. With sedimentation the sludge in the waste water treatment plant is separated from the water phase by gravity settlement. After dewatering this sludge by means of filter presses, a sludge cake with up to 40 % dry solids can be achieved, whereas belt presses produce a sludge cake with up to 20 – 25 % dry solids. Centrifuges achieve up to 25 – 45 % dry solids and thermal treatment up to 90 % dry solids. Energy is an important factor in these processes.

European tanneries' waste water effluent is treated in many different ways. There are situations in which an individual tannery applies all the above-described waste water treatment steps on site. In other situations an individual tannery may apply (on site) only pre-treatment or a part pre-treatment or no treatment at all, sending the effluent to a communal effluent treatment plant; these may be jointly owned and are usually dedicated to processing tannery effluent. A tannery might also treat its effluent partly on site, but then discharge to a municipal sewage works and make some financial arrangement for effectively sharing the role of effluent treatment.

Waste management and treatment

The above-mentioned process-integrated measures will directly or indirectly also prevent the arising of waste. It is also important to treat waste that cannot be prevented in such a way, e.g. by separating of specific fractions, that efficient treatment is possible. Several options for the recycling or re-use of organic waste fractions are available:

- gelatine and glue from untanned wastes can be produced; in some Member States untanned wastes are processed to produce sausage casings
- tallow recovery from raw trimmings, fleshings and splits is performed in rendering plants. Limed trimmings, fleshings and splits may need pre-treatment before conversion
- fat can be separated and recycled, but this is practicable only in exceptional cases
- recovery of protein (protein hydrolysate) from e.g. splits, for conversion into fertiliser
- recovery of collagen from e.g. lime trimmings and splits. Collagen has various uses as meat and bakery product additives, in pharmaceuticals and cosmetics, and as additives to rubber products
- tanned wastes can be used in leather fibreboard production.

Further treatment options for organic waste and sludges from waste water treatment are composting, recycling in agriculture, anaerobic digestion, landfill and thermal treatment. The applicability of the techniques in sludge disposal depends on the composition of the sludge, especially the chrome content, and has to be assessed on a case-by-case basis, taking into account national regulations and strategies.

Other residues may require further (off-site) treatment. This includes the following wastes: salt, organic solvents and chemicals used as process chemicals, auxiliaries, cleanser, sludges from finishing, solids from air abatement (activated carbon, sludges from wet scrubbers) and packaging material.

Air abatement

Releases to air can arise from various process steps carrying different substances and particulates. Preventative measures and end-of-pipe techniques are available to prevent or abate emissions from organic solvents, ammonia, hydrogen sulphide, sulphur dioxide, total particulate together with the odour which might arise from those substances.

Energy

Very little information is available on energy use in tanneries. For collecting more information it is necessary to record the energy consumption for electricity, heat (steam and heating) and compressed air, particularly for the units with highest consumption, such as waste water treatment and drying procedures.

Noise, vibrations

There is no information at all on this subject.

Monitoring

Standardised analysis and measurement techniques exist for monitoring waste water effluent parameters, but it is important to use the same units to make those data comparable. In this document data are sometimes expressed as concentrations or in relation to the leather produced or the raw hides input. This makes it very difficult to compare emission data and the performance of the techniques used. Information about the monitoring of gaseous emissions, waste, energy and noise is not available.

Decommissioning

General decommissioning operations are described, but information specific to the decommissioning of tanneries is not available.

BAT in tanning industry (Chapter 5)

Management & good housekeeping

Operation and maintenance

Commitment of tannery management is a prerequisite for good environmental performance. Technology by itself is not sufficient; it needs to go together with good housekeeping measures.

A key to good performance is awareness of the inputs to and outputs of the process with regard to the characteristics of the materials, the quantities, and their potential environmental impacts. Criteria that ensure a better environmental performance can then be taken into account as well as technological criteria that focus on the properties of the end product.

Reduction of spills, accidents, water wastage and chemical usage is achieved by the choice of appropriate techniques, good maintenance and operation control – by monitoring and adjusting process parameters – and good staff training.

BAT is to implement provisions for segregation of waste streams in order to allow for recycling of certain waste streams. These provisions include training of personnel.

Accident prevention

Chemicals used in the tannery should be stored and handled in such a way as to minimise the risk of spillages and accidents. BAT is:

- to store chemicals appropriately. Basic requirements are: separation of chemicals which could react to generate dangerous emissions; labelling and use of appropriate containers; adaptation of storage rooms and areas to provide proper ventilation and soil protection, especially for halogenated and non-halogenated organic solvents and waste containing these substances
- to implement measures such as information and training of personnel; technical provisions for safety, personal protection and organisation to minimise handling of potentially harmful agents:
  - handling and accidental spillage might lead to unforeseen chemical reactions such as, e.g., the release of sulphides
  - protection has to be provided against releases of harmful substances. To substitute organic solvents and other agents where possible
  - to ensure that Material Safety Data Sheets for all chemicals and preparations used and stored on site are available and easily accessible
- to provide first-aid facilities and to establish evacuation procedures
- to make contingency plans for avoiding shock loads to sewage treatment plants
- to monitor the operation of end-of-pipe abatement measures
- to have clean-up materials readily available for dealing with spillages
- to ensure efficient capture of waste water from clean-up operations
- to keep records of accidents and incidents.

Substitution of chemicals

For the substitution of chemicals, BAT is:

- to substitute less harmful chemicals for agents and auxiliaries that are known to be harmful to the environment
- to maintain an inventory of inputs and outputs, their fate in processes and releases
- to measure appropriate parameters to monitor the environmental releases
- to exercise responsible management including e.g. awareness of the chemicals applied in the process (including ready-made supplies), staff training, information and safety measures for workforce and environment.

In Table 5.1, substances to be substituted are listed in the left column. BAT substitutes are listed in the right column.

SUBSTANCE	BAT SUBSTITUTE
Biocides	• Products with the lowest environmental and toxicological impact, used at the lowest level possible e.g. sodium- or potassium-di-methyl-thiocarbamate
Halogenated organic compounds	• They can be substituted completely in almost every case. This includes substitution for soaking, degreasing, fatliquoring, dyeing agents and special post-tanning agents - Exception: the cleaning of Merino sheepskins
Organic solvents (non-halogenated) The finishing process and the degreasing of sheepskins are the major areas of relevance.	Finishing: • Aqueous-based finishing systems - Exception: if very high standards of topcoat resistance to wet-rubbing, wet-flexing and perspiration are required • Low-organic solvent-based finishing systems • Low aromatic contents Sheepskin degreasing: • The use of one organic solvent and not mixtures, to facilitate possible re-use after distillation
Surfactants APEs such as NPEs	• e.g. alcohol ethoxylates, where possible
Complexing agents EDTA and NTA	• EDDS and MGDA, where possible
Ammonium deliming agents	• Partially with carbon dioxide and/or weak organic acids
Tanning agents - Chromium - Syntans and resins	• 20 – 35 % of the fresh chrome input can be substituted by recovered chrome • products with low formaldehyde, low phenol and low acrylic acid monomer content
Dyestuffs	• De-dusted or liquid dyestuffs • High-exhausting dyes containing low amounts of salt • Substitution of ammonia by auxiliaries such as dye penetrators • Substitution of halogenic dyes by vinyl sulphone reactive dyes
Fatliquoring agents	• Free of agents building up AOX - Exception: waterproof leathers • Applied in organic solvent-free mixtures or, when not possible, low organic solvent mixtures • High-exhausting to reduce the COD as much as possible
Finishing agents for topcoats, binders (resins) and cross-linking agents	• Binders based on polymeric emulsions with low monomer content • Cadmium- and lead-free pigments and finishing systems
Others: - Water repellent agents - Brominated and antimony-containing flame retardant	• Free of agents building up AOX - Exception: waterproof leathers • Applied in organic solvent-free mixtures or, when not possible, low organic solvent mixtures • Free of metal salts - Exception: waterproof leathers • Phosphate-based flame retardants

Table 5.1: BAT for the substitution of chemicals

Process-integrated BAT measures

With the implementation of BAT in the process rather than choosing an end-of-pipe abatement, improvement is gained with regard to:

- consumption of chemicals
- substitution of hazardous chemicals by less hazardous ones
- water and waste management
- emissions to air
- energy savings.

It is therefore essential in selecting BAT that the equipment used, e.g. processing vessels, the dosage of chemicals and the process control devices are also examined for their efficiency and compatibility with the above-mentioned goals. These pre-requisites are also discussed in the section on Management & Good housekeeping

Table 5.2: (Process-integrated BAT Measures) describes BAT – where possible – for every separate process unit in a tannery. In two cases no consensus was reached in the TWG.

The first case is the recycling of the pickle liquor. Spent pickle liquors from the pickling process can be recycled into the pickling process or be re-used in the tanning process in order to reduce the amount of salt and effluent discharged to sewer. Experts representing one Member State and some experts representing industry in the TWG did not fully support this view, because it can have a negative effect on the quality of leather, especially aniline leather. A split view is recorded.

The second case is about chrome tanning. The majority of the TWG agreed that the best available technique for chrome tanning is to increase the efficiency of the chrome tanning process through careful control of pH, float, temperature, time and drumspeed, all in combination with chrome recovery through precipitation for waste water streams containing total chrome > 1 g/l. They also agreed that, when chrome recovery is not possible (either individually or in a common plant), then high-exhaustion tanning methods are the best-performing alternative. Experts representing one Member State and some experts representing industry do not fully support this BAT. Their opinion is that a separate treatment of chrome-containing liquors is not currently economically viable for a large part of the European leather industry, particularly in situations where a common specialised treatment plant is not available. Although they agree that BAT is to increase the efficiency, they assert that chrome recovery cannot be BAT when common specialised recovery plants are not available. Nor, in their view, can chrome recovery be BAT when the recovered chrome cannot be recycled into the tanning process. This is the case when high quality leathers are produced, because high quality leather can only be produced with "fresh" chrome, not with any addition of recovered chrome or with high-exhaustion chrome tanning agents. In their view, chrome recovery is not economically viable in this situation. A split view is recorded.

	PROCESS UNIT	BAT is:
BEAMHOUSE	**Curing and soaking**	• To process fresh hides as far as they are available Exceptions: - When long transport time is necessary (max 8 - 12 hours for fresh, unchilled hides; 5 - 8 days if a cooling chain of 2 °C is maintained) - For certain types of end-products - Sheepskins, calf skins • To reduce the amount of salt used as far as possible.
	Unhairing & liming	• To use hair-save technology, but economics can be an issue for existing plants when re-use of the saved hair is not possible • To reduce sulphide consumption by the use of enzyme preparations; not for sheepskins • To recycle spent liquors only when processing sheepskins, which are dewoolled by painting
	Splitting	• To use lime splitting Exceptions: - When the starting material is wet blue - When a firmer leather has to be produced (e.g. shoe-leather) - When a more uniform and accurate thickness is needed in the final product • To maximise the use of split
TANYARD OPERATIONS	**Deliming and bating**	• To make a partial substitution of ammonium salts with CO_2 and/or weak organic acids
	Sheepskin degreasing	• To optimise wet degreasing using surfactants, with or without organic solvents • Closed machines with abatement for air and waste water releases when organic solvents are used to degrease skins in dry state
	Pickling	• To use partial recycling or re-use of pickle liquors **(*) split view; see below** • To use a volume of floats in the range of 50 – 60 % (based on fleshed weight) for ovine skins and bovine hides in order to reduce salt consumption
	Tanning **(**) split view; see below**	• To increase the efficiency of the chrome tanning process through careful control of pH, float, temperature, time and drumspeed, all in combination with chrome recovery through precipitation for waste water streams containing $Cr_{total} > 1$ g/l **(**)** • To use high-exhaustion tanning methods where chrome recovery is not possible **(**)** • To maximise exhaustion of the vegetable tanning liquor with counter-current (pit system) or recycling (drum tanning)
POST-TANNING OPERATIONS	**Retanning, chrome fixation and neutralisation**	• To enhance exhaustion of post-tanning treatment agents and fixation of tanning agents in the leather • To reduce the salt content of spent liquors
	Dyeing	• To enhance exhaustion of dyestuffs
	Fatliquoring	• To enhance exhaustion of fatliquor
	Drying	• To optimise mechanical dewatering prior to drying where possible
	Applying a surface coat	• To use roller coating • To use curtain coating • To use HVLP spray guns • To use airless spray guns Exception for all four above-mentioned techniques: - When very thin finishes are applied, e.g. on aniline and aniline-type leather

(*) split view on Pickling: The majority in the TWG agreed that partial recycling or re-use of pickle liquors is BAT. Experts representing one Member State and some experts representing industry in the TWG did not fully agree because in their view an exception has to be made. In their view BAT is:
• To use partial recycling or re-use of pickle liquors with an exception for high quality leathers.

(**) split view on Tanning: Experts representing one Member State and some experts representing industry do not fully support this BAT. Their opinion is that a separate treatment of chrome-containing liquors is not currently economically viable for a large part of the European leather industry, particularly in situations where a common specialised treatment plant is not available. In their view BAT is:
• To increase the efficiency of the chrome tanning process through careful control of pH, float, temperature, time and drumspeed
• To use chrome recovery through precipitation
   Exceptions: - When common specialised recovery plants are not available
                     - When the recovered chrome cannot be recycled in order to produce high quality leathers
• To use high-exhaustion tanning methods
   Exception: - High quality leather production.

Table 5.2. Process-integrated BAT measures

Water management and treatment

BAT for water management and treatment comprises:

- reduction of water consumption
- good housekeeping
- process-integrated measures (listed in Table 5.2) and, finally,
- effluent treatment.

Within these areas, BAT is:

GOOD HOUSE-KEEPING AND PROCESS - INTEGRATED MEASURES	To improve the matching of water flow to the requirements of the process
	To use 'batch' versus 'running water' washes
	To modify existing equipment to use short floats
	To use modern equipment for short floats
	To re-use waste water in less critical processes
	To recycle or re-use process liquors where possible (see Table 5.2)
EFFLUENT TREATMENT	To keep sulphide-containing effluent from the beamhouse separate and at high pH until the sulphide is removed. The associated emission level after treatment is 2 mg S^{2-}/l in a random sample in the separate effluent. After the sulphide is removed (on site or in a jointly used dedicated treatment plant) the effluent can be mixed. **(***) split view; see below**.
	To collect chromium-containing partial effluent (e.g. from tanning and samming) with a concentration of $Cr_{total} > 1$ g/l separately and send it for chrome recovery. Chrome recovery can be done on or off site **(****)**
	To treat (on or off site) chromium-containing effluent with a concentration of $Cr_{total} < 1$ g/l in combination with other effluent **(****)**
	To use mechanical treatment (on or off site)
	To use biological treatment (on or off site)
	To use post-purification sedimentation and sludge handling (on or off site)

(***) split view on sulphide and chromium treatment:
Industry supports the conclusion that separate treatment of sulphide-containing effluent is BAT, but in their view the mixed treatment – on site – of sulphide- and chrome-containing effluent is also BAT. The arguments are the following:
- lower costs
- less chemicals have to be used
- the technique is simple and reliable
- emission levels for the total effluent – depending on the mixing rate – of 2 mg S^{2-}/l and 1 mg Cr_{total} /l can be achieved. (e.g. if 50 % of the mixed effluent consist of the chrome-bearing effluent and 50 % of the mixed effluent consist of the sulphide-bearing effluent, emission levels for the total effluent will be 1 mg S^{2-}/l and 0.5 mg Cr_{total} /l).

(****) see split view on chrome recovery in note **(**)** on Table 5.2 **and** see split view on separate treatment in note **(***)** on this table.

Table 5.3: BAT for water management and treatment

For all the techniques mentioned in Table 5.3, it has to be decided site-specifically whether primary, secondary or even tertiary treatment is more environmentally and economically efficient on site or in a jointly used dedicated waste water treatment plant. It can also be efficient for a tannery to treat its effluent partly on site and then discharge it to a municipal sewage treatment works. The removal of particular substances from the waste water effluents e.g., biocides, halogenated organic compounds, surfactants and other process agents that need specific treatment, also has to be decided on a case-by-case basis.

Waste management and treatment

In waste management and treatment, BAT, in order of priority is:
- prevention
- reduction
- re-use
- recycling / recovery
- thermal treatment for certain types of waste.

Landfill is not BAT, although in some cases it is the only option available.

A large amount of waste, in particular organic waste, is inherent to production in tanneries. Both organic waste fractions and other residues can be prevented and reduced to a large extent by using BAT in the process units. Recycling options are numerous and carried out on site and off site. The potential for recycling should be exploited by ensuring segregation of waste. Of equal importance is commercialisation of wastes as by-products and co-operation between tanners to make recycling and re-use options economically feasible.

Waste that arises in the tannery has to be handled and stored in such a way as to avoid leaching, odour problems and emissions to air.

In Table 5.4 re-use, recycling / recovery and treatment options are given in the first column and waste fractions that can be used for the respective option are listed in the second column. BAT is to identify opportunities to implement these measures where feasible, ensuring that actions are carried through.

Re-use / recycling / recovery and treatment	Type of waste
Leather production	Splits
Leather fibre board production	Tanned wastes in general, e.g., splits, shavings, trimmings
Small leather goods etc.	Splits and tanned trimmings
Filling material, wool	Hair and wool
Gelatine and/or hide glue	Raw trimmings, green and limed fleshings and splits
Sausage casings	Untanned splits
Fat recovery	Raw trimmings, green and limed fleshings
Protein hydrolysate	Hair, raw and limed trimmings, green and limed fleshings, green, limed and tanned splits and shavings
Collagen	Limed trimmings and splits
Agriculture and fertiliser	Hair for the nitrogen content, residues from composting and anaerobic digestion, sludges from waste water treatment. The legal requirements for the application of waste to land require sophisticated waste separation and treatment of the various fractions
Composting	Hair, green and limed fleshings, green, limed and tanned splits and shavings, fats, grease and oil; sludges from waste water treatment
Anaerobic digestion	Hair, raw trimmings, green and limed fleshings, green, limed splits, fats, grease and oil; sludges from waste water treatment
Thermal treatment	Fats, grease, mixtures of non-halogenated organic solvents and oil
Recycling of organic solvents	Organic solvents (no mixtures)
Regeneration of air abatement filters	Activated carbon filters
Re-use and recycling of packaging material by feeding it back to the supplier via an appropriate recycling system	Container, pallets, plastic, cardboard

Table 5.4: BAT for waste management

Air abatement

BAT is to prevent the generation of odours through process control, maintenance and proper handling and storage of raw hides and wastes, in some cases requiring the installation of filters, e.g. at waste water treatment plants or for VOC releases.

BAT to prevent releases of e.g. hydrogen sulphides, ammonia, VOCs and dust, are mentioned in Table 5.1, Table 5.2 and/or Table 5.3. In addition, the following end-of-pipe measures are BAT for the abatement of hydrogen sulphides, ammonia and VOCs in particular:

- wet scrubbing, for example, to abate ammonia and hydrogen sulphides from deliming, pickling and dyeing
- wet scrubbing, absorption, bio-filters, cryogenic removal or incineration to abate VOC from degreasing, drying and finishing
- wet scrubbing, absorption or bio-filters to abate various releases from waste water treatment.

Techniques exist that are suitable for the abatement of a combination of releases, e.g. wet scrubbing for removal of aerosols, organic solvents and odours. Too little information is available to come to detailed conclusions on BAT.

Energy

BAT is to record the energy consumption for electricity, heat (steam and heating) and compressed air, particularly for the units with the highest consumption, such as waste water treatment and drying procedures.

Operators therefore need a system for monitoring energy usage and performance. The scale of this needs to match the level of energy usage, but the following activities should be considered:

- recording actual energy usage, split by energy type and major end-uses, on a specified and appropriate regular basis (e.g. hourly, daily, weekly, etc.)
- generating energy performance indicators (historical energy performance or normalised to an indicator of production/external temperature/building occupancy etc.)
- monitoring energy performance, including mechanisms to alert the operator to significant variations from predicted energy performance
- ensuring appropriate investigative and corrective action is taken, and recorded, in response to variations
- delivering concise, appropriate and timely energy performance information to all individuals with identified responsibilities for energy management
- setting, reviewing and revising performance targets.

Too little information is available to come to detailed conclusions on BAT.

Decommissioning

In general, BAT for decommissioning of a tannery includes all provisions and measures that have to be taken into account to prevent environmental impact during and after the shut-down process. The aim is to prevent impact on the environment in general, and in particular the immediate surroundings, by activities that have to be carried out to leave the area in such a way that it can be re-used (depending on the enforcement bodies' decision on land use planning). This includes activities from the shut-down of a plant itself, the removal of buildings, equipment, residues etc. from the site, and contamination of surface water, groundwater, air or soil. Too little information is available to come to detailed conclusions on BAT.

Concluding remarks (Chapter 7)

Level of consensus

This BREF has met support from most of the TWG members, although on three BAT conclusions the following split views had to be noted:

1. The majority in the TWG agreed that partial recycling or re-use of pickle liquors is BAT, but experts representing one Member State, and some experts representing industry in the TWG, did not fully agree. In their view BAT is to use partial recycling or re-use of pickle liquors with an exception for high quality leathers.

2. Experts representing one Member State and some experts representing industry do not fully support this BAT conclusion on chrome recovery. Their opinion is that a separate treatment of chrome-containing liquors is not currently economically viable for many individual tanneries where a common specialised treatment plant is not available.

3. Industry supports the conclusion that separate treatment of sulphide-containing effluent is BAT, but in their view also the mixed treatment – on site – of sulphide- and chrome-containing effluent is BAT.

Recommendations for future work

For future BREF reviews, all TWG members and interested parties should continue to collect data on the current emission and consumption levels and on the performance of techniques to be considered in the determination of BAT. For the review, it is also important to collect more data on the achievable emission and consumption levels and the economics of all tanning processes and tanning agents. Information on reference plants and actual performance data are also scarce; for the revision of this document the missing information should be provided. Apart from these general areas, mention have been made in the body of the BREF of more specific areas in which data and information are lacking.

Recommendations for future R&D work

The previous paragraph highlights many areas for attention in future work. Much of the future work concerns the collecting of information to be used in reviewing this BREF. Proposals for future R&D work focus on the techniques that are identified in this BREF, but are too expensive or cannot be used yet because of the high risk of damaging the hides, the skins and/or the leathers. Proposals for future research into new techniques for tanneries, including those relevant to water and sludge, solid waste, air and soil are also addressed in Chapter 7.

The EC is launching and supporting, through its RTD programmes, a series of projects dealing with clean technologies, emerging effluent treatment and recycling technologies and management strategies. Potentially these projects could provide a useful contribution to future BREF reviews. Readers are therefore invited to inform the EIPPCB of any research results which are relevant to the scope of this document (see also the preface of this document).

PREFACE

1.   Status of this document

Unless otherwise stated, references to "the Directive" in this document means the Council Directive 96/61/EC on integrated pollution prevention and control. As the Directive applies without prejudice to Community provisions on health and safety at the workplace, so does this document.

This document forms part of a series presenting the results of an exchange of information between EU Member States and industries concerned on best available technique (BAT), associated monitoring, and developments in them. It is published by the European Commission pursuant to Article 16(2) of the Directive, and must therefore be taken into account in accordance with Annex IV of the Directive when determining "best available techniques".

2.   Relevant legal obligations of the IPPC Directive and the definition of BAT

In order to help the reader understand the legal context in which this document has been drafted, some of the most relevant provisions of the IPPC Directive, including the definition of the term "best available techniques", are described in this preface. This description is inevitably incomplete and is given for information only. It has no legal value and does not in any way alter or prejudice the actual provisions of the Directive.

The purpose of the Directive is to achieve integrated prevention and control of pollution arising from the activities listed in its Annex I, leading to a high level of protection of the environment as a whole. The legal basis of the Directive relates to environmental protection. Its implementation should also take account of other Community objectives such as the competitiveness of the Community's industry thereby contributing to sustainable development.

More specifically, it provides for a permitting system for certain categories of industrial installations requiring both operators and regulators to take an integrated, overall look at the polluting and consuming potential of the installation. The overall aim of such an integrated approach must be to improve the management and control of industrial processes so as to ensure a high level of protection for the environment as a whole. Central to this approach is the general principle given in Article 3 that operators should take all appropriate preventative measures against pollution, in particular through the application of best available techniques enabling them to improve their environmental performance.

The term "best available techniques" is defined in Article 2(11) of the Directive as "the most effective and advanced stage in the development of activities and their methods of operation which indicate the practical suitability of particular techniques for providing in principle the basis for emission limit values designed to prevent and, where that is not practicable, generally to reduce emissions and the impact on the environment as a whole." Article 2(11) goes on to clarify further this definition as follows:

"techniques" includes both the technology used and the way in which the installation is designed, built, maintained, operated and decommissioned;

"available" techniques are those developed on a scale which allows implementation in the relevant industrial sector, under economically and technically viable conditions, taking into consideration the costs and advantages, whether or not the techniques are used or produced inside the Member State in question, as long as they are reasonably accessible to the operator;

"best" means most effective in achieving a high general level of protection of the environment as a whole.

Furthermore, Annex IV of the Directive contains a list of "considerations to be taken into account generally or in specific cases when determining best available techniques ... bearing in mind the likely costs and benefits of a measure and the principles of precaution and prevention". These considerations include the information published by the Commission pursuant to Article 16(2).

Competent authorities responsible for issuing permits are required to take account of the general principles set out in Article 3 when determining the conditions of the permit. These conditions must include emission limit values, supplemented or replaced where appropriate by equivalent parameters or technical measures. According to Article 9(4) of the Directive, these emission limit values, equivalent parameters and technical measures must, without prejudice to compliance with environmental quality standards, be based on the best available techniques, without prescribing the use of any technique or specific technology, but taking into account the technical characteristics of the installation concerned, its geographical location and the local environmental conditions. In all circumstances, the conditions of the permit must include provisions on the minimisation of long-distance or transboundary pollution and must ensure a high level of protection for the environment as a whole.

Member States have the obligation, according to Article 11 of the Directive, to ensure that competent authorities follow or are informed of developments in best available techniques.

3. Objective of this Document

Article 16(2) of the Directive requires the Commission to organise "an exchange of information between Member States and the industries concerned on best available techniques, associated monitoring and developments in them", and to publish the results of the exchange.

The purpose of the information exchange is given in recital 25 of the Directive, which states that "the development and exchange of information at Community level about best available techniques will help to redress the technological imbalances in the Community, will promote the world-wide dissemination of limit values and techniques used in the Community and will help the Member States in the efficient implementation of this Directive."

The Commission (Environment DG) established an information exchange forum (IEF) to assist the work under Article 16(2) and a number of technical working groups have been established under the umbrella of the IEF. Both IEF and the technical working groups include representation from Member States and industry as required in Article 16(2).

The aim of this series of documents is to reflect accurately the exchange of information which has taken place as required by Article 16(2) and to provide reference information for the permitting authority to take into account when determining permit conditions. By providing relevant information concerning best available techniques, these documents should act as valuable tools to drive environmental performance.

4. Information Sources

This document represents a summary of information collected from a number of sources, including in particular the expertise of the groups established to assist the Commission in its work, and verified by the Commission services. All contributions are gratefully acknowledged.

5. How to understand and use this document

The information provided in this document is intended to be used as an input to the determination of BAT in specific cases. When determining BAT and setting BAT-based permit conditions, account should always be taken of the overall goal to achieve a high level of protection for the environment as a whole.

The rest of this section describes the type of information that is provided in each section of the document.

Chapters 1 and 2 provide general information on the industrial sector concerned and on the industrial processes used within the sector. Chapter 3 provides data and information concerning current emission and consumption levels reflecting the situation in existing installations at the time of writing.

Chapter 4 describes in more detail the emission reduction and other techniques that are considered to be most relevant for determining BAT and BAT-based permit conditions. This information includes the consumption and emission levels considered achievable by using the technique, some idea of the costs and the cross-media issues associated with the technique, and the extent to which the technique is applicable to the range of installations requiring IPPC permits, for example new, existing, large or small installations. Techniques that are generally seen as obsolete are not included.

Chapter 5 presents the techniques and the emission and consumption levels that are considered to be compatible with BAT in a general sense. The purpose is thus to provide general indications regarding the emission and consumption levels that can be considered as an appropriate reference point to assist in the determination of BAT-based permit conditions or for the establishment of general binding rules under Article 9(8). It should be stressed, however, that this document does not propose emission limit values. The determination of appropriate permit conditions will involve taking account of local, site-specific factors such as the technical characteristics of the installation concerned, its geographical location and the local environmental conditions. In the case of existing installations, the economic and technical viability of upgrading them also needs to be taken into account. Even the single objective of ensuring a high level of protection for the environment as a whole will often involve making trade-off judgements between different types of environmental impact, and these judgements will often be influenced by local considerations.

Although an attempt is made to address some of these issues, it is not possible for them to be considered fully in this document. The techniques and levels presented in chapter 5 will therefore not necessarily be appropriate for all installations. On the other hand, the obligation to ensure a high level of environmental protection including the minimisation of long-distance or transboundary pollution implies that permit conditions cannot be set on the basis of purely local considerations. It is therefore of the utmost importance that the information contained in this document is fully taken into account by permitting authorities.

Since the best available techniques change over time, this document will be reviewed and updated as appropriate. All comments and suggestions should be made to the European IPPC Bureau at the Institute for Prospective Technological Studies at the following address:

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Best Available Techniques Reference Document on the Tanning of Hides and Skins

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SCOPE

The scope of the BREF for the tanning industry is based on Section 6.3 of Annex I of the IPPC Directive 96/61/EC as 'Plants for tanning hides and skins where the treatment capacity exceeds 12 tonnes of finished products per day'. In this sector the interpretation of '12 tonnes of finished products per day' is critical in deciding whether a specific installation requires an IPPC permit. This document does not address this issue of interpretation.

The processes to be included in the BREF will be following the technical definition of tanning as stabilising hides and skins and all associated activities[1]. These are any up- or down-stream activities carried out on a site. Thus, the scope comprises the core process and the associated activities, even if they are not all carried out by every plant covered by the IPPC Directive.

The types of hides and skins are restricted to those of ovine and bovine origin, because the production capacities for any other type of raw material for the production of leather and furs are far below the threshold value in the Directive.

Abatement of emissions from incineration processes for energy supply and from waste treatment processes generally carried out off site are not included in this document.

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[1] For comparison number 441 in EC's NACE classification scheme refers to tanning and dressing of leather, where it includes the following: tanning and dressing (441.1); manufacture and imitation of leather based on natural leather (441.2); and currying, dyeing and finishing of leather (441.3).

1 GENERAL – STRUCTURE OF THE INDUSTRY

The use of leather goes back to prehistoric times. The principal raw material is the hide or skin of animals including, to a small extent, reptiles, fish and birds. The tannery operation consists of converting the raw skin, a highly putrescible material, into leather, a stable material, which can be used in the manufacture of a wide range of products. The whole process involves a sequence of complex chemical reactions and mechanical processes. Amongst these, tanning is the fundamental stage, which gives to leather its stability and essential character. Preserving pelts by tanning and performing various steps of pre- and after-treatment, generates a final product with specific properties: stability, appearance, water resistance, temperature resistance, elasticity- and permeability for perspiration and air, etc.

Leather is an intermediate industrial product, with numerous applications in downstream sectors of the consumer products industry. For the latter, leather is often the major material input, and is cut and assembled into shoes, clothing, leather goods, furniture and many other items of daily use. These different applications require different types of leather.

The tanning of hides and skins also generates other by-products, which find outlets in several industry sectors such as pet and animal food production, fine chemicals including photography and cosmetics, and soil conditioning and fertilisers.

The process of making leather has always been associated with odour and pollution, and as it seemed to be an inevitable consequence of the activity at the time, in some cultures people engaged in this industry rarely enjoyed a high social status. Most of the basic stages of leather-making are still the same, but the tanning industry has undergone important changes and with respect to environmental protection, major improvements have been made.

A considerable potential impact of tanning and associated activities on air, on surface and ground water, soil and resources arises from the chemicals applied, the raw materials used, and the effluents, waste and off-gas releases generated in the process. Therefore provisions for pollution control, waste generation and disposal, chemical safety, accidents, and raw material, water, and energy consumption are essential.

The solutions for a better environmental performance are frequently complex and have to be assessed with regard to their potential impacts on other process units and particularly their benefits for the environment as a whole. Best available techniques will be balanced against these criteria and therefore include changes within process units as well as end-of-pipe abatement techniques.

Sophisticated treatment and processing techniques play an important part in achieving improved environmental performance. Competent operation and regular maintenance are as essential as the choice of technology. As is mentioned in the definition of techniques, this includes: good management decisions/practices; education and supervision of the workforce, on matters of workplace safety and accident prevention and, finally, monitoring of processes and environmental performance.

Other major influences for the potential environmental impact are the geographic location, the planning of the site, and the relation of the company with its surroundings and other stakeholders. Environmental concerns play an important role, but social and economic factors and the policies framework for business activity are just as important. These factors steer not only decisions affecting the core – the process itself – , but all activities of the industry, particularly emission and consumption, options for abatement techniques and re-use/recovery. However, these aspects will not be mentioned in the BREF, as it will focus on technical information for the guidance of permitters.

1.1 Overall production in Europe and world wide

The production of raw hides and skins depends on animal population and slaughter rate and is related mainly to meat consumption. On a world scale, significant cattle populations are to be found in the USA, Argentina, the former USSR and the EU. Sheepskins originate predominantly in New Zealand, Australia, the Near East and the EU. The main centres for raw skin production do not coincide with the major leather production centres, thus indicating the necessity of proper storage and means of transport. Typically hides and skins are traded in the salted state, or increasingly as intermediate products, particularly in the wet-blue condition for bovine hides and the pickled condition for ovine skins.

While developing countries hold over 75 % of the world bovine herd they together produce about 56 % of the world hide output by value or 43 % of total output by weight. With respect to sheepskins, developing countries account for about 59 % of the global number of skins produced.

Globally 39 % of the output of raw hides enter international trade. Within developing countries, exports from Latin America and Africa have fallen, while those of the Near East and the Far East have increased. For sheepskins, Oceania remains the dominant exporting region.

The tendency for bovine hides and skins is that developing countries change from being a net exporter to being a net importer, reflecting an expansion in tanning capacity in most developing countries, especially in the Far East and in Latin America. Conversely, the role of developed countries has changed from that of a net importer to net exporter of cattle hides. Japan and Western Europe are still net importers. Wet-blue is imported from a wide range of sources: the USA, Argentina, Brazil, South Africa, Australia, Russia and Eastern Europe.

As regards sheepskins, developing countries became net importers in the mid-nineties. Conversely, the developed countries as a whole are net exporters; Europe again, though, remains a net importer.

The origin of EU imports is presented in Figure 1.1[2].
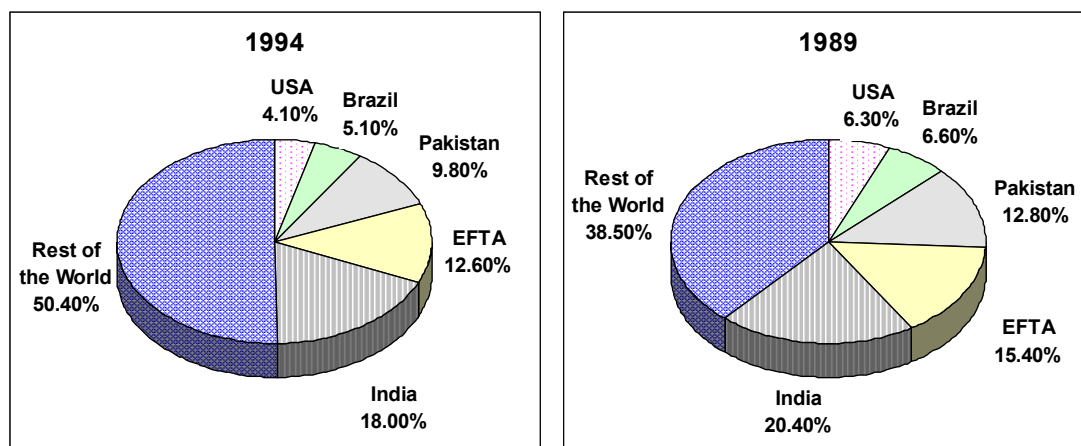
Figure 1.1: Origin of EU imports
Source: COTANCE, tan/tm/23/Panorama

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[2]   Data on a) rawhide and skin import (split ovine and bovine) and b) intermediate products (e.g. wet-blue) are not comprehensive yet. For data in Figure 1.1 it is not clear from the reference if the figures correspond to raw material or to finished leather and there is no split in ovine and bovine products.

Statistical data: raw hide and skins Trade% of weight (not price ratio):
UK:1996: 40 % import, 60 % export; 1997: 34 % import, 76 % export;
tan/tm/16/Spain: 70 % of bovine raw hides and 40 % of ovine raw skins are imported.
tan/tm/39/Italy: 80 % imported as raw hides or wet-blue from EC and non-EC
tan/tm/40/Protugal: 80 % imported as raw hides (30 %) or wet-blue (70 %), mainly from Brazil

Apart from the EU, the major leather production centres in the world are found in Mexico, Brazil, Japan, South Korea, China, India, and Pakistan. Korea, Japan, and Italy import hides from countries with high meat production (USA, Australia, other European countries), whereas the South American countries − for example, Argentina and Brazil − process mostly their own hides. Sheepskins are almost all exported from Australia, New Zealand, and the United Kingdom. Goatskins are produced in great quantities in China.

The global output of heavy leather increased in the mid-nineties. The principal producing regions are the Near East and Far East. Output of heavy leather continued to decline in developed regions. The sustained expansion of tanning capacity in developing countries is reflected in the growth in output of light bovine leather. The global output of sheep and goat leather expanded less rapidly than that of light bovine leather.

The tanning industry suffered over a long time in northern European countries such as Germany and the UK. Impressive growth rates in Italy and Portugal are levelling out. The EU's share on world markets tends to shrink with the development of the leather industry in other regions of the world such as Asia and the Americas.

Globally approximately 5.5 million tonnes of raw hides on a wet salted basis were processed to yield about 460000 tonnes of heavy leather and about 940 million square meters of light leather, including split leather. In comparison Europe produced about 74000 tonnes of heavy leather and about 240 million square meters of light leather. For goat and sheep world-wide 621000 tonnes of raw skins on a dry basis were converted into almost 385 million square meters of sheep and goat leather [tan/tm/46/FAO 1998]. The light leather production from goat and sheepskins in Europe yielded approximately 99 million square meters. All figures represent an average of the years 1994 to 1996 [tan/tm/46/FAO 1996 and FAO 1998].

With a positive trade balance of 746.3 million ECU in finished leather, the EU tanning industry is successfully resisting the gradual increase in imports in quantitative terms. In the reference tan/tm/23/Panorama no reference year is provided; it is assumed that the data apply for 1994. The EU is still the world's largest supplier of leather in the international marketplace. Italy alone represents 14 % of the world's cattle and calf leather production, 23 % of sheep and goat leather production and 11 % of sole leather production. Exports account for some 40 to 90 % of the tanning sector's turnover in the different EU Member States. Asia's growing economies, in particular the Far East, have become increasingly important markets for EU tanners.
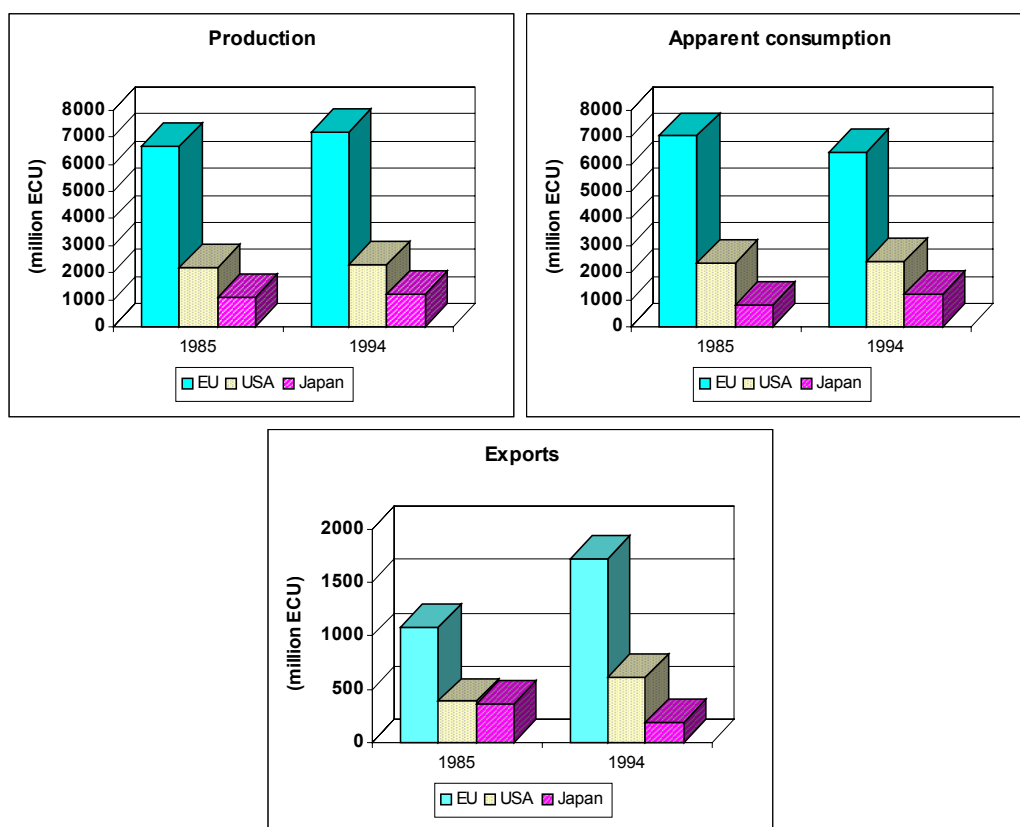
Figure 1.2: International comparison of main indicators in current prices
Source: COTANCE, DEBA GEIE, tan/tm/23/Panorama

1.2 Distribution of the EU tannery industry

Italy is by far the leather sector's most important location in Europe in terms of establishments, employment, production and turnover. Spain ranks second and with France, Germany and UK accounts for most of the balance in the EU leather industry. Other European Member States also have a dynamic leather industry of which Portugal's looks particularly promising.

In 1997 Italy alone accounted for 65 % of the production in the EC and 15 % on a world-wide basis [tan/tm/39/Italy]. Italy has about 2400 tanneries, Spain about 255, Portugal 100 and Germany less than 40. Production units in Italy are generally much smaller than in the other countries. Austria has 7 tanneries on an industrial scale and about 60 small ones. In the Nordic countries tanning used to be a major industry, but only a few tanneries remain. In 1999 there were 3 tanneries in Denmark (1 in Greenland), 5 in Sweden, and approximately 9 of importance are operating in Finland [tan/tm/027/Finland(1997)].
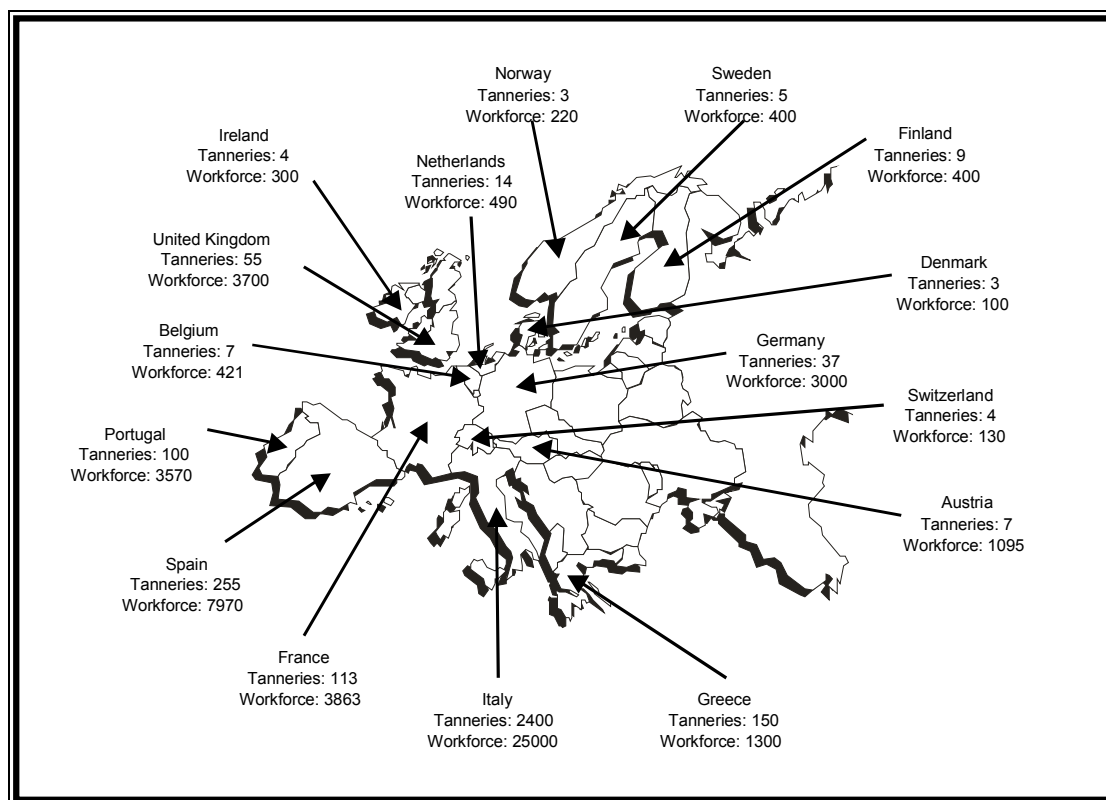
Figure 1.3: Geographical distribution of tanneries in Europe

Certain regions within EU Member States present characteristic concentrations of tanneries and municipalities whose local socio-economic life heavily depends on this sector's activity. These are more frequent in Southern European countries and in particular in Italy where, in Tuscany (S. Croce sul Arno and Ponte a Egola with 960 companies), Vicenza (Arzignano, Zermeghedo and Montebello Vicentino with about 640 companies), Avellino (Solofra), Naples (about 350 companies) and Piemonte (Turbigo, Castano Primo with about 80 companies) most of the EU tanning sector's operators are concentrated. Santa Croce and Arzignano are the centres of bovine leather tanning in Italy. The major part of leather production in Santa Croce is directed at the shoe industry. In Arzignano production is concentrated on upholstery leather, clothing, and the shoe industry; classical high quality leather is manufactured on a larger scale and in a more industrial (as opposed to artisan) manner than in Santa Croce. In Spain, about 60 % of tanners are located in Catalonia (near Barcelona), and about 35 % in Valencia, Murcia and Madrid. In Portugal about 85 companies are concentrated in Lisbon and Tagus Valley Region (Alcanena) and in the Northern Region (Porto) are about 15 companies. In Athens in Greece are other smaller tanning regions, which is the same for the Midi-Pyrénées in France.

In Figure 1.4 the production share of the largest producers within the EC for bovine and ovine leather is presented. The up-dated figures from tan/tm/46/FAO 1998 coincide approximately with the COTANCE figures given in Figure 1.4 for cattle and calf leather. However, for sheep and goat skins there is a considerable difference between the 75 million square meters quoted by COTANCE and the 99 million square meters quoted by tan/tm/46/FAO 1998. It is assumed that the shares in percentages of the production capacities nevertheless indicate the distribution in European sheep- and goatskin accurately enough.
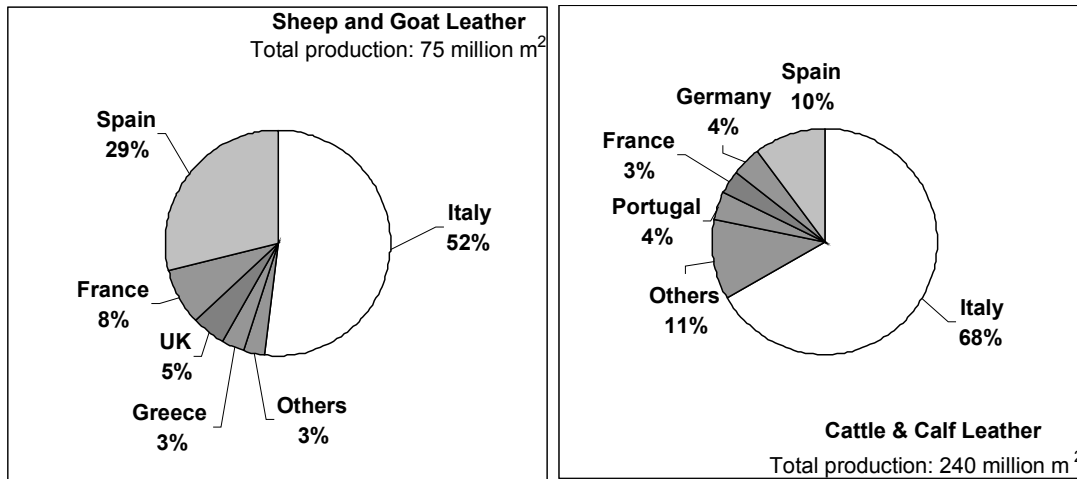
Figure 1.4: Production share of EC Member States for bovine and ovine leather
Source: COTANCE 1996

1.3 Economic situation, investments and employment in the EU tannery industry

Despite the enlargement of the EU to include Sweden, Finland and Austria, the total number of tanneries continues to decline. In 1998 there were over 3000 tanneries in the EU and about 50000 workers. Over the last decade the tanning sector has lost 1/4 of its industrial capacity and 1/3 of its work force. Most of the loss in industrial apacity has been in Northern European countries. Germany and the United Kingdom have suffered a particularly sharp decline in the number of tanneries.

Tanneries in Europe are small and medium sized enterprises (SMEs) of which only 10 are reckoned to employ more than 200 people [tan/tm/023/Panorama]. Only 1 % of companies in this sector employ between 101 and 200 people and (only) 8.5 % employ between 21 and 100 people. Companies are generally family businesses with a long tradition.

In Europe, the trend has been a reduction in capacities and volume of output, but a slow rise in turnover. Sole leather production is measured in tonnes, for other leather types the reference measure is square metres.

Country	Employment	Companies	Turnover [1000 EUR]	Exports/ imports %	Production (1000 m²)	
					Cattle/calf	Sheep/goat
Belgium	421	7	64766	90 %	1226	1000
Denmark	100	3	25000	90 %	1300	
France	2863	113	335000	39 %	6600	5700
Germany	3000	37	408000	38 %	10600	200
Greece	1300	150	90000	50 %	2100	2500
Italy	25000	2400	5789500	46 %	155500	39000
Ireland	400	3	36000	100 %	4000	250
Netherlands	490	14	68800	70 %	3617	
Spain	7970	255	1150000	39 %	25200	21965
Portugal	3570	100	230000	11 %	9700	980
UK	3700	55	510000	70 %	10000	3500
Sweden *	400	5	60000	70 %	2200	22
Finland	400	11	35000	60 %	1841	
Austria	1095	7	133358	90 %	5011	
EU-15	**50709**	**3160**	**8935424**		**238895**	**75117**
Norway	220	3	31000	85 %	1100	40
Switzerland	130	4			5440	88
TOTAL	51059	3167	8966424		245435	75245
* also 200000 m² leather from elk and reindeer is produced.						

Table 1.1: Structure of the European leather industry, 1996
Source COTANCE

Hides and skin are imported as raw hides or as partly processed products, for example wet-blues. This means that certain steps of the processes of integrated tanneries are transferred to other countries, particularly to Third World countries. From the environmental point of view this development has two consequences. First, environmentally important steps are transferred to other countries, and secondly, particular agents, which are restricted or prohibited within the EC, might be applied and are consequently imported via the hides and skins into the EC.

	Raw hide to leather	Raw hide to crust	Raw hide to wet-blue	Raw hide to pickled hides	Crust to leather	Wet-blue to leather	Pickled to leather	Others	Total
Belgium									7
Denmark	3								3
France									113
Germany	17	3	1	0	2	8	3	3	37
Greece									150
Italy									2400
Ireland									3
Netherlands									14
Spain – Catalonia [1]	27		79			74			180 (255)
Portugal	60				5	35			100
UK									55
Sweden	5								5
Finland									11
Austria									7
Europe total									**ca. 3500**
Notes: (1) tan/tm/16/Spain; A tendency to perform all stages from raw hide to leather (finished product) in one company is observed.									

Table 1.2: Distribution of tanneries with respect to traded products

Demand for leather depends on a multitude of factors, which fundamentally relate to the perception of this material by consumers. Price plays a fundamental role, particularly in the middle and lower end of the market. Higher quality or fashion oriented leathers are more sensitive to consumer spending patterns than to price.

EU tanners are adjusting their production towards higher quality output and high fashion content leathers. In certain cases they specialise in some particularly demanding niche markets requiring careful technological control of the process or lucky anticipation of market trends. The transition from quantity to quality has swept through much of Western Europe's leather industry.

Footwear remains overall the most important outlet for EU tanners' production with a share of 50 %. The clothing industry takes approximately 20 % of all finished leather produced in the EU. Leather for furniture and automotive upholstery represents some 17 % of EU tanners' output and the leather goods sector, 13 %. These ratios vary widely from one Member State to another.

	(%)
Footwear industry	50
Clothing industry	20
Upholstery	17
Other industries	13

Table 1.3: Destination of European leather output, COTANCE 1996

Leather tanning is a raw materials and labour intensive industry. Raw materials account for 50 to 70 % of production costs, labour 7 to 15 %, chemicals about 10 %, energy 3 %. EU tanners' environmental costs are estimated at about 5 % of their turnover [tan/tm/23/Panorama]. The remaining 5 to 15 % are other production costs. These figures refer to Europe in general. The tanning industry is labour intensive. It involves a series of batch processes during some of which each hide must be processed separately and partly manually.

To the extent that innovations take place in this industry related to environmental performance, the focus is more on chemicals than on machines. The biggest changes have taken place in the finishing of leather. A case in point is the shift to water-based solvents that was driven by environmental requirements. New chemicals and processes have been developed that make it possible to produce leather according to a number of different specifications. With finishing chemicals, reasonably high quality leather can be manufactured from hides and skins with defects. High quality aniline leather requires comparatively little finishing.

The high cost of raw materials makes it risky to experiment with unproven technological solutions and can be a barrier to investment. Investment in environmental improvements tends to be driven by legislation and/or cost minimisation. A barrier to the introduction of new techniques is that the new technological solutions often have to be tailor-made – as is the case in most industries – to the tanneries in question. This is particularly true for the tanners who compete in the very high quality niche markets and traditional family tanneries.

1.4 Environmental relevance of the tannery industry

The tanning industry is a potentially pollution-intensive industry. EU tanner's environmental costs are estimated at about 5 % of their turnover. For comparison, in the pulp and paper (chemical) industry, which is frequently referred to as pollution-intensive, the abatement costs can amount to about 2 % (almost 4 % in 1993) of their turnover. [tan/tm/23/Panorama]

Environmental concerns in a tannery include waste water, solid waste, air pollution, soil protection and health and safety aspects. The releases potentially contain toxic, persistent or otherwise harmful substances. A huge variety of chemicals is released, but no adequate data are available for a balancing of possible impacts.

The environmental effects that have to be taken into account comprise not merely the load and concentration of the classic pollutants, but also the use of certain chemicals: e.g., biocides, surfactants and organic solvents. Furthermore, contamination of soil and groundwater may be caused through accidental releases, spillages and leakages of certain agents as well as by the treatment of effluents and wastes. A further aspect to be aware of in tanneries is the potential hazard to human health and the environment from handling, storing, transporting and packaging of chemicals.

Table 3.2 will comprise a detailed list of raw materials and most important auxiliaries, the releases to waste water and air, and the residues for each process step.

About 20 – 25 % of the raw (salted) bovine hide weight is transformed to leather in the tanning process; for sheep or goat skins this number is 12 – 15 %, based on salted raw skins. When sole leather is produced, the number is approximately 65 %. 15 % of the organic material is released as solids or dissolved in the waste water. In a conventional process, the majority of the weight is lost to waste of various kinds, all of which has to be disposed of. 1 tonne of raw hides generates approximately 600 kg of solid waste and 15 - 50 m^3 of effluent containing about 250 kg COD and 100 kg BOD [tan/tm/09/UNIDO]. About 500 kg of various chemicals are added (compare with p. 26). The quantities and qualities of emissions and waste produced by tanneries strongly depend on the type of leather processed, the source of hides and skins and the techniques applied.

Of world tanneries, 80 – 95 % use chromium (III) salts in their tanning processes. The issue of chrome is perhaps one of the most debated issues between authorities and the tanning industry because of the difference in opinion about the toxicity of chromium (III) salts used in the tanning industry (see also Section 3.1.4). Where industry has the view that the chromium (III) tanning agent is not toxic and can be compared with table salt, authorities opinion is that chromium (III) should be considered toxic, especially for aquatic life. Both opinions are supported by the references used for writing this document. What is agreed is that chromium (VI) is much more toxic than chromium (III). The following text from several places in reference [tan/tm/31/Irwin] supports this: "The potential hazards and benefits of chromium are complex and are highly related to chemical speciation. The toxic mechanism of action differs for hexavalent versus trivalent chromium. Hexavalent chromium causes cellular damage via its role as a strong oxidizing agent, whereas trivalent chromium can inhibit various enzyme systems or react with organic molecules. As in the case of other metals, the overall hazard presented by chromium may be partly related to the solubility of the specific form of chromium. For example chromium (III) fluoride, which is relatively insoluble in water is far less toxic than chromium (III) sulphate, which is much more soluble. Chromium (III), the naturally occurring form, has low toxicity because it is non-corrosive and passes poorly through membranes, bute chromium (VI) is highly toxic because it has strong oxidation characteristics and passes readily through membranes."

The leather industry feels that the main reason why there is pressure on chromium tanning is that there is confusion between the toxicity of chromium (VI) and chromium (III). Chromium (VI) is toxic; it is known to be a skin irritant and thought to be a carcinogen. The toxicity of chromium (III) expressed in LD$_{50}$ (rat oral) is 3530mg/kg and is comparable to table salt. The use of chromium (III) salts in tanneries was thought to have detrimental effects on the health of workers but epidemiological studies of tannery workers have failed to find elevated incidences of cancers or allergy compared to the general population [IARC; Stern, 1987; Pippard, 1985]. A recent study [Chattopadhyay, 2000] on the impact of the use of chromium-containing effluents for irrigation of aqua-culture ponds concluded that total chromium

concentrations of between 0.025 - 1.70 mg/l had no impact on the growth of the fish or plants studied. [tan/tm/58/BLC].

Much of the chromium (III) used in the tannery is recycled or re-used, and most of the chromium (III) which enters the tannery waste streams is removed on-site by precipitation as the [insoluble chromium (III) hydroxide which may then go to landfill. The residue passes to the sewage treatment works and of this, 99 % is also insoluble. This relative insolubility prevents chromium (III) entering the water system or leaching from landfill. Where soluble chromium (III) is added to soils through sewage waste it rapidly disappears from solution and is transformed into insoluble hydroxides or oxides. An examination of available data on the disposal of chrome-containing tannery wastes to landfill concluded that there was no migration or oxidation of chromium (III) or contamination of groundwater by chromium (III). [Rutland, 1991; tan/tm/58/BLC]. Measurements in Denmark, however, show an average of 0.2 mg Cr/l in the leachate from a controlled landfill in which, two Danish tanneries deposit their chrome tanned shavings [Danish comment].

Chromium will only exist in the environment in the trivalent state. In soil, chromium (VI) is rapidly reduced to chromium (III) by its oxidative action upon organic material. This is supported by the very low recovery rates for chromium (VI) when added to columns of farm soil. The explanation given for this observation was that the chromium (VI) had been reduced to chromium (III) which subsequently precipitated or fixed to the soil. [Donmez, 1989; tan/tm/58/BLC].

Chrome is mentioned in list 2 of the Annex to Council Directive 76/464/EEC of 4 May 1976 on pollution caused by certain dangerous substances discharged into the aquatic environment of the Community. Tannery wastes containing chromium are not included in the European Hazardous Waste List on the basis that the wastes do not possess the characteristics necessary for classification as a hazardous waste.

Despite the fact that chromium has been under pressure from some regulatory authorities, the extent of substitution of chromium tanning agents has been limited. The main reason for this is that chromium is the most efficient and versatile tanning agent available, and it is relatively cheap. Some leather users are beginning to demand the use of alternative tanning agents, such as gluteraldehyde, aluminium and vegetable tannins, but the scientific basis for this is unproven. Reich came to the conclusion that chrome-free leather and a chrome-free tanning process are not generally superior. [tan/tm/77/Reich].

Most of the steps of the tannery's operations are performed in water. Consequently waste water effluent is one of the major concerns in tanneries. The characteristics of (untreated) waste water are a high chemical and biological oxygen demand, high salt content and toxic releases. The data have to be interpreted in the context of the processed hide weight; concentrations have to be discussed with regards to the loads. Variations in concentrations of three orders of magnitude may occur due to different water consumption and process types [tan/tm/18/UNEP-Tan, tan/tm/15/Reemtsma].

In Table 1.4 data for the tanneries on a world-wide scale and for tanneries in the EC are compared to present an indication for the quantity discharged [tan/tm/06/Europe].

	World Tanneries		EC Tanneries	
	Production in Million t/yr	Water consumption in Million t/yr	Production in Million t/yr	Water consumption in Million t/yr
Bovine (40 – 50 m³/t)	5	200 – 250	0.8	32 – 40
Sheep, goats (70/80 m³/t)	0.5	35 – 40	0.3	21 – 24

Table 1.4: Water consumption in general as a rough average

Tanneries in Europe usually discharge their waste water effluents to large waste water treatment plants, which are either municipal waste water treatment plants or plants operated for large tanning complexes. Few tanneries discharge directly to surface water. Most tanneries discharging to sewer have some form of on-site effluent treatment installed, ranging from pretreatment to biological treatment.

Overall, European bovine tanners are estimated to produce 400000 tonnes of sludge a year and around the same amount of other solid residues with moisture content between 40 – 80 %. In general, tanneries generate a solids load during primary treatment equivalent to a sludge volume of about 5 to 10 % of the total volume of effluent being discharged. The settled sludge resulting from these operations is normally in the form of a liquid with a solids content of typically 3 - 5 % dry solids (DS). When employing biological treatment on-site, the total sludge generation may be increased by 50 – 100 % compared to the sludge generated during primary treatment. Most tanneries will dewater their sludges to reduce the volume of sludge for disposal. Typically, dewatered sludges have a dry matter content of 25 – 40 %. The benefits of reducing the pollutants in waste water treatment have to be weighed against the additional production of sludges.

The solid waste consists of organic material such as protein, fat, dirt and process chemicals. The content and amount of waste generated and consequently the possible treatment options depend strongly on the types of processes used.

For many residues further re-use and recycling options exist. The viability of these options is strongly dependent on the composition of the residues. Landfilling of wastes with high organic content and toxic substances is increasingly coming under pressure in many Member States. However, landfilling is a legal option for many of these waste fractions in several Member States and in many cases the only available disposal route. Current environmental policies and legislation do not sufficiently encourage recycling or recovering operations in the tanning industry. Council Directive 1999/31/EC on the landfill of waste, adopted in 1999, is expected to have a considerable impact on trends to re-using and recycling versus landfilling. It lays down that by July 2003 Member States shall have established a national strategy for the reduction of biodegradable waste going to landfills. This strategy should include reduction measures by means of, in particular, recycling, composting, biogas production or materials/energy recovery.

A survey conducted by COTANCE suggests that European tanneries generate more than 300000 tonnes of dry sludge per year. This is equivalent to 1200000 tonne of sludge at a dry matter content of 25 %, which can generally be achieved after filter pressing the sludge. More than 80 % of these sludges contain chromium.

The volume of sludges quoted above is not the total volume of sludges generated by tanneries in Europe. More than 80 % of tanneries in Europe discharge their effluent to sewer, with the exception of Italy where the majority of tanneries are connected to a communal effluent treatment plant discharging directly to surface water. Further sludge will be generated in municipal treatment plants that treat tannery effluents in combination with other industrial and domestic effluents. It is not known how much sludge is generated as a result of the treatment of tannery wastes in municipal treatment plants.

Waste disposal routes for waste water treatment sludges differ in all Member States and are strongly dependent on the acceptability of applying sludge to agricultural land. Table 1.5 gives an estimate of the disposal routes for tannery sludges in several European countries in 1997 (COTANCE).

Disposal route	B	D	E	F	IRL	I	N	NL	S	UK
Ordinary landfill		98 %	90 %	70 %	60 %			70 %	50 %	90 %
Cost per tonne (EUR)		150	35	60	25			77	17	50
Special Landfill	66 %	2 %		25 %		100 %	100 %	30 %	50 %	
Cost per tonne (EUR)	219	600		185		55 - 73	40	103	110	
Incineration	17 %									
Cost per tonne (EUR)	125									
Agriculture	17 %		10 %	5 %	40 %					10 %
Cost per tonne (EUR)	$7.5/m^2$		20	30	n/a					n/a
B = Belgium	F = France				N = Norway			UK = United Kingdom		
D = Germany	IRL = Republic of Ireland				NL = The Netherlands			E = Spain		
I = Italy	S = Sweden									

Table 1.5: Disposal routes of sludges from waste water treatment in tanneries in Europe
Source: COTANCE

Air emissions can be toxic and/or odorous substances, e.g., sulphides, ammonia, organic solvents, particulate, and standard gas emissions from energy supply and other incineration processes. The assessment of the impact of air emissions has to cover emissions to the workplace and emissions to the surroundings. The emission of organic solvents is regarded as a major problem in tanneries.

Emissions of toxic substances like sulphides, ammonia and many organic solvents may reach critical levels at the workplace [tan/tm/18/UNEP-Tan]. Leather dust from mechanical operations can also pose a hazard when limit values are exceeded. Furthermore, in the handling of chemicals, particularly powdery agents, the protection of the workforce has to be taken into account. Both types of dust can cause serious problems at the workplace because of the particle size.

For ambient air quality emissions of VOC, NH_3, sulphides, and emissions from incineration processes for power supply are relevant. For the incineration of waste from tanneries, further toxic releases (chrome (VI), PCDD/F due to halogenated organic compounds, PAH) have to be taken into consideration.

The odour from substances like sulphides, mercaptans, and organic solvents and odour from putrefaction may constitute a major problem.

Soil and possibly groundwater can be affected directly by the activities of a tannery, particularly from accidental releases, spills and leakage, handling and storing, even temporarily, of process chemicals and wastes.

Skins and hides – and consequently – any waste fraction arising from skins and hides treatment before alkaline treatment might contain infectious material. Special care has to be taken in these cases not only to stop the infection spreading within the tannery, but also in the treatment of residues and waste water.

Faecal coliforms indicate contamination by manure and sewage. Pathogenic micro-organisms may also occur in water courses. Whereas anthrax has practically disappeared from European farm animals, dried hides and skins imported from parts of the world where anthrax is still endemic may still present a risk to employees handling these materials.

Effects such as excessive noise and air emissions from open burning or other operations should not happen in a tannery with modern management standards.

2 APPLIED PROCESSES AND TECHNIQUES

The production processes in a tannery can be split into four main categories: hide and skin storage and beamhouse operations (Section 2.1), tanyard operations (Section 2.2), post-tanning operations (Section 2.3), and finishing operations (Section 2.4). Furthermore, tanneries employ abatement techniques (Section 2.5) for the treatment of waste water, waste and air emissions generated during these processes. Operations carried out in the beamhouse, the tanyard, and the post-tanning area are often referred to as wet processes, as they are performed in processing vessels filled with water. After post-tanning the leather is dried and operations are referred to as dry processing.

The leather manufacturing industry is extremely varied and the categorisation given above can only serve as an indication of the type of processes employed in tanneries. Processes employed in each of these categories change depending on the raw materials used and the final products produced. Hence the environmental impacts are widely different from tannery to tannery and a more detailed assessment is necessary at the individual site. An indication of the complexity of tanning processes is given in Table 2.1, categorising some of the types of leather manufacturing processes, raw materials, and products which could be used in installations which are within the scope of IPPC.

Depending on the circumstances, different options for the process will be applied and consequently different environmental impacts may occur, ranging e.g. from toxic effects to long-term pollution in soil and water.

Raw material used	Type of leather manufacture	Finished products
Cattle	Fellmongery	Shoe upper
Sheep	Raw to wet blue	Shoe lining
Goat	Raw to crust	Sole leather
Pig	Raw to finished	Upholstery leather for furniture
Buffalo	Wet-blue to finished	Upholstery leather for automotive use
	Crust to finished	Clothing
		Protective clothing (fire resistant, water resistant)
		Fancy goods
		Gloving
		Bookbinding
		Chamois
		Saddlery
		Belting

Table 2.1: Variation in the types of raw materials, type of leather manufacture, and finished products

After the hides and skins are flayed from the carcass at the abattoirs, they are delivered either to the hide and skin market or directly to the tannery or to the fellmongery. Where necessary, hides and skins are cured before transport to the tannery and fellmongery in order to prevent the hides and skins from putrefying. Upon delivery to the site, hides and skins can be sorted, trimmed, cured and stored pending operations in the beamhouse. The following processes are typically carried out in the beamhouse of a tannery: soaking, unhairing, liming, fleshing and splitting. Fellmongeries typically (although not in every Member State) carry out the following processes: soaking, fleshing, painting, pulling, liming, deliming, bating, pickling and fleshing. Pickled skins are tradable intermediate products, and fellmongers generally do not carry out any tanning on their site. The wool is dried and sold as a product to wool scourers. Variations to these processing sequences in tanneries and fellmongeries exist for certain types of products. In this document the term 'tannery' will be used to refer to both fellmongery and tannery, unless specific differences between fellmongeries and tanneries exist.

Typically, the following processes are carried out in the tanyard: deliming, bating, pickling, and tanning. Sheepskin tanneries may degrease the skins prior to or after pickling or after tanning (wool-on sheepskins). The tanned hides and skins are tradable intermediate products as they have now been converted to a non-putrescible material called leather.

The following processes are typically carried out in post-tanning operations: samming, setting, splitting, shaving, retanning, dyeing, fatliquoring and drying. At this stage the leather is called 'crust'. 'Crust ' is a tradable intermediate product.

Finishing operations include several mechanical treatments as well as the application of a surface coat. The selection of finishing processes depends on the specifications of the final product. Tanneries generally use a combination of the following processes: conditioning, staking, buffing, applying a finish, milling, plating and embossing.

The listing of the above-mentioned processes' functions is designed to give an indication of the complexity of tanning. This list is by no means complete and many other processes exist which are used by specialised tanneries. However, for the purpose of this document only the most widely applied processes are being described.

	Chrome tanned leather	Vegetable tanned leather	
		Strap and russet Upper leather	Sole leather
	Raw hides	Raw hides	Raw hides
Beam-house	Soaking	Preliminary soaking Soaking	Soaking
	Liming	Liming	Liming
	Fleshing Splitting	Fleshing Splitting	Fleshing
Tanning	Deliming Bating	Deliming, Bating Washing, Dripping	Deliming Bating
	Pickling Chrome tanning	Vegetable pit Tanning	Vegetable pit Tanning
	Samming	Dripping, Washing Samming	Washing Samming
Wet-blue	Shaving	Shaving	
	Washing	Fatliquoring (drum)	Fatliquoring
	Neutralisation	Drying	Drying
Wet finishing	Washing	Retanning Dyeing Fatliquoring (drum)	
	Retanning Dyeing, Fatliquoring		
	Washing	Samming, washing	
	Drying	Drying	
Crust	Buffing	Staking	
Dry finishing	Lacquering	Buffing Toggling	
	Mechanical finishing	Ironing	Staking (Rolling)

Figure 2.1: Process steps for the production of leather from raw hides
Source: tan/tm/37/Germany

Sheepskins		Dressed sheepskins

Raw material

Soaking		
Liming		Cr(III) – retanning
Fleshing	Dressing	Rinsing
Washing		Dyeing
Pickling		Rinsing
Chrome(III)-tanning / Tanning		Fatliquoring
Dyeing		Drying
Drying		De-greasing
Degreasing		Finishing:
Finishing:		Buffing
Buffing		Brushing
Stretching		Re-shearing
Shearing		Ironing
Ironing		
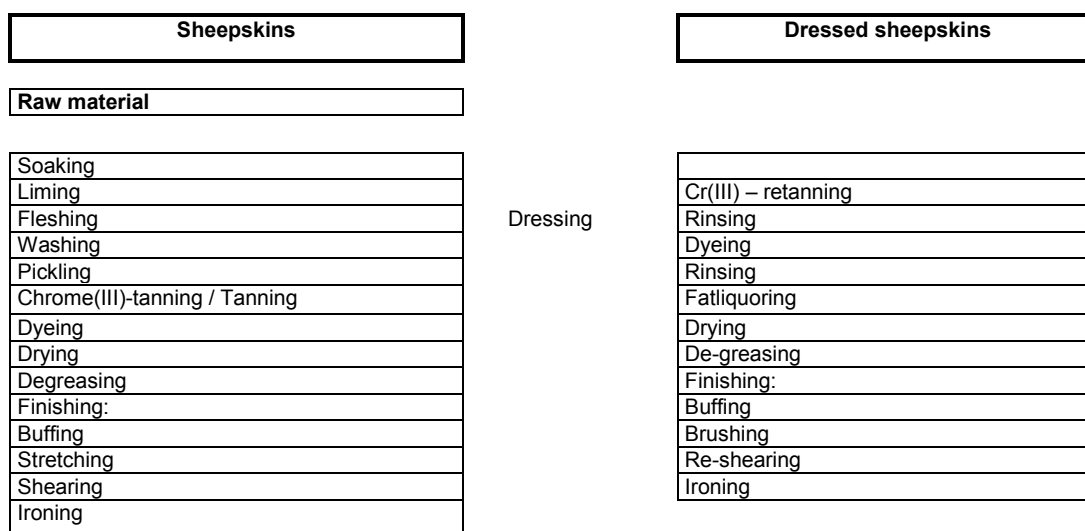
Figure 2.2: Process steps for the production of leather from raw skins
Source: tan/tm/37/Germany

2.1 Hide and skin storage and beamhouse operations

2.1.1 Sorting

On receipt, hides and skins may be sorted into several grades by size, weight, or quality. Hides are also sorted by sex.

2.1.2 Trimming

Trimming is generally carried out during the sorting process. Some of the edges (legs, tails, face, udders, etc.) of the raw hides and skins can be cut off. Usually this process step is done in the abattoir, but it can also be carried out in tanneries.

2.1.3 Curing & storing

Curing is a process that prevents the degradation of hides and skins from the time they are flayed in the abattoir until the processes in the beamhouse are started [tan/tm/02/HMIP, tan/tm/04/Austria, tan/tm/17/Frendrup].

When the raw material cannot be processed immediately ("green"), it must be cured. The methods for curing for long-term preservation (six months) are: salting, brining, drying and salt drying.

Methods for short-term preservation (2 - 5 days) are cooling, using crushed ice or refrigerated storage, and biocides.

Curing is done in the abattoir, at the hide market, or at the tannery. In certain cases it might be necessary to repeat the step in the tannery, e.g. if chilled hides are salted for longer storage or salting was not efficient enough.

Hides and skins are generally stored as they are received by the tannery on pallets in ventilated or air conditioned and/or cooled areas, depending on the method of curing chosen. From storage the hides and skins are taken to the beamhouse.

2.1.4 Soaking

Soaking is carried out to allow hides and skins to re-absorb any water which may have been lost after flaying, to clean the hides and skins (removal of dung, blood, dirt etc), and to remove interfibrillary material.

The soaking methods depend on the state of the hides. The process is mostly carried out in two steps: a dirt soak to remove the salt and dirt and a main soak [tan/tm/03/UwHB-Tech]. The process is carried out in processing vessels, such as mixers, drums, paddles, pits, or raceways. Raceways and pits are more commonly used for the processing of sheepskins. The duration of soaking may range from several hours to a few days.

Depending on the type of raw materials used, soaking additives can be used such as surfactants, enzyme preparations and bactericides.

2.1.5 Unhairing & liming of bovine hides

The function of liming and unhairing is to remove hair, interfibrillary components and epidermis and to open up the fibre structure.

Hair removal is performed by chemical and mechanical means. The keratinous material (hair, hair roots, epidermis) and fat are eliminated from the pelts mainly with sulphides (NaHS or Na_2S) and lime. Alternatives to inorganic sulphides include organic compounds such as mercaptans or sodium thioglycolate in combination with strong alkali and amino compounds. Enzymatic preparations are sometimes added to improve the performance of the process.

The process of liming and unhairing can be carried out in process vessels such as drums, paddles, mixers, or pits.

2.1.6 Painting & liming of sheepskins

The aim of painting is to bring about the breakdown of the wool root within the skin so that as much undamaged wool fibre as possible can be pulled easily from the pelt.

Paint, generally consisting of a mixture of sodium sulphide and lime, is applied to the flesh side of the skin and left for several hours. Application of the paint can be through a spraying machine or manually. After several hours the wool can be 'pulled' from the skin, either manually or mechanically. After pulling, the skins are limed in process vessels, with the same purpose as the liming of bovine hides.

Wool-on skins are not painted, unhaired or limed.

2.1.7 Fleshing

Fleshing is a mechanical scraping off of the excessive organic material from the hide (connective tissue, fat, etc.). The pelts are carried through rollers and across rotating spiral blades by the fleshing machine [tan/tm/35/BLC].

Fleshing can be carried out prior to soaking, after soaking, after liming or after pickling. The process of fleshing is called green-fleshing if the removal is done prior to liming and unhairing. If fleshing is performed after the liming and unhairing it is called lime-fleshing. Sheepskins may be fleshed in the pickled state.

2.1.8 Splitting

By mechanical splitting the thickness of hides and skins is regulated and they are split horizontally into a grain layer and, if the hide is thick enough, a flesh layer. Splitting is carried out on splitting machines, fitted with a band knife. Splitting can be done in limed condition or in the tanned condition.

2.2 Tanyard operations

2.2.1 Deliming

The aim of deliming is to remove residual lime from the pelts and to take the pelts to the optimum condition for bating. This involves a gradual lowering of the pH (by means of washing and addition of deliming chemicals), an increase in temperature and the removal of residual chemicals and degraded skin component.

Generally, deliming is performed in a processing vessel such as a drum, mixer or paddle.

2.2.2 Bating

Bating is a partial degradation of non-collagenic protein achieved by enzymes to improve grain of hide and the subsequent run and stretch of leather. In this process the rest of the unwanted hair roots and scud can be removed. [tan/tm/52/Handbook].

2.2.3 Degreasing

Excess grease must be eliminated from fatty skins (sheep, pig) to prevent the formation of insoluble chrome-soaps or prevent the formation of fat spues at a later stage. Degreasing is most relevant in processing sheepskins, where the natural fat content is about 10 % - 20 % on dry weight. The nature of this fat makes it difficult to remove because of the presence of cerides and a high melting temperature.

The three different methods commonly used for degreasing are:

1. degreasing in aqueous medium with organic solvent and non-ionic surfactant
2. degreasing in aqueous medium with non-ionic surfactant
3. degreasing in solvent medium.

2.2.4 Pickling

Pickling is carried out to reduce the pH of the pelt prior to mineral tanning and some organic tannages (e.g. chrome tanning, gluterdialdehyde tanning, vegetable tanning).

The choice of the exact pickling parameters depends on the subsequent tanning step.

Very often tanning is carried out in the pickle liquor; however, pickled pelts, e.g. sheepskins, can be traded. Pickeled pelt sheepskins must contain fungicides to protect them from mould growth during storage [tan/tm/02/HMIP, tan/tm/09/UNIDO].

2.2.5 Tanning

In the tanning process the collagen fibre is stabilised by the tanning agents such that the hide is no longer susceptible to putrefaction or rotting. In this process the collagen fibres are stabilised by the cross-linking action of the tanning agents. Furthermore their dimension stability, resistance to mechanical action and heat increase. [tan/tm/03/UwHB-Abfall, tan/tm/03/UwHB-Stoffe, tan/tm/02/HMIP].

The various agents can be categorised in three main groups:

- mineral tannages
- vegetable tannins
- alternative tanning agents, which can be subdivided into
    - syntans
    - aldehydes
    - oil tannage

Chromium and vegetable tanning agents are the most commonly used tanning agents.

2.2.6 Draining, samming and setting

After tanning, the leathers are drained, rinsed and either horsed up to age, or unloaded in boxes and subsequently sammed to reduce the moisture content prior to further mechanical action, such as splitting and shaving.

The setting out operation can be carried out to stretch out the leather. Machines exist which combine the samming and setting action.

After samming and setting, hides and skins can be sorted into different grades after which they are processed further or sold on the market.

2.2.7 Splitting

The function of the splitting operation is to cut through skins or hides at a set thickness. If the hide/skin is thick enough splitting can yield a grain split and a flesh split which can both be processed into finished leather. Splitting can be performed before tanning, after tanning or after drying.

2.2.8 Shaving

The shaving process is carried out to achieve an even thickness throughout the skin/hide, and it can be carried out on tanned or crusted leather. Shaving is carried out where splitting is not possible or where minor adjustments to the thickness are required.

2.3 Post-tanning operations

Post-tanning involves neutralisation and washing, followed by retanning, dyeing and fatliquoring, mostly done in a single processing vessel. At this stage of the process, specialist operations may also be carried out to add certain properties to the leather such as water repellence or resistance, oleophobing, gas permeability, flame retarding, abrasion, anti-electrostatics.

2.3.1 Neutralisation

Neutralisation is the process by which the tanned hides are brought to a pH suitable for the process of retanning, dyeing and fatliquoring.

2.3.2 Bleaching

Vegetable tanned skins and leathers with wool or hair may need to be bleached in order to remove stains, or to reduce the colouring in the hair, wool, or leather prior to retanning and dyeing.

2.3.3 Retanning

The retanning process can be carried out with the following objectives:

- to improve the feel and handle of the leathers
- to fill the looser and softer parts of the leather in order to produce leathers of more uniform physical properties and with more economical cutting value to the customer
- to assist in the production of corrected grain leathers
- to improve the resistance to alkali and perspiration
- to improve the wetting back property of the hides which will help the dyeing process.

A wide variety of chemicals can be used for the retannage of leather. They can generally be divided into the following categories: vegetable tanning extracts, syntans, aldehydes, mineral tanning agents and resins.

2.3.4 Dyeing

The dyeing process is carried out to produce level colours over the whole surface of each hide and skin and exact matching between hides in a commercial pack. Typical dyestuffs are water-based acid dyes. Basic and reactive dyes are less commonly used.

2.3.5 Fatliquoring

Leathers must be lubricated to achieve product-specific characteristics and to re-establish the fat content lost in the previous procedures. The oils used may be of animal or vegetable origin, or might be synthetics based on mineral oils [tan/tm/12/Ullmann p. 276, p. 138].

Stuffing is an old technique used mainly for heavier vegetable-tanned leather. The sammed leather is treated in a drum with a mixture of molten fat. [tan/tm/12/Ullmann p. 276].

The retanned, dyed, and fatliquored leather is usually washed before being piled on a 'horse' to age (let the fat migrate from the surface to the inside of the pelt).

2.3.6 Drying

The objective of drying is to dry the leather whilst optimising the quality and area yield. There is a wide range of drying techniques and some may be used in combination. Each technique has a specific influence on the characteristics of the leather.

Drying techniques include samming, setting, centrifuging, hang drying, vacuum drying, toggle drying and paste drying. Generally samming and setting are used to reduce the moisture content mechanically before another drying technique is used to dry the leather further.

After drying, the leather may be referred to as crust. Crust is a tradable intermediate product.

2.4 Finishing

The overall objective of finishing is to enhance the appearance of the leather and to provide the performance characteristics expected of the finished leather with respect to:

- colour
- gloss
- handle
- flex, adhesion, rub fastness, as well as other properties including extensibility, break, light- and perspiration fastness, water vapour permeability and water resistance as required for the end use.

Generally, finishing operations can be divided into mechanical finishing processes and applying a surface coat.

2.4.1 Mechanical finishing processes

A wide range of mechanical finishing operations may be carried out to improve the appearance and the feel of the leather. The following list of operations includes commonly used mechanical finishing operations. However, the list is not exhaustive and many other operations exist for special leathers such as sole leathers, wool-on skins, and special effects leathers:

- conditioning (optimising the moisture content in leather for subsequent operations)
- staking (softening and stretching of leather)
- buffing/dedusting (abrading of the leather surface and removing the resulting dust from the leather surface)
- dry milling (mechanical softening)
- polishing
- plating/embossing (flattening or printing a pattern into the leather).

These operations may be carried out before or after applying a coat, or between the application of coatings.

2.4.2 Applying a surface coat

The purpose of applying a surface coat is:

- to provide protection from contaminants (water, oil, soiling)
- to provide colour either to modify dyed colour or reinforce that provided by the dyes, to even the colour or to disguise defects
- to provide modifications to handle and gloss performance
- to provide attractive fashion or fancy effects
- to meet other customer requirements.

There is a wide range of application methods each of which has its advantages and disadvantages. A combination of methods can be used to achieve the desired effect on the finished product. In principle the following types of application methods can be distinguished:

- padding or brushing the finishing mix onto the leather surface
- spray coating, which involve spraying the finishing material with pressurised air in spray cabinets
- curtain coating, which is passing the leather through a curtain of finishing material
- roller coating, which is an application of finishing mix through a roller
- transfer coating, which is the transfer of a film/foil onto leather previously treated with an adhesive.

2.5 Abatement of potential releases to the environment

Generally any release from a tannery (gaseous, solid, liquid) has to undergo treatment to meet (local) environmental regulations. The main releases are to waste water or are residues.

2.5.1 Waste water streams

Tanneries generate effluents that are typically high in organic and inorganic pollutants. Since tanneries employ a sequence of batch processes, and a wide range of raw materials, their effluent is complex in nature with variation in characteristics from time to time, process to process and tannery to tannery.

Tannery effluents have to be treated before they can be discharged to surface water. Depending on local economic conditions and their geographic location, tanneries may treat waste water on site, discharge directly to sewer or use a combination of these options. Furthermore, some tanneries can discharge their treated effluent directly to surface water.

The waste water treatment strategies employed by tanneries are so varied that it is difficult to generalise, but broad descriptions are:

- mechanical pretreatment: consists in skimming of fats, oil and grease, and gravity settling (sedimentation)
- physico-chemical treatment: includes oxidation, precipitation, sedimentation, flotation, equalising flows and neutralisation. It is mainly performed to remove organic matter, sulphide from beamhouse effluents and chrome from tanning and post-tanning operations
- biological treatment: the high organic content is reduced. A nitrification / denitrification step is gradually being introduced in countries with strict nitrogen discharge limits. During the nitrification, sometimes, biological oxidation of sulphides takes place
- sedimentation: is used to separate activated sludge from the purified overflow. The primary sludge which comes out of the mixing and equalising tank, as well as the surplus sludge from biological treatment, is collected and treated in a sludge buffer tank.

Dewatering is often practised to reduce the volume of sludge for disposal. This is mostly done by mechanical equipment to press out water, sometimes followed by a drying process. Prior to de-watering, sludge thickeners can be employed to further thicken sludges.

2.5.2 Waste

Only 20 % - 25 % of the weight of the raw hide is processed to leather, depending on, among others things, the animal species and product specification. The rest of the weight plus the chemicals input ends up as either waste or by-products, assuming that emissions are not discharged by the waste water effluents.

Residues can be solid or liquid. They include salt, hair or wool, trimmings, fleshings, splits, shavings, fats, grease, waste machinery oil, sludges from waste water treatment, waste treatment, and waste process chemicals from finishing operations, organic solvents, and chemicals used in other than finishing processes, solids from air abatement, packaging material, and others. [tan/tm/02/HMIP, tan/tm/03/UwHB-Abfall].

Residues from tanneries can be tradable products, non-hazardous waste or hazardous waste. The classification, re-use, recycling and disposal depend on the legal context in the respective Member State, but also on markets and facilities for treatment and re-use/recycling available. The situation differs broadly within the Member States.

Currently many residues are being disposed of, generally in landfills, as this is the cheapest option. Some residues, such as fleshings, lime splits, grease, shavings, and trimmings, may be sold or given away as raw materials to other industry sectors. Depending on specific local conditions, some of the wastes may be treated on site before being sold or disposed of. Such treatments could include dewatering, compacting, fat rendering, anaerobic digestion, composting and thermal treatment.

Due to high investment costs many treatment options are not economically feasible on a small scale. Therefore tanneries often share off-site treatment plants or they transport residues to treatment plants as a complement to other wastes. Problems with the residues arise through chemical contamination, infectious material and odours.

From the technical point of view, further treatment, re-use or disposal options depend on the contamination the respective waste fractions carry. This contamination and the amounts of waste might vary significantly according to the process chosen for tanning or waste water treatment.

2.5.3 Air emissions

Compared to emissions to water, air emissions occur generally in relatively small quantities. Traditionally tanneries have been associated with odour rather than any other air emissions, although the emissions of organic solvents are a major problem. Whether a tannery has the following air emissions depends on the type of processes employed:

- particulate
- organic solvents
- hydrogen sulphide
- ammonia
- odour.

Emissions to air have effect beyond the tannery site, but also affect the workplace and possibly the health of the tannery workforce. Apart from odours, particular mention should be made here of organic solvent emissions, aerosols and dust (buffing dust and powdery chemicals).

The main emissions to the environment in general arise from odour, organic solvents (VOCs) and total particulate, though emission limit values are also set for ammonia and sulphides.

Particulates
The majority of particulate emissions arise from dry processes, such as milling, buffing and spray finishing operations. These emissions can be abated by using filters, down flow booths, chemical dosing equipment and/or dust free chemicals (dust free bates, liquid dyes and liquid retanning agents).

Organic solvents
The principal source of organic solvent emissions in tanneries is from finishing operations. Abatement techniques, such as scrubber units, are used and are effective in capturing a large part of the organic solvent emissions. Tanneries employing solvent based degreasing processes (mainly sheepskins) have also organic solvent emissions requiring special abatement.

Hydrogen sulphide
The generation of hydrogen sulphide is pH dependent. Hydrogen sulphide can be formed during deliming and pickling processes and when alkaline effluent streams containing sulphide are mixed with acidic effluent streams. To prevent the generation of hydrogen sulphide, the liquors from the deliming and pickling processes are treated by means of oxidising the sulphide with sodium metabisulphite or hydrogen peroxide. This treatment is not applicable for waste lime liquors or mixed effluent due to the presence of too much organic substances.

Extraction fans above processing vessels or improved process control can also minimise odours. Optimisation of washing processes in order to sufficiently remove sulphide before deliming and pickling will further reduce the odour emissions.

Hydrogen sulphide is also formed in waste water treatment by anaerobic bacteria from sulphates and therefore presents problems in waste water treatment, sludge storage, and dewatering operations. Hydrogen sulphide can also be formed in the sewerage system when sulphide-containing effluent is not treated carefully.

Ammonia
Ammonia can be formed in deliming processes and the dyeing process. Good housekeeping practices, such as effective washing and process control, can minimise these emissions. Extraction fans above processing vessels or improved process control can also minimise odours.

These ammonia and hydrogen sulphide emissions can be abated as VOCs, usually by wet-scrubbing or bio-filters.

Odour
Odour emissions from raw hides can be controlled by ensuring correct curing procedures, improving storage conditions and ensuring adequate stock rotation. Cool and dry conditions should be maintained in storage facilities and doors should remain closed.

Odours may arise from degradation of organic matter or from chemical substances that are also toxic. Odours can arise from storing hides and skins, from beamhouse operations (sulphides, ammonium), from ammonia releases in dyeing, from VOC released in finishing processes and from the waste water treatment.

Odour is one of the main reasons for complaints from neighbours.

Other
Sulphur dioxide emissions might occur during bleaching (see Table 3.2).

If combustion facilities are used for energy generation, emission limit values are generally set for emissions depending on the size of the facility and the local environmental legislation in place for such facilities.

3 CURRENT EMISSION AND CONSUMPTION LEVELS

This chapter aims to give some information as to the typical emissions and consumption levels of tanneries. Due to the wide versatility of tanneries, both in terms of the type of hides and skins used and the range of products manufactured, these levels will generally be indicative. They are not prescriptive, but merely serve to give an indication as to what type of emission and consumption levels can be expected in a wide range of tanneries. Where possible, a range for consumption and emission levels for particular processes will be given. The figures will strongly depend on the raw material processed, the quality and specifications of the final product, the processes chosen and local requirements. The figures are given for the performance of a conventional tannery. The possible achievements will be presented in Chapter 4.

The environmental impacts from tanneries originate from liquid, solid and gaseous waste streams and they arise from the consumption of raw materials such as raw hides, energy, chemicals and water. Furthermore, the nature of some of the processes and the materials consumed in those processes may potentially have an impact on health and safety at work, and possibly on soil and groundwater contamination. Also, the use of certain techniques for production processes and abatement may result in some cross-media effects.

The main releases to waste water originate from wet processing in the beamhouse, the tanyard, and the post-tanning operations. The main releases to air are due to the dry-finishing processes, although gaseous emissions may also arise in all other parts of the tannery. The main sources of solid wastes originate from fleshing, splitting and shaving. A further potential source of solid waste is the sludge from the effluent treatment plant (but not in all tanneries is this an activity on site). However, many of these wastes may be classified as by-products as they may be sold as raw materials to other industry sectors.

For a rough estimate in calculating consumption and emission levels with respect to the weight of several hides, the following assumptions can be made: one bovine hide weighs 15 – 40 kg, one sheepskin weighs 1 – 6 kg and this is the same for a goatskin. One pigskin weighs 2 – 4 kg.

Raw material	Bovine	Ovine	Other	Total	Source
Austria	~ 60000	–		~ 60000	tan/tm/04/Austria 1997
Belgium					
Germany	120000	n/a		120000	Germany/Cotance
Denmark	5000 - 6000	n/a		5000 - 600	Denmark/Cotance
Spain	245000	74000	16000	335000	CEC/AIICA 2000
Finland	4820	1560	1850	8400	tan/tm/27/Finland 1997
France					
Greece					
Italy				no data	tan/tm/39/Italy
Ireland					
Luxembourg	n/a	n/a		n/a	
Netherlands					
Portugal	65000	5700	< 1000	72000	tan/tm/40/Portugal 1997
Sweden					
United Kingdom					
TOTAL					

Table 3.1: Amount of raw material consumed by European tanneries

The raw materials used by the European tanneries, which are dealt with in this BREF, are bovine or ovine. They originate from EU and non-EU countries. The tanneries use either salted, pickled, wet-blue or crust hides and skins. The quantities of various raw materials consumed by European tanneries are presented in Table 3.1. The import statistics are given in Figure 1.1.

Figure 3.1 provides a rough overview of the input and output flows in a tannery running a conventional process.

INPUT

OUTPUT

Chemicals	~ 500 kg

Leather	200 -250 kg

Water	15 – 50m³

Water	15 – 50 m³	COD	230 – 250 kg
		BOD	~ 100 kg
		SS	~ 150 kg
		Chrome	5 – 6 kg
		Sulphide	~ 10 kg

Rawhide	1 t

Solid waste	~ 450 – 730 kg	Untanned	Trimmings	~ 120 kg
			Fleshings	~ 70 – 350 kg
		Tanned	Splits, Shavings, Trimmings	~ 225 kg
		Dyed / Finished	Dust:	~ 2 kg
			Trimmings	~ 30 kg
		Sludge from treatment	(~ 40 % dry matter content)	~ 500 kg

Energy	9.3 – 42 GJ

Air	~ 40 kg	Organic solvents

Figure 3.1: Input / output overview for a conventional (chrome-tanning) process for bovine salted hides per tonne of raw hide treated

Table 3.2 lists the main raw materials used in tanneries, specified for each individual process unit. The table does not include the hides and skins themselves. Furthermore, where the input is considered to be insignificant, it is not included. For example, all processes require some amount of energy and most processes require the use of steam or water. Raw materials are only included in the table if their consumption levels are significantly higher than in other processes.

Section 3.7 discusses in more detail and for each process step the input chemicals, the most important auxiliaries, the emissions to waste water and air and the residues. Special remarks are pointing out particular advantages or problems in a process unit to facilitate the search for particular information.

The sequence of process steps can change and processes can be combined into one batch procedure. Fleshing, splitting and degreasing, for example, can be performed at various stages of the process. The input and output therefore change accordingly. In Table 3.2 the most commonly found sequence is presented.

Process Unit	Inputs	Waste water	Waste	Air emission	Remark
Hide and skin storage and beamhouse operations					
Trimming			• parts of the raw hides (trimmings)		
Curing & Storing	• salt • energy for cooling / drying • biocides	see soaking	• salt		waste water released in soaking and residues depend on the curing method used
Soaking	• water • alkali • sodium hypo- chlorite • wetting agents, surfactants, enzymes • biocides	• BOD, COD, SS, DS from soluble proteins, dung, blood etc., • salts • org.-N • AOX • emulsifiers, surfactants, biocides			
Fleshing (*)	• (cold) water	• BOD, COD, SS, DS from fat, grease	• fat, connective tissue, lime		contamination depends on choice of green fleshing or lime fleshing. Blood is found in green fleshing
Liming & Unhairing	• water • lime, alkali sulphides • thioalcohols • enzymes • surfactants	• sulphides, • BOD, COD, SS, DS – emulsified and saponified fat, protein, degradation products from hair • lime • high pH, • org.-N, NH$_4$-N, • biocides	• hair • sludge from liming effluents (waste water treatment)	• sulphides • odour	
Rinsing after Unhairing	• water	as from liming and unhairing			
Splitting (**)	• water	same as liming	• lime split (flesh-side) • trimmings		• problems in waste fractions: pH ~ 12 and sulphides • splitting in tanned condition
Tanyard operations and post-tanning operations					
Deliming / Bating	• ammonium salts • org. and inorg. acids and their salts • carbon dioxide • enzymes • water	• BOD, COD, DS from epidermis, skin and pigment residues, degradation products and excess bating agents • NH$_4$- N • sulphides • calcium salts (mainly sulphates)		• NH$_3$ • H$_2$S • dust from bating agents	• NH$_4$ – N depends on deliming method • prior treatment using H$_2$O$_2$ or (Na-bisulphite to oxidise the sulphides • dust emission from bating agents depend on the agents and the method in which they are applied
Rinsing	• water	as from deliming / bating			
Degreasing	• surfactants and water • organic solvents	• BOD, COD, DS, • organic contents (fat, solvents) • surfactants	• distillation residues • waste water treatment residues		• chlorinated / non-chlorinated hydrocarbons • workplace conditions for VOCs

Process Unit	Inputs	Waste water	Waste	Air emission	Remark
Pickling	• water • organic and inorganic acids, salt • fungicides	• BOD, COD, SS, DS • Salt • low pH, • fungicides		• hydrogen sulphide • acid fumes	• fungicides • addition of some hydrogen peroxide may be necessary
Tanning	• water • organic and inorganic acids, salt • basifying salts • fungicides • complexing agents	• contents according to tanning process [see tan/tm/02/HMIP p. 102, fig. 8.2] • SS, DS, BOD, COD, low pH • complexing agents • fungicides	• hides due to operating errors • tanning liquors • waste water treatment sludge		• toxicity of tanning agents (aldehydes) • complexing agents: masking; sequestering agents for water treatment
Rinsing	• water	• same as in tanning			
Draining, Samming & Setting		• same as in tanning			• noise as in all mechanical processes
Splitting & Shaving			• split and shavings • trimmings	• dust if dry shaving is performed	• noise as in all mechanical processes • content of the residues depending on tanning techniques
Rinsing		• leather fibres from shaving			
Neutralisation	• water • organic and inorganic acids, alkali salt • neutralising tanning agents	• DS, SS; BOD, COD • rest of tanning agents		• ammonia and sulphur dioxide can be released into the air	
Rinsing	• water	• same as in neutralisation			
Retanning	• as tanning				
Bleaching	• water • organic and inorganic acids, alkali salt	• organic load • others, depending on the agents used		• sulphur dioxide	
Dyeing	• dyestuff • ammonia • organic solvents • auxiliaries: surfactants, chlorinated organic compounds • water	• high colour • organic solvents • dyeing agents • AOX	• residues of chemicals • dyeing agents	• NH_3 • phenols • formaldehyde	• toxicity of dyestuff • toxicity of auxiliaries
Rinsing	• water	same as in dyeing			

Process Unit	Inputs	Waste water	Waste	Air emission	Remark
Fatliquoring	• synthetics – mineral based oils • (sulphonated) animal, vegetable oil fish oil • chlorinated organic compounds • surfactants • other auxiliaries • water	• high oil • chlorinated organic compounds (AOX) • surfactants			• chlorinated organic compounds (AOX) • surfactants • toxicity of auxiliaries
			Finishing		
Staking / other mechanical operations			• dust		• other mechanical operations like polishing, embossing, plating, rolling, etc. • noise as in all mechanical processes
Drying	• energy • biocides			• heat • acid fumes	• moth protection for wool-on sheepskins, fungicides for crust
Milling / Buffing			• dust	• dust [tan/tm/03/UwHB-Stoffe]	• noise as in all mechanical processes
Coating	• lacquers (solvent based) • lacquers (water based) • binder and cross-linking agents • auxiliaries • water	• finishing agents in water or in aqueous solutions (organic solvents, heavy metals) • auxiliaries	• residues from chemicals, sludges from finishing agents(over-spray, etc.	• organic solvent use and release: aerosols • formaldehyde as fixing agent [tan/tm/03/UwHB-Abluft]	• workplace protection • toxicity and health effects of water based agents and organic solvents, binders, cross-linking agents, and auxiliaries
Trimming			• final trimmings		• with or without finish
			Abatement		
Air abatement	• filter matrices • water, acidic and basic agents for wet-scrubbers	• waste water from wet-scrubbers	• sludges from waste water from wet-scrubbers • filter matrices • dust	• not abated emissions	• depending on the method of air abatement for various effluent streams
Waste water abatement	• energy • precipitation agents • other treatment agents (flocculation, etc.)		• sludges • coarse material • filters (e.g. from special treatment)	• according to waste water stream and process (e.g. sulphides, ammonia, odour)	• depending on the method of waste water abatement for various effluent streams
Waste treatment	• energy • other treatment agents according to process	• according to waste fraction and process	• according to waste fraction and process	• according to waste fraction and process	• depending on the method of waste water abatement for various effluent streams

Notes:
(*)   Fleshing can be performed before or after liming resulting in different releases.
(**)   Splitting can be performed with limed or tanned hides and skins with crust resulting in different releases.

Table 3.2: Steps in the tannery showing main consumption and releases

3.1 Chemicals

The amount of chemicals used varies significantly with the specification of the final product, the pelts treated and the process chosen. Figures for consumption of chemicals can therefore only be given within a broad range. The water content must also be taken into account when comparing consumption figures. The inorganic chemicals generally used are sodium sulphide, calcium hydroxide, acids, carbonates, sulphites and sulphates. The standard organic chemicals are organic acids and their salts. About 20 – 50 % of the pelt weight will be added as inorganic standard chemicals, about 3 – 40 % as organic chemicals. The biggest variable is the amount of tanning agents used. Table 3.3 gives an example of overall consumption levels given [tan/tm/11/Nordiske Seminar].

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

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

The above-mentioned potential environmental effects of each substance have to be assessed. The potential impact of chemicals will depend on many factors:

- the chemical chosen
- the medium in which it is released, i.e. solid waste, ambient air or atmosphere, aqueous environment or soil
- the actual concentration received by the environment. It should be noted that the quantities in the waste water are not strictly a function of the input quantities. Some agents are almost totally absorbed, react in the process or are precipitated in the waste water treatment
- transformation of the chemicals due to chemical and biological processes before and after discharge to the environment. The substances might react during the process or with other constituents of the effluents; or they are degraded in the waste water treatment plant; they can also be distributed to different outlets of a factory, e.g. the products, waste and waste water
- continuous or batch discharge
- characteristics of the receiving environment. For example in a water course, essential factors are: the stress of organisms due to other water constituents; inhibitory or synergetic effects due to other chemicals; flow characteristics; light and temperature.

There are few data about the fate of biocides, surfactants and other process chemicals in the environment, particularly in the aquatic environment, even for widely used substances. If data about toxicity are available they include almost exclusively acute toxicity data for a few species, with very few values on chronic toxicity, carcinogenic, mutagenic or teratogenic properties, no–observed–effect–concentrations (NOECs) or no–observed–acute–effect–concentrations (NOACs). Hardly any data exist on the effects of chemicals that act as endocrine disruptors (e.g. certain organophoshates used as biocides), even though this is an issue of growing importance.

The reliability of available data is sometimes questionable because they are often derived from laboratory experiments and not from observed aquatic systems.

Current legislation does not require aquatic fate studies to be carried out, and monitoring of these substances by companies is seldom required specifically. There is therefore very limited availability of experimental protocols on long-term effects; acceptability levels; accumulation; degradation and formation of by-products. Data on transition and degradation products are even scarcer than data on the parent compound.

As organic substances, they contribute small amounts to COD and BOD; however, summary parameters do not adequately reflect the impact of the waste water effluents. Chlorinated organic compounds from soaking (and dyeing and fatliquoring) as well as reaction products of hypochlorite with organic matter contribute to the AOX. An AOX emission limit value is not set in all Member States.

In some cases summary parameters may even be misleading in the interpretation of the impact on the environment, meaning that data for particular emissions have to be added, e.g. for certain biocides and surfactants. However, data about other than summary parameters are hardly monitored. Without this information an assessment of the fate in the environment of the applied chemicals is impossible.

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

Table 3.3: Main and auxiliary process chemicals for a conventional tanning process for salted, bovine hides

3.1.1 Salt

The discharge of electrolyte into the environment might have a significant effect on both aquatic and plant life, with most fresh water species unable to tolerate even relatively low concentrations of electrolyte in the water. Discharge of electrolyte is even more of a problem in areas where fresh water is scarce, and contamination of the watercourse by salt can have a highly adverse effect. Salt substitutes mineral nutrients in soil. Furthermore, monitoring of aquatic toxicity can be hindered by high salinity.

The importance attributed to the total salt load released is dependent on the specific environment of the site; that is, the sewage treatment plant or type of surface water into which the tannery or the sewage treatment plant discharges. Also, where waste water is used to irrigate land, the impact of the salt content on the land has to be assessed.

3.1.2 Sulphides

Sulphide flake, used in the unhairing process, is hazardous as the dust is very caustic and is an irritant. Sulphide solution is also toxic. However, the biggest problem is due to the release of hydrogen sulphide gas to the atmosphere and the oxygen depletion of water caused by sulphide oxidation. Sulphide can be transformed to highly toxic hydrogen sulphide gas.

Fatalities have occurred opening drums during the deliming process, through cleaning operations/sludge removal in gullies and pits, and bulk deliveries of acid or chrome liquors being pumped in to containers holding solutions of sodium sulphide. There are dangers of low level exposure over long periods of time. Typical effects are headache, nausea, and eye irritation. One of the problems with the gas is that although the odour can be detected at low levels, these are often higher than levels acceptable for extended exposure. At concentrations above 100 ppm hydrogen sulphide cannot be detected by smell and can be lethal.

There is also a risk of formation of hydrogen sulphide under anaerobic conditions due to the action of sulphur-reducing bacteria.

Aliphatic thioles are used as auxiliaries in the unhairing process. They are also built by the degradation of sulphur-containing proteins in the waste water treatment. They are volatile and make air abatement measures in waste water treatment necessary; the remaining thioles in the waste water are biodegraded.

3.1.3 Nitrogen

The potential as nutrient for aquatic plants is indicated by nitrogen content, typically measured as total Kjeldahl nitrogen (TKN). However, nitrogen also has a high oxygen demand and, like phosphor, stimulates eutrophication. Ammoniac nitrogen is toxic to aquatic life. During biological waste water treatment, ammoniac nitrogen can be converted to nitrates. Nitrates are regulated, because of harmful effects on drinking water.

3.1.4 Tanning agents

Different agents can affect the environment in different ways. The environmental impact of mineral and vegetable tanning systems, and to a lesser extent the environmental impact of retanning agents and of the minerals present in dyestuff and pigments should be assessed.

The information from the three references mentioned below (Font, BLC and Slooff) shows different opinions about the environmental impact of chromium. These conflicting expert opinions are one of the main reasons why **chromium basic sulphate,** used in tanneries**,** is still under debate.

Water soluble trivalent chromium compounds are normally salts of strong mineral acids and are themselves acidic including, e.g. the chromium sulphates which are the normal salts used in leather tanning. Whilst these salts have significant acute toxicity to aquatic species, once absorbed by the hides during the tanning process, the trivalent chromium becomes substantially fixed in the leather and has little or no measurable toxicity. In a recent paper by Font et al is concluded:

- "only in one sample of the semi processed waste was the EC_{50} of the eluates with photobacterium phosphoreum close to 3000 ppm. The toxicity of this sample is probably due to the aromatic esters of 1,2 benzenedicarbosylic acid and to benzothiazol
- other tests such as reactivity, corrosivity, biotests with Daphnia Magna and Sprague-Dawley (rats) gave negative results about the toxicity of these samples". [Font, 1998].

Chrome (III) oxide and hydroxide which are generally found in tannery effluents and sludge are not toxic in any environmental medium, as they are not bio-available. For example, chromium hydroxide has a solubility product of 2.9×10^{-29} and would remain insoluble in the normal environmental pH range. [tan/tm/58/BLC]

Another, less recent, paper concluded that based on both the LC_{50}- and the NOEC-values, no significant difference can be found in the toxicity of chromium (III) and chromium (VI) for organisms in fresh water [Slooff, 1989].

Other minerals can be used to produce tanned leathers, although the overall characteristics of the leathers produced will not be comparable with the ones obtained in chrome tanned leathers. The following minerals can be used:

Aluminium as a substitute is still under debate because of assumed long-term toxic effects, with an indication that it might have considerable adverse effects on human health and environment.

Titanium in the form of titanium dioxide is quite inert, a fact often used to support the claim that titanium is environmentally harmless. However, titanium dioxide is not used as a tanning agent but rather water soluble quadrivalent titanium salts containing the TiO^{2+} ion which are highly acidic. So the assumption, based on the properties of titanium dioxide, should not be made that other titanium salts have low impact and toxicity,

Zirconium is often reported to be harmless. As with titanium, it is not valid to apply conclusions about one substance (salt) to the eco-toxicity of other salts.

Other tanning agents like vegetable tanning agents, syntans, and aldehydes mainly affect in principle the surface watercourse. Problems arise due to their low biodegradability and their toxicity for aquatic life.

Vegetable tanning agents are poly-phenolic compounds. Vegetable tannins may be classified as:

1. hydrolysable pyrogallol (Myrabolan, Oak, Sumac, Chestnut, etc.), or
2. condensed tannins based on catechol (Mimosa, Quebracho).

The vegetable tanning agents used are typically 15 – 70 % of commercial extract, often sulphited, then spray dried or concentrated. However, the extracts contain 20 % or more non-tannins (gums, sugars, mineral salts, organic acids, insoluble matter), which end up mostly in the waste water.

The effluents carry a high load of COD and show a low biodegradability. A further problem may be the phenol content and the colour of these effluents (see also Section 3.7.4.4.2).

Syntans, Resins, and Polyacrylates are agents used alternatively or in addition to chrome and vegetable tannins.

Syntans are sulphonated condensation products of hydroxyl-substituted aromatic compounds (phenol, cresol or naphtalene) with formaldehyde and often with amides [tan/tm/28/BASF, tan/tm/02/HMIP]. Production of syntans might be a source of large environmental impact. There is a wide variety of syntans, some of which are hardly biodegradable, whereas other are

biodegradable to a great extent. On the market syntans with low levels of free phenols which have a lower impact on the environment are available.

Syntans can cause a high COD and the degradation of sulphonated polyphenols is aerobically and anaerobically insufficient. The degradation products of the sulphonated polyphenols (and the phenols themselves) are strong pollutants. These substances are hardly reduced by adsorption on particulate matter and are highly mobile [tan/tm/15/Reemtsma]. It is expected that these substances are not retained in the sewage treatment and are released to the surface water. Even though they have low acute aquatic toxicity, their persistence and mobility are classified as negative to the environment with respect to ground and drinking water quality. Aromatic sulfonacids are xenobiotic substances, often with similar effects to detergents. Some syntans are sources of nitrogen.

As syntans react with proteins, ecological problems are caused. Adverse effects (their strength depending on the syntans) on fish and bacteria in biological treatment plants (blocking activity of the bacteria) have been recorded [tan/tm/09/UNIDO].

Attention has to be paid to the monomer content of syntans. Residual amounts of formaldehyde and phenol are detected in many products.

Sulphonated polyphenols are used not only as tanning agents, but also as dispersing agents, surfactants, wetting agents, auxiliaries for suspensions, and stabilising agents. These broad applications by many users lead to small but continuous releases from seemingly diffuse sources.

Resins are derived from aliphatic compounds such as polyurethanes, dicyandiamide and melamine. Resins contain (low) concentrations of free formaldehyde and inorganic fillers [tan/tm/28/BASF]. Monomers of formaldehyde are found in the resins.

Acrylic acid condensates exist in a vast number of derivatives. Since polyelectrolytes on the basis of acrylic acid condensates are used in the treatment of drinking water, it is assumed that the acrylic acid condensates behave similarly and are precipitated because they are absorbed on organic particulate matter. As with syntans, free monomers are still to be found in the product. The acrylic acid monomer is carcinogenic, the aquatic toxicity however is low. Acrylic acids and the condensates are anaerobically and aerobically biodegradable [tan/tm/15/Reemtsma].

Glutardialdehyde is the most commonly used **aldehyde,** but formaldehyde is still used [tan/tm/03/UwHB-Stoffe]. Aldehydes have to be carefully evaluated with respect to work space safety. Aldehydes react completely with the proteins found both in the hides/skins and in the effluents. Therefore they do not create an environmental problem at the end-of-pipe treatment.

As a carcinogen, formaldehyde requires special measures.

Glutardialdehyde has bactericidal effects and is therefore also used as a disinfectant. Glutardialdehyde is only degraded to a limited extent, has high toxicity and probably influences biological treatment negatively. The principal concern for workplace safety is occupational asthma, irritation of eyes, nose and throat. It is a skin sensitiser and can produce allergic dermatitis. Glutardialdehyde is undoubtedly a stronger mutagenic substance than formaldehyde, although less volatile [tan/tm/15/Reemtsma].

3.1.5 Organic solvents

Organic solvents other than the above-mentioned aldehydes are used mainly in the finishing process, but also in degreasing.

Solvents usually are categorised (varying in the Member States) according to their toxicity. Due to their volatility, organic solvents are emitted into air. A number of organic compounds are directly harmful to human health or to the environment. Moreover, many organic solvents undergo chemical reactions in the atmosphere, that cause a number of indirect effects, in particular the formation of photochemical oxidants and their main constituent, ozone. Pollution by tropospheric ozone is a widespread and chronic problem within the community.

The European Commission has therefore developed and published Council Directive 1999/13/EC of 11 March 1999 on the limitation of emissions of volatile organic compounds due to the use of organic solvents in certain activities and installations (Official Journal L 085, 29/03/1999). This VOC-Directive will have a **direct** impact on the use of volatile organic compounds in the finishing process in tanneries where the organic solvent consumption is more than 10 tonnes per year. Where the organic solvent consumption per year is more than 10, but less than 25 tonnes, the total emission limit value is 85 g/m^2. Where it is over 25 tonnes per year, the limit is 75 g/m^2. The emission limits are expressed in grams organic solvent emitted per m^2 of end-product.

This VOC-Directive will affect not only the finishing process but also degreasing activity. When compounds specified in article 5, paragraph 6 and 8, of this VOC-Directive are used and organic solvent consumption is between 1 and 5 tonnes/year, than the emission limit value in the waste gas is 20 mg/Nm^3 and the fugitive emission value as a percentage of the organic solvent input is 15 %. When more than 5 tonnes/year is consumed, the emission limit value is the same, but the fugitive emission value is 10 %.

When more than 2 tonnes/year of **other compounds** are used, the emission limit value in the waste gases is 75 mgC/Nm^3; when less than 10 tonnes/year is consumed, the fugitive emission value is 20 %, when more than 10 tonnes/year is consumed, the fugitive emission value is 15 % (of the organic solvent input). For the use of these **other compounds**, there is one exemption from application of the above-mentioned emission values and these are installations which demonstrate to the competent authority that the average organic solvent content of all cleaning material used does not exceed 30 % by weight.

The foregoing is only a brief outline of the main points of the VOC-Directive that relate to tanneries. The Directive should be consulted for details of when the emission limit values have to be met and when exceptions are made, e.g. when abatement techniques are used.

Table 3.4 shows some of the organic solvents used in finishing operations in tanneries; Table 3.5 gives similar information for degreasing of sheepskins.

Esters	Glycol Ethers
Isopropyl acetate	2-Ethoxyethanol
n-Butyl acetate	2-Butoxyethanol
Ethyl acetate	2-Ethoxyethyl acetate
n-Propyl acetate	2-Butoxyethyl acetate
n-Amyl acetate	1-Methoxy-2-Propanol
	1-Methoxy-2-Propyl acetate
Alcohols	
Methyl alcohol	
Ethyl alcohol	**Hydrocarbons**
n-Propyl alcohol	Xylene
Iso-propyl alcohol	Toluene
n-Butyl alcohol	
Di-acetone alcohol	
Ketones	
Acetone	
Methyl ethyl ketone	
Methyl isobutyl ketone	
Cyclohexanone	
Di-isobutyl ketone	

Table 3.4: Organic solvents used in finishing

Degreasing of pickled pelts	Degreasing of dry leather
Paraffin	Tri-chloroethylene
White spirits	Tetra-chloroethylene (=Perchloroethylene)
	Butyl oxitol
	Ethyl oxitol

Table 3.5: Organic solvents used in degreasing of sheepskins

Releases from processes, handling and storage at the workplace call for abatement depending on the potential effects on health of the work force. Explosion and fire hazards require special protection measures. Organic solvents are mainly released to air, but they also occur in waste water effluents. As wastes they are usually classified as hazardous waste.

Storage and handling of organic solvents requires special equipment and precautions for the particular agents used. These measures aim to reduce releases into air and spillage onto the ground, which causes contamination of soil and in many cases groundwater. Chlorinated organic compounds can, for example, easily pass through concrete floors. Fire and explosion protection is of minor importance for halogenated solvents.

Special attention has to be paid to **highly volatile halogenated hydrocarbons** and other halogenated hydrocarbons. Depending on the particular substance, they have impacts on the environment where, in particular, persistency and accumulation in the biosphere have to be mentioned. Their properties are different from that of non-halogenated solvents in many respects.

Certain halogenated organic compounds are ozone depleting substances. In compliance with the Montreal Protocol, the European Commission has, by adopting the VOC-Directive, taken steps towards a total phasing-out of the use of these halogenated substances. In the past, substances such as CFC-113, CFC-11, carbon tetrachloride and 1,1,1-trichloroethane (not to be confused with trichloroethylene) were used in solvent degreasing and dry cleaning of leather. However, it is thought that these substances are no longer used in the European leather industry.

Chlorinated organic compounds may be released in the following processes: soaking, degreasing, dyeing, fatliquoring and finishing. Either the pure solvent is used or products like biocides and auxiliaries used in the finishing process may contain halogenated organic compounds [tan/tm/43/World Leather June/July 1996]. In the different processes, these chemicals serve a wide range of purposes; all they have in common is the halogen substitution on an organic compound

Per-chlor-ethylene, mono-chlor-benzene and per-chlor-benzene are examples of halogenated organic solvents used in degreasing sheepskins and pigskins.

Emission and consumption standards currently mandatory in the Member States show large variations, but this will change with the adoption of the above-mentioned VOC-Directive.

Table 3.6 shows the permitted emission levels of several organic solvents in Germany and the Netherlands. In the Netherlands these emission levels meant that most tanneries had to achieve a reduction level of 90 – 95 % to meet these limits (situation in 1995) [tan/tm/59/Spin].

Solvent	Category	Permitted mg solvent / m^3 air	Mass flow rate (kg/h)
2-Butanol	III	150	3
Butyl acetate	III	150	3
Butyl glycol	II	100	2
Cyclohexanone	II	100	2
Diacetone alcohol	III	150	3
Ethyl acetate	III	150	3
Ethyl glycol	II	100	2
Isopropanol	III	150	3
Methyl ethyl ketone (MEK)	III	150	3
Toluene	II	100	2
Xylene	II	100	2

Table 3.6: Organic solvents and their emission levels (TA-Luft)
[tan/tm43/World Leather June/July 1996]

From a survey in the UK in the year 1991/1992, the estimated consumption of finish and the emission of organic solvents in the UK leather industry as a whole are shown in Table 3.7.

type of coating	projected industry usage (tonnes/year)	organic solvent content (%) average	estimated organic solvent emission (tonnes/year)
organic solvent thinnable (incl. thinners)	2000	90	1800
water thinnable materials	535	38	200
water based systems	2500	4.8	120
total	5035		2120

Table 3.7: Solvent usage in the UK leather industry for finishing operations
[tan/tm/66/BLC]

Abatement techniques:
Releases of VOC require special abatement techniques [tan/tm/03/UwHB-Luft]. Simple organic solvent mixtures can be removed by adsorption, using activated carbon (or other media) followed by recovery of the solvent through the regeneration of the carbon bed. Alternatively, organic solvents may be recovered by absorption of the gas into a liquid via a mass transfer system, such as a scrubber or a packed tower. Recovery is enabled by distillation, as one example, if the organic solvent does not react with the liquor. A third recovery technique is

condensation, using either liquid nitrogen (cryogenic condensation) or cooled brine; the choice of coolant depending on the volatility of the organic solvent. This is a highly efficient - and in the case of cryogenic condensation, a highly expensive - recovery method [tan/tm/55/EPA].

Abatement techniques such as activated carbon filters are feasible but not standard in tanneries; in the Netherlands 1 out of 27 companies uses an adsorption medium in its aerosolfilter [tan/tm/59/Spin].

Emissions:
Untreated organic solvent emissions from the finishing process can vary between 800 and 3500 mg/m^3 in conventional processes. 50 % of emissions arise from spray-finishing machines, 50 % from dryers.

Organic solvent content	Spraying			Roller Coating	
	g / m²	kg / t raw hide		g / m²	kg / t raw hide
	UNEP [tan/tm/17/Frendrup]	UNEP	Nordiske Seminar [tan/tm/11/Nordiske Seminar]	UNEP	UNEP
Solvent based	143 (− 215)	> 25	30	52	9
Water based	31	5.4	2 [(1)] (- 93 %)	18 (minimum ca. 5)	3.2 (minimum ca. 1)

Notes:
(1)   It is not specified if this figure is for solvent free & roller-coating, or only solvent free, or only roller coating
Data are given for chrome tanned bovine hide.

Table 3.8: Consumption of finishes for different types of processes

Table 3.9 shows a comparison of the average of VOC-emissions and emission concentrations between the several types of finishes from a survey in the Netherlands [tan/tm/59/Spin].

	Emission (kg/h)	Emission concentration (g/m^3)
Solvent based finish[1]	50	3
Water based finish[2]	5	0.3
Solvent free finish[3]	<1	-

Notes:
1)   Percentage organic solvent > 75 %
2)   Percentage organic solvent 10 – 75 %
3)   Percentage organic solvent < 10 %

Table 3.9: Comparison VOC-emissions of different types of finishes

By using a water-based finish, half applied by roller coating and half by low pressure spraying, Scandinavian Leather in Denmark (year 1995) achieved a VOC emission level of < 700 μg/m^3 (99 % fraction). The corresponding massflows are < 1.3 kg/h for category II VOCs and < 4.6 kg/h for category III VOCs. (See Table 3.6 for the categories).
In Austria, due to the application of water based and - as far as possible - solvent free top coats and the use of the roller coating technique in the finishing process, every tannery meets the emission level of 35 mg VOC/m^2 produced leather. [tan/tm/04/Austria].

The following Table 3.10 shows the results of measurements made at six tanneries in the UK, producing a wide range of both ovine and bovine leathers. The conclusion of this measurements was that when organic solvent-based finish systems are employed, the levels of VOCs in the discharges from both the spray cabin and the drier sections, although covering a wide range, are greatly in excess of the Guidance Note PG6/22(1992) limit of 50 mg/m^3 VOC. In worst cases, reductions in excess of 98 % would be necessary to meet the requirements.

	VOC emission concentration (mg/ m³)	
	Spray cabin	**Drier**
Organic solvent systems		
A	1980 - 3710	394 - 603
B	1200	505
C	2730 - 3695	1200 - 1225
D	3540	5316
Aqueous systems		
A	115	-
B	810, 210	40
C	7 - 180	nil to 100
D	135	14

Table 3.10: VOC contents of air discharged from spray finishing machines
[tan/tm/66/BLC]

3.1.6 Surfactants

Non-ionic, anionic, cationic, or amphoteric surface-active agents might be added as main reaction agents or emulsifiers but also as abrasion reduction agents, water-repellent agents or anti-electrostatic agents. They might also be added to allow the dispersion of oils in water.

Non-ionic surfactants, such as alkoxylates, are commonly incorporated into the beamhouse area of processing where they function as detergent to clean the skin or hide and to help emulsify and remove fats. Non-ionic surfactants can be aromatic or aliphatic poly-ethoxylates. The well-known nonylphenol ethoxylates (NPEs) are the most commonly used surfactants in the group of alkyl phenol ethoxylates. These surfactants have traditionally been used within the leather industry, for example as detergents, fatliquoring auxiliaries or as auxiliaries in other agents. NPEs are not only degraded only partially in aerobic conditions [tan/tm/15/Reemtsma], they most importantly form phenolic degradation metabolites (particularly nonylphenol (NP)), which are highly toxic for aquatic environments. Furthermore, the degradation products like nonylphenol are accumulated in the waste water treatment sludge, which is of minor importance when the sludge is incinerated. NPEs are thought to act as endocrine disrupters. A commitment to phase out the use of NPEs in the future already exists in many EC Member States. NPEs might have a negative effect on biological waste water treatment. They can be detected in surface and drinking water [tan/tm/15/Reemtsma]. Research in Spain has shown that with inlet values of 190 micrograms NP/l and 250 mg NPE/l into a biological waste water treatment, emission values of 25 micrograms NP/l and 6 mg NPE/l can be achieved. The high level of NPE degradation and a parallel reduction of NP level were verified, without any increase in NP level of the outlet stream. The tanneries drain this treated effluent to a sewer with further communal biological treatment. In the year 2000 a new study is being conducted of the inlet and outlet streams of the common biological waste water treatment plant.

Aliphatic polyethoxylates are used as substitutes for NPEs. They do not degrade with phenols as metabolites and are anaerobically and aerobically degradable, but not sufficiently.

Alkyl polyglycosides can be used as an alternative to NPEs, and are readily biodegradable under aerobic and anaerobic conditions. But they are limited to minority ingredients in some commercial formulations, due to the foam level generated and the limited advantages afforded.

Anionic surfactants, such as aliphatic sulphonates (mostly fatty acid sulphonates), ether sulphonates and fatty acid sulphates might be included in the degreasing process and dyeing operations.

Their biodegradability depends strongly on the substituting alkyl group. The more these groups are branched the more difficult degradation will be. Depending on the surfactant, aerobic or anaerobic degradations is possible.

Linear alkylated benzenesulphonacids (LAS) are well assessed because they are broadly applied in household detergents. Linear alkylbenzene sulphonates are readily biodegradable [Ullmann], and are being used in tanneries. There are other surfactants, such as sulphonated poly-phenols, that are used only in industry and that are found in effluents of tanneries. They are far less well understood, but it is known that they are not biodegradable and have a higher mobility than LAS [tan/tm/15/Reemtsma].

Cationic surfactants, such as quarternary ammonia salts, are used as surfactants, complexing agents and as bactericides. They are only partially biodegradable.

Amphoteric surfactants, such as glycinates, are not commonly used in tanneries.

3.1.7 Fatliquoring agents

Fatliquoring agents are either insoluble in water or alternatively emulsifiable or soluble in water. The water-insoluble products include natural (animal, vegetable, fish) and synthetic fatty acid ester and petrochemical products. By sulphonation or other chemical processes fatliquoring agents can be made water-emulsifiable (e.g. fatty acid methylester sulphonates).

Chlorinated hydrocarbons of chain length C16-30 (chlorinated paraffins) may also be applied [tan/tm/06/Europe]. Chlorinated organic compounds increase the AOX and might even exceed existing emission limit values. These substances can in principle be degraded aerobically and anaerobically but, with multiple chlorination, degradation is more difficult. Instead of microbial degradation the substances can also be integrated in the bio-mass of the bacteria. [tan/tm/15/Reemtsma]

Alkaline earth salts[3], carbohydrates, natural and synthetic mucilaginous substances and preparations thereof (stuffing agents [tan/tm/08/TEGEWA]) are added to the preparation.

3.1.8 Other post-tanning operation agents

In order to correct the hydrophilic properties of the leather due to prior addition of surfactants or to impregnate the pelts in order to achieve water-proof properties, natural, mineral, or synthetic fatty substances, polymers, polycondensates, polyaddition products, metallic acid complexing compounds, silicon derivatives and perfluorinated organic compounds are used.

Further impregnating agents to improve wearing qualities are agents that achieve oil-repelling or anti-electrostatic properties, reduce permeability to gas, or are flame retardant and abrasion reduction agents.

Oil-repellent agents and agents to reduce the permeability of gas are essentially solvent-containing or solvent-free preparations of perfluorinated organic compounds.

Flame retardants are often phosphorus-based, but can also be based on antimony trioxide and/or other metallic oxides, as well as on boron and nitrogen compounds [tan/tm/08/TEGEWA].

Abrasion reduction agents are very similar to the water-repellent agents. Anti-electrostatic agents are mostly anionic or cationic surface-active agents. Polycondensates and polymers are also used.

Emissions to waste water from the fatliquoring agents and the impregnating agents are significant. Like dye stuff, these agents not only increase the COD and BOD, but sometimes

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[3]   An oxide of an alkaline earth metal (lime); alkaline earth metals are: calcium, barium, strontium and radium.

also the AOX, so may have to be assessed as single substances due to their high potential impact on the environment or the workers handling them. For many of the substances used, no assessment is available yet.

Sequestering agents and wetting agents are problematic substances due to their ability to form stable complexes with heavy metals. Thus they not only prevent effective precipitation, they cause the re-mobilisation of heavy metals from sediments. Some of these substances are hardly biodegradable and include ethylen-diamin-tetra-acetate (EDTA) or carboxylic acids/dicarboxylic acids and their respective salts, e.g. respectively oxalic acid, formic acid, sodium oxalate, sodium formate and phthalic acid, sodium phthalate, etc.

Phosphoric acid esters are used as wetting agents and emulsifying agents. For example tri-butoxy-ethylphosphate is found in the effluents. This substance is problematic due to its solubility in water and low biodegradation rates.

Other complexing agents are used in chrome tanning as masking agents. "Masking" the chrome tannage often gives a plumper, softer leather. Carboxylic acids and the respective salts and di-carboxylic acids and the respective salts can act as masking agents. The di-carboxylic acids cause problems in the precipitation of chrome in the waste water treatment. Certain phthalates, such as di-sodium phthalates (DSP), are also used as masking agents in chrome tanning. While it is currently not known whether DSP is an endocrine disrupter substance, its use in tanneries is likely to be called into question in the near future.

3.1.9 Dyes and dyeing auxiliaries

3.1.9.1 Dyes

The number of different types of dyestuff used by tanneries varies with their product range, and the extent to which their products follow fashion world. Because each tannery can use between 50 and 100-plus types of dyestuffs, these chemicals have to be grouped in categories.
Even small amounts of dyestuff in the effluent stream can discolour the waste water efluents. Many dyestuffs are hard to biodegrade (increasing COD, BOD, SS) and in the case of some reactive dyes they could contribute to the AOX levels in the waste water effluents.

The dyestuffs used in tanneries can be classified in two families: anionic and cationic dyestuffs. The leather industry widely uses anionic dyestuffs, which are divided into the following families:

- acid dyes
- direct dyes
- mordant dyes
- pre-metallised dyes
- solubilised sulphur dyes.

Reactive dyes, although part of the anionic group of dyes, are not widely used in tanneries due to their method of application. The use of basic dyes is also limited.

From the chemical point of view the dyestuffs are predominantly azo dyes, or anthraquinone dyes. Triphenylmethane dyes may also be used.

Special attention has to be paid to a number of azo dyes that can split, under reduction conditions, into any of twenty carcinogenic amines.

Azo- and anthraquinone dyes are applied as either dispersion or solutions.

There is a Commission draft of a European Parliament and Council Directive, amending for the 19th time Directive 76/769/EEC on the harmonisation of the laws, regulations and administrative provisions of the Member States relating to restrictions on the marketing and use of certain dangerous substances and preparations. This amendment deals with azo dyes and mentions 22 aromatic amines.

Metal complex dyes consist of a central metal ion and one or two azo dye legends. The central ion can be iron, chrome, nickel, copper and cobalt. It is thought that metal complex dyes containing lead and cadmium are no longer used. Metal complex dyes may require carriers (such as certain ethoxylation products and emulsions of chlorobenzene or esters of phosphoric acid) to produce dark shades. Fixing agents are added to minimise the transfer of dyes released by the leather goods produced.

Experiments have shown that metal-complex dyes do not impair the compostability of chrome free leather shavings to a great extent. Shavings containing metal-complex dyes are degradable, apart from those containing copper. Copper has fungicidal and bactericidal properties; thus high concentrations inhibit degradation.

Vegetable dyes are extract of logwood, red wood, fustic or sumac leaves. These dyes give a restricted range of colour compared to the range provided by other types of dyestuff.

During the dyeing operation wetting agents, levelling agents, bleaching agents, shade intensifiers, after treatments and fixing agents can be applied. All these products have different effects on the dyestuff and on the leather. Some will help the uptake of the dye, others will help the penetration of the dyestuff. Some products are used to improve the fastness properties of the leathers produced. Some auxiliary products, like most chemicals, can contain potentially harmful substances, which could be present in the waste waters if their uptake is poor.

3.1.9.2 Dyeing auxiliaries

Surfactants may be added to dyestuff. Chemically they can be classified as follows:

- dispersing agents: e.g., sulphated acid esters and amide, fatty acid condensates, alkyl aryl sulphonates or ethoxylation products
- wetting agents (auxiliaries) can be divided in anionic (e.g. alkyl-sulphates, alkane-sulphonates, alkyl aryl sulphonates, etc.), non-ionic (e.g. phosphoric acid esters, etc.), and cationic (e.g. alkyl aryl amine polyglycol ethers, amine derivatives, betains, polyamine condensates, etc.).

Solvents may be used to promote the dissolution of dyestuffs in water. Solvents which can be used in this way are: alcohols, esters, polyols, thio-esters and mixtures thereof.

Sequestering agents to be added to the water can be divided into the following groups: nitrilo-tri-acetate (NTA), ethylendiamine-tetra-acetate (EDTA), polyphosphate (Calgon), Carboxylic acids.

pH regulators are: organic acids, acids, buffering salts, or mixtures of these chemicals.

Anti-foaming agents are low-foaming standardisation of wetting agents, mixtures of alcohols of higher valence and neutral phosphoric acid esters.

After-treatment and fixing agents are surface-active substances, particularly cationic poly-quaternary ammonium compounds, cationic formaldehyde poly-condensates and other nitrogen derivatives as well as inorganic complexing agents, metallic salts and preparations thereof.

Stripping agents are used generally on vegetable tanned leathers to level out the colour of the substrate prior to the dyeing operation. More rarely this operation is carried out on chrome tanned leathers. The chemicals used for this type of process are: salts releasing sulphur dioxide, oxalic acid, EDTA, bleaching syntans, etc. In certain cases there may be the need to strip a certain amount of dye from dyed leathers; this operation can be done using either alkali, e.g. ammonium bicarbonate, sodium bicarbonate, etc, or using bleaching syntans or using a combination of the two.

3.1.10 Finishing products

The basic components of leather finishes are binders, colouring agents (pigments and dyes), auxiliaries and lacquers.

Binders
A binder is the main film-forming constituent of a leather finish. It binds pigments and other materials, together and by its adhesive properties, adheres the film to the leather. Protein binders generally consist of preparations based on albumen and casein. They may also contain additives such as waxes and shellac. They are available as a powder and can be dissolved using sodium hydroxide, ammonia or borax. Protein binders use plasticisers, such as sulphated castor oil or polyethylene glycol.

Resin emulsions are the most commonly used binders in tanneries. This includes acrylics, butadienes, polyurethanes, and vinyl acetates. Resins are water-based emulsions.

Colouring agents
Colouring agents include dyes and pigments. Dyes may be used in finishing formulations for particular application. Dyes used in finishing are supplied in liquid form, and are generally pre-metalised dyes.

Pigments form the most significant colouring agents used in leather finishing. The main types of pigments are organic and inorganic pigments. Inorganic pigments are for example iron oxides, titanium dioxide and carbon black but also heavy metal compounds, e.g, lead chromate, lead molybdate and cadmium sulphate [tan/tm/28/BASF]. Inorganic pigments containing lead, chromate or cadmium are known to be toxic and harmful. These harmful substances were banned in Europe five years ago. Occasionally tanners buy cheap pigments containing banned substances from third world countries, so they may still be used in some circumstances.

Auxiliaries
For dispersion of the pigments in various organic solvents and/or water surface-active substances may be added. The preparations can furthermore contain waxes, plant mucilages, cellulose products or polymers as protective colloids, natural or synthetic oils as softening agents.

For special properties bottoming, grain tightening, penetrating agents, agents to prevent sticking, thickening and stabilising agents, plasticisers (phthalates), dulling and fixing agents are applied.

Cross-linking agents
Cross-linking agents are used to join the various polymers in the finish formulation, and reduce the water solubility of the compounds. The following cross-linking agents may be used:

- poly- isocyanates (for both base- and top-coats) are applied for polyurethane finishes
- carbodiimides for polyurethane base- and top-coats
- aziridines are highly toxic and for this reason they have been replaced by poly-aziridines, which are less toxic and can be used for base-coats and top-coats
- epoxies can only be used for top-coats
- formaldehyde for casein and protein finishes
- ethylene-imine-based cross-linking agents for top-finishes. Ethylene-imine is toxic and carcinogenic
- metal oxides for butadiene finishes for splits.

Lacquers and lacquers emulsions
Lacquer or lacquers emulsions form the top or fix coat of a finish. Lacquers are made by dissolving nitrocellulose in solvents (e.g. ethyl acetate, methoxypropanol, methyl isobutyl ketone). These solutions can be emulsified with water and surfactant to give lacquer emulsions. Polyurethane lacquers are also used.

Carriers
Carriers are used to produce suspensions/dispersions of binders used in finish formulations. Water and organic solvents are considered carriers. The organic solvents used can be divided into two categories: solvents which actually dissolve the binders (e.g. ethyl acetate) and diluents which enable the ready-made solution to be diluted to spraying viscosity or the desired concentration (e.g. methoxypropanol, iso-propyl alcohol etc).

3.1.11 Biocides

Biocides can be applied in various tannery processes to protect the substrate against either bacterial or fungal attack. Generally biocides are included in most liquid chemical formulations such as dyes, fatliquors and casein finishes. Furthermore, raw hides and skins may contain biocides applied to the animal to protect it from disease during its life. Clearly, all biocides are potentially toxic since they are designed to kill certain life forms.

It is important to understand that biocides are a subgroup of pesticides, and are divided into two main categories: b**actericides and fungicides**.

Bactericides are used mainly at the beginning of the leather making process, when hides and skins are more vulnerable to bacterial degradation, e.g. curing and soaking.

Fungicides are used from the pickling stage to the drying stage, because the pH conditions in these processes are ideal for mould growth.

To prevent bacteria and fungi becoming biocide-resistant and to reduce the risk of skin sensitisation, best practice is to change the active ingredients in the bactericide and fungicide on a regular basis; say, every six months.

Pesticides are used in farm animal husbandry (e.g. ectoparasiticides) to prevent animal pests, fly infestation, moth larvae damage, and beetle attack so that they cannot damage hides and skins prior to slaughtering. They are also used on raw hides and, if the hides and skins are intended for long transport, they may also be used on intermediate and finished products.

Different pesticides can be used on sheep and cattle. Table 3.11 shows the most common pesticides used in animal husbandry and their application methods.

Compound	Application Method	Treatment for	
		Sheep	Cattle
Organophosphates			
Phosmet	pour-on		√
Fenthion	pour-on		√
Diazinon	dip	√	
Propetamphos	dip	√	
	spray	√	
Synthetic Pyrethroids			
Cypermethrin	dip	√	
	pour-on	√	√
	spray		√
Deltamethrin	spot-on	√	√
Flumethrin	dip	√	
Permethrin	pour-on		√
Avermectins			
Ivermectin	bolus		√
	injection	√	√
	pour-on		√
Abamectin	injection		√
Doramectin	injection		√
Moxidectin	injection		√
Others			
Amitraz	dip	√	
Cyromazine	pour-on	√	

Table 3.11: Commonly used ectoparasiticides and application methods
Source: BLC

Currently, there is a trend to substitute organophosphates with synthetic pyrethroids, but synthetic pyrethroids are reported to be more toxic to aquatic life than organophosphates and both groups of pesticides have been reported to have endocrine disrupter effects. Synthetic pyrethroids and organophosphates survive the aggressive chemical conditions in the tanning processes and are consequently found in significant quantities with respect to environmental quality standards in the waste water effluents.

The use of some pesticides such as HCH, DDT and naphthalene is prohibited in Europe[4] but they may be imported through raw hides from non-EU member states in South America, Far East, Africa or India, for example. The European Commission has regulated the discharge of biocides through EC Directive 76/464/EEC on Pollution Caused by Certain Dangerous Substances Discharged into the Aquatic Environment of the Community. The situation may be different in developing countries. Some pesticides, such as "drins" and lindane can be found in skins imported from Africa. Arsenic is still used for animal treatment in some developing countries. Mercury should no longer be in use anywhere.

Biocides applied in the tannery industry are essentially non-oxidising biocides. They can be categorised as quaternary ammonium compounds (QACs), isothiazoles, halogenated organic compounds e.g., Bronopol (2-bromo-2-nitro-propane-1,3-diol), thiocarbamates and others, e.g. sulphur containing hetero-cycles like derivatives of benzothiazole (for example thiocyanomethylthiobenzothiazole (TCMTB)), and glutaraldehyde. Traded biocide products usually contain a mixture of biocides.

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[4] 'blacklisted substances' = Substances listed in the appendix to the Commission Communication to the Council (dated 22 June 1982) concerning hazardous substances, which should be included in List I of the Directive 76/464/EEC. See also the IRPTC (International Register of Potentially Toxic Chemicals).

Halogenated phenols were applied for a long time in tanneries but have been phased out. Although the use of chlorinated phenols such as PCPs is restricted in the EC, similar chemicals, such as phenol, o-phenylphenol and p-chloro-m-cresol are still used. Mixed phenols and, for example, p-chloro-meta-cresol are found in the effluents.

TCMTB in particular is used as a substitute for chlorophenols but due to the limited biodegradability and potential aquatic toxicity, it seems that benzothiazoles are of higher environmental concern than previously recognized [tan/tm/48/Reemtsma, Jekel].

If phenolic based chemicals are used during the leather making process it is strongly advised not to use sodium hypochlorite (bleach) as, under acidic conditions, the bleach can release chlorine dioxide which can subsequently oxidise phenols.

Handling of hides and skins contaminated with pesticides and handling of the biocides themselves pose a hazard to the work force.

Biocides can have negative effects in biological treatment of waste water [tan/tm/15/Reemtsma, tan/tm/48/Reemtsma, Jekel].

Table 3.12, lists the bacteria and bactericides that can be used during curing and processing.

Chemicals added to salt to prevent halophilic bacterial growth "red heat"	Short-term preservation chemicals	Bactericides added to soak liquors	Fungicides used during pickling, tanning and post-tanning operations
pH Controllers	**Inorganic Compounds**	Methylene bis-thiocyanate (MBT)	Mixed phenolics+Pyrithion (3-Methyl-4-chlorphenol, 2-Phenylphenol)
Sodium carbonate	Boric acid	2-bromo-2-nitro-propane-1,3-diol (Bronopol)	Isothiazolone
Boric acid	Hypochlorites	Sodium or Potasium dimethyldithiocarbamate	2-thio-cyano-methyl-thio-benzothiazole (TCMTB)
Sodium bisulphate	Chlorites	Thiadiazine	Methylene bis-thiocyanate (MBT)
	Sodium metabisulphite		TCMTB/MBT mix
	Sodium silico fluoride		
Inorganic compounds	Sodium fluoride		
Sodium metabisulphite	Zinc compounds		
Sodium silico fluoride			
Sodium fluoride			
Zinc compounds			
Organic compounds	**Organic compounds**		
Dichlorophen (5,5'-dichloro-2,2'-dihydroxy diphenyl methane).	Quaternary ammonium compounds		
Substituted benzothiazole	1,2 benzisothiazolin-3-one (BIT)		
Mixed phenolics			

Table 3.12: Biocides used in tanneries
Source: BLC and LAWA

3.2 Water & waste water

Water consumption consists of two main components: process water and technical water needed for energy generation, waste water treatment operation, sanitary purposes etc. The latter is estimated to account for about a fifth of total water consumption [tan/tm/42/Unido-Mass]. Process water consumption varies greatly between tanneries, depending on the processes involved, the raw material used and the manufactured products. The water consumption of tanneries manufacturing finished leather from intermediate products is low compared with that of integrated tanneries or those generating intermediate products. This difference is also partly due to more or less stringent water reduction measures, e.g. in rinsing steps. For a traditional tannery, average water consumption lies in the range of 25 to 80 m³/t of processed hide [tan/tm/18/UNEP-Tan, tan/tm/04/Austria]. For 12 tonnes of processed hides a day the annual effluent of a tannery would be up to about 200000 m³/yr.

The water used in the different processes is usually taken from nearby rivers, municipal waterworks or from company owned wells. Initiatives to reduce water consumption depend strongly on the source of the water supply and on the costs of waste water treatment.

Water consumption	% (rough average)
Soaking	$\sim 15 - 25$
Liming **Rinsing**	$\sim 23 - 27$
Deliming / Bating **Rinsing**	$\sim 10 - 15$
BEAMHOUSE SUM	$\sim 50 - 65$
Pickling / Tanning **Rinsing after Tanning** **Neutralisation** **Rinsing**	~ 10
Retanning, Dyeing, Fatliquoring, Rinsing	~ 30
POST-TANNING OPERATIONS SUM	$\sim 30 - 40$
Finishing	~ 10
TOTAL	100

Table 3.13: Water consumption in various process units for a conventional process for bovine salted hides and chrome tanning
Source: tan/tm/01/HMIP, tan/tm/07/Zimpel, tan/tm/38/Denmark, tan/tm/42/Unido-Mass

The most commonly monitored parameters for setting the requirements for waste water effluents are chemical oxygen demand (COD), biochemical oxygen demand (BOD_5), suspended solids (SS), total nitrogen (N-tot, TKN), ammonium nitrogen (NH_4-N), sulphide (S^{2-}), $chrome_{(total)}$, grease and fat content, pH and temperature. Salt as chloride and/or sulphate (Cl^-, SO_4^{2-}), total dissolved solids (TDS), phosphorous (P_{total}), absorbable organic halogenated compounds (AOX), surfactants, pesticides, phenols and fish toxicity are not as common. The composition of waste water effluents varies greatly between tanneries.

It is estimated that effective utilisation of process chemicals leads to an up-take of about 15 % in the final product, implying that 85 % enters the waste or waste water streams. [tan/tm/42/Unido-Mass]

Table 3.14 gives the composition of an average untreated tannery effluent, with a breakdown by source and technique. Aquarno, Cuoiodepur and F.I.C., are common waste water treatment plants in Italy that treat the waste water from about 150 to 400 tanneries. The data in this table is the incoming waste water that is treated in those plants. See the discription of those three treatment plants above Table 3.23. See also annexes (pages 210 - 211) for the figures of the plants Cuoiodepur and F.I.C.

Untreated waste water	Water	SS	BOD	COD	Cr	S^{2-}	TKN	Cl^-
	m³/t raw hide	kg / t raw hide						
conventional 1)	50	~150	~ 60 –100	~175–250	~ 5– 6	~ 6 – 10	~ 14	
		milligrams / litre						
conventional 1)	50	3000	800 - 2000	3500 - 5000	100	100 - 200	300	
conventional 2)	20 - 30			4000 - 9000	100 - 400	50 - 200	400 - 800	
Aquarno		45000	5000	10000 - 12000	40 -60	120	300 -400	6000
Cuoiodepur		10000		11000 - 12000	30 - 40	200		8000
F.I.C.		2700		6500	10	60	600	

1): Source is tan/tm/04/Austria, tan/tm/11/Nordiske Seminar
2): Source is tan/tm/37/Germany, and the data are an example of homogenised overall (not treated) complete waste water flow combinations for the manufacture of chromium leather made from cattle hides, based on raw hide weight.

Table 3.14: Overall emission loads to waste water
Source: tan/tm/04/Austria, tan/tm/11/Nordiske Seminar, tan/tm/37/Germany, Italy

The figures given in Table 3.16 for goat skins (also valid for the processing of bovine hides) and conventional techniques (from tan/tm/43/World Leather November 1996[5], p. 13) are considerably lower. This reveals not only large differences between tanneries but also within the term 'conventional'.

About 60 % of total tannery chloride stems from salt used for curing and released in the soaking effluents. The rest stems from the pickling and to some extent from tanning and dyeing processes. Where unsalted hides are used, the share of chloride emissions shifts to over 70 %.

About 75 % of the BOD and COD load is produced in the beamhouse, with the main load coming from unhairing that does not use a hair saving technique [tan/tm/11/Nordiske Seminar]. A significant proportion of the COD (about 45 %) and BOD (about 50 %) load stems from liming/unhairing [tan/tm/18/UNEP-Tan]. Liming /unhairing is also the main generator of SS (about 60 %). In total the beamhouse emissions rise to about 90 % of total SS.

The majority of total nitrogen matter (TKN) is discharged from the liming process. Beamhouse operations as a whole account for about 85 % of the tannery's TKN load.

About 65 – 70 % of the total chrome in effluents stem from tanning. The German leather industry association has estimated that 80 – 90 % of total chrome emissions stems from the tanning process (bovine). The remainder stems from post-tanning wet processes, from stock drainage and wringing.

Waste water from the beamhouse processes (soaking, fleshing, unhairing and liming) and from the associated rinsing is collected together. It contains hide substance, dirt, blood, dung (high BOD and SS), excess lime (depending on the liming process) and sulphides. It has a high salt content and high alkalinity.

The waste water from deliming and bating contains sulphides, ammonium salts and calcium salts (depending on the deliming process) and has a weak alkalinity.

After the pickling and tanning process, the main contaminants of the waste water are determined by the tanning techniques used. For chrome tanning, these are chrome salts and acids (pH about 4). Vegetable tanning increases the COD and possibly the phenol concentration.

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[5]   Source used in this article is a publication from: the Int. Environment Commission (IUE) Friedrichshafen, Germany, (1995).

Combinations of different tanning techniques are common. The effluents arise from pickling, tanning, draining, samming and the post-tanning operations. If fatliquoring is performed, additional substances are found in the waste water, again, depending on the techniques used.

Table 3.15, Table 3.16, Table 3.17, Table 3.18, Table 3.19 and Table 3.20 show consumption and emission values from several types of raw material, several processes and several sources.

Waste water	Soaking	Unhairing	Deliming	Σ beamhouse	Pickling / Tanning	Post-tanning operations
% from kg / t raw hide	%	%	%	%	%	%
SS	ca. > 15	ca. 60 ± 10	ca. < 5	ca. 90 ± 5	ca. > 5	ca. > 5
COD	ca. > 20	ca. 45 ± 5	ca. < 5	ca. 75	ca. > 5	ca. >15
BOD	ca. > 15	Ca. 50 ± 5	ca. 5	ca. 70 ± 5	ca. 5	ca. > 20
TKN	ca. 10	ca. > 40	ca. < 40	ca. 85 ± 5	ca. > 5	ca. 5
S^{2-}	—	<100	some	ca. 100	—	—
Cr	—	—	—	0	65 – 70	ca. 30 – 35 [(1)]
Cl^-	ca. 70 ± 10	some	some	ca. 70 ± 10	Ca. 30 ± 10	
Notes: (1) 20 % samming and 20 % post-tanning operations [tan/tm/09/UNIDO]						

Table 3.15: Averages of loads of emissions to waste water for the first process units as percentages of total loads as summary from various references for salted bovine hides with chrome tanning

Bovine	Water	SS	COD	BOD	TKN	S^{2-}	Cr	Cl^-
	m³/t	%	%	%	%	%	%	%
Beamhouse	7 – 25	ca. 80 ± 5	ca. 75 ± 10	ca. 75 ± 10	ca. 85 ± 5	100	—	ca. 75 ± 5
Tanning operations	1 – 3	ca. > 5	ca. < 10	ca. < 10	ca. < 5	—	ca. 70 ± 5	ca. 20 ± 5
Post-tanning	4 – 8	ca. > 10	ca. 15 ± 5	ca. 15 ± 5	ca. > 10	—	ca. 30 ± 5	ca. < 5
Finishing	0 – 1	ca. < 5	ca. < 5	ca. < 5	—	—	—	—

Ovine	Water	SS	COD	BOD	TKN	S^{2-}	Cr	Cl^-
	m³/t	%	%	%	%	%	%	%
Beamhouse	65 – 150	ca. 85	ca. 70 ± 10	ca. 70 ± 5	ca. 70 ± 5	100	—	ca. 65 ± 10
Tanning operations	30 – 70	ca. < 10	ca. 25± 10	ca. 20 ± 5	ca. 20 ± 5	—	ca. 85 ± 5	ca. 30 ± 10
Post-tanning	15 – 35	ca. > 5	ca. 10	ca. 10	ca. 10	—	ca. 15 ± 5	ca. < 10
Finishing	0– 10	some	—	some	—	—	—	—

Table 3.16: Averages of loads of emissions to waste water for goat skins (in tan/tm/39/Italy, stated as also valid for processing bovine hides) and ovine skins from beamhouse, tanyard, post-tanning and finishing operations as percentages of total loads
Source: Percentages are calculated from kg/t bovine hide and l/kg ovine skin from the data in tan/tm/43/World Leather November 1996 (see Table 3.17).

Bovine	Water m³/t	SS kg/t	COD kg/t	BOD kg/t	TKN kg/t	S^{2-} kg/t	Cr kg/t	Cl^- kg/t	SO_4^- kg/t
Beamhouse 1)	7 – 25	70 - 120	120 - 160	40 - 60	9 - 14	4 - 9		120 - 150	5 - 20
Tanning operations	1 – 3	5 - 10	10 - 20	3 - 7	0 - 1		2 - 5	20 - 60	30 - 50
Post-tanning	4 – 8	10 - 20	15 - 40	5 - 15	1 - 2		1 - 2	5 - 10	10 - 40
Finishing	0 – 1	0 - 5	0 – 10	0 - 4					
TOTAL	12 - 37	85 - 155	145 - 230	48 - 86	10 - 17	4 - 9	3 - 7	145 - 220	45 - 110
Notes: 1) soaking to bating									

Table 3.17: Typical pollution values related to conventional tannery processes for bovine salted hides in chrome tanning process
Source: tan/tm/43/World Leather November 1996, tan/tm/39/Italy

	Water l/skin	SS g/skin	COD g/skin	BOD$_5$ g/skin	TKN g/skin	S^{2-} g/skin	Cr^{3+} g/skin	Cl$^-$ g/skin	SO$_4$$^{2-}$ g/skin	TDS g/skin
Sheepskins										
Beamhouse	65 - 150	150 - 300	250 - 600	100 - 260	15 - 30	6 - 20		150 - 400	5 - 40	
Degreasing-Tanning	30 - 70	15 - 30	50 - 300	20 - 100	4 - 10		8 - 12	40 - 200	30 - 50	
Post-tanning	15 - 35	10 - 20	30 - 100	15 - 35	2 - 4		1 - 3	20 - 40	10 - 20	
Finishing	0 - 10	0 - 2	0 - 5	0 - 2						
TOTAL	**110 - 265**	**175 - 352**	**330 - 1005**	**135 - 397**	**21 - 44**	**6 - 20**	**9 - 15**	**210 - 640**	**45 - 110**	
Wool-on sheepskins										
Beamhouse	220	100	550	150	16			400		600
Tanning operations	40	15	150	45	2		15	460		650
Dyeing operations	100	80	80	25	3		5	50		270
TOTAL	**360**	**195**	**780**	**220**	**21**		**20**	**910**		**1520**

Table 3.18: Typical water consumption and pollution values for conventional tannery processes for ovine leather
Source: IUE Commission, 1999

		Chemicals used, composition and volume of effluents		
No.	Operation	Chemicals used and effluent constituents	Concentration [mg/l]	Effluent volume [m^3/t] raw hides
1	Soaking	Alkali, wetting agents, biocides (AOX), dung, blood, soluble protein, curing salt	COD 2500 - 10000 BOD$_5$ 1800 - 2300 pH 7 - 10	2 - 4
2	Liming and rinsing	Lime, alkali sulphides, thioalkohols, enzymes, residual protein from hair and skin, emulsified fat, degradation products	COD 17000 -25000 BOD$_5$ ca. 3000 pH 12 - 13 Sulphide 600 - 4000	3 - 8
3	Deliming Bating Rinsing	Ammonium salts, oxalates, citrates, CO$_2$, enzymes, epidermis-,hair- and pigment residues, non collagenic proteins, soluble Ca salts	COD up to 10000 BOD$_5$ 800 - 1700 pH 7 - 9 Sulphide ca. 50	1- 4
4	Pickling and chrome tanning	Pickling salts (NaCl), organic and inorganic acids, Cr(III) salts, sodium carbonate, fat, fungicides, leather fibres	COD up to 10000 BOD$_5$ 350 - 1500 pH 3 - 4 Cr$_{(tot)}$ up to 5000	0.5 - 3
5	Dripping Samming	Residues from 4	as under 4	ca. 0.2
6	Washing Neutralising Washing	Organic and inorganic acids, alkali salts, tanning agents for neutralization, Cr(III) salts, leather fibres	COD 1000 - 4000 BOD$_5$ ca. 150 pH 4 - 6	ca. 3 - 6
7	Retanning Dyeing Fatliquoring	Formic acid, Cr(III) and/or Zr salts,Al salts, vegetable and synthetic tanning agents, dyes, fat, ammonia (AOX)	COD 8000 - 22000 BOD$_5$ ca. 800 pH 4 - 5 Cr$_{(tot)}$ - 500	ca. 2 - 6
8	Washing Samming	Residues from 7	as under 7	3 - 5
9	Finishing	Lacquer polymeres, solvents (lacquering with wet separator), dye and lacquer sludge, emulsifiers	-	-
	Total			15 - 30

Table 3.19: Manufacture of chrome leather from bovine hides
Source: tan/tm/37/Germany

Part I: Processing of preserved raw hides to produce wet blue (2.3) (standard ranges; deviations possible depending on actual practices and water consumption)

No.	Operation	Chemicals and Auxiliaries used	Effluent							Remarks
			Volume [m³/t] *	Constituents	Concentration ranges [mg/l]					
					pH	COD	$N_{org.}$	NH₄ - N	Sulphide	Cr (III)	
1.1	Soaking	Alkali, wetting agents, biocides, enzymes	2 - 3	Soluble proteins, dung, blood, preservation salts, biocides	7 - 10	2500 to 10000	ca. 200	20 to 50			Preservatives/biocides may cause input of AOX
1.2	Liming/ drum painting	Lime, alkali sulphides, thioalcohols, enzymes	1 - 3	Sulphides, alkali, emulsified fat, proteins e.g. hair, epidermis, protein degradation products	12 - 13	17000 to 80000	2000 to 5000	100 to 300	1200 to 4000		
1.3	Washing/ rinsing		2 - 4	as under 1.2	Dependent on the volume of wash water						
1.4	Fleshing		~	as under 1.2	Production-specific volumes and concentration ranges						Mechanical process
1.5	Splitting		~	as under 1.2	Production-specific volumes and concentration ranges						Mechanical process
1.6	Deliming/ bating	Organic and inorganic acids and salts thereof, e.g. ammonium salts; Carbon dioxide, enzymes	1 - 4	Calcium salts; epidermis, skin and pigment residues; ammonium salts	7 - 9	1000 to 17000	300 to 900	30 to 900	30 to 7000	to 30	Ammonium concentration varies as a function of the deliming method used
1.7	Washing		3 - 4	as under 1.6	Dependent on the volume of wash water						
2.1 2.2	Pickling/ chrome tanning	Organic and inorganic acids, pickling salt (NaCl), Cr(III) salt, fat, basifying agents e.g. magnesium oxide, acid sodium carbonate, fungicides	0.5 - 3	Cr(III) salts, pickling salt, leather fibres, fat, fungicides	3 - 4	3000 to 12000	ca. 200	to 300		300 to 4000	Cr(III) concentration varies as a function of the tanning method used; tanning may be followed by washing
2.3	Samming		ca. 0.2	as under 2.2	Concentration ranges as under 2.2						wet blue

Part II: Processing of wet blue to produce crust (3.8) and finished leather (3.9)   (Standard ranges; deviations possible depending on actual practices and water consumption)

No	Operation	Chemicals and auxiliaries used	Effluent								Remarks
			Volume [m³/t] *	Constituents	Concentration ranges [mg/l]						
					pH	COD	$N_{org.}$	NH_4 - N	Sulphide	Cr (III)	
3.1	Shaving		-	not applicable							Mechanical process
3.2	Washing		3 - 4	Cr(III) salts, pickling salt, fungicides, fat	Dependent on wash water volume						Leather fibres from shaving
3.3	Neutrali-sation	Organic and inorganic acids, alkali salts, neutralising tanning agents	2 - 3	Cr(III) salts from tanning, dissolved salts, leather fibres	4 - 6	1000 to 4000	ca. 200	500 to 1000		10 to 500	
3.4	Washing		1 - 3	as under 3.3	Dependent on wash water volume						
3.5	Dyeing, Fatliquoring Filling, Retanning	Dyes, ammonia, fat, fillers, Cr(III)-, Zr- and Al-salts, vegetable and synthetic tanning agents	2 - 6	Vary as a function of the chemicals and auxiliaries used	3.5 - 5	8000 to 24000	ca. 200	100 to 900		10 to 500	Cr(III) concentrations will be higher in chrome retanning; fats may cause input of AOX
3.6	Washing		2 - 5	as under 3.5	Dependent on wash water volume						
3.7	Setting out		~	as under 3.5	Production-specific volumes and concentration ranges						Mechanical process
3.8	Drying		-	not applicable							Crust
3.9	Finishing	lacquer polymers, solvents, colour pigments, coagulants	~	Vary as a function of the chemicals and auxiliaries used	Production-specific volumes and concentration ranges						Finished leather

Legend:

    ~ ... insignificant volumes
    *) ... reference weight   1.1- 1.3   putting-into-work weight   f = 1.00
                                    1.6 - 3.1   pelt weight   f = 0.65
                                    3.2 - 3.9 shaving weight   f = 0.50

                                    f ... conversion factor for effluent volume relative to putting-into-work weight

Table 3.20: Operations, chemicals used, composition and volume of effluents, illustrated by the example of the manufacture of chrome leather from bovine hides
Source: tan/tm/37/Germany

	Average analytical values		Removal efficiency
PH	7 – 9	–	
BOD	2000 – 3000	mg/l O_2	98 – 99 %
COD	4000 – 8000	mg/l O_2	96 – 98 %
SS	3000 – 7000	mg/l	> 99 %
Sedimentable solids	50 – 7000	mg/l	> 99 %
Sulphides	150 – 2500	mg/l	> 99 %
Chromium	1500 – 2500	mg/l	> 99 %
Chlorides	3000 – 8000	mg/l	60 – 75 %
Ammonia	100 – 300	mg/l	> 99 %

Table 3.21: Average analytical values for pollutants in waste water and removal efficiency
Source: Leather No.1, January 1998, changed due to comments from Germany and BLC

Table 3.23 gives the input and output of the waste water loads (data received in 1999) of three common treatment plants in Italy. See annexes (pages 210 - 211) for figures of the plants Cuoiodepur and F.I.C. S.p.A.

In the UK, a commercial relationship exists between the tannery and the sewerage operater to share the treatment of the waste water. All tanneries treat their waste water to some degree before discharge to sewer. Typical discharge levels in total (i.e. mixed) effluent from UK tannery waste water treatment plants to sewer are:

pH	6 - 10	
Sulphides	2 - 5	mg/l
Chromium	1 - 20	mg/l
Soluble solids	500 - 1000	mg/l
COD	2000 - 6000	mg/l
Chlorides	5000	mg/l
Sulphates	1000 - 1200	mg/l
Ammonium	10 - 1000	mg/l

Table 3.22: Typical discharge levels in total effluent to sewer from UK tannery waste water treatment plants
Source: BLC

Aquarno is the common treatment plant in Santa Croce Sull'Arno and treats waste water from about 400 tanneries (10000 m³ per day) and municipal waste water from 2 villages (500 m³ per day). The main problems are the high COD and the salt contents. To meet the standard of 160 mg COD/l, hydroxy peroxide is sometimes added. The amount of sludge from the activated sludge process is 120000 tonne/year (40 % dry contents) and is disposed of. The cost of disposal is ITL 150 per kg (about EUR 80 per tonne sludge). The sludge can be used for agriculture because it meets the Italian standard, but there is no market for it.

Cuoiodepur is another common treatment plant in Santa Croce. 3500 m³ of municipal waste water per day has to be treated together with the waste water from 150 tanneries (6000 m³ per day). 95 % of the tanneries discharging to this plant are using vegetable tannins. It is a very modern plant and totally covered; the removed air is led through a scrubber and the final contents of H_2S is 0.4 ppm (the Italian standard is 5 ppm). The sludge produced is dried to a water content of 15 – 20 % (about 30000 tonne/year based on 85 % dry contents); with the aim of using it as a fertilizer as soon as the authorities give their approval. At the moment it is used in civil engineering works. In treating the waste water, problems arise with the high ammonium sulphate content of 300 - 400 mg/l; the nitrification-denitrification process takes 17 days. To meet the standard (160 mg/l) for COD, iron salts are added. For salt the standard is 1200 mg/l and this cannot be met.

The third common treatment plant is F.I.C. S.p.A in the Arzignano area. In this plant 30000 m³ per day of waste water from 160 tanneries and 150 other industrial activities, and 8000 m³ per

day of municipal waste water is treated. 90000 tonnes of sludge per year is produced with a water content of 65 %. After the sludge is treated in a beltpress and platepress, a thermal treatment dries the sludge to a water content of 10 %. This dried sludge is put in big bags and landfilled on their own site. But because this landfill is almost completely filled, new alternatives are being investigated. An incineration plant is one of the options. The drying system is an energy saving cogeneration system. It produces 5360 kWh electrical energy, which is almost sufficient to meet the total plant requirement of 5500 kWh. The sludge cannot be used in agriculture because of the 3 % chrome content based on the dry matter. The nitrification/denitrification process takes a lot of energy and the reduction time is 3.5 to 5 days.

Influent	Water m³/day	COD mg/l	SS mg/l	TKN mg/l	S^{2-} mg/l	Cr mg/l	Cl^- mg/l	SO_4^{--} mg/l	Costs EUR [4]
Aquarno [1]	10000	10000 - 12000	45000	300 - 400	120	40 - 60	6000	2000 - 3000	
Cuoiodepur	9500	12000	10000	300 - 400	200	30 - 40	8000	2000 - 2500	
F.I.C [2]	30000	6500	2700	550	60	110	-	-	
Effluent									
Aquarno [1]		200 - 400		20 - 30					6
Cuoiodepur		200 - 250	30	3 - 4	0	0	4500	1800	11
F.I.C [2]		120 - 130 [3]	10	1 - 5	0	0.3	2000 - 2500	1000 - 1500	2.5 - 3

Notes:
1) Municipal waste water not included.
2) Waste water from tanneries and other industrial activities; no municipal waste water
3) Hypochlorite is added to achieve these data
4) Costs for treating 1 m³ of industrial waste water, inclusive air treatment and sludge treatment

Table 3.23: Waste water loads of three common treatment plants in Italy

The table below gives data of the waste water of a vegetable tanning process.

Manufacture of vegetable tanned leather - chemicals used, composition and volume of effluents						
	A) Strap and russet upper leather (e.g. belts, handbags, suitcases)			B) Sole leather		
Current .Nr.	Operation	Efflu-ent m³/t	Chemicals used, Effluent constituents	COD % load	Efflu-ent m³/t	Operation
1	Preliminary Soaking	ca.15	Alkali, wetting agents, biocides, dung, blood, soluble protein, curing salt, AOX	ca.50 %	6 - 8	Soaking
	(Soaking) liming		Lime, Na-sulphide, Na-hydrogen sulphide, residual protein from hair and skin, fat, degradation products			Liming
3	Deliming, Bating, washing		Ammonium sulphate, oxalates, CO_2, citrates, enzymes; epidermis, hair and pigment residues, non-collagenic proteins, soluble lime salts			Deliming, Bating
4	Pit tanning* (removal of content at 4 - 6 week intervals)	ca.8	Vegetable and synthetic tanning agents (A: ca.20 % tanning agent/pelt weight; B: ca. 25 - 30 % tanning agent/pelt weight); leather fibres, organic degradation products,	ca. 50 %	ca. 2	Pit tanning (removal of content at 2 - 6 month intervals)
5	Dripping, washing Samming					Washing, samming
6	Fat-liquoring	1 - 2	Greasing agents, emulsifiers, leather fibres			
7	Retanning, dyeing, greasing washing	ca.5	Vegetable and synthetic tanning agents, dyes, fat, emulsifiers, leather fibres			
8	Samming					
		∑ 15 - 30			ca.10	
	COD ca.150 kg/t, 5000-10 000 mg/l			COD ca. 100kg/t; 10 000-12 000 mg/l		

* Drum tanning used only in split manufacture; here, the volume of waste water is ca. 1 m³/t raw hides; COD: up to 10000 mg/l; BOD_5: up to 3000 mg/l.

Table 3.24: Example of effluent composition of a vegetable tanning process
Source: tan/tm/37/Germany

Treated and untreated waste water may be used for irrigation under certain circumstances, see e.g. the Igualada waste water treatment plant and reference [tan/tm/42/Unido-Mass]. The long- and short-term effects on soil and groundwater have not yet been comprehensively assessed, but, given the possible contents of waste water effluents, there is potential for harmful environmental impact. A comprehensive assessment would require more data.

3.3 Waste

Quantities of solid waste produced by tanneries depend on the type of leather processed, the source of hides and skins and the techniques applied. On average, at the end of the process about 20 % of the weight of the raw hides is (grain side) leather.

The EC recently rejected a call by some member states of the EU to include tannery wastes containing chromium in the European Hazardous Waste List on the basis that the wastes did not possess the characteristics necessary for classification as a hazardous waste. The table below shows the wastes included in the European Waste Catalogue[6]. Those deemed to be hazardous are marked with an asterisk.

04 01	**Wastes from the leather and fur industry**
04 01 01	fleshings and lime split waste
04 01 02	liming waste
04 01 03*	degreasing waste containing organic solvents without a liquid phase
04 01 04	tanning liquor containing chromium
04 01 05	tanning liquor free from chromium
04 01 06	sludge, in particular from on-site effluent treatment, containing chromium
04 01 07	sludges, in particular from on-site effluent treatment, free from chromium
04 01 08	waste tanned leather (blue sheetings, shavings, cuttings, buffing dust) containing chromium
04 01 09	waste from dressing and finishing
04 01 99	waste not otherwise specified

On the following page, Table 3.25 lists the residues from the process units and the associated processes. In the column for 'Further treatment / Disposal / Recycling' all possible options are listed, regardless of whether they are applied, BAT or emerging techniques.

[6] Commssion Decision of 3 May 2000, replacing Decision 94/3/EC establishing a list of wastes pursuant to Article 1(a)of Council Directive 75/442/EEC on waste and Council Decision 94/904/EC establishing a list of hazardous waste pursuant to Article 1(4)of Council Directive 91/689/EEC on hazardous waste.

Process Unit	Type of waste	Content	Further Treatment / Disposal/ Recycling
Trimming	• parts of the raw hides (trimmings)	collagen, hair, fat, connective tissue, blood,…	• production of hide glue/gelatine • animal feed stuff • biogas • thermal treatment • landfill
Curing	• solid salt • brine	NaCl and possibly additives	• re-use – problems with infectious material on salt • landfill
Liming and Unhairing	• hair / wool	Keratin rich material	• wool is sold • re-use as filling material • production of lanolin from sheep wool • fertiliser / agriculture / animal feedstuff • composting • biogas • landfill
Fleshing (*)	• fleshings	fat, blood (green fleshing) possibly with liming and unhairing chemicals	• splits can be processed to leather • production of hide glue/gelatine (sausage casings only splits) • protein hydrolysate • recovery of fat (fleshings only) • composting • biogas • landfill
Splitting (**)	• lime split (flesh-side)	same as fleshings	
Solvent degreasing **Aqueous degreasing**	• distillation residues • waste water treatment residues	• organic solvents and fat • surfactants • emulsified and not emulsified fat • pre-tanning agent residues (e.g. aldehyde, etc)	• recycling of organic solvents • re-use of fats • thermal treatment of non-halogenated-organic-solvent containing waste • recovery of fat using acid cracking for possible use in the cosmetic industry • low pH waste waters to be treated
Tanning / Retanning	• tanning liquors	for chemical composition of agents see Section 3.1.4	• recovery of chrome in tanning liquors
Splitting & shaving	• tanned split and shavings, • trimmings	organic matter with contents according to tanning	• leather fibre board production • protein hydrolysate • composting • agriculture • thermal treatment • landfill
Fatliquoring	• obsolete chemicals	for chemical composition of agents see Section 3.1.7	• disposal of chemicals according to their characteristics
Dyeing		for chemical composition of agents see Section 3.1.9	

Process Unit	Type of waste	Content	Further Treatment / Disposal / Recycling
Milling / Buffing	• dust	organic matter with contents according to tanning	• landfill • thermal treatment
Finishing (Coating)	• residues from finishes, • sludges from finishing agents (over-spray, etc.)	• for chemical composition of agents see Section 3.1.10 • solvents • heavy metals	• landfill • thermal treatment
Trimming (final)	• trimmings with or without finish	leather with contents according to tanning and finishing	• leather fibre board production for not lacquered trimmings • other re-use (patchwork, small leathergoods etc.) • landfill • thermal treatment
Air treatment	• depending on the abatement techniques: activated carbon, sludges from wet-scrubbers, filter dust etc.	depending on the off-gas stream	• organic compounds (e.g., solvents) – recovery • sludges see waste water treatment • thermal treatment • landfilling
Waste water treatment	• sludge from waste water treatment	depending on the separation of waste water streams	• re-use in agriculture • composting • biogas • landfill • thermal treatment
Waste treatment	• residues from on-site waste treatment	residues from rendering, anaerobic or aerobic digestion	• re-uses in agriculture • landfill • thermal treatment
Packaging	• pallets • paper • plastic • containers for chemicals		• recycling • landfill • thermal treatment
Other	• obsolete chemicals • scrap metal and defunct equipment		• recycling • landfill • thermal treatment

Notes:
(*)   Fleshing can be performed before or after liming resulting in different releases.
(**)   Splitting can be performed with limed or tanned hides and skins with crust resulting in different releases.

Table 3.25: Overview for all waste fractions

As waste fractions are separated and merged in different ways, depending on the options for re-use/recycling and disposal, differences in the figures reported occur.

Data for the percentage of various waste fractions with respect to the total waste production for salted bovine hide are compiled from various sources [tan/tm/11/Nordiske Seminar, tan/tm/37/Germany, tan/tm/18/UNEP-Tan, tan/tm/04/Austria, tan/tm/09/UNIDO, tan/tm/15/Reemtsma] and shown in Table 3.26.

	% of raw hide weight
	average
Trimmings from raw hides	2 – 5
Lime fleshing	10 – 40
Lime split [1] and pelt trimmings	10 – 20
(Chrome) shavings [1]	
(Chrome) split [1]	20 – 30
(Chrome) leather trimmings	
Buffing dust	0.2 – 1.0
Painting, lacquer and other chemicals	0.5
Sludge from waste water treatment	40 – 50 [2]
Packaging	1.5
Notes: (1) Amount depending on splitting in limed or tanned condition. (2) A figure cannot be accurately given, since the reference parameters (moisture, efficiency of waste water treatment are not given for the figures quoted from other references. Assuming the amount of suspended solids according to the figure in Table 3.14, the total quantity of sludge generated by sedimentation and biological treatment is about 400 to 500 kg t wet salted hides. [tan/tm/42/Unido-Mass]	

Table 3.26: Amount of organic waste for salted bovine hides

Apart from the summary of waste treatment options summarised in Table 3.25, recycling, re-use and disposal of all waste fractions will be discussed in detail in Section 4.7.

The stricter the requirements for waste water purification (emission limit values for certain parameters), the higher the quantity of sludge produced. To compare data the dry matter content and the removal efficiency have to be reported.

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

Other waste fractions not shown in Table 3.26 are salt, organic solvents, residues of process chemicals and auxiliaries, fats from degreasing, finishing sludges, residues from air abatement other than buffing dust, such as activated carbon filters and sludges from wet-scrubbers, and residues from waste treatment.

3.3.1 Hair / wool

Depending on the techniques applied, hair is either separated or released together with the effluents of the beamhouse, thus contributing to the COD loading of the effluent and the subsequent amount of sludge generated in the waste water treatment. If the hair is separated it can be used in various ways (see Table 3.25 and Section 4.7). The majority of tanneries employ a hair-burn system whereby the hair is completely dissolved and released in the effluent.

Wool from sheepskins is sold as raw material to the textiles industry.

3.3.2 Trimmings / fleshings / splits / shavings / dust

Figures in the following paragraphs apply only for bovine hides.

The residues arising from the initial **trimming** of the rawhides are pieces of the raw hides, which carry curing agents and possibly biocides or perhaps infectious material.

Hides may be sorted and trimmed before processing. Trimmings may also arise during fleshing, splitting, or rounding. The disposal routes for trimmings are summarised in Table 3.25.

Trimmings from later stages in the process, such as after tanning, post-tanning or finishing can be re-used in the production of leather fibre board production (if they are not lacquered) [tan/tm/37/Germany]. Trimmings that are not recovered or re-used are landfilled (when allowed).

The figures for the amount of trimmings from raw salted bovine hides range from 2 % [tan/tm/11/Nordiske Seminar] to 5 % [tan/tm/17/Frendrup]. If trimmings after lime splitting are included, the amount is estimated to about 12 % [tan/tm/04/Austria]. It should be stressed that the amount of trimmings generated strongly depends on the type of processing employed. Whereas some tanneries may generate no trimmings in the beamhouse, others may generate up to 10 % of trimmings.

The equivalent of approximately 10 – 40 % of the weight of raw hides is removed as wet fleshings.

Fleshings and non-tanned split are putrescible material consisting of protein and fat. Additionally they contain chemicals carried over from previous process steps. Thus, depending on the sequence of the processes, these waste fractions may have varying chemical compositions. For example lime fleshings will contain process chemicals from liming and unhairing, such as lime and sulphide. Furthermore, the pH of these lime fleshings will be approximately pH 12. Therefore, each waste stream requires specific handling procedures taking into consideration the risks associated with the chemical composition of the waste.

Splits can be generated after limings or after tanning. The flesh side of the splitting, also referred to as the split, can be used to make leather without a grain.

Shavings which are generated in levelling the surface of the leather, are smaller pieces than splits. Splits from tanned leather, shavings and **dust** from milling and buffing contain the tanning chemicals. Any further re-use and treatment depends on the particular chemical composition.

3.3.3 Sludges from waste water treatment

Sludges are produced directly in the tannery from first treatment steps or from a full waste water treatment on-site or at the waste water treatment plant to which they are released. Both sources have to be taken into account when figures for the amounts of sludge produced are discussed. The amount of sludges generated is influenced directly by the requirements set for waste water effluents. In practice, however, it is very difficult to obtain figures if industrial effluents and municipal effluents are treated jointly. The quality of the sludge produced depends on the chosen treatment. Any further treatment options will depend on this choice.

A typical composition for waste water treatment sludges is given for Italian tanneries from tan/tm/39/Italy. The figures are percentages of sludge from a biological treatment plant after dewatering.

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

Table 3.27: Typical composition for waste water treatment sludges
Source: tan/tm/39/Italy

For the disposal of sludge several options are available. However, because of new regulations some will not be available in the future or might require further pretreatment steps.

- landfilling of sludge
- anaerobic digestion
- application of sludge in agriculture
- incineration of sludge.

Landfilling of sludge
Landfilling of sludges will become increasingly difficult for two reasons: the availability of landfills is diminishing and new environmental legislation, such as the Landfill directive aiming to prevent or reduce negative effects on the environment from landfilling waste came into force. Consequently alternative disposal routes and pretreatment options need to be developed for larger quantities of sludge.

The Federal Environmental Agency of Germany (UBA) expects that using only anaerobic treatment or pyrolysis is not enough to reduce the organic carbon content of sewage sludge to the level which as of 2005 will be required in Germany as a condition for the depositing of sewage sludge on landfills for domestic refuse. In Austria landfilling of sludge with a total organic carbon (TOC) content higher than 5 % will be forbidden from January 2004. Thereafter, sludge from biological waste water treatment plants cannot be disposed to landfill without additional treatment.

Anaerobic digestion

Anaerobic digestion of organic wastes is not a common technique for sludges yet, because other disposal options have been more readily vailable. This technique needs careful planning and management to achieve a reliable performance. Anaerobic digestion offers the advantage of energy gains from the produced methane. The residues of the process have to be disposed of, however this is feasible more easily than disposal of untreated sludges.

Application of sludge in agriculture in Europe

Though application of sewage sludge to land is a generally accepted practice in Europe (although not in every country), there is increasing pressure to restrict this route. The main reasons for concern are: contamination of soils with chromium, pesticides, pathogens or other pollutants; nutrient saturation of soils; distance from waste water treatment plants to sufficient farmland; local opposition because of nuisance problems and an image problem. Pretreatment, e.g. anaerobic digestion or composting, might be necessary. Anaerobic digestion, as a stand-alone technique, is not sufficient to meet the 5 % TOC criterion that will be applied in Austria from January 2004 to determine whether the sludge is allowed to be landfilled.

Environmental legislation[7] sets limits for the concentrations of several heavy metals in sewage sludge (lead, cadmium, mercury, copper, zinc, and nickel) and limits for the amounts of heavy metals which may be added to the soil in sewage sludge. Furthermore it lays down certain requirements when applying sewage sludge to land.

Thermal treatment of sludge

Incineration, gasification, or pyrolysis of sludges as a means of disposal, whilst recovering energy from waste is currently under investigation. However, it is thought that this option is only economically attractive if alternative disposal routes are being restricted or becoming too expensive.

Emission limits to air may have an impact on the quality of sludge that can be incinerated and on the cost of abatement of gaseous emissions. The residues of the process still have to be disposed of, but this is more easily achieved than with untreated sludges.

A study done in Austria gave the following results. Incineration of dewatered sludge involves a high consumption of energy; the temperature must be over 800°C to avoid noxious smells spreading to the environment. Moreover, about 5 to 10 % of total chromium is converted from chromium (III) to the carcinogenic chromium (VI). The installation of incineration plants and especially the filter equipment for air pollutants is very expensive. Given the environmental legislation and people's resulting sensitivity to waste treatment, there is no acceptance for incineration plants in Austria. [tan/tm/04/Austria]

The waste disposal routes for waste water treatment sludges differ in all Member States. The feasibility of a disposal route is strongly dependent on the costs and on the acceptability of applying sludge to agricultural land. Table 1.5 gives an estimate of the disposal routes for tannery sludges in several European countries.

In Table 3.28 data for the different options of waste treatment for organic wastes discussed in the previous chapters are given for Austria as an example. The main disposal routes are highlighted for each waste fraction (compare with Table 3.25). Similar data were not available for other countries; the disposal routes for the various waste fraction might be very different.

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[7]   Council Directive 86/278/EEC and legislation in Member States.

AUSTRIA	Hair	Trimmings		Fleshings	Splits	Shavings	Dust	Sludges
Unit: [%]		raw	tanned					
Renderer / Separation of contents		100		100 [(1)]	C/P 20 [(2)]	C/P 70		
Composting								
Anaerobic digestion								
Agriculture								
Thermal treatment								
Other re-use/recycling	C/P 100 [(3)]		66 [(4)]		80 [(5)]	C/P 30 [(6)]		
Landfill [(8)]	No		33	---			100	100 [(8)]

Notes:
(1) Animal feedstuff and tallow production.
(2) Splits processed at renderers' or for separating the contents, if they are not tanned. The products derived gelatine (from 80 % of untanned splits) and sausage casings (20 % of untanned splits).
(3) C/P stands for chemical/pharmaceutical production. Only sheep's wool is recovered, bovine hair is destroyed.
(4) Trimmings can be re-used as shavings to produce leather fibre board. Only vegetable tanned trimmings are used for leather fibre board production and heating.
(5) 80 % of the splits are used to produce to leather without a grain layer.
(6) Shavings are re-used to produce leather fibre board. If they do not contain chrome, shavings are used for the production of animal feedstuff and fertilisers. Chrome containing shavings are deposited or used for leather fibre board production.
(7) Legislation in Austria has changed recently. After the transition period it will not be possible to dispose organic waste fraction without special pretreatment.
(8) In the future sludges with low chrome content will be used in agriculture.

Table 3.28: Organic waste treatment routes currently used in Austria
Source: tan/tm/03/UwHB-Stoffe, tan/tm/03/UwHB-Abfall, tan/tm/04/Austria

3.3.4 Other waste fractions

Salt can be re-used in curing or for pickling liquors if it is sufficiently sterilised and clean. In some Member States landfilling of solid salt is practised.

Organic solvents can be re-used within the process for minor applications such as cleaning; in particular cases, organic solvents can be recovered by distillation for repeated process-integrated use or external re-use. Finally, (non-halogenated) organic solvents can be thermally treated.

Residues of chemicals and auxiliaries have to be disposed in the light of their risk to human health and the environment. Some chemical waste may need to be treated off-site in specialised waste treatment plant or taken back by the chemical supplier. Other chemical waste can be classified as non-hazardous waste and disposed of with other non-hazardous wastes.

Residues from degreasing contain fats and – depending on the process chosen – organic solvents or surfactants. Fat and solvents can be recovered or the residues are treated thermally.

Finishing sludges can contain hazardous substances depending on the finishes used. They can be treated physico-chemically, thermally or be landfilled.

Activated carbon filters from **air abatement** can be regenerated several times; final disposal is by thermal treatment or landfill. Leather dust can be thermally treated or it can be landfilled. Dust may also be compacted before disposal to facilitate handling. Sludges from wet-scrubbers are landfilled.

Residues from **waste treatment** of organic wastes on-site can be re-used in agriculture, treated thermally or be landfilled, depending on their composition.

Packaging material (containers for chemicals, palettes, plastics) is either sent back to the supplier, treated thermally or is landfilled.

Table 3.29 presents figures for the different disposal routes for other wastes. The principally viable or in practice used disposal routes are highlighted for each waste fraction (compare with Table 3.25).

Unit: [%]	Salt	Organic solvents	Chemicals	Fats from degreasing	Pigment sludges	Air abatement	Waste treatment	Packaging material
Re-use within process	x	x						x
Re-use in agriculture							x	
Physical/ chemical treatment	x			x		(1)		
Thermal treatment		x	x				x	x
Other re-use/ recycling		x	x	(2)				x
Back to supplier								x
Landfill	(3) x	(3)	(3)	(3)	x	x	x	x
Notes: (1) Regeneration of activated carbon (2) Recovery of organic solvent and fat (3) Landfilling might still be allowed in some Member States.								

Table 3.29: Waste treatment routes for various wastes in Europe / in Member States

3.4 Air

For air emissions, the distinction has to be drawn between emissions to the workplace and emissions to the environment in general. Emissions to the workplace include odour, dust of powdery chemicals (tanning, dyeing agents), organic solvents and leather dust, but they cannot be quantified. Exposure limits are set for some substances.

For air emissions to the environment in general, data are only available for VOC in general (often giving only the consumption of organic solvents and using different monitoring systems). Volatile halogenated hydrocarbons require special attention, as some of these constitute a high environmental risk. They are used predominately in the degreasing of sheepskins. Abatement techniques such as activated carbon filters are feasible but not standard in tanneries; furthermore, fugitive emissions may be a major part of the total emissions. Odours are not quantifiable, but they frequently give rise to complaints from neighbours.

Relevant air emissions are: sulphides from the beamhouse and the waste water treatment; ammonia from the beamhouse; tanning and post-tanning operations; sulphur dioxide from post-tanning operations; dust/total particulate from various operations, such as storage and handling of powdery chemicals, dry shaving, buffing, dust removal machines, milling drums and staking.

Incineration processes for energy supply and for waste treatment require further monitoring and abatement. For incineration, particularly the oxidation of chrome (III) to chrome (VI) under particular conditions and organic emissions (PCDD/F, PAH) have to be taken into account.

Many Member States have implemented specific regulations, which apply to all emissions to air, to protect the environment and the immediate vicinity from offensive odours and harmful substances. The emission limit values are usually set for ammonia, hydrogen sulphide, volatile organic compounds (VOC), total particulate matter and, for the incineration process, carbon

monoxide and nitrogen oxides. On a European level, the European Commission has restricted the use and emissions of leather coating with the Solvents Directive.

3.5 Energy

Of particular interest are the energy demands of drying operations, the preparation of warm water and the effluent treatment plant. From the environmental point of view, besides the demand for thermal and electrical energy, major points of concern are: the type of the energy source; boiler and fuel types and energy conservation.

Energy consumption in tanneries depends mainly on the following factors:

- production type, capacity and size
- equipment for process units
- air exchange rates to meet workplace safety conditions
- heat losses in buildings and process units
- type of waste water treatment on-site
- type of waste treatment and recovery of energy from waste on-site

Energy is required as thermal energy for processes like drying, warm water, heating of working areas, air pressure (solvent use, dust) and as electrical energy for machinery, light etc.

Several studies of energy consumption were conducted in the 70s and 80s. Based on these studies it appears that approximately 85 % of all energy consumption is thermal energy and 15 % is electrical energy.

Table 3.30 gives an indication of energy consumption by type of energy used.

		% of overall consumption
Thermal energy	Drying	32 – 34
	Hot water	32 – 34
	Space heating	17 – 20
Electric energy	Machinery and process vessels	9 – 12
	Pressurised air	1.5 – 3
	Light	1.5 – 3

Table 3.30: Consumption of thermal and electrical energy
Source: BLC and tan/tm/03/UwHB-Energie, tan/tm/17/Frendrup

Many tanneries have one central or several departmental boilers on-site to raise steam (thermal heat). Boilers generally run on gas, oil, or coal, but sometimes waste, such as fat, tallow and pallets, may also be used as a source of energy. Most tanneries use electrical energy from the public supply.

The climate has a decisive influence on the energy requirement of a tannery, hence large variations in energy consumption between tanneries in Northern Europe and Southern Europe are likely. It is thought that the requirement of a tannery for thermal energy is reduced by 2 % for each degree the annual average temperature increases.

The electric energy consumption needed to operate a biological waste water treatment may account for more than 50 % of total energy consumption of the complete effluent treatment plant.

A survey carried out to compare energy consumption between European tanneries revealed that energy consumption can range from 9.3 - 42 GJ per tonne of raw hides.

The following data are average taken from real consumptions in a representative number of Spanish tanneries, from 1996.

- energy consumption (fuel):   80.2 g fuel/sq ft finished leather
- electricity consumption: 174.3 Wh/sq ft finished leather
- water: 11.3 l/sq ft finished leather

The principal sources of energy losses are exhaust hot air, exhaust hot water, distribution losses and chimney or stack losses.

Collation of data on energy usage in UK tanneries, processing bovine hides, gave the following overall results, indicating a need to separate out data into comparable operations:

- raw to wet blue: average energy usage is 28.58 kWh/tanned hide (range 29.78 - 31.39)
- tanned to finish: average energy usage is 17.7 kWh/m^2 finished leather (range 6.7 - 35.7)

3.6 Noise

Some mechanical operations are the source of noise problems, both with high frequency (Health & Safety in the workplace) and with low frequency (domestic nuisance). Proper design and maintenance should reduce noise to acceptable levels and additional workplace protection generally resolves the problem in tanneries [tan/tm/36/UK].

3.7 Typical emission and consumption from process units

This section discusses each of the process units described in Table 3.2 and explores in further detail what emissions and consumption levels are likely to be expected in European tanneries. It should once again be stressed that this information is indicative and not prescriptive. Variations may occur depending on types of raw materials used and types of products produced.

3.7.1 Trimming

Hides and skins may be trimmed in the tannery upon receipt. This generates trimmings that are either disposed off or can be sold for rendering, glue or gelatine manufacture, or when possible for further tanning (see Section 3.3.2). Where hides and skins have not been preserved for long time storage, trimmings are putrescible.

3.7.2 Curing

Consumption
The hides and skins are brought from the abattoirs to the tanneries either directly or through hide markets, hide merchants and even other tanneries. The raw material has to be transported from the abattoir to the tannery or from the abattoir to the hide and skin market and then to the tannery. Temporary storage may be necessary at any stage.

Tanneries stock hides and skins to optimise the efficiency of their batch processes. There is a wide choice of methods to prevent the degradation in transit of hides and skins that cannot be processed immediately. The choice depends mainly on the period of time envisaged for preservation.

Long-term preservation methods are:

1. salting
2. brining
3. drying
4. salt drying.

These four methods of curing are effective for up to six months without jeopardising the quality of the leathers produced.

Salt is a biostat and acts by inhibiting the growth and activity of bacteria by lowering the moisture content in rawstock. Various methods of salt curing can be applied. In general, hides and skins are spread out, covered with salt, and then stacked, sandwiched with more salt. The hides and skins may need to be resalted if they are stored for a long time. As an alternative to throwing salt on the pelts, they can be agitated in a brine solution. This generally takes place in processing vessels such as drums and raceways.

In salting, the quantity of salt (sodium chloride) used depends largely on the storage time required, but is typically 15 % of the salted hide weight. Brining is a preservation technique mainly used in the USA and involves dragging the hides through a salt solution.

In some cases selected biocides may be included in the salt to prevent the growth of salt-tolerant bacteria, though it is thought that this is not common in Europe. Several proprietary biocidal products are on the market. These include potassium dimethyldithiocarbamate (> 0.3 % of hide weight for brine curing), p-dichloro-benzene, sodium silico-fluoride and borax. More commonly known biocides such as boric acid and sodium metabisulphite might occasionally be used as preservatives.

Skins originating from countries with a very hot climate may have been dried or dry-salted. Dry and dry-salted skins may contain insecticides such as pyrethrum and permethin, which are added either to the raw material or to the salt to keep insects away from the eatable substrate during and after the drying process.

Drying in ventilated areas is used predominantly for skins, but bovine hides are preserved by drying in some countries (Russia, Africa) [tan/tm/39/Italy].

Short-term preservation methods are:

1. ice
2. refrigerated storage
3. biocides.

One of the short-term preservation methods is cooling. If the time between flaying and processing in the tannery is no more then 5 - 8 days, it is possible to cool the hides/skins, after draining the blood, to a temperature of 2 ºC. Crushed ice, ice-water or cooled storage may be used for this purpose. The cooling chain must not be interrupted during transport and storage. With this technique - processing fresh hides - the use of salt is avoided. Processing fresh hides may not be feasible when a long transport time is necessary (max 8 - 12 hours for fresh, unchilled hides; 5 - 8 days if a cooling chain of 2 ºC is maintained), for certain types of end-products and when processing sheepskins and/or calf skins.

In general there are no biocides used in the preservation of raw <u>bovine</u> hides in Europe. Biocides that were used in the past include PCPs, DDT, benzene hexachloride, HCH, dieldrin, arsenic and mercury based ones. The use of these biocides is prohibited in Europe. Nevertheless, skins imported from South America, the Far East, Africa or India, could still be treated with biocides already banned in the EC. Furthermore, hides and skins could contain

traces of biocides because of animal treatment with these substances prior to slaughtering (see biocides in Section 3.1).

The selection of preservation methods largely depends on the market structure (consistent supply from abattoir, hide and skin market) and geographical distribution of raw material.

Country	% - age of raw hides processed as fresh hides	Source
Austria	60 – 70	tan/tm/04/Austria, tan/tm/17/Frendrup
Germany	60 – 70	tan/tm/17/Frendrup
United Kingdom	30	BLC
Denmark	0	
South America	75	tan/tm/09/UNIDO

Table 3.31: Processing of green hides in Member States

Emissions
Process-specific substances, such as salt, biocides and pesticides can be found in the joint effluents after subsequent process steps are performed. Salted and brined hides can produce a leachate which is contaminated with dirt, bacteria, blood, salt etc. There can also be solid waste salt from the curing process that needs to be disposed of. It is not common to re-use waste salt as this would increases the risk of contamination with salt-tolerant bacteria.

3.7.3 Beamhouse operations

3.7.3.1 Soaking

Consumption
Soaking of hides and skins takes place in processing vessels filled with water. Water consumption may be between 200 % (very clean hides) and 3000 % (dried or very dirty hides) of the weight of the hides and skins depending on the source of the raw material and the state of contamination with dirt and dung (compare Table 3.13). Sheepskins generally require more water in wet processing than hides, because of the nature of the wool. In most tanneries the float of the soaking is renewed at least once. The first float is called the dirt soak and the second float is called the main soak.

In some cases biocides may be added to the float in order to minimise bacterial damage to the hides. The biocides are added particularly if the soaking is performed at elevated temperature, at a rate of about 0.1 % of the hide weight. Chlorinated alkanes are used as conserving agents in soaking [tan/tm/15/Reemtsma].

Furthermore, alkali, surfactants and enzymes may be added to improve the efficiency of the soaking process. Sometimes sodium hydroxide (0.2 - 2 g/l) or up to 1 g/l sodium hypochlorite [tan/tm/11/Nordiske Seminar] is added, although the latter might cause problems with AOX in the waste water effluents. Alternatively weak acids such as formic acid or sodium bisulfite can be used. Generally, biocides, alkali e.g. caustic soda or sodium carbonate, surfactants and enzymes are added each in amounts less than 1 % of the weight of the salted hides and skins. For example alkyl ether sulphates and alkyl sulphates with non-ionic alkyl(phenyl)polyglycol ethers may be used, for example nonylphenol ethoxylates (NPEs).

Emissions

The soak liquor is discharged to the waste water treatment plant. The effluent contains the dirt, dung, blood, fat and other hide components, which results in high COD loading of the effluent. Furthermore, if the hides and skins were preserved, the effluent contains most of the salt and biocides which were on the hides. Also, the additives added in the soaking operation are largely contained in the soak liquor. These releases are monitored by the parameters BOD, COD, SS and chloride in the final effluent.

There is hardly any specific monitoring of some other environmentally important or potentially important substances and, consequently, no data are available. These substances include biocides, surfactants, organic solvents and chlorinated alkanes. As organic substances, they make some contribution to COD and BOD, but these broad indicators are inadequate measures of their environmental effects. The level of bactericides used in soaking can be monitored during processing by the use of dip slides that allow the tanner to optimise the amount applied, thereby reducing waste water to a minimum and saving on the cost of chemicals. Chlorinated organic compounds from soaking (and dyeing and fatliquoring) as well as reaction products of hypochlorite with organic matter contribute to the AOX. An AOX emission limit value is not set in all Member States.

The following table shows the range of concentrations of types of pollutants that may be found in the effluent from the soaking process. The actual loads and concentration of pollutants varies widely from tannery to tannery depending on the raw materials used, the process operated and the specifications of the products.

Pollutants in Waste water		Examples for emission loads from conventional soaking processes for Salted bovine hides in [kg / t raw hide]			
		Tan/tm/11/ Nordiske Seminar	Tan/tm/39/Italy	Tan/tm/58/BLC	Tan/tm/17/ Frendrup
Total Solids					160
Suspended Solids	X	15		15	15
COD	X	40		30 - 50	27
BOD	X	8 – 10		8 - 10	10
Chloride	+	200 ± 50	60 - 200	200 ± 50	85
Biocides	+				
Detergents	+				
Enzymes	/				
Notes: X = always + = often / = sometimes					

Table 3.32: Pollutants in waste water from soaking

60 %of tannery chloride originates from salt used for curing; the remainder comes from the pickling and tanning processes. The importance attributed to the total salt load released is dependent on the specific environment of the site; that is, the sewage treatment plant or type of surface water into which the tannery or the sewage treatment plant discharges. [tan/tm/11/Nordiske Seminar, tan/tm/09/UNIDO]

Further possible problems are odours due to putrefaction and releases of hydrogen sulphide and ammonia. [tan/tm/16/Spain].

3.7.3.2 Liming & unhairing

Consumption

The unhairing and liming of hides generally takes place in the same float. It requires the use of alkali and sharpening agents to attack the hairs. The following chemicals are commonly used for this purpose:

- sodium sulphide
- sodium hydrogen sulphide
- lime
- surfactants
- enzymes
- amines.

The most common mixture is 150 – 400 % water, 3 – 6 % hydrated lime and 1 – 5 % Na_2S (or plus NaHS). Water consumption, including the rinsing afterwards, is considerable (almost a quarter of overall consumption; cf. p. 47).

Furthermore, some tanneries may use thiols, mercaptoethanoates, amines or enzyme preparations to (partly) substitute sodium sulphide. Caustic soda, sodium carbonate and calcium chloride can also be used as sharpening agents. Ammonia is formed naturally in old lime liquor, which can be helpful here [tan/tm/52/Handbook].

The concentration of chemicals varies greatly depending on the type of raw stock processed. For example, small calf skins will require higher chemical concentrations to achieve successful hair removal. A broad range of % (based on the raw material weight) of chemicals used during processing is:

Water (including washes)	150	-	3000 %
Hydrated Lime	3	-	6 %
Sulphides	1	-	5 %
Amines	0.2	-	1 %
Enzymes	0.5	-	1 %

[tan/tm/58/BLC]

Germany reports a consumption level of enzymes (to reduce the consumption of sulphides) of about 0.1 % enzymes + 0.1 % NaOH, which is already added during the soak (based on raw material weight).

Emissions

The effluents of liming and unhairing are characterised by their high alkalinity, their high sulphide content and high COD and suspended solids loading. It is estimated that the pollution load of the liming process accounts for more than 50 % of total suspended solids and more than 70 % of the BOD loading of the beamhouse [tan/tm/11/Nordiske Seminar]. Where a hair-save technology is used in unhairing, the hair is generally separated from the effluent, resulting in a solid waste and a subsequent reduction in effluent loading. A quarter of the overall nitrogen releases stems from liming and unhairing (see Table 3.15).

Where tanneries use sulphides for the unhairing process, the effluents need to be treated with care. Sulphides might be released to air from any effluents carrying sulphides (used and spent liquors, recycled liquors, rinsing water, etc.) as well as skins and hides if the pH drops below 9, e.g, by mixing sulphide-bearing effluent with acidic effluent. Low emissions of sulphides might even arise if no sulphide-containing agents are used, because some degradation products from keratin are alkyl-sulphides. Thiols, which are added or are built due to degradation of sulphur containing proteins, are found in waste water effluents. Some are highly volatile, so might cause an odour problem in the waste water treatment and may need abatement measures [tan/tm/15/Reemtsma]. If the sulphide solution is alkaline (pH above 8.5 - 9), hydrogen sulphide

is not released. Hydrogen sulphide, which is very toxic to humans in relatively low concentrations, is released if the solution is neutral or acid.

Further releases to air of ammonia can occur. Ammonia is split off at high pH from amino acids and, if the liming is too strong, ammonia is produced because the organic matter of the skin is degraded.

3.7.3.3 Painting and pulling of sheepskins

Consumption
The paint sprayed onto the flesh side of sheepskins in preparation for wool removal generally consists of a mixture of water, lime and sodium sulphide or sodium hydrogen sulphide. In some cases sodium hydroxide may be added to the paint. Whereas lime is the preferred paint thickener, a wide range of alternatives may be used such as chemically modified starches, gums, natural clays and poly-acrylates.

After painting, the skins are left for several hours for the paint to penetrate the skins and react with the hair roots. After this, the wool is pulled from the skins, either manually or mechanically. The wool is then dried and sold. The pulled skins are limed, similarly to the liming process described in the previous section, with the difference that there is carry over of lime and sulphide in the pulled skins, requiring reduced chemical addition for the subsequent liming action. It is common practice that the spent liquors in this process are recycled.

Emissions
Generally the paint will be contained in the skins and will all be carried over to the liming stage, and there is no, or minimal, waste paint to be disposed of. Pulling of wool may result in some wool being discarded where it is considered to be of low grade or contaminated with paint.

3.7.3.4 Processing of wool

The wool is generally washed before it is carded and dried in a drying tunnel. After drying, the wool is baled and sold to woolscourers.

Emissions
The effluent of the wool washing stages is discharged to sewer and contains dirt, grease and sulphides. At this stage some hydrogen sulphide may be released.

The drying of the wool requires energy to reduce the moisture content of the wool. This process may create odorous emissions.

3.7.3.5 Fleshing

Fleshing can be carried out at several stages of the process. The different fleshing operations are the following:

- green fleshing (raw fresh and chilled hides/skins)
- green fleshing (soaked -salted- hide/skins)
- lime fleshing
- pickle fleshing.

The fleshing operation aims to remove excess connective tissue and fat from the flesh side of the hides and skins. If fresh hides are being used, green fleshing takes place before soaking. If salted hides are used, green fleshing is carried out after soaking. Lime fleshing is carried out

after liming. Sheepskins can also be fleshed after pickling. Sheepskins are generally fleshed at two stages in the process, whereas hides are generally fleshed once.

There are no chemicals used for fleshing of hides and skins, other than that operators may use sawdust or an alternative to get a better grip of the slippery hides. The fleshing machines generally use water to wash away the fleshings.

In Germany at least five tanneries (year 1999) are processing green fleshing; two are processing salted bovine hides, the other three both salted and fresh hides. Those tanneries produce, amongst other things: shoe leather, upholstery leather and leather for bags. Two tanneries in Austria and several in the UK apply green fleshing. The two main tanneries in Denmark don't apply green fleshing but only lime fleshing because of the high quality required for upholstery leather.

Emissions
About 10 to 40 % of the weight of hides and skins are removed as wet fleshings. Fleshing of pickled skins and green fleshing generally generates the least quantities of fleshings, whereas lime fleshing generates the largest quantities.

Depending on the state in which the hides are fleshed, the fleshing may be putrescible. This in turn will decide what disposal route is feasible for the fleshings. The disposal route for fleshings largely depends on the local infrastructure for those wastes. In some Member States fleshings can be landfilled without prior treatment or after treatment, such as digestion or composting. Often fleshings will be sold for the production of e.g. hide glue, gelatine or for fat recovery. A traditional outlet is rendering.

3.7.3.6 Splitting

Consumption
Splitting can be carried out most commonly on the following substrates:

- limed pelts
- pickled pelt sheepskins
- tanned leathers
- crust leathers.

Depending on where the splitting is carried out, the use of chemicals and water in subsequent processes will be reduced, as only the required part of the hide is processed. Therefore, the earlier splitting is carried out, the fewer chemicals and the less water used to process the hides and skins. However, tanneries do not always split in the limed stage for technical reasons or the specifications of the final product.

When sheepskins are split in the pickled state to produce chamois leathers, a solution of surfactants is used on the splitting blade to increase the grip on the greasy skins, and reduce fat build up on the blade.

Emissions
Splitting creates a grain layer and a flesh layer. If the flesh layer is thick enough it can be processed into particular types of leather, such as suede. Sometimes, the flesh layer will be split again, depending on the thickness of the split and the end-use of the splits. Splits (flesh layer) obtained from lime splitting that are too thin to make leather can be sold to the gelatine, glue or sausage casings industry. Splits obtained from tanned splitting that are too thin to make leather can be sold to leather board manufacturers or be discarded as waste.

During lime splitting a waste water stream is created containing wood flour (or alternative chemicals used to aid gripping) and other unhairing and liming chemicals.

Sheepskin flesh layers are called chamois, and the grain layers are called skivers. Skivers can be sold to be processed as book binding material. During this splitting operation soapy water is used, leading to the production of an acidic waste water stream containing surfactants.

3.7.4 Tanyard operations

3.7.4.1 Deliming and bating

Consumption

In order to reduce the alkalinity and remove the calcium from the limed hides, a combination of washes and deliming agents is used. Generally, the calcium held on the surface of the hides can be removed through washing. Adding deliming salts, such as ammonium chloride or ammonium sulphate and organic ammonium salts can further reduce the pH [tan/tm/28/BASF]. The amount added is about 2 – 3 % of the weight of raw hides [tan/tm/16/Spain, tan/tm/17/Frendrup], while BLC [tan/tm/58/BLC] reports a use of 2.5 – 4 %.

Carbon dioxide can also be injected into the float as a full or partial replacement for ammonium salts. The amount of CO_2 ranges between 1 and 2.2 % [tan/tm/16/Spain, tan/tm/17/Frendrup], while Finland reports a typical carbon dioxide consumption of 0.75 - 1.5 % (of the weight) [tan/tm/50/FinlandCO2]. When thick hides are processed, deliming with CO_2 reaches its limits and ammonium compounds or organic or inorganic auxiliaries (e.g. boric acid) are added to aid the speed of the deliming process [tan/tm/17/Frendrup].

For both types of process, about 200 % of the raw hide weight of water is necessary (see Table 3.13), although Finland reports the use of about 30 % in a normal tanning process. Further alternative deliming agents, which may be used on their own or in combination with traditional deliming salts, include organic acids and sodium bisulphite. Auxiliary surfactants are added at the rate of 0.2 % of weight of raw hide [tan/tm/16/Spain].

Bating enzymes sold for tannery use contain only 1 – 5 % of either pancreatic or bacterial enzymes (active ingredient). The remaining 95 – 99 % of bating agent consist of inert carriers (wood flour, kaolin) and salts (ammonium chloride in most cases) [tan/tm/58/BLC].

Emissions

If the pH is sufficiently low, sulphides carried over with the hides from the liming give rise to free hydrogen sulphide in the drum. This is the case in CO_2 deliming (and in pickling).

When using ammonium salts for deliming, the ammonium reacts with the alkaline liquors to form ammonia gas, which is released to air. Good ventilation is usually installed. In the Swedish tannery Elmo Calf AB, the emission of ammonia to air has been measured twice. The results were 27.47 mg NH_3/m^3 and 32.8 mg NH_3/m^3, which means 8 tonnes annually as an average of 0.68 kg NH_3/ t raw hide (see Annex I.3).

Furthermore the ammonium salts contribute to a large extent to the total NH_4-N release [tan/tm/17/Frendrup]. A reduction of these releases might be necessary to meet the nitrogen discharge limits. The nitrogen discharge limits can be achieved by reducing the ammonium consumption of the process and/or an end-of-pipe solution such as a nitrification/de-nitrification in a waste water treatment plant.

If carbon dioxide (CO_2) is used as a deliming agent to completely or partly substitute ammonium, the reduction of ammonium in the waste water is considerable (see Table 3.33).

A comparison of the emission levels from the deliming and bating operation using either ammonium salts or carbon dioxide is shown in Table 3.33.

Emissions to waste water from deliming/bating [kg / t raw hide]	NH$_4$	CO$_2$
BOD	3 [1]	3 [1]
COD	6 [1]	6 [1]
TS	45 [1]	30 [1]
N-total	5 [1]	1.5 [1]
NH$_4$-N	4.1 [1]	0.1 [1] - 0.2 [2]
Notes: [1] tan/tm/11/Nordiske Seminar [2] tan/tm/17/Frendrup		

Table 3.33: Emission to waste water from deliming/bating

Bating chemicals are often added as powdery agents. For workplace safety, measures to prevent dust emissions have to be taken (see Section 4.8).

3.7.4.2 Pickling

Consumption
Hides and certain skins are pickled in salt and acid in order to prepare them for the tanning process. The combination of acids added to the pickle depends on the type of tanning employed and the desired properties of the tanned leather. The most common acids being used are sulphuric acid and formic acid. Other acids that can be used include hydrochloric acid, boric acid and other weak organic acids, e.g. acetic acid, lactic acid.

Typically, acids would be added as 0.5 % – 3 % of the weight of the raw materials. Common salt is usually used in concentrations between 6 % (bovine hides) and 14 % (mainly pickled pelt skins). Alternative salts include sodium sulphate and potassium chloride.

If pickled pelt sheepskins are going to be vegetable tanned, they will firstly be de-pickled using either sodium acetate or sodium bicarbonate.

As pickled skins are often stored for a considerable time, sometimes in excess of a year, a fungicide needs to be added to the pickle float [tan/tm/02/HMIP, tan/tm/30/Renner, tan/tm/18/UNEP-Tan]. A wide variety of commercial fungicides are on the market e.g, TCMTB, thiobenzothiazole and the fairly toxic p-chlorometacresol. Substances like p-nitrophenol, tri- or PCP, beta-naphtol and mercury compounds are regarded as too toxic in industrialised countries. Fungicides are typically applied in low quantities, up to 0.2 % of the weight of the pelts.

Emissions
Effluent from pickling is acidic (as low as pH 2) and very high in salt concentration. Together with soaking liquors, pickling liquors constitute the main sources of salinity in tanneries.

Many tanneries will not discharge the pickling float but will continue to carry out the tanning process in the same float. In that case, emissions from pickling will be contained in the tanning float.

If sulphides have not been completely removed during deliming, residual sulphides may be released into the air. Adding oxidation acids, such as hydrogen peroxides and sodium metabisulphate, to the float can prevent these emissions.

3.7.4.3 Degreasing

The laboratories CTP Centre Technique de Papier Grenoble and ITF Lyon Institut Textile de France have carried out a research to definitively evaluate the toxicity of leather industry effluents; the results are published in March 1993 in Industrie du Cuir. Authors are Michel Aloy and Arlette Vulliermet, CTC.

Five different processing floats were selected from different companies; a soaking float processing calf hides, a degreasing float processing sheep skins, a dyeing float processing goat skins, a fatliquoring float processing cattle hides and a finishing float also processing cattle hides. From those floats the following parameters were determined; pH, COD, BOD_5, Total SS, Biodegradability (COD/BOD_5), Daphnic toxicity, Microtox test, AOX and the colouration.

The overall conclusion of this research was that it seemed that toxicity can be evaluated in different ways, depending upon which test is adopted, and that the most toxic floats are not the least biodegradable. It may well prove possible to process them biologically, after suitably adapting the flora.

However, on the basis of all the criteria, the degreasing floats prove to be the most toxic, even in the absence of conventional organic solvents. In the opinion of the authors of this article, these floats should receive priority of research to reduce their impact on the environment.

The other results were - examining the various criteria of toxicity using biodegradability, the daphnic test and the microtox test - that the finishing float was considered as the least toxic and the dyeing- and fatliquoring floats were around the middle of the toxicity scale. Finally, the soaking float, the least biodegradable, gives the lowest microtox test result but lies in the middle of the Daphnic test results.

Consumption/emissions

Bovine hides are not degreased in a separate process. Where necessary, degreasing of bovine hides may be stimulated during soaking and liming with surfactants. Generally, only sheepskins and pigskins are degreased.

The three different methods commonly used for degreasing are [AIICA and Italy]:

1. degreasing in aqueous medium with organic solvent and non-ionic surfactant
2. degreasing in aqueous medium with non-ionic surfactant
3. degreasing in organic solvent medium.

1. Degreasing in aqueous medium with organic solvent and surfactant is the traditional method to degrease dewooled sheepskins, in which petroleum or white spirit is used as solvent for the natural fat. This is done by adding the solvent that is already mixed with small amounts of non-ionic surfactant. The surfactant is needed to emulsify the solvent. Once the fat is dissolved, the fat-solvent mixture is emulsified with some more non-ionic surfactant to be removed from the skins into the float. After this, several washes are carried out with brine (approximately 5 degrees Beaumé) and small amounts of non-ionic surfactant. The non-ionic surfactants, and in particular the nonylphenol ethoxylates, are the most efficient ones. The need to use salted water for washing (4 – 5 % sodium chloride) can be avoided if the skins are previously neutralized. The amount of petroleum/white spirit used in this process can be as high as 20 % based on the lime weight. The amount of nonylphenol ethoxylates is relatively low (2 - 3 % total). [AIICA].

This system is rather polluting from the waste water point of view, as more than 60 % of the petroleum is recyclable by distillation and the added COD and toxicity in the effluent are concequently very high. The waste water contains the removed fat plus petroleum plus non-ionic surfactant. Another important drawback is the danger implied by the presence of a flammable solvent in the drainage system. The leakage of 20 – 40 % of the used solvent to the

drainage system and to the waste water treatment plant is caused mainly by the many washes that follow the main degreasing float, in which no recovery is possible due to the relatively low solvent content. [AIICA].

2. Degreasing in an aqueous medium with non-ionic surfactant. With this technique the natural fat from dewooled sheepskins is directly emulsified in water by means of the non-ionic surfactant. The most effective non-ionic surfactant is nonylphenol ethoxylate with 8 - 8.5 moles of ethylene oxide. The amount to use depends on the fat content of the skins, but it is usually between 4 and 6 % based on lime weight. Usually the surfactant is added in a very short float in order to distribute the product uniformly and, after running for a certain period, more water is added to emulsify the fat. The emulsified fat is finally removed by draining. After this, several washes with water and some surfactant are required. There are several types of non-ionic surfactants able to work properly in this process, but none of them offers the same effect as nonylphenol ethoxylates, either in the efficiency of the degreasing by emulsion or afterwards in the treatment of the effluent by breaking the emulsion and separating the fat phase from the aqueous one. [AIICA]. Depending on the surfactant used, the amount needed is in the range of 3 – 10 % to achieve a fat residu in the pelts of 2 – 5 % [Italy]. See Section 3.1.6 Surfactants, for the environmental and health problems of nonylphenol ethoxylates.

There are some variations according to the specific characteristics of the skins, the fat content and its nature. Usually a certain pre-tannage is required to increase the shrinkage temperature. This enables the fat to emulsify and to flow easily when its melting point is too high. [AIICA]. The shrinkage temperature of the skins must be at least 20 ºC higher than the operation degreasing temperature, which can be up to 60 ºC [tan/tm/17/Frendrup]. Pre-tanning agents that could be used (1 – 3 %), include glutardialdehyde, aluminium sulphate, or syntans [tan/tm/17/Frendrup].

Another possibility is to neutralise the skins in the first float, before washing, in order to avoid the addition of salt to the water and effluent. Finally, there are some intermediate versions that incorporate some organic solvent with the surfactant (usually 2 – 3 %). This helps the removal of the natural fat and eases its emulsion in the water. This system adds a lower level of COD to effluent water and, depending on the adequacy of the surfactant, permits the emulsion to be broken and a cleaner waste water to be separated from the fat and surfactant mixture in a more or less simple way. A recent (European) research project about ovine leather degreasing demonstrated, contrary to what was previously thought, that the use of enzymes hinders the degreasing process. [AIICA].

Sodium carbonate can be used in the degreasing process as a de-pickling agent to facilitate the extraction of the emulsion once the skins have been treated with surfactants, but it cannot be considered as a degreasing agent. [AIICA].

Emissions [AIICA]
The emission values - before treatment - for the aqueous degreasing with surfactants for dewoolled ovine leather are:

NPEs : 20 - 60 g/skin*
Fats   : 30 - 120 g/skin*
COD   : 130 - 500 g/skin*
(* the base is lime weight and is about 1 kg.)

The amount of water in the whole degreasing process (main float and further washes) is about 8 - 10 l/skin considering. The first float (1.5 - 2 l/skin) is treated separately, as the fat and surfactant content (7 – 9 %) is much higher then the rest. This treatment consists in breaking the emulsion of fat and surfactant by increasing the temperature to 90 ºC. With this procedure, widely used industrially in Spain, 60 – 80 % of the generated COD is eliminated. After this treatment a normal physico-chemical treatment is carried out. The values obtained after those two treatments and before the biological treatment are 190 micrograms NP/l and

250 milligrams NPE/l. In the outlet of the biological waste water treatment plant, those values are 25 micrograms NP/l and 6 milligrams NPE/l. The elimination of NP in the biological waste water treatment plant is around 90 % and of NPE 98 %. Considering that NP is formed as an intermediate in the degradation of NPE, the rate for NP degradation is even higher. (NP = nonylphenol, NPE = nonylphenol ethoxylate).

3. Dry degreasing in organic solvent medium is applied by extraction at an intermediate temperature directly in solvent, usually tri-chloroethylene or per-chloroethylene. The use of the chlorinated solvents is due to the non-flammability of these products, in contrast to other solvents. Normally this process is applied to wool-on sheepskins in crust stage to equalize the residual fat and to assure a steady dyeing in further operations. The degreasing is carried out in closed machines; the used solvent is automatically distilled and re-used. The distillation is quite effective, although never absolutely total. [AIICA]. As the technique uses solvent alone, the pelts have to be in dry state otherwise the solvent cannot come into contact with the fat. And because non-tanned pelts cannot be dried completely, the pelts have to be tanned before drying. The limited size of the closed machines is the reason why this technique only is used when aqueous degreasing is not possible or not efficient enough and has to be completed by degreasing in the dry state. Possible cases are wool-on sheepskins, very fatty skins (domestic English, Australian, etc.) and fatty wet-blue imported as such. [Italy].

Emissions

The residual fat remains with a considerable amount of the chlorinated solvent [AICCA]. Also the waste water contains chlorinated solvent which can be removed by using activated carbon. The emission level set in Germany for this treated waste water is 0.1 mg chlorine/l as the sum of tri-chloroethylen, tetra-chloroethylen, 1.1.1-tri-chloroethan and di-chloromethan in a random sample. The emission level in Germany of the stripped air from this treatment is 20 mg VOC/Nm^3 (273 K, 101.3kPa).

3.7.4.4 Tanning

Consumption

In order to convert hides and skins into non-putrescible material, tanning agents are introduced to the pelts and fixed to the collagen. Different leathers are produced depending on the type and quantity of the tanning agent added to the pelts.

The following types of tannage can be used in a tannery:

Type of tannage	Tanning agents used	Auxiliaries used
Chrome tannage	Basic sulphate complex of trivalent chrome	Salt, basifying agents (magnesium oxide, sodium carbonate, or sodium bicarbonate), fungicides, masking agents (e.g. formic acid, sodium diphthalate, oxalic acid, sodium sulphite), fatliquors, syntans, resins
Other mineral tannages	Aluminium, zirconium, and titanium salts	*Masking agents, basifying agents, fatliquors, salts, syntans, resins, etc.
Vegetable tannage	Polyphenolic compounds leached from vegetable material (e.g. quebracho, mimosa, oak, etc.)	Pre-tanning agents, bleaching and sequestering agents, fatliquors, formic acid, syntans, resins, etc.
Synthetic tannage (Resin-syntans)	Sulphonated products of phenol, cresol, naphthalene, cresylics, poly-acrilatess, melamine resins, etc.	Fixing agents, either acid or alkali, fatliquors.
Aldehyde tannage	Glutaraldehyde and modified aldehydes and di-aldehydes	Alkali, bleaching agents, tanning agent carrier.
Oil tannage	Cod oil and marine oils	Catalysts such as manganese, copper, or chrome. Sodium bicarbonate or other alkali, aldehydes, emulsifiers.
Notes: *The auxiliary used vary depending on the mineral used and the type of cross link with the collagen.		

Table 3.34: Type of tannage, main tanning agents, and auxiliaries

For the tanning process a large variety of chemicals is necessary and only a part of these chemicals are taken up in the hides and skins. As a result, effluents are generated from tanning operations that have a low pH and carry the part of the chemicals that was not integrated. The substances released depend on the type of tanning applied. The following paragraphs discuss the consumption and releases of chrome- vegetable- and other tanning methods.

Tanning auxiliaries are intended to produce a desired modification of the tanning effect without developing a tanning action. Complex active and buffering substances are used for mineral tanning. Surfactant auxiliaries are added to disperse the tanning agents and accelerate the complete penetration of tannin as well as to influence the emulsion and electrolyte stability of other auxiliaries (for mineral and vegetable tanning). Sequestering agents in water treatment can combine with the hardening constituents of the water to produce more stable complexes. Fixing agents reduce souring losses of vegetable and/or syntan tannins by the formation of water-insoluble compounds. These products are mainly aluminium or manganese salt, albuminious materials, usually cationic nitrogen-containing organic compounds or organic or inorganic compounds, which condense in the leather.

Spent tanning liquors are disposed of via the waste water. Residues are the sludges of the waste water treatment and residues from chemicals and auxiliary agents.

3.7.4.4.1   Mineral tanning:

Although tanning with chrome agents was introduced only about 100 years ago, this is the most commonly used procedure. Chrome tanned leather accounts for approximately 90 % of all the leather produced in the world. The main tanning agent is a basic sulphate complex of trivalent chrome. The agent can be added as a powder or liquor, and tanning is generally carried out in process vessels such as drums or paddles. Other mineral tannages include aluminium, titanium and zirconium.

For a conventional process the ***chrome*** salts are mostly added as a powder with offers between 8 % - 12 % based on the raw material weight, on the limed split pelts weight or on the pickled pelts weight. This offer of chrome tanning powder will provide only ¼ of active tanning material (2 % - 3 % Cr_2O_3), the remaining components found in the powder do not take part in the tanning process. For the high-exhaustion chrome tanning process only $5 - 6$ % are added, based on the raw material weight, on the limed split pelts weight or on the pickled pelts weight. As basifying salt, about 1 % of sodium bicarbonate or 0.5 % of magnesium oxide can be added, based on the raw material weight, on the limed split pelts weight or on the pickled pelts weight. For a short float, $40 - 60$ % of pelt weight water is necessary.

To optimise the speed of the chemical penetration, masking agents (formic acid, phthalate or salts of dicarboxylic acids for complexation of Cr^{3+}) are sometimes introduced. Masking increases the precipitation point of the complex. The amount of masking agent can vary from 0.5 % to 1.0 % [tan/tm/58/BLC].

If the wet-blues are stored or traded, fungicides may be added at the rate of about 0.1 % of pelt weight. [tan/tm/02/HMIP]

In a conventional tanning process, between 60 and 80 % [tan/tm/58/BLC] (70 % [tan/tm/52/Handbook]) of the chrome oxide may be fixed on the leather, the remainder being left in the water phase. Several options exist to reduce the releases of chrome into the environment from this process step. Further chrome releases occur from the subsequent steps in the tannery either because the chrome is not totally fixed in the hides and skins and is washed off, or because more chrome powder is added.

The waste water contents depend on the exact combination of process units (e.g., pickling and tanning in the same float). The effluents have a low pH (3 – 4) and contain chrome, a mixture of salts, complexing agents, natural grease and traces of fungicide.

In Table 3.35 the consumption of water and main effluent parameters for liquors from chrome tanning are summarised from various references.

Liquors	Drain	Cr^{3+}-salts in spent liquors	Salt (Cl^-)	TDS	SS	BOD	COD	TKN	NH_4 - N
m^3 / t	m^3 / t	kg/t	kg/t	kg/t	kg/t	kg/t	kg/t	kg/t	kg/t
0.2 [1]	0.3– 0.5 [1]	5 – 10[2]	30– 100 [3]	~ 175 [4]	~ 5 [4]	~ 3 [4]	~ 14 [4]	~ 1 [4]	~ 0.5 [4]
Notes: [1] tan/tm/07/Zimpel [2] tan/tm/58/BLC [3] tan/tm/12/Ullmann, tan/tm/30/Renner; tan/tm/58/BLC [4] tan/tm/12/Ullmann									

Table 3.35: Water consumption and emissions to waste water from pickling and chrome tanning per tonne of raw hide

Besides chrome, some tanning, retanning or pre-tanning is done using aluminium, zirconium and titanium. Aluminium, zirconium and titanium cannot be used as substitutes for chrome in the tanning process, as the leathers tanned with chrome can have quite different characteristics (e.g. hydrothermal stability) compared to the leathers tanned with other mineral tanning agents.

Aluminium as a tanning agent produces a white leather which is, however, not sufficiently water- or heat-resistant. It is used in pre-tanning (Wet-white option, see p. 128) [tan/tm/03/UwHB-Tech, tan/tm/02/HMIP, tan/tm/03/UwHB-Abfall]). Occasionally aluminium is used in chrome tanning to increase the uptake of chrome [tan/tm/12/Ullmann], or for the production of fur (sheep and lamb skins) and of leather for glacé gloves.

Aluminium tanning can be combined with vegetable tanning to give leather with a higher shrinkage temperature. For a combination of aluminium tanning with vegetable tanning the dosage would be in the range of 6.4 % mimosa tannin and 1 % aluminium oxide or 3.6 % mimosa tanning and 3 % aluminium oxide [tan/tm/17/Frendrup]. For a reduction of chrome the dosage could be ~ 1.5 % Cr_2O_3 (~ 12 kg / t raw hide) and 0.25 % aluminium oxide.

Aluminium salts can also be combined with aldehydes; such as glutardialdehyde and formaldehyde. About 0.25 – 0.5 % glutaraldehyde can be added to the aluminium salt. Due to restrictions on the grounds of Health and Safety, formaldehyde is no longer used in Europe. The main used glutaraldehyde is the modified glutaraldehyde, which is considered much safer.

Zirconium (IV) gives a white, strong and stable leather. As with aluminium, zirconium salts are sometimes used in chrome tanning and in combination with other tanning agents.

Mostly zirconium sulphate is used as tanning material. Initially a lower pH (1.3 – 1.5) than for chrome tanning is required. Sometimes citric acid is used as a complexing agent to achieve a lower pH. At least 7 % salt is needed, based on the raw material weight, on the limed split pelts weight or on the pickled pelts weight.

Zirconium has been used in various combinations, e.g, following a pre-tannage with formaldehyde or as a retannage for chrome leather in combination with aluminium or chrome salts [tan/tm/09/UNIDO].

Titanium salts are excellent pre- and retanning agents and they can be used successfully in combination with other mineral tanning agents [tan/tm/58/BLC]. Proprietary products based on titanium-aluminium complexes are commonly found on the market. They can be used either to produce white leathers or as capping agents. Ammonium titanyl salts will increase the nitrogen load in the waste water.

3.7.4.4.2   Vegetable tanning

The plant extracts applied for vegetable tanning are either polyphenolic compounds (condensed vegetable tannins) or esters of glucose and gallic acid (hydrolisable vegetable tannins), which are leached (with water) from wood, barks, leaves, roots etc. [tan/tm/03/UwHB-Tech; tan/tm/17/Frendrup; tan/tm/12/Ullmann; tan/tm/58/BLC]

The most commonly used vegetable tannins extracts are:

- natural quebracho
- soluble quebracho
- mimosa
- natural chestnut
- sweetened chestnut
- myrobolans
- valonia.

Three techniques of vegetable tanning can be distinguished:

- pit tannage
- drum tannage
- pit and drum tannage.

The basic principle of pit tannage is a counter-current system, whereby the hides are first put into much used and almost exhausted liquors, and then into progressively stronger liquors to fix more tan. As these stronger liquors become denuded of tan they are "run" (pumped) down the yard and used in the earlier stages, so that as much tan as possible is used. Vegetable material (e.g. bark) can be used directly in the pits, or vegetable extracts can be used.

Another principle is based on the Liritan system, whereby the pelts are pre-tanned using Calgon and they are subsequently tanned in the same strength liquor [tan/tm/58/BLC].

Pit tannage can last between several weeks and a year, depending on the tanning agent and the tanning system used.

Drum tannages have been developed in more recent times to accelerate the vegetable tanning process and can be used to produce medium and light vegetable tanned leathers.
Drum processes require less water than pit processing, but they can produce a higher polluting load due to the high concentration of tanning liquor used and the lack of need for low concentration tanning liquors. The tanning process can be completed in one to three days, depending on the thickness of the pelts.

In the combined pit tannage and drum tannage, vegetable tannage can be carried out in pits for a few days; at least long enough to fix the grain of the pelts to give it enough resistance to mechanical action. After this process, full penetration of vegetable tannins can take place in a drum [tan/tm/58/BLC]. This tanning system is capable of tanning medium/heavy weight leathers in five days.

In sole leather, about 350 – 500 kg/t of tanning extracts (equals 475 kg extract per tonne of raw hide) are applied. These extracts typically contain 60 – 70 % tannins, the remainder consisting of non-tannins such as gums, sugars, organic acids, mineral salts and insoluble matter.Sole leathers are typically very heavy, as they are "stuffed" with vegetable tannins. Typically 1 tonne of raw hide can produce approximately 600 - 650 kg sole-leather, as against approximately 200 - 250 kg of chrome tanned leather.

Vegetable tanning may be preceded by pre-tanning, shaving and splitting stages.

Depending on the type of vegetable tanning employed, vegetable tanned leather can be used to produce shoe sole leather, upper leather, harnesses, saddles, belts, leathergoods, leather for clothes and upholstery.

Emissions
The non-tannins remain largely in solution and are present in the effluent discharged from this operation. Vegetable tanning effluents typically have a high load of COD (up to 120 g/kg hide), some of which has a low biodegradability. A further problem may be the colour and phenolic compounds of these effluents.

The volume of the effluent largely depends on the technique employed, but ranges between 3 and 5 m^3 per tonne hides processed. Traditional pit tannage requires more time and more water than the drum processes.

	Traditional technology (1)	Average unit (1)	Drum technology
Water volume, m^3/t	5	3 - 4	3 - 4
Total solids, kg/t	200 - 300	110 - 200	65 - 100
Suspended solids, kg/t	100 - 125	10 - 15	10 - 15
BOD5, kg/t	40 - 75	40 - 75	25 - 35
COD, kg/t	120 - 220	120 - 220	70 - 110
Chloride (Cl-), kg/t	50	50	4 (2)
[1] Counter-current pit technology [2] Salt free pickling			

Table 3.36: Rough data of typical waste water loads per tonne raw hide vegetable tanning (from pickling, tanning, washing and bleaching)
Source: [tan/tm/17/Frendrup]

3.7.4.4.3   Other organic tanning

Syntans, resins, and polyacrylates
Synthetic tanning agents, or syntans, are sulphonated aromatic compounds [tan/tm/02/HMIP]. Some syntans are substituting other tanning agents, or are used in pre- and retanning (e.g., acrylic polymers, sulphonated phenol-formaldhyde and naphthalene formaldehyde), some are used as auxiliary to induce certain leather properties (e.g., ureaformaldehyde and melamine resins).

Depending on the combination with other tanning methods, 1 – 15 % of the pelt weight of syntans are applied [tan/tm/04/Austria, tan/tm/18/UNEP-Tan].

Emissions
The effluents of these processes may carry a high load of COD and show a low biodegradability. However, proprietary products are on the market which can significantly lower the COD loading of these effluents.

Some of these formulations may result in the release of formaldehyde and phenols into the effluent. Formaldehyde may also be released to the air.

Aldehydes

Some aldehydes are used as tanning agents [tan/tm/17/Frendrup]. Glutaraldehyde and modified glutaraldehydes are used for pre- and retanning, but also as a tanning agent which produces leather with special properties (very soft and full, yellowish with high wash and sweat resistance) for special purposes, e.g. golf gloves or woolskin bedspreads for hospitals.

Formaldehyde is not used in the <u>standard</u> tanning process in any European country because of the health risks. It is possible to cross-link aldehydes (oxazolidine) with vegetable tannins and thus substitute any metal salt. It is also used in pre-tanning to accelerate vegetable tanning and to fix hairs of fur and sheep wool [tan/tm/12/Ullmann].

Emissions

Tanning agents based on gluteraldehydes are associated with health risks and strict health and safety requirements may be imposed on the use of these tanning agents. Gluteraldehyde is generally fully exhausted in the process. Any residual glutaraldehyde that may reach the waste water treatment plant will react quickly with the proteins from other effluent streams and generally does not pose a problem in effluent treatment.

Oil tannage

A traditional tanning procedure is chamois tanning or cod oil tanning performed with unsaturated vegetable or animal oils, particularly for sheepskins and deer hides. They require oxidation with catalysts like Mn-, Cr-, or Cu-oxides. After wringing of excess cod oil and washing with alkaline (Na_2CO_3), they may be subject to some after-treatments, such as dyeing. In an alternative a pre-tanning step with glutardialdehyde is performed, before the cod oil is applied to the hides and with warm air blowing into the vessel. [tan/tm/03/UwHB-Tech]

Emissions

The cod oil has a particular smell, which may give rise to some odour problems. Cod oil tannage may result in effluent with a high loading of COD in the form of oxidised natural oils.

3.7.4.5 Draining & samming

Emissions

The waste water from draining and samming the hides after the tanning process could contain various degrees of tanning agents depending on the efficiency of the tanning process. Whereas the same types of contaminants may be found in these effluents as in the spent tanning liquors, the concentrations are often lower for samming waste water. About 0.2 m³ of effluent per tonne limed hide can be generated [tan/tm/07/Zimpel].

3.7.4.6 Shaving

The shaving process is carried out to achieve an even thickness throughout the hide. This involves a shaving cylinder scraping off small strips of leather from the flesh side.

Emissions

The residue from this process is shavings, which typically constitute between 2 – 20 % of the weight of the tanned hides. Shaving is generally minimised by accurate splitting. Where splitting is carried out very accurately, the amount of leather which needs to be shaved will be minimal and result in small dust-like leather particles.

Shavings constitute solid waste, which has to be disposed of or can be sold as a raw material in the manufacture of a wide range of products such as leatherboard and fertiliser or for the manufacture of hydrolysate following de-tanning.

Shaving operations may cause considerable noise on the work floor and dust may be generated if the hides are shaved in a relatively dry state.

If dry-shaving is performed, attention has to be paid to adequate dust collection systems (see Section 4.8)

3.7.5 Post-tanning operations

3.7.5.1 Neutralisation

Neutralising agents are mild alkali. The following neutralising agents can be used:

- sodium carbonate, sodium and ammonium bicarbonate
- sodium bisulphite, sodium metabisulphite and sodium thiosulphate
- ammonia
- borax
- sodium formate, calcium formate, sodium acetate
- polyphosphates (used on vegetable tanned leathers)
- neutralising syntans.

Combinations of the above agents may be added in quantities up to 4 % of the weight of tanned leather.

Emissions
The waste water effluents from all post-tanning operations and from rinsing are collected jointly. Figures for emissions are therefore not available for every process unit. Post-tanning operations normally account for about 10 – 20 % of the COD of all tannery effluent.

3.7.5.2 Retanning

A variety of retanning agents is available producing different properties in the final leather product. The most important types are:

- vegetable tanning agents
- syntans, polymeric and resin tanning agents
- aldehydes
- mineral tanning agents.

Several types of retanning agents may be combined to get the desired properties in the leather. Quantities added range from 3 % of shaved weight for clothing leather, up to 15 % for shoe uppers.

Emission
The main environmental problems stem from high COD from incomplete exhaustion of chemicals and non tannins contained in vegetable tanning agents, residual monomers contained in syntans (formaldehyde and phenol) and polymeric tanning agents, chromium from mineral tannages or the tanning process and inorganic salts originating from syntans.

Some of the retanning formulations may also cause dust emissions during handling.

3.7.5.3 Stripping and bleaching

This operation is carried out regularly on vegetable tanned leathers to clear off the excess tanning agent from the leather surface, and to improve the uniformity of the colour of the substrate prior to further processing.

It is optional to strip the leather with sodium carbonate, sodium bicarbonate, borax or oxalic acid at 1 – 4 % of shaved weight. Stripping prepares hides for retanning and dyeing in selected cases.

Sulphuric acid and hydrogen peroxide can be used to bleach hides and skins in preparation for dyeing of pale shades and the removal of stains. Alternatively, sulphites, metabisulphites, hydrosulphate or thiosulphate followed by acidification to release sulphur dioxide can be used.

Chamois leather may be bleached in sunlight or by drumming in a solution of potassium permanganate and sodium bisulphite.

Emissions
The release of sulphur dioxide gas may constitute a risk to human health.

Oxidising bleaching agents have the potential of oxidising chrome (III) to chrome (VI) in the leather.

3.7.5.4 Dyeing

The dyeing process is carried out to produce leathers with a selected uniform shade of colour. Typical dyes for leather are either anionic dyes (acid, direct, sulphur, mordent, reactive and premetallised) or basic dyes.

Reactive dyes, although part of the anionic group of dyes, are not widely used in tanneries due to their method of application. The use of basic dyes is also limited.

From the chemical point of view the dyestuffs are predominantly azo dyes, or anthraquinone dyes. Triphenylmethane dyes may also be used.

Metal complex dyes consist of central metal ion and one or two azo dye ligands. The central ion can be iron, chrome, nickel, copper and cobalt. It is assumed that metal complex dyes containing lead and cadmium are no longer used.

Vegetable dyes are extract of logwood, red wood, fustic or sumac leaves. These dyes can give a range of colours which is restricted when compared to the range provided by other types of dyestuff.

During the dyeing operation, as well as a mixture of various dyestuffs, other chemicals are used, e.g. wetting agents [tan/tm/08/TEGEWA], levelling agents, bleaching agents, shade intensifiers, after-treatments and fixing agents. These products are used to aid the dyeing operation, and they contribute towards improving colour fastness.

The dyeing operation is completed by adding mainly organic acids, e.g. formic or acetic acid; in a few cases mineral acids are used, e.g. hydrochloric acid.

The addition of dyestuff may range from 0.05 % of the shaved weight of the leathers (pale shades), up to 20 % for deep shades (this is up to 10 % of the wet-blue shaved weight or up to 20 % of the dry crust weight). Pigments may also be added to aid the build up of a shade, particularly for white leathers.

The exhaustion of the bath depends on the type of dye used, the tanning agents applied earlier, the nature of the leather and the process parameters used (pH, temperature, time, concentration and agitation).

Emissions
Emissions from the dyeing process occur mainly to waste water. Ammonia emissions to air and residues from dyestuff and auxiliaries, which have to be disposed of, are of comparatively minor importance. Special caution has to be applied to workplace safety in handling the chemicals, in particular with the control of dust.

Dyeing is one of the most expensive processes carried out in the tannery due to the cost of the dyestuffs. Tanneries therefore seek to maximise bath exhaustion. Exhaustion levels in excess of 90 % are typically achieved, with near complete exhaustion being possible under certain conditions.

Chemicals applied in the dyeing process, but not retained in the leather, are released to the waste water. These chemicals not only increase the COD, but may also result in the release of absorbable organic halogens (AOX), particularly when halogen-containing dyes are used. Several halogenated dyestuffs are on the market. Dyes in effluent are difficult to remove and may result in a colouring of the receiving waters. This creates undesirable aesthetic pollution and may have a negative impact on the environment as it could influence the penetration of light in surface waters. Some single substances may have a high negative impact on the environment. For many of the substances used, no assessment is available.

3.7.5.5 Fatliquoring

Fatliquoring is generally carried out after retanning and dyeing. Electrolyte stable fatliquors can be used in pickling or chrome tannage and cationic fatliquors can be used after main fatliquoring and fixation to create a waxy surface or to impart a silky nap on suede. The amount of fatliquoring agent added varies between 3 – 15 % based on shaved weight, with shoe uppers requiring less fatliquor than upholstery [tan/tm/18/UNEP-Tan, tan/tm/04/Austria, tan/tm/09/UNIDO]. Smaller amounts of fat (1 – 4 %) are sometimes applied during chrome tanning in the tanning bath, enhancing the penetration of the fat and the dispersion of the chrome tanning agent.

Before addition, fatliquors are emulsified. These emulsions are generally oil-in-water emulsion, but in some cases water-in-oil emulsions can be prepared. Emulsifiers are generally incorporated in the fatliquor formulation. Fatliquoring is generally carried out in floats at high temperatures (up to 65°C) in order to maintain the emulsion. Acidification completes the process of binding the product to the leather. The most commonly used chemicals for adjusting the pH of fatliquoring, and therefore controlling penetration and fixation, are ammonia and formic acid.

Stuffing is an old technique used mainly for heavier vegetable-tanned leather [tan/tm/12/Ullmann]. The wet leather is treated in a drum with a warm mixture of molten fat containing also special emulsifiers. The resultant fat content amounts to 20 – 30 % and for further finishing the surface must be degreased. Stuffing agents consist generally of alkaline earth compounds, carbohydrates as well as natural and synthetic mucilaginous substances and preparations thereof [tan/tm/08/TEGEWA].

Agents may be applied in order to achieve particular properties and wear qualities, e.g. water-repellent or water-proof properties, oil-repelling or anti-electrostatic properties, reduced permeability to gas, flame retardant and abrasion reduction.

The surfactants used in wet processes could increase the hydrophilic properties of leather. To correct this, hydrophobic chemicals such as silicones or organic chlorofluoro-polymers

dissolved in organic solvents can be applied. For permanent protection the leather must contain 5 – 10 % of the waterproofing agent.

Emissions
Emissions to waste water from the fatliquoring agents and the impregnating agents contribute to the COD and BOD in the effluent. Most significantly, the discharge of fatliquors is a principal source of oil and grease in the effluent. Furthermore, when chlorinated fatliquors have been used, the effluent may contain AOX.

Emissions to waste water from conventional post-tanning operations	kg/t raw hide
TS	65
SS	7
BOD	14
COD	20 – 30
N-tot	0.8 – 1
NH_4^+	0.6 – 0.8
Cr	1
Cl^-	2 – 5

Table 3.37: Emissions to waste water from conventional post-tanning operations
Source: [tan/tm/11/Nordiske Seminar; tan/tm/30/Renner]

3.7.5.6 Drying

There are a number of ways to remove moisture from leather, each having their specific impact on the final properties of the leather and the surface area yield. Often more than one drying technique may be used to achieve the desired moisture content of the leather.

Generally, leather is first sammed and set before being dried in a drying machine. Drying machines all involve the use of large amounts of energy. Temperatures for drying range between ambient temperature and 100°C, depending on the drying technique employed, the type of leather processed and the drying time allowed for.

Paste drying involves the application of a paste to the leather consisting of a mixture of carbohydrates, cellulose derivatives, albuminous products or synthetic polymers. This paste is used to adhere the grain side to the drying plate during the drying process.

Drying is one of the most energy intensive processes in the tannery, and may account for up to 45 % of total energy consumption. However, it is estimated that the total energy costs do not exceed 3 % of the overall production costs in a tannery. Some tanneries have installed low temperature drying systems to improve the area yield of the leathers produced, and to save energy. Energy saving efforts mainly concentrate on insulating pipes and drying equipment and controlling the temperature and humidity of the air.

3.7.6 Finishing

3.7.6.1 Mechanical finishing operations

Mechanical operations consume energy. Most mechanical operations create noise, both high frequency and low frequency. They may also create vibrations. Dust may also be generated at this stage.

In milling, the leather is treated mechanically in drums to soften the product; in buffing, the surface is abraded. This treatment produces wet or dry leather particles as residues with a high organic content and, if the leather was chrome tanned, a high chrome content. The dust from milling and buffing is exhausted from the workplace. In some tanneries dust is compacted and bricketed, after being collected by various systems (see Section 4.8). Currently, these residues are landfilled.

3.7.6.2 Coating / finish

The different types of finishing processes were mentioned in Section 2.4.2

Padding can be carried out manually or by machine. This operation has a relatively low throughput, and requires a high level of manpower. The level of waste will vary, depending on the operators (manual operation).

The spray line is mostly chosen to deliver a smaller quantity of finish onto the leather surface than can be achieved using a roller or a curtain coater. Fine adjustments to the colour of the leather can be achieved more easily using the spray line in the final coats. The leather is fed into chambers to protect the surrounding areas from the over-spray (aerosols, organic solvents). The spray booth must be closed during processing in order to avoid the release of emissions into the working environment. Exhaust air must be abated to meet local emission limits for particulate and organic solvent emissions.

In wet coating aqueous or solvent-based lacquers are applied by spray guns. Waste includes residual finish formulations, sludges from finishes, sludges from air abatement techniques and pretreated organic solvent and heavy metal containing waste water. Assessing the VOC a distinction between the applied solvents according to their toxicity has to be made. Formaldehyde, for example, is used for fixing protein finishes (and ironing wool-on sheepskins) [tan/tm/18/UNEP-Tan]. It is carcinogenic and requires special precautions. Previsions for organic solvent recycling include a careful selection of organic solvents, otherwise recycling can be impossible (see Section 4.1.4).

Computer aided spraying means that automated systems sense the area, either by a mechanical feeler, electric eye or ultrasonic system and control the opening of the guns so that they only spray when the leather is passing directly beneath them. Automated systems can prevent 75 % of the finish being lost as overspray. The technique is widely available in more or less sophisticated versions. Care must be taken that the detection equipment is properly adjusted.

The roller coater is more versatile compared to the curtain coater. More type of finishes can be applied using a roller coater.

Foam coating is a finishing technique rather than a type of application. Foam coating can be applied both by roller coaters and by spray lines. This finishing system is rather new and many tanneries are still experimenting with the technique, and this may be the reason why there is not much data on this technique compared to the others.

Various finishing coats, e.g., waxes and lacquers, can be applied to either side of the leather. Typically leather is finished with a base coat, intermediate coat, and a topcoat. Quantities of surface coats applied to leather range from 0.2 g/m^2 for sole leather up to 400 g/m^2 for heavily finished leathers, such as corrected grain, pigmented splits and oily leathers.

The main finishing coats and their components are shown in Table 3.38.

Type of coat	Main components	Additives
Base coats	Water/organic solvent	Waxes
	Pigments/dyes	Surfactants
	Resins	Thickening agents
		Fillers
Intermediate coats	Water/organic solvent	Waxes
	Pigments/dyes	Thickening agents
	Resins	Fillers
Top coats	Water/organic solvent	Waxes
	Solvent based lacquers	Silicon based agents
	Water based lacquers	Matting agents
	Binders	Cross linkers

Table 3.38: Finishing coats: main components and additives

Most water-based products still contain small amounts of organic solvents. Pigment colours are intended to colour the finishing agent, which forms the film coat. The preparations can also contain protective colloids or softening agents. Formaldehyde may be used as a fixing agent for casein finishes or hard-formulated polyacrylate dispersions and for ironing of wool-on sheepskins. The chemicals used in finishing will determine the surface handle and appearance of the leather. [tan/tm/03/UwHB-Abluft, tan/tm/12/Ullmann]

Processes such as padding, plating or ironing are done to achieve the desired final appearance (see Section 2.4). Sometimes ammonia is used for opening the surface before a finish is applied. After the application of the finish the leather is dried, for example by passing it through a drying tunnel. Drying tunnels are generally integrated in the finishing line, and heating can be done by steam, gas or electricity (infrared).

Emissions
Different emissions arise, depending on the type of chemicals and process used. The main problem with solvent-based coating agents (see Section 3.1.5) is the emission of volatile organic solvents (VOC) released during and after the coating process. The releases of VOC require special abatement techniques [tan/tm/03/UwHB-Luft]. Furthermore, particulates may be released from the finishing operations. 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. Scrubbers create an effluent containing finish mixes and water-miscible organic solvents. Organic solvents that are not water-soluble will be emitted to air. Most countries have emission limits on the amount of organic solvents emitted, expressed either in organic solvent consumption per square meter of leather, or a concentration of organic solvents per cubic meter of air.

Furthermore the toxicity of chemicals, such as formaldehyde, other organic solvents and certain cross-linking agents might constitute a severe problem if they are released to the workplace.

Formaldehyde may be released where protein finishes are used or wool-on sheepskins are ironed.

Residual finish mixes are disposed of according to the particular components of the mix. Residues are sludges containing lacquers from coating, sludge from wet air abatement techniques and paper with lacquers from dry exhaust. These residues are disposed of in appropriate incineration plants [tan/tm/07/Zimpel]. Organic solvents may be recovered and re-used on site or collected for recovery, recycling or incineration off site.

A waste fraction occurs from a final trimming of the coated leather. Currently, this waste is sold to small leathergoods manufacturers, is collected for re-use or is landfilled.

Water-based finishes exist which have low or near-zero concentrations of organic organic solvents. Water-based finishes require longer drying periods than organic solvent-based systems.

Further finishing operations

Fur skins of lamb and sheep can be sheared to obtain special effects [tan/tm/12/Ullmann].

Ironing is used to stretch the pelts and to improve the appearance of hair. Water, to which surfactants can be added, is used as an ironing solution. To achieve special effects formaldehyde together with water-soluble alcohols and acid are used.

4 TECHNIQUES TO CONSIDER IN THE DETERMINATION OF "BAT"

Efficient raw material and energy usage, optimum process chemical utilisation, recovery and recycling of waste, and substitution of harmful substances are important principles of the IPPC Directive. For tanneries the focal points are water consumption, efficient use and substitution of potentially harmful process agents, and waste reduction within the process in conjunction with recycling and re-use options.

This chapter will set out commercially available techniques that represent technical alternatives with the best environmental and economical performance or possibilities for improvement to achieve integrated prevention and control of pollution. Both process-integrated measures and end-of-pipe measures are included, but it is acknowledged that a certain overlap exists between internal solutions and external control measures. The list of techniques is not exhaustive and may be extended when this document is reviewed.

A standard structure is used to outline each technique, covering:

- a description of the technique, including its applicability to new and existing plants
- the advantages and disadvantages
- the main emission values achieved
- cross-media effects
- economics
- reference plants and
- reference literature.

The above-mentioned objectives are linked to each other, with achievements in one sector entailing positive achievements in another. There are, however, often adverse effects on the environment, and they have to be considered, too. The different environmental impacts of best available techniques will be assessed and compared as far as possible. The effects for the environment as a whole will be discussed in the section about 'cross-media effects'.

Environmentally preferable techniques exist for many process units. However, a technology is only as effective as its operation, maintenance and upkeep allows it to be. Advanced technology often requires greater skill in operation, and higher chemical and energy consumption. Much can be achieved through good housekeeping practice. It is important to note that some improvements will focus on a particular process unit. Many techniques may require changes in the whole process line. BAT then has to be considered as an integrated system of techniques.

For particular substances the goal is a complete substitution with safer substances. This includes, for example, substitution in favour of chemicals that are easier to abate, have a lower toxicity for workers, are easily biodegradable and are not bio-accumulative. Before substituting chemicals it is crucial to be aware of what exactly is introduced in the process. In the interests of avoiding and/or reducing hazardous substances, the chemicals suppliers and the tanners need to provide information about the effects on products and processes of any newly-introduced substance.

Environmental improvement also strongly depends on market acceptance of the design, the product specifications and properties, as well as any other tradable by-product. For example, hair save technology can be implemented the to get a cleaner waste water effluent, with the advantage of recovering high-quality and possibly tradable hair.

The costs of raw material, process agents, equipment, abatement and disposal options vary greatly. The cost of any modification has to be assessed in terms of avoided abatement costs as well as direct payback. Not every measure that has to be taken to ensure adequate environmental protection can be expected to pay off on the microeconomic scale of a tannery, however.

4.1 Substitution of substances

The priorities selected for the substitution of harmful substances by less harmful substances may also differ, depending on the local conditions and legislation. Many of these environmentally important or potentially important substances are not monitored, e.g. pesticides, biocides and surfactants. For the risk assessment of chemicals, various methods are applied in different countries and by different interested parties. However, in many cases there are no assessments or, at least, no comprehensive assessments of these substances for their possible impact on the environment. So, a comparison with other options is in most cases impossible. There are of course some substances whose impact on the environment has been discussed extensively in the past and led to restrictions by legislation. The more difficult decisions, however, arise from cases where far too little is known for the risk to be assessed.

	Process	Agents and auxiliaries [tan/tm/28/BASF]	Substitution	Process change
BEAMHOUSE	Curing	Substitution of biocides	4.1.5	
		Substitution of salt	4.2.1.1	
	Soaking	Substitution of surfactants	4.1.1	
		Substitution of biocides	4.1.2, 4.1.5	
	Liming	Low-sulphide and sulphide-free liming		4.2.3
	Deliming	Low-ammonium and ammonium-free deliming processes		4.3.1.1, 4.3.1.2
	Degreasing	Substitution of halogenated solvents; non-halogenated solvents	4.1.2.2	
		Substitution of surfactants	4.1.1	
		Aqueous degreasing with organic solvents and non-ionic surfactant		4.3.3.1
		Aqueous degreasing with non-ionic surfactants		4.3.3.2
		Optimising the use of organic solvents in dry-degreasing		4.3.3.3
	Pickling	Low-salt and salt-free pickling processes		4.3.2.4
		Substitution of biocides	4.1.5	
TANNING	Tanning	Improved exhaustion and fixation		4.3.4.2
		Non-chrome tanning agents		4.3.4.5
		Substitution of biocides	4.1.5	
		Substitution of surfactants	4.1.1	
		Substitution of complexing agents	4.1.6	
POST-TANNING OPERATIONS	Retanning	Improved exhaustion and fixation		4.4
		Low-salt liquid retanning agents		4.4
		Selection of polymeric tanning agents		4.4
		Low phenol and low-formaldehyde syntans		4.4
		Low-formaldehyde resin tanning agents		4.4
		Selection of aldehyde tanning agents		4.4
	Dyeing	Dedusted powder dyes	4.4.2	
		Liquid dyes	4.4.2	
		Selection of dyes	4.4.2	
		Selection of fixing agents	4.4.2	
		Selection of dyeing auxiliaries	4.4.2	
		Substitution of surfactants	4.1.1	
		Substitution of complexing agents	4.1.6	
	Fatliquoring	AOX-free fatliquors	4.1.2	
		Polymeric fatliquors with high-exhaustion	4.1.2	
		Substitution of surfactants	4.1.1	
		Substitution of complexing agents	4.1.6	
	Other post-tanning agents	Substitution of water repellents	4.1.2	
		Substitution of flame retardant	4.1.2	
FINISHING	Finishing	Aqueous finishing systems	4.1.4	4.5.2
		Substitution of particular organic solvents	4.1.4	
		Agents with low aromatic content	4.1.3	
		Substitution of heavy metals in pigments	4.4.2.3	
		Substitution of binders and cross-linking agents	4.1.3	
		Substitution of biocides	4.1.5	

Table 4.1: Options for substitution of chemicals in tannery processes

Table 4.1 lists the substitute agents and auxiliaries that will be discussed. Chapter references are given in the last two columns. Some substitutions cause minor process changes or are valid for different process units. These substitutions are covered in Section 4.1. In some cases the implications for the process are significant or very process-specific (e.g. low-ammonium and ammonium-free deliming). They are discussed with other techniques in the chapter for the respective process unit.

Many agents used during the process are added in particulate form including dyes, organic and inorganic salts, bating agents, syntans, retanning and tanning agents. Many of these emit dust during handling, mixing and feeding into process drums. If the agents cannot be applied in a de-dusted or liquid form, protective gear or dust abatement has to be used to provide for workplace safety. For the abatement of dust emissions see Section 4.8.

Responsible management by the tanner requires awareness of substances and their fate in and after the process. Information has to be demanded from the supplier primarily, as safety data sheets do not usually provide sufficient information about environmental risks.

Unless otherwise indicated the substitutions can be made in existing and new plants.

4.1.1 Substitution of surfactants

Surfactants are used in many different processes throughout the tannery, e.g., soaking, liming, degreasing, tanning and dyeing. Environmental concern about surfactants is mainly related to their biodegradability, the toxicity of metabolites and the parent products and the potential to act as endocrine disrupters.

Concerns currently focus on the use of alkyl phenol ethoxylates (APEs), a range of non-ionic surfactants. A degradation product of APEs is octylphenol. Research carried out at Copenhagen's main university teaching hospital Rigshospitalet, the Royal Veterinary College and Odense university, claimed to be the first to establish a possible link between human fertility and octyl phenol.

The APE surfactant most commonly used in the leather industry is nonylphenol ethoxylate (NPE). Whilst these detergents have the desired detergent and emulsifying properties, their harmful effects on the environment are well known. NPEs can be degraded to smaller chain NPEs and nonylphenol, both of which are toxic. Nonylphenol is also implicated as an endocrine disrupter. Several countries and retailers have already placed restrictions on the use of NPEs.

The main alternatives in the leather industry are **alcohol ethoxylates**.

A lack of data means that no assessment can be made of many surfactants. There are, however, indications that many of them, e.g. linear alkylated benzenesulphonacids and quaternary ammonium compounds, give rise to negative effects on the environment.

Enzymes (lipases) can be used to degrade natural grease during the soaking operation of bovine hides. The soaking process containing lipases will usually make it possible to reduce the input of the surfactant used to emulsify the degraded fatty matter. In a recent (European) research project about ovine leather degreasing, however, it was demonstrated that the use of enzymes hinders the degreasing process.

Aqueous degreasing with detergents is commonly used to substitute halogenated and non-halogenated solvents. Generally, only sheepskins and pigskins are degreased. Bovine hides are not degreased in a separate process.

Surfactants are generally not monitored, even if foam is a visible problem in the effluents of a waste water treatment plant. Therefore only a few data on emission and impact are available (see Section 3.7.4.3)

Main achieved emission levels: Elimination of potentially toxic endocrine modulator. In Spain further research will be carried out on waste water containing nonylphenol ethoxylates and nonylphenol that is treated in a communal biological treatment plant (see Section 3.7.4.3).

The substitution of organic solvents in the degreasing step by surfactants, clearly shifts the contamination risk away from air emissions, waste and soil to the watercourse. Neither a quantitative nor a qualitative assessment of cross-media effects can be carried out, since insufficient data are available for any single medium.

4.1.2 Substitution of halogenated organic compounds

Emissions of adsorbable organic halogens (AOX) are restricted in certain countries for environmental reasons. Chlorinated organic compounds give rise to AOX emissions.

In many cases, a comparison with other options is not possible, since no comprehensive assessment has been made of the possible environmental impact of these substances.

4.1.2.1 Halogenated organic compounds for soaking

Chlorinated alkanes may be used as preserving agents in soaking [tan/tm/15/Reemtsma]. See Section 4.1.5 for the substitution of those biocides.

4.1.2.2 Halogenated organic compounds for degreasing

Possibilities for substituting halogenated organic compounds are either using non-halogenated solvents or changing over to an aqueous degreasing system.

Alkylpolyglycolether, carboxylate, alkylethersulphate, alkylsulphate and sulphonate can be substitutes for halogenated solvents [tan/tm/64/LAWA]. Solvent degreasing will result in some air emissions of solvents, even though solvents are recovered. Storage, handling and transport require special precautions in order to prevent contamination of the soil through spillage and protect the workforce from fugitive emissions. Prevention measures such as closed systems, solvent recycling, emission abatement techniques and soil protection can considerably reduce the emissions.

When halogenated solvents have to be used, prevention and abatement measures have to be adapted specifically. Fugitive emissions from closed solvent degreasing systems can be minimised in order to minimise the impact on health and safety at work and on solvent emissions into air, soil or effluent.

Wastes of greasy residues (at a rate of 10 – 20 % of pickled weight [tan/tm/09/UNIDO]), organic solvents and the filters from air abatement of organic solvents must be disposed of.

Residues of grease-containing halogenated solvents, solvent and waste waters from the solvent degreasing process do not lend themselves to further treatment.

4.1.2.3 Halogenated organic compounds for fatliquoring agents, auxiliaries and other post-tanning operation agents

For the substitution of surfactants see Section 4.1.1.

Fatliquors
The use of AOX-free fatliquors is triggered essentially by existing AOX emission limit values [tan/tm/09/UNIDO].

There are fatliquors available that do not require stabilisation by organic solvents, do not contribute to the AOX, for example fish oils [tan/tm/04/Austria, tan/tm/30/Renner], and perform with improved exhaustion [tan/tm/28/BASF, tan/tm/06/Europe].

Fatliquors containing HOC are necessary in the case of waterproof leathers; substitutes have not yet proved satisfactory.

Water repellent agents
Like fatliquors, water repellent agents can also contain organic solvents and organic halogenated compounds. Some water repellents contain emulsifiers and need fixing, which is most efficiently done with metal salts of aluminium, zirconium, calcium or chrome.

There are water repellent agents available which contain no organic solvents and which require no metal salts for fixing. They result in a decrease of the COD and the elimination of AOX in the waste water.

Agents with the above-mentioned properties are available, but the substitution of metal salts (chrome, aluminium, zirconium, calcium) as fixing agents is not generally applicable, particularly for very high standards of water resistance

Flame retardants
Flame retardants are classified as "durable"or "non-durable" [tan/tm/65/Ohio].

1) non durable flame retardants
The non-durable flame retardants are water-soluble inorganic salts, e.g.: borax, boric acid, ammonium borate, and ammonium bromide. Their low cost in achieving effective flame retardance ensures their use in applications not subject to leaching. In the production of upholstery leather, where exposure to aqueous leaching in normal product use is most unlikely, the non-durable flame retardants are becoming increasingly important. The Environmental Protection Agency (USA) suggests that no reasons have been found for environmental concerns relative to the use of these non-durable flame retardants in textiles.

2) durable flame retardants
In the context of flame retardants, durability is simply the ability to withstand leaching with water and, to some extent, dry-cleaning organic solvents. Often the durability of the flame retardant is established through appropriate cross-linking agents. Tetrakis (hydroxymethyl) phosphonium compound (THP) is one of the most important flame retardants. Until the discovery of THP, the most successful durable flame retardant employed a urea-phosphate treatment; other compounds have sometimes been combined with the urea-phosphate, e.g. cyanamide, ammonium sulphamate, chlorinated paraffin wax or antimony oxide.

In the magazine World Leather, November 1999, Roy Kittmer from Hodgson Chemical Ltd, UK wrote the following about fire retardants: "There are already movements away from the use of brominated and antimony-containing fire retardants. This is due to their potentially toxic combustion products. The natural successors will almost certainly be phosphate-based." So obviously brominated fire retardants are still used.

Further post-tanning operation agents
Surfactants and complexing agents are used as auxiliaries. These substance classes are discussed in Sections 4.1.1 and 4.1.6, respectively.

4.1.3 Substitution of binders and cross-linking agents

Resins with low monomer content (e.g. binders) are commercially available and are used in finishing to replace conventional polymeric products.

Isocyanates and aziridines are extremely toxic and for this reason they are not used in their monomer form in the leather industry. Commercial products may have used high molecular weight chemicals with isocyanates or aziridines groups, thus considerably reducing the volatility and toxicity of these compounds compared to the monomer, but strict safety precautions are generally required.

Alternatively, self-cross-linking reactive polymers containing N-methylolamine groups can be used.

4.1.4 Substitution of organic solvents in the finishing process

In the finishing process, water-based systems are increasingly favoured because of environmental concerns about organic solvents and in order to comply with regulations [tan/tm/58/BLC, tan/tm/17/Frendrup]. For applying the coating layers, different techniques can be used (compare Section 4.5.2). Organic solvent based processes in closed spray cabinets and closed drying systems, which offer an acceptable environmental performance, require cost intensive abatement techniques (compare Section 4.8).

Base coats are generally water-based. If very high standards of topcoat resistance to wet-rubbing, wet-flexing and perspiration are required, then solvent-based systems cannot always be substituted by aqueous-based systems [tan/tm/17/Frendrup, tan/tm/09/UNIDO]. In some situations upholstery for automotive and furniture use are examples of such applications.

The main advantage of water-soluble lacquers is the considerable reduction of organic solvent consumption and releases. Most water-based finishing products still contain a low amount of organic solvents.

Finishing system	Organic solvent content% [tan/tm/17/Frendrup]
Organic solvent thinnable lacquer	80 – 90
Water thinnable lacquer emulsion	40
Water-based system	5 – 8

Table 4.2: Organic solvent content in finishing systems

In order to achieve equal characteristics with low-organic solvent and water-based systems, cross-linking agents for the finishing polymers often have to be used. The toxicity of these agents is problematic, but commercial products offer the agents in a less toxic (workplace safety) and less volatile form. Nevertheless, special measures have to be taken to prevent accidents in handling (protective clothing) and applying these agents.

Organic solvents are either added in the formulation of the finish or are already incorporated in the finishing chemicals (i.e. lacquers) by the supplier. Many of the finishing chemicals do not specify the composition of the finish in terms of the type and quantity of organic solvent used. The safety data sheets are generally the only source of information for the tanner.

For any organic solvent applied in the process that cannot be substituted by aqueous systems, the alternative is to use organic solvents with the lowest impact on workplace safety and the environment and, in order to make recycling feasible, to avoid mixtures.

The main parameters for an assessment of organic solvent-based finishing agents are:

- the type of organic solvent used with regard to toxicity and the recycling options
- the efficiency of abatement in all processes where organic solvents can be released consequently, i.e. also in drying and storage
- the ratio of recycling or re-use of organic solvent.

The minimum requirement for organic solvent-based coating is the recording of solvent consumption, to include not only the solvents bought as solvents, but also the solvents contained in the finishing chemicals. This is the only acceptable way to calculate the overall emissions of VOC, because it is not possible in practice to monitor fugitive emissions. (VOC releases from leather during storage are estimated as 10 % of the applied organic solvents that remain in the leather and about 60 % of the amount emitted in the drying tunnel. The rest is emitted during storage [tan/tm/03/UwHB-Luft p.20]).

Halogenated solvents are discussed in Section 4.1.2.2.

A further cross-media effect is the higher energy consumption for drying water-based top-coats.

4.1.5 Substitution of biocides

Biocides may be used in the curing, soaking, pickling, tanning and post-tanning processes

Halogenated organic compounds, e.g. bronopol, thiadiazine, have been used for a long time in tanneries and halogenated biocides are still sold. Sodium- or Potassium- di-methyl-di-thiocarbamate is considered to be a more environmentally friendly bactericide, due to its lower persistency and toxicity levels [tan/tm/58/BLC].

BLC reports that the use of e.g. 0.05 % (of the weight of raw hides) bronopol can offer adequate protection. Portugal (CTIC) reports a range of 0.05 to 0.1 %, Italy 0.1 to 0.5 % depending on the type and concentration of the commercial product.

The uptake of bactericide can be measured by using dip slides. The dip slides should show the presence of bacteria in the soaking float, the bacteria count should be reduced to safe levels and the bactericide should therefore be fully utilised.

Pesticides that are prohibited in Europe may be imported through hides from non-EU member states. When those hides are processed, special attention has also to be paid to workplace safety to avoid infection of the work force from skin contact with infected hides and skins before beamhouse processing. The possible infections include anthrax infection, but the incidence is infrequent.

One way for European tanners to avoid importing these prohibited substances is to reject contaminated hides and skins. Alternatively European tanners could try to persuade their suppliers not to use pesticides that are prohibited in Europe.

Main achieved emission levels: According to Neuber, Leder- und Häutemarkt 6, 1998, the following calculation can be made for the use of biocides.

It is assumed that the water consumption in leather manufacture is 32 m^3/t (IFU, 1995). The breakdown is as follows:

Beamhouse: 20 m^3
Tanning: 1 m^3
Washing: 1.5 m^3
Finishing: 2.3 m^3
Washing and cleaning equipment: 7.2 m^3

For the purposes of the calculation that follows, it is assumed that the batches (100 % liquor) for tanning consist of 10 tonnes hides and that 0.1 % preservative is used with a 15 % content of active ingredient; this gives a usage of 10 kg of preservative per batch, containing 1500 g of active ingredient per 10 tonnes of hides (150 mg/kg). 95 % of the active ingredient supplied is absorbed by the hides, i.e. 142.5 mg/kg of it end up absorbed by the hides and 7.5 mg/l in the tanning liquor (75 g in liquor for a 10 tonnes batch).

During washing and finishing (together 3.8 m^3 of water) 10 % of the active ingredient is extracted, i.e. 128.3 mg/kg remains on the hides and 14.3 g of active ingredient ends up in the wash water (3.8 m^3).

The estimate gives a total amount of 89.3 mg of active ingredient in 32 m^3 of waste water per tonne of hides processed, i.e. the concentration in the waste water is 2.8 mg/l.

A series of measurements carried out on a batch in a wet-blue tannery in operational practice showed that the uptake of the active ingredient had actually been completed after 3 hours. Only about 5 % of the active ingredient remained in the tanning liquor, and its concentrations in the liquor remained at that level in the further course of the tanning process.

4.1.6 Substitution of complexing agents

Complexing agents such as e.g. EDTA (ethylen-diamine-tetra-acetate) and NTA (nitrilo-tri-acetate), are brought into the water as sequestering agents. Apart from impeding the waste water treatment, complexing agents have an adverse impact on the environment.

EDTA, and NTA to a lesser extent because it has a higher biodegradability than EDTA, poses a particular hazard. Possible substitutes can be DTPA (di-ethylene-triamine-penta-acetate) or PDTA (Propylene-diamine-tetra-acetate (both aminopolycarbon acids), but there is no information available whether those substances are any safer than EDTA. More environmentally friendly alternatives are EDDS (ethylene-diamine-di-succinate), which is very biodegradable and MGDA (methyl-glycine-di-acetate), which is also very biodegradable but expensive. IDS-Na salt can be an alternative but might not be powerful enough. (tan/tm/72/UBA). There is no information on whether those substances are used in tanneries or not.

4.2 Beamhouse

The following tables show the consumption and emission levels for the beamhouse process.

Bovine hides	COD (kg/t)	S^{2-} (kg/t)	NH_4^+ (kg/t)	Cl^- (kg/t)
Soaking				60 - 200
Liming/unhairing	80 - 100	5 - 12		
Deliming	8 - 10		5 – 10	

Dry goat-and sheepskin	COD (kg/t)	S^{2-} (kg/t)	NH_4^+ (kg/t)	Cl^- (kg/t)
Soaking				60 - 200
Liming/unhairing	200 - 350	10 - 25		
Deliming	15 - 30		6 - 12	

Table 4.3: Waste water loads from processing salted bovine hides and dry goat- and sheepskins
Source: tan/tm/39/Italy

Emissions to Waste water from:	Water m^3/tonne	BOD mg / litre	COD mg / litre	S^{2-} mg / litre
Soaking	2 - 4	1800 - 2300	2500 - 10000	
Liming Rinsing	3 - 8	~3000	17000 - 25000	600 - 4000
Deliming/bating Rinsing	1 - 4	800 - 1700	up to 10000	50

Table 4.4: Emissions to waste water from the beamhouse process, from the manufacture of chrome leather from bovine hides
Source: tan/tm/37/Germany, see alsoTable 3.18

The ideal solution for reducing the environmental impact of the beamhouse process is washing, chilling, trimming, fleshing and – if necessary – salting of the hides in the abattoir. This system ensures the maximum value of trimmings and fleshings as raw material for the production of animal foodstuffs, as they are not contaminated by any chemicals and their water content is relatively low. The washing facilitates the subsequent fleshing; and the fleshing ensures a minimum of salt consumption at the same time as a maximum conservation effect because the salt penetrates the hide from the flesh side. Fewer chemicals and less energy are wasted on material that is not converted into leather.

In the case of sheep's wool, 40 – 50 % of the total waste water load can be caused by matter attached to the wool (urine, fat, manure, dirt, loam). There are requirements (EC legislation on hygiene standards) for abattoirs which mean that the hides and skins they provide to the tanneries should be from washed animals. In practice a wide variation in the cleanness of the hides is found, depending on the abattoir and the season – cattle which are not kept inside are much cleaner. Problems arise because tanners buy their hides from different sources with different quality standards.

The quality of the hides has taken a downward trend; from 27 % in 1980, 17 % in 1990, the estimated proportion of quality hide in the total world hide population for 2000 is 12 % (source LMC/Philip Hadley, BLC). According to a survey in the UK, 10485 hides carried on average 6 % manure. The manure ends up in the tannery waste, and the 60 kg manure per tonne raw hide corresponds to a waste water load of approximately 12 kg total solids, 3 kg suspended solids, 2 kg BOD, 5 kg COD and 0.6 kg total Kjeldahl nitrogen [tan/tm/17/Frendrup].

For this reason, ten European partners, under the auspices of COTANCE, started the FAIR Project: Improving Hide and Skin Quality. By surveying the existing initiatives in Denmark, Sweden, New Zealand, Australia, UK and the Netherlands, the following common success factors were found [tan/tm/43/World Leather, May 1999]:

- the supply chain should be as short as possible
- the supply chain should be integrated in terms of ownership, joint ventures and/or communication
- agreements on collection/price between abattoirs and suppliers should be long-term and stable (e.g. monthly rather than weekly)
- hides/skins should be priced by quality
- incentives for quality help cement longer term relationships by encouraging added value through the chain, making increased rewards available to all the participants in the chain.

Apart from improving the quality standard of the leather this project may ultimately result in less waste. It would be useful if this were monitored as well.

4.2.1 Curing and soaking

The following table show emission data from soaking from several sources.

Pollutants in Waste water		Examples for emission loads from conventional soaking processes for salted bovine hides in [kg/t raw hide]			
		Tan/tm/11/ Nordiske Seminar	Tan/tm/39/Italy	Tan/tm/58/BLC	Tan/tm/17/ Frendrup
Suspended Solids	X	15		15	15
COD	X	40		30 - 50	27
BOD	X	8 – 10		8 - 10	10
Chloride	+	200 ± 50	60 - 200	200 ± 50	85
Biocides	+				
Detergents	+				
Enzymes	/				
Notes: X = always + = often / = sometimes					

Table 4.5: Pollutants in waste water from soaking

The salt and other additives applied in curing and soaking are transferred to the effluents in the soaking process. The main contamination is the high COD and salt content in the waste water effluent. Further problems arising might be odours due to putrefaction, sulphides and ammonia [tan/tm/16/Spain]. Certain bactericides (sodium hypochlorite) and certain surfactants can also contribute to the AOX level in the waste water.

For curing and soaking, reported techniques to reduce emissions are:

- substitution of salt
- reduction of salt, where a complete substitution is not possible
- recovery of the used salt
- environmentally optimised treatment of salt waste water effluents and waste (recycling and re-use options for solid salt or waste water)
- substitution of specific substances: biocides, surfactants, hypochlorite (see Sections 4.1.1 and 4.1.4)
- optimisation of water consumption and process control.

These techniques or technologies are described in the following sections. After those measures are taken the following emission loads can be achieved:

Waste water loads per tonne raw hide[1]				
	Traditional technology	Average unit	Available technology	
			Salted hides	Salt free raw hides[2]
Water volume, m^3/t	10[3]	6	4	2
Total solids, kg/t	160	125	130	45
Suspended solids, kg/t	15	13	10	10
BOD$_5$, kg/t	10	10	10	12
COD, kg/t	27	23	23	23
Total Kjeldahl nitrogen, kg/t	3.8[4]	1.5	1.5	2
Chloride (Cl$^-$), kg/t	85	65	55	5
[1] Calculated on the basis of salted weight [2] Fresh or chilled hides [3] By soaking of dried hides and/or rinsing with running water, up to 20 m^3/tonne raw hide [4] Dirty hides				

Table 4.6: Waste water loads that can be achieved
Source: tan/tm/17/Frendrup.

The figures in this table are exclusive of contributions from manure etc.; e.g. 12 kg total solids, 2 kg BOD$_5$, 5 kg COD, 0.6 kg total Kjeldahl nitrogen per tonne raw hide or more. If a detergent is used, the amount might typically be 10 kg per tonne raw hide.

4.2.1.1 Substitution of salt

Substitution of sodium chloride by potassium chloride

Potassium chloride, while chemically quite similar to sodium chloride, does not present the same environmental difficulties. Where sodium displaces metals in the soil that are essential for plant growth, potassium is a 'required' plant micro-nutrient and its application would enhance the soil rather than damage it. Länderarbeitsgemeinschaft Wasser (LAWA) Germany, has another opinion. This institute states that it is not the cation sodium or potassium that is the problem in the receiving water, but the anion chloride. Although potassium is a 'required' plant micro-nutrient, organisms living in this receiving water are much more sensitive to potassium chloride than to sodium chloride.

An advantage of using potassium chloride is that it will eliminate the problem of "red heat". A disadvantage is the (lower) solubility of potassium chloride. When the temperature drops, the

level of potassium chloride needed in the hide is not achieved and a companion bactericide is still necessary.

Cross-media effects: the use of bactericide is necessary.

Economics: the cost is about four times greater than sodium chloride.

Reference literature: Dr. D.G. Bailey, Eastern Regional Research Centre, USA, World Leather, November 1999.

Drying

In countries with low relative humidity and warm temperatures, an environmentally friendly and cost-effective long-term preservation method is the drying of skins, as long as either low environmental impact bactericides or no bactericides are used. Under adverse weather conditions, the drying of raw materials becomes more difficult and more expensive.

Cooling and processing of fresh hides

Description: Chilling the hides/skins is considered a short-term preservation method, and is environmentally friendly for short storage periods. Chilling, based on reducing the hide temperature to 10 - 15 ºC, has been used for many years e.g. in Australia. If the refrigeration temperature is reduced to ±2 ºC, hides can be stored for three weeks without suffering damage. The temperatures to which hides and skins should be chilled depends on the required duration of preservation.

Cooling of the hides can be carried out in several ways:

- by spreading the hides immediately after stripping on a clean marble floor with the flesh side in contact with the cold floor
- by processing the hides immediately after stripping in a mixer containing chunks or cubes of ice
- by passing the hides immediately after stripping through a tank of glycol-cooled water and adding ice to the storage container
- by using CO_2 snow
- by using refrigerated storage units.

There are, however, several restrictions when using short-term preservation methods:

- ideally the slaughterhouse must be relatively close to the tannery (not overseas)
- the raw material must be processed almost immediately (depending on the chilling method, between one day and twenty days)
- raw stock cannot be bought in great quantity when prices are lower
- the transport costs can be greater due to either extra weight (ice) or the cost of refrigerated units
- the energy consumption can become prohibitive if the hides are stored for more than one week
- the system of collecting/trading hides in any individual country or region may not suit the use of short-term preservation methods; for example, if a substantial proportion of hides are imported or exported, the system may not be practical/economically viable.

All the above points can militate against short-term preservation as it can increase the cost of the raw material. In practice, chilling can be adopted in all countries, but in some countries it is less cost effective than in others.

The cost of an ice-making machine is not as high as the capital investment required for chilling units and cold stores.

Carbon dioxide cooling meets the needs of small abattoirs. Hides can be cooled rapidly by simple, economic and efficient means to provide preservation lasting several weeks. Investment costs are low because most firms producing hides as a by-product already have cold storage facilities. In adequately ventilated premises, carbon dioxide gas presents no health or safety risk. This technology has found a use in Australia and New Zealand.

Some of the above-mentioned options depend strongly on the local conditions, particularly on the distance of tanneries from the abattoir and good management of the input stock of the raw hides. On the other hand some options, in particular good management practice, can be applied in both, existing and new plants and do not depend on the local conditions. The cooling techniques can eliminate common salt from preservation, but cold conditions have to be maintained.

Advantages of processing cooled hides
- under normal circumstances no salt in the waste water from the soaking
- the quality of the hides is better; they are softer and have more regular neck parts, so easier to process
- 1 - 1.5 % better yield
- no need to de-salt in a de-salting drum.

Disadvantages of processing cooled hides
- 'green' fleshed hides can't be split as accurately in the lime as salted hides can be
- lower prices (profit) on split butts achievable due to flesh remnants on the sub-cutaneous (hypodermis) connection tissues of the butts - irrespective of whether the butt has been pickled in the pelt or sold as wet blue.

Main achieved emission levels: A reduction of nearly 100 % in salt consumption is achieved.

Cross-media effects: Cooling and chilling require energy. Depending on the existing national legislation on food hygiene, there may be better re-use options for the wastes generated in trimming and fleshing.

It is reported from the Netherlands that more biocides are needed when processing fresh hides, because the cooling process takes several hours, during which bacterial growth will start to develop.

Salt facilitates the elimination of some proteins and therefore some salt is in any case added at the soaking process; enzymes can be used instead of salt.

Reference plant: Gribitsch & Wollsdorf Leder, Austria, year 1999.
The following information comes from Gribitsch & Wollsdorf Leder from Austria. In Austria about 60 – 70 % of raw (in majority cattle) hides are processed as fresh hides.

This tannery's transport costs vary between DEM 0.03 and 0.06 /kg (about EUR 0.015 - 0.03 /kg), depending on the distance. Basically there is no difference in transport costs of fresh hides versus salted hides, as a refrigerated truck/container is not required for the transport of fresh (cooled) hides. For distances up to 3 hours driving time, no cooling at all is necessary. For longer transit times the hides are stored either in lattice boxes with a layer of ice splinters (1 - 2 shovels) over each hide, or stored in lattice boxes only (without using ice splinters). Once the hides arrive at the tannery, they are stored in a cold storage house with a capacity of about 1200 hides.

Better transport methods are, however, only applicable if the supplier (abattoir) has a cold-storage facility where the hides are stored at a temperature of +2 ºC prior to transport. The hides must be hanging and must not touch each other.

For this specific tannery, the distance to the suppliers is up to 1500 km and the transportation is contracted out to transport companies.

The decision whether to process cooled or salted hides depends very much on the end-product.

Reference literature: tan/tm/58/BLC, tan/tm/17/Frendrup, tan/tm/04/Austria.

4.2.1.2 Reduction of salt

Various options exist to achieve a reduction of the salt input. They are mainly a question of optimising the management of the process and the input chemicals rather than applying particular techniques.

Reduction in the abattoir/hide market
Although abattoirs and hide markets are outside the scope of this document, the following information may be useful. It should be understood that measurements meant for industries other than tanneries cannot be defined as BAT for tanneries.

Description: The performance of washing, trimming, fleshing and curing in the abattoir reduces the overall weight of the rawstock leading to a reduction of salt necessary for the curing operation. The washing facilitates the subsequent fleshing and ensures a minimum of salt consumption at the same time as a maximum conservation effect, because the salt penetrates the hide from the flesh side.

In the USA, 75 % of all hides are processed in this way and do not need any re-fleshing in the tannery. However, this type of processing presupposes a supply to the abattoirs of large numbers of reasonably similar animals; for this reason it has only become common practice in the USA with its big abattoirs (1000 - 10000 animals per unit per day). A centralised beamhouse plant did exist for some years in the Netherlands but closed down as it was uneconomic. [tan/tm/17/Frendrup]

This option also depends strongly on the local conditions; e.g. not all abattoirs are allowed to process raw material on site.

Since this option does not depend on the standards in the tannery, it can be applied in both existing and new plants.

For the siting of a new tannery the possibilities in the abattoir for this kind of pretreatment might be one of the crucial factors to be considered.

Main achieved emission levels: According to experience from the USA, the weight of the hide is reduced by 18 – 24 % through this treatment (3 – 4 % manure, 5 % trimmings and 10 – 15 % fleshings). If 35 % salt is added, calculated on this reduced weight, the salted weight will be 884 kg instead of 1000 kg without pretreatment, and the amount of chloride in the tannery waste water, deriving from the raw hides, will be 108 kg instead of 122 kg (both figures calculated on the basis of 1140 kg fresh weight) [tan/tm/17/Frendrup]. This results in a reduction in salt consumption of about 12 %.

Cross-media effects: With this technique the pollution load from the organic material is generated in the abattoir instead of the tannery. The raw material trimmings and fleshings can be immediately rendered and re-used by the abattoir.

Chemicals are saved and consequently not transferred to the effluents or wastes. Less weight has to be transported.

Reference plant: This technique is applied with great success in very large abattoirs in the United States.

Economics: There has to be a relatively high number of similar animals to make this kind of pretreatment cost-efficient in the abattoir and there are some specific regulations for abattoirs which prohibit these treatments, for example in Germany [tan/tm/06/Europe].

Reference literature: tan/tm/18/UNEP, tan/tm/06/Europe, tan/tm/17/Frendrup, tan/tm/58/BLC

Application of biocides

With the addition of inorganic or organic biocides the salt consumption can be reduced. Biocides can be applied by spraying, dip immersion or mechanical systems such as drums or mixers.

The assessment of environmental advantages and disadvantages of this technique is necessary to qualify this technique. The technique can be applied in both existing and new plants.

Cross-media effects: The energy input has to be assessed in comparison with the salt releases and the use of biocides. The by-products containing biocides such as fleshings and splits may not be used by the food industry.

4.2.1.3 Recovery of salt

Description: Salt can be recovered by shaking off any excess; this operation can be carried out either manually, or mechanically using purpose built drums. In both cases 8 % of the original salt content of the hide is eliminated, corresponding to about 5 % of the total salt discharge from the tannery.

The re-use of salt might be problematic due to contamination (bacteria, organic material); the salt might be too dirty to be used in the pickle liquors without sterilisation with heat. Mechanically shaking off the salt can influence the quality of the hides, because the solid salt can scratch or produce abrasion of the grain during drumming. The cost of this operation and of the proper treatment to make the salt suitable for re-use is not effective due to the low price of salt. For all those reasons it is often difficult to get acceptance for this technique in a tannery. The technique can be applied in both existing and new plants.

Main achieved emission levels: The overall salt emission level is limited to the salt dissolved in the raw material. About 5 % of the salt usually found in the effluent streams is recovered. Although currently not economically feasible, the salt can be sterilised, washed and dried before recycling in the tannery, either in the preservation step or in a process step.

Cross-media effects: The main disadvantage is the problem with the disposal of solid salt. Landfilling of solid salt is not an environmentally sound option (high solubility) and is consequently forbidden in some Member States.

Economics: The cost of salt recovery is prohibitively expensive in comparison with the cost of fresh salt.

Reference literature: tan/tm/58/BLC, tan/tm/17/Frendrup

4.2.1.4 Reduction of water consumption during soaking, and re-use of brine liquors

Description: It is possible to re-use some process liquors such as the water at the end of the bating process, which is used to rinse and cool the pelts prior to the pickling operation. This water could be used for the dirt soak to reduce water consumption.

Pickle liquors and liquors from high-exhaustion tanning processes can also be recycled, thus reducing the salt consumption and emissions in the tannery (see Sections 4.3.2.2, 4.3.2.3, and 4.3.4.3.)

It is necessary to install storage tanks and appropriate pumping and dosing systems to treat the recovered bath prior to re-use. The treatment can include a separation of suspended solids (e.g. coarse filters), strengthening the concentration of the active chemicals, addition of bactericides, addition of fresh water, precipitation and recovery of processing chemicals, e.g. chrome.

When recycling soak liquors for usage during dirt soak, it is important to pay attention to bacterial contamination, which might require either the addition of sodium hypochlorite or the use of bactericides.

Main achieved emission levels: Water consumption can be reduced to the equivalent of the water being recycled.

For the reference plant in St. Croce (compare liming in Section 4.2.3.3 and pickling in Section 4.3.2.2), 200 % of water savings on hide weight are reported.

The combination of recycling soaking, liming and pickling liquors leads to savings of 24 – 31 % in suspended solids, 25 – 26 % in COD, 98 – 99 % of chrome, 50 – 57 % of sulphides and 40 % of chlorides at the plant in St. Croce.

Cross-media effects: Biocides have to be considered for an assessment of cross-media effects, particularly with regard to waste water, waste water treatment, and implications for recovery of fleshings for the tallow industry [tan/tm/35/BLC].

Reference plant: St. Croce, Italy [tan/tm/43/World Leather November 1996].

Economics: Financial benefits of about ITL 200 million (about EUR 100000) are reported for the waste water treatment due to water savings and the reduction of suspended solids.

Reference literature: tan/tm/58/BLC, tan/tm/43/World Leather November 1996

4.2.2 Green fleshing

Description: Fleshing hides in green or soaked state is a useful procedure for producing chemical-free solid residues and it allows a more rapid and uniform penetration of chemicals into the hide. Unfortunately, the process is difficult and risks damaging the hides, because of the differences in thickness of raw hides due to uneven hair length or mass of dung that the fleshing machine is not able to identify. Green fleshing requires a well-set machine, where blades are exactly adjusted to avoid a further fleshing step after liming.

Green fleshing can also be complicated or made impossible if dung, dirt etc. are not sufficiently removed by washing and soaking. If the washing is not sufficient, a machine operation for the dung removal is sometimes necessary as well. However, where there is a significant amount of dried dung on the hides, de-dunging may not be feasible due to damage to the hides (dung ball damage). [tan/tm/17/Frendrup]

The green fleshing can be done with the raw hides in the abattoir (see Trimmings, p. 15) but only when a careful sorting has been carried out to select batches of hides of similar size and thickness. Or it can be done after a dirt soak. If a through process to the wet blue is being operated, green fleshing can be carried out before soaking.

If green fleshing has not produced a sufficiently clean flesh side, a further fleshing before lime splitting might be necessary. And if this additional operation is needed, green fleshing becomes an undesirable technique with significant drawbacks in terms of production. For example the introduction of green fleshing may increase the total processing time as hides may have to be unloaded and loaded between soaking and liming. The fleshings are collected and kept separately from other waste fractions and can be treated in the same way as the waste from trimming the raw hides.

The grease and fats in the water used in green fleshing can be more easily skimmed off if cold water is used. A renderer may be reluctant to handle this material because of the higher energy costs he would incur in evaporating the water. Fleshings can be processed into tallow by the tannery if a tallow recovery plant is installed on-site.

The technique can be applied to both existing and new plants. A retrofit is certainly economically more feasible if process steps are changed, because new machines have to be installed for green fleshing. The reference tannery in Germany reports that investments of millions (DEM) are necessary for this process change and for the new machines.

Main achieved emission levels and cross-media effects: The presence of excessive dung may prevent green fleshing, unless it is first removed by a thorough wash. Large quantities of dung may not be removed by washing and the use of de-dunging machines may therefore be necessary prior to soaking.

Fleshing can be sold to renderers or the tannery may have a rendering plant in which fleshings are turned to tallow. When deciding on whether to green flesh or lime flesh it is important to take into consideration the product specifications of the renderer. Though the quality of tallow recovered from green fleshing is higher than from limed fleshings, there may be a problem with tallow if biocides have been applied.

If green fleshing is applied (and no repeat fleshing is needed) the consumption of chemicals and water in the beamhouse are reduced by 10 – 20 % [tan/tm/58/BLC]. Consequently the waste water volume in the unhairing/liming step is reduced.

Green fleshing allows a more rapid and uniform penetration of chemicals into the hide.

Reference plant: Fa. HELLER-Leder, Germany

Economics: Investments for the change of process steps and the new machines needed runs into millions (DEM). The savings on chemicals and the higher price these fleshings fetch are not enough to repay the investment cost. The reference plant also reports that the market for green fleshed, limed hides is not as good as that for conventionally processed hides.

Reference literature: tan/tm/58/BLC, tan/tm/03/UwHB-Abfall, tan/tm/03/UwHB-Stoffe, tan/tm/02/HMIP

4.2.3 Unhairing & liming

The following tables show emission loads from conventional and average unhairing/liming processes for bovine hides. Sheepskins are also 'unhaired' by pulling the wool from the skin, but there are almost no data concerning sheepskins; all the data refer to bovine hides unless otherwise mentioned.

Typical waste water loads per tonne raw (soaked) hides: liming/unhairing		
	Conventional technology[1]	Average unit[2]
Water volume, m^3/t	12	9
Total solids, kg/t	187	150
Suspended solids, kg/t	93	66
BOD_5, kg/t	50	40
COD, kg/t	130	100
Total Kjeldahl nitrogen (TKN), kg/t	5.8	5.8
Ammonia nitrogen, kg/t	0.4	0.4
Sulphide (S^-), kg/t	8.5	5
Chloride (Cl^-), kg/t	15	15
Grease and oil, kg/t	5	5
Notes: [1] Hair-dissolving process, carried out with high quantities of chemicals (5 % lime, 1.6 % S^{2-}) [2] Hair-dissolving process with good chemicals economy (2 % lime, 0.8 % S^{2-})		

Table 4.7: Waste water load of liming-unhairing process
Source: tan/tm/17/Frendrup

Italy has provided average data referring to different types of leather produced from bovine hides and average data for processing goatskins and, to a lesser extent, sheepskins.

	COD (kg/t)	S^{2-} (kg/t)
Bovine hides	80 - 100	5 - 12
Dry goat- and sheepskins	200 - 350	10 - 25

Table 4.8: Waste water load of conventional liming-unhairing process
Source: tan/tm/39/Italy

Techniques to reduce the emissions are:

- hair-save technologies
- reducing the sulphide consumption
- recycling spent sulphide liquors
- removing sulphide from the effluent.

They are discussed in the following paragraphs.

4.2.3.1 Hair-save technologies

Description: Hair-save processing has been developed for processing bovine hides [tan/tm/03/UwHB-Abfall; tan/tm/58/BLC, tan/tm/17/Frendrup, tan/tm/02/HMIP, tan/tm/12/Ullmann, tan/tm/28/BASF, tan/tm/18/UNEP-Tan, tan/tm/09/UNIDO]. This involves manipulating the conditions of alkalinity and reducing the agent in such a way that the hair comes out of the follicle without being pulped and without destroying the hair shaft. A recirculation system with a screen is used to separate the intact hair. This waste is landfilled or, where possible, used as new raw material elsewhere, rather than being discharged to the effluent. This brings about a reduction in levels of solids and BOD. Hair causes a very high organic load, which results in a high production of sludge.

Several commercial hair-save processes are on the market. Although these processes are not suitable for all types of raw hides and leather products, high quality leathers are already being produced [tan/tm/45/World Leather, November 1999; Carlos S. Cantera, CITEC]. In Italy this

technique is applied to bovine hides for footwear, leather goods and upholstery, but not to bovine leather used for the production of sole leather or to goatskin [tan/tm/39/Italy].

A hair-save technology for sheepskins, called painting, consists of the application of a semifluid paste on the flesh side of the skin, composed of an inert material (kaolin or other) containing sulphide and lime. The treatment is carried out in a warm environment (max. 30°C) and takes some hours. The painting of sheepskins is not further discussed in this section.

The hair-saving techniques, for bovine hides, are well known but they demand precise operating conditions and control. There are several tanneries in Europe which have implemented this technique; for example Fa. HELLER-Leder in Germany. There the unhairing is done in two steps. Where they normally add in one step calciumoxide and sodium sulphide, in the hair-saving process they add in the first step 2/3 of both calciumoxide and sodium sulphide plus thioglycol-acid. The thioglycol-acid prevents the hair from being destroyed. After this first step a rotating screen removes the - undestroyed - hair from the float. The remaining 1/3 of the chemicals is then added to finish the unhairing process. The main reason for this tannery adapting this technique was the reduction of sludge by 15 – 30 %.

Elmo Calf AB in Sweden has implemented hair-saving since the end of 1998 for all production. A local farmer uses the saved hair as a fertiliser. The main reason to install rotating screens to remove the hair from the waste water was to decrease the COD and nitrogen content. All flesh split from lime splitting used to be processed for fat recovery, which also caused an emission of nitrogen to the waste water. At the moment they send about half of the lime fleshings to a plant for the production of biogas. The intention is to send all lime fleshings to anaerobic digestion in order to decrease the emission of nitrogen even further. Those two measures - hair-saving and sending lime splits partially to anaerobic digestion - have reduced the emission of organic nitrogen by 50 % and the total nitrogen load in the waste water by 20 % i.e. from 15 kg N_{tot}/tonne raw hide to 12 kg N_{tot}/tonne raw hide

The techniques can be applied to both existing and new plants. However, the processing vessels need to be adapted to allow for the recovery of the hair from the float during the process. Some process vessels may be difficult to adapt to operate a hair-save system.

Main achieved emission levels: Table 4.9 shows the emission reductions achieved using hair-save technology, whether or not in combination with recycling and filtering the bath, from various sources.

Reduction in waste water from liming / unhairing section	1	2	3
SS		- 80 %	
BOD		- 60 %	
COD	- 60 %	- 65 %	- 30 – 40 %
TKN	- 35 %	- 57 %	
Sulphide	- 50 %	- 92 %	- 30 – 40 %
Ammonia nitrogen		- 25 %	- 20 – 30 %
Notes: (1) tan/tm/35/BLC; tan/tm/28/BASF (2) tan/tm17/Frendrup: hair-saving process, carried out with recycling and filtering of the bath (3) tan/tm/39/Italy: hair-saving process, carried out with recycling and filtering of the bath			

Table 4.9: Reduction of emissions for hair-save technology compared to conventional techniques

The volume of sludges coming from the waste water treatment plant is reduced by 15 – 30 % (reported by the German reference tannery). Frendrup [tan/tm/17/Frendrup] reports a reduction of the amount of sludge dry matter to 100 - 110 kg per tonne raw hide.

The amount of hair saved varies from 30 - 50 kg dry hair per tonne raw bovine hide up to more than 100 kg per tonne calf, sheep or goat skins [tan/tm/17/Frendrup]. Although it is difficult to find an economic outlet, hair can be re-used as filling material or as a fertiliser (low rate of releasing nitrogen). See Section 4.7.1.

Cross-media effects: Positive effects for the environment are:
* a reduction of organic loads in the waste water
* a lower volume of sludges for landfilling or treatment and
* a saving on waste water treatment chemicals.

If there is no recovery option, a balance has to be struck between, on the one hand, the saving in the waste water, the landfilling of hair (separately from other waste water treatment sludges) and the different chemical agents used, and, on the other hand, the process without hair removal (high BOD in effluents, high volume sludge). For an example see: Figure 3.1. Assume that 500 kg sludges (40 % dry matter content) and, because hair-save technologies have been used, 75 kg hair (also 40 % dry matter = 30 kg dry hair) are produced per tonne raw hide. This results in a reduction of 10 % of the sludge produced, which means 50 kg less sludge to be landfilled; but 75 kg hair needs to be landfilled instead when there is no other outlet available. With a sludge-reduction of 30 % (150 kg less sludge) and 125 kg hair (both based on 40 % dry matter, assuming 50 kg of hair is saved), the net weight to be landfilled is 25 kg per tonne raw hide less when using the hair-save technology.

Hair-save technology may not be viable where, on the one hand, landfill is the only disposal option for the saved hair and, on the other, the waste water treatment plant can handle the high organic load of burned hair **and** high sludge production is not a problem because the sludge is treated and therefore suitable for re-use as, e.g. fertiliser. A careful balance has to be struck, taking each case on its merits.

Reference plant: Igualada (Spain), Swewi (Denmark), Fa. HELLER-Leder (Germany), Elmo Calf AB (Sweden).

Economics: There are few options for re-use of the recovered hair (see Section 4.7.1.) To make the hair removal and recovery process economically feasible, a strong incentive is a market for the hair, which exists more commonly for e.g., sheep and goat hair [tan/tm/09/UNIDO]. When enzymes are used in the hair-saving process, the hair is no longer suitable for the production of felt.

The technique requires high capital investment for existing tanneries.

Lime suitable for the hair-saving process is more expensive.

Reference literature: tan/tm/35/BLC, tan/tm/38/Denmark, tan/tm/39/Italy, tan/tm/74/Germany, tan/tm/03/UwHB-Abfall, tan/tm/28/BASF, tan/tm/02/HMIP, tan/tm/12/Ullmann, tan/tm/17/Frendrup, tan/tm/18/UNEP-Tan, tan/tm/09/UNIDO, tan/tm/43/World Leather November 1998.

4.2.3.2 Reducing the sulphide consumption

Description: A total substitution of the sulphides used as an unhairing agent is currently not possible in practice, but they can be reduced considerably [tan/tm/17/Frendrup, tan/tm/09/UNIDO, tan/tm/28/BASF]. In ovine skins, the necessary upgrading of the wool as by-product hinders the reduction in the sulphide consumption for the unhairing operation.

Enzymes and amines can be added to facilitate the unhairing and reduce the consumption of sulphides [tan/tm/16/Spain, tan/tm/18/UNEP-Tan, Germany (comments)]. Mechanical removal can then be performed easily.

Combinations of enzymes with sulphides are used to make the hair removal more efficient. The hair has to be removed continuously to prevent it from dissolving in the float. Many tanners do not feel confident enough to use enzymes in this application, as there is a significant risk of grain damage. For ovine skins the partial replacement in the painting process of sulphide by thioles, amines or enzymes is at present not possible.

The process has to be monitored by chemical analysis.

The technique can be applied to both existing and new plants.

Main achieved emission levels: COD and sulphide are reduced by 40 – 70 % each [tan/tm/39/Italy].

Cross-media effects: When enzymes are used, the water consumption increases because an additional rinsing step is required to block the enzymatic activity and the saved hair is not suitable for the production of felt.

The generated solid waste fraction is difficult to dispose of.

Sulphides have the advantage of not only attacking the hair, but also of opening the fibre structure for a better tanning process; enzymes don't have this quality.

Economics: In Germany (1999) 1 kg enzymes cost DEM 2 - 3 (about EUR 1 - 1.5); sulphide cost DEM 0.30 - 0.40 (about EUR 0.15 - 0.20)

Reference literature: tan/tm/39/Italy, tan/tm/17/Frendrup, tan/tm/09/UNIDO, tan/tm/28/BASF

4.2.3.3 Recycling spent sulphide liquors

Description: Suspended and dissolved solids are a problem for the recycling of the floats [tan/tm/17/Frendrup; tan/tm/58/BLC; tan/tm/16/Spain]. Large size solids can be filtered out (hair-save systems, separation of solids > 1mm) by screening, centrifugation and/or sedimentation. After filtration the unhairing liquors must be analysed, and their chemical concentration has to be corrected before re-circulating into the process.

Alkali-stable enzymes can be added at the end of the unhairing process to clarify the liquors (preventing them from becoming glutinous, soupy), though care has to be taken that the enzyme activity is stopped before the liquor is recycled. Recycling requires laboratory analysis and process control.

The technique has been in use for over 10 years in tanneries [tan/tm/17/Frendrup: France (but are closed now, Australia]. The recycled bath can be re-used a maximum of ten times.

Laboratory analysis, process control and well trained staff are necessary. The quality of leather might be affected if the process is not carefully controlled, because the efficiency of the unhairing is reduced by the organic substances and salts from the unhairing chemicals that build up in the recycled liquors. For high quality leather lime recycling is not feasible. The recycling of the spent liquors is common practice in processing sheepskins.

Main achieved emission levels: The main effect is observed in the reduction of the loads in the effluents and the water consumption. As a consequence, in the waste water treatment, input chemicals are saved and the amount of sludge produced is reduced. Between 50 and 70 % of the float (and of the chemicals) can be recovered and recycled (comments Italy).

Emission reduction in waste water	1	2	3	4
COD in total effluent)	15 – 40 %	40 %	30 – 40 %	
TKN in total effluent	15 – 40 %		35 %	
Sulphide in effluent	50 – 70 %			
Total solids	50 %	50 %		
Input of sulphide	20 – 40 %		40 %	20 – 50 %
Input of lime	20 – 40 %		50 %	40 – 60 %
Water volume	70 %			
Notes: (1) tan/tm/58/BLC (2) tan/tm/16/Spain (3) tan/tm/38/Denmark (4) tan/tm/18/UNEP-Tan				

Table 4.10: Reduction of emissions in total effluent by recycling spent sulphide liquors

The next table is the same as already presented in Section 4.2.3.1

Reduction in waste water from liming / unhairing section	1	2	3
SS		80 %	
BOD		60 %	
COD	60 %	65 %	30 – 40 %
TKN	35 %	57 %	
Sulphide	50 %	92 %	30 – 40 %
Ammonia Nitrogen		25 %	20 – 30 %
Notes: (1) tan/tm/35/BLC; tan/tm/28/BASF (2) tan/tm17/Frendrup: hair-saving process, carried out with recycling and filtering of the bath (3) tan/tm/39/Italy: hair-saving process, carried out with recycling and filtering of the bath			

Table 4.11: Reduction of emissions for hair-save technology with regard to conventional techniques

Cross-media effects: Lime-protein sludge and grease sludge can be recycled after further treatment (see Section 4.7), but not re-used in tannery processing. The sludges are difficult to dispose of.

The bath may need to be heated up before it is recycled. The energy for warming the bath and the electrical energy for the process are outweighed by the savings in energy in the waste water treatment and sludge treatment.

Because the protein concentration increases after every recycling, odour can become a problem.

Reference plant: For the reference plant in St. Croce, Italy (compare soaking in Section 4.2.1.4 and pickling in Section 4.3.2.2), 200 % of water savings on hide weight are reported. Detailed data on environmental performance and economic savings are presented in Section 4.2.1.4.

Economics: Laboratory analysis, process control and well trained staff are necessary for environmentally sound and cost-efficient production.

The process requires a holding tank for the liquors to allow for screening and re-use. The refitting of existing drums might be costly.

Reference literature: tan/tm/35/BLC; tan/tm/38/Denmark, tan/tm/16/Spain, tan/tm/39/Italy, tan/tm/17/Frendrup, tan/tm/43/World Leather November 1996

4.2.3.4 Prevention of H₂S emissions

Description: It is common practice to treat sulphide-bearing effluents from the beamhouse separately to reduce the sulphide levels in the waste water treatment plant, and in order to prevent the release of toxic hydrogen sulphide gas when acidic effluents are mixed with sulphide-containing effluents. (See also sulphide emission problems in deliming.) Treatment for the prevention of the release of hydrogen sulphide gas can take place in the processing vessels or in the separately collected beamhouse effluent.

The sulphides in the deliming and pickle liquors can easily be oxidised in the drum by adding hydrogen peroxide, sodium metabisulphite or sodium bisulphite. The catalytic oxidation of the sulphides in the vegetable tanning process can also be achieved by adding the exhausted liquor from the tanning process.

Sulphide removal from effluent can be achieved by catalytic oxidation to thiosulphates and, in smaller quantities, into sulphates (aeration in the presence of manganese salts). The thiosulphate then decomposes into sulphur and sulphite with which it forms a balance. Hydrogen peroxide is expensive and when it is used, it is mostly in combination with aeration in presence of manganese salts or iron (II) salts to avoid odour.

Sulphides in effluents can also be removed by means of precipitation with iron (II) salts and aeration. Due to the aeration, iron (III) hydroxide and sulphur are formed; the black sludge turns brown and settles easily. Together with the iron (III) hydroxide, the bulk of the organic substances will settle. Iron salts can be used when treating either mixed tannery effluents, or separated waste water streams. This precipitation generates very high volumes of sludge, and if the sedimentation is not sufficient the iron salts give a brown colour to the effluents.

Sulphide oxidation in the drum can be complete, but it may need to be carried out in combination with sulphide oxidation of the effluent in a designated treatment facility.

Aeration can eliminate the problems with sulphides and it can be achieved by blowing air at the base of a tall tower, through a set of diffusers, or alternatively by surface or sub-surface aerators. Surface turbine aerators are simple, robust and not subject to clogging, but tend to have high noise levels. The manganese salts may be added manually for a batch process. Continuous sulphide oxidation systems are available with full automatic control.

Foaming can be reduced through use of auxiliary agents, or a limited application of kerosene.

The catalytic oxidation does not irreversibly turn the sulphides into sulphates; in fact the reaction creates reversible compounds able over time to revert back to sulphides. For this reason the treatment is not deemed suitable for lagoons. If catalytic oxidation of sulphides is carried out, there is a chance that amine-containing compounds can be stripped from the effluent, resulting in odour emissions.

In vegetable tanning, aluminium salts can be used because iron salts form black ink with the vegetable tannins.

Main achieved emission levels: Concentrations of sodium sulphide in separated effluents may be 0.6 to 8 g/l. Careful control can achieve sulphide concentrations in the final effluent of 0.5 mg/l.

The German reference tannery, using manganese sulphate for the oxidation of sulphide, achieves a concentration of sulphide lower than 2 mg/l in the separated effluent, before mixing this effluent with the other effluents [tan/tm/74/Germany].

Cross-media effects: After destroying sulphides, proteins can be precipitated and liquors recycled to wash or deliming baths when a hair-save technique has been employed.

Sulphide oxidation results in the formation of sulphate. The release of sulphate into the sewer may need to be limited because of the damage sulphates can cause to the concrete sewer infrastructure. The use of iron salts may turn the effluent black and also increase the volume of primary sludge generated. Under anaerobic conditions, sulphates may revert to sulphides.

Reference plant: Most tanneries already oxidise sulphides in the effluent.

Economics: Recycling to wash or deliming after destroying sulphides and eliminating proteins is considered to be too expensive.

Reference literature: tan/tm/18/UNEP-Tan, tan/tm/58/BLC, tan/tm/74/Germany.

4.2.4 Lime splitting

Description: In most cases, splitting of limed hides is more environmentally friendly than splitting after tanning (blue-splitting).

Lime splitting has several advantages compared to either tanned stock or crust splitting:

*   the area yield is improved compared with blue-splitting due to maximum relaxation of the grain surface [tan/tm/09/UNIDO]
*   chemical consumption in subsequent wet processes is reduced
*   processing time is reduced, due to a reduction in the overall thickness of the leathers
*   flexibility to carry out different tannages on split and grain layers
*   reduction in tanned solid waste
*   the limed split hides used for the production of upholstery and automotive leathers can take advantage of the environmentally advantageous carbon dioxide process, as the penetration of the deliming agents through a split pelt is easier.

On the other hand, limed pelts are more difficult to handle than to either tanned or crust leathers, and the accuracy of lime splitting is not as high as can be achieved by splitting tanned stock. Another disadvantage is the fact that handling a pelt in the limed state with a pH of 12 causes more personal risk than handling wet-blue pelts.

Bovine hides used for the production of either upholstery or automotive leathers are typically split in limed condition. The resultant split will have an uneven surface due to differential swelling during the liming operation, and will need additional shaving to achieve the desired final thickness. When a firmer leather has to be produced, e.g. for the production of shoes, lime splitting is not usually done.

The flesh split from lime splitting can be used either for processing into leather or for the manufacture of collagen products (gelatine split: gelatine, food casings, and dog chews). National foodstuff regulations may limit the use of green and limed splits, if they contain bactericides, enzymes, or chemicals other than sulphide and lime.

Lime, pickle, tanned and crust splitting require different splitting machines.

Main achieved emission levels: The consumption of all chemicals and water in the subsequent process is reduced, because only the parts of the hides processed into leather are treated. Savings in chemicals per square meter leather produced in the process between liming and shaving are directly proportional to the weight of the lime split waste [tan/tm/35/BLC].

Cross-media effects: The waste fraction and the subsequent waste treatment options are certainly influenced by the choice of the procedure, i.e. if the splitting takes place in a tanned or untanned condition. The utilisation options for tanned splits that are too thin to be processed

into leather are limited and generally these are landfilled. However, they may also be used in the manufacture of fertiliser or leather fibreboard if such markets are accessible. In some member states there may be recycling routes available for waste splits which are tanned with non-chromium agents.

Hides split in the limed stage may need more shaving than leather split in the tanned stage, because the splitting in the limed state is not as accurate as in the tanned stage. This might lead to a higher amount of shavings created when employing lime splitting. So when a more uniform and accurate thickness is needed in the final product, lime splitting is not an environmentally better option. Furthermore, where hides are relatively thin, splitting in the limed stage may result in a loss of split yield. In those cases, splitting in the tanned stage may result in less wastage, as the split can be further processed into leather.

Reference plant: Generally introduced across Europe.

Economics: Because wet-blue is a tradable intermediate product, the next customer might want an unsplit hide, thus limiting the possibility of some tanneries to introduce lime splitting.

The investment costs for a new lime splitting machine may be as high as GBP 200000 (year 1999) (EUR 130000).

Reference literature: tan/tm/58/BLC, tan/tm/17/Frendrup, tan/tm/09/UNIDO.

4.3 Tanyard operations

4.3.1 Deliming and bating

Bating agents are often added in powder form. Handling of these chemicals requires protection for the workforce because the enzymes in the agents may cause serious health effects if they are breathed in.

4.3.1.1 CO_2–deliming and reduction of ammonia

Description: Carbon dioxide deliming is generally regarded as a practicable, cleaner technology that can considerably reduce the environmental impact of this operation. A complete substitution of ammonium deliming agents is possible for bovine hides, but the process can be very slow with thicker hides. If sufficient deliming cannot be achieved using CO_2 alone, auxiliary agents other than ammonium salts, e.g. organic acids, can be used. This technique is in current use [tan/tm/50/Finland].

Carbon dioxide dissolves readily in water, forming carbonic acid (weak acid), which causes the desired gradual reduction in pH of the hides. The way the CO_2 is introduced into the float depends on the type of vessel used. In drums, CO_2 can be injected in gaseous form through the gudgeon, or preferably, if the drum is equipped with a recirculation device, the CO_2 can be added there to ensure better mixing. In mixers, the CO_2 is introduced directly by a lance. In pit-type vessels, the CO_2 is mixed in by a sparger pipe. [tan/tm/35/BLC, tan/tm/03/UwHB-Abfall]
Typical carbon dioxide consumption is 0.75 - 1.5 % w/w. With thick or unsplit hides the consumption is greater, and additional chemicals or extended processing is needed. The deliming is faster at higher temperatures (32 - 35°C), but the temperature should not be so high as to damage the hides [tan/tm/50/Finland].

The advantages of applying gaseous carbon dioxide are that little process control is necessary and the gas is easily injected into process vessels.

Releases of H_2S can be prevented by oxidising with hydrogen peroxide (0.1 - 0.2 %) or (cheaper) sodium bisulphite. However, sodium bisulphite releases sulphur dioxide. Hydrogen peroxide can be corrosive to wood and sodium bisulphite is used instead [tan/tm/17/Frendrup]. A system for automatic (stoichiometric) dosage of hydrogen peroxide has been developed, said to prevent both H_2S generation and surplus H_2O_2 in the drum. Air filters can abate odour problems.

Generally the deliming time has to be extended [tan/tm/16/Spain, tan/tm/17/Frendrup]. For thick, unsplit hides, accelerating auxiliary agents are available [tan/tm/09/UNIDO], or a small amount of ammonium salts or organic acids can be added.

If CO_2 is used in the deliming, the final pH at the end of the process can be somewhat lower (pH 6.7 - 6.9) than when using ammonium salts (pH 8.8 - 9.2). Careful control of carbon dioxide deliming can allow the pH at the end of the process to be between 8.8 and 9.2. If the pH at the end of the deliming process is below or above the pH recommended for optimal activity of conventional bating enzymes, the subsequent bating step may require adaptation by using different bating enzymes with optimal activity in the lower pH range [tan/tm/35/BLC].

The technique can be applied to both existing and new plants, and is applicable to bovine and, to a lesser extent, to ovine material. The problem with the use of CO_2 in deliming ovine skins is that in the previous processes a large amount of sulphide has to be used. The large amount of sulphide released, originating from the application of CO_2, cannot be compensated by oxidising with hydrogen peroxide, due to the large amount required and the cost.

Apart from a possible adjustment of the bating process, no significant process changes are needed in later processes. The technique is easy to handle and can be automated. CO_2 deliming requires the installation of a pressurised storage tank for CO_2, diffusers and a warming chamber that has to be checked regularly by trained personnel. The process can be applied to produce all types of leather.

Main achieved emission levels: CO_2 deliming can eliminate nitrogenous discharges and reduce the BOD-load. In comparison to conventional techniques, with nitrogen emissions of 3.8 kg N/t w-s, carbon dioxide deliming can reach levels of 0.02 kg N/t w-s or lower. A 20 - 30 % decrease in total Kjeldahl nitrogen emissions and a 30 – 50 % reduction in BOD in the effluent from the tanning process can be achieved [tan/tm/50/Finland]. See for comparison Table 3.33.

Together with hair-save technology it is possible to achieve ammonia discharges of lower than 750 mg/kg hide processed [tan/tm/09/UNIDO].

Cross-media effects: If the final pH of deliming is lower than the pH after ammonium deliming, there is a risk of hydrogen sulphide being generated. Prevention measures for H_2S releases have to be taken. (See also sulphide treatment in the liming process.)

The quality of the final product will be the same as or better than with conventional methods. The amount of chemicals used will decrease. A disadvantage with conventional deliming is that acid is added in concentrated form, which causes a localised pH drop, forcing open the pores and making the finished hide much coarser. The use of carbon dioxide eliminates this effect, as it does not cause a sudden drop in the pH, since it is added in small doses either continuously or intermittently, thus reducing the pH gradually to the desired level. The result is a cleaner hide with no enlarged pores. The reduced coarseness means that the colour bonds better in the dyeing stage. Carbon dioxide deliming also improves the degreasing action, which may result in less detergent being used in the process or the use of milder detergents. [Tan/tm/50/Finland].

Reference plant: Carbon dioxide deliming is used at several plants in Europe. In Australia carbon dioxide deliming has been implemented at most wet blue plants for deliming of unsplit hides, usually incorporating 1 % of ammonium salt. In Finland nine tanneries are operating

carbon dioxide deliming, of which two are using AGA's deliming method; Lapuan Nahka Oy in Lapua and Geson Ab in Kronoby [tan/tm/50/Finland].

Economics: The economics of the process are affected by prolonged production times and the cost of CO_2 and alternative bates as compared with the cost of ammonium salts [tan/tm/17/Frendrup]. Cost savings are possible, especially in the treatment of ammonium and COD in the effluent. In Australia the chemical savings are reported to give a rapid payback on the capital expenditure.

The cost of running the process may be slightly higher than for conventional deliming. A tannery processing 25 t raw hides per day would need to invest USD 50000 (about EUR 50000).

Finland reports [tan/tm/50/Finland] that carbon dioxide deliming requires low capital investment. This includes a concrete pad for the container, piping to the deliming vessels, and control equipment to control the flow of carbon dioxide into the vessels. The tannery usually leases the container. The process costs are comparable to traditional deliming methods. However, considerable savings can be achieved if deliming using organic acids is replaced with carbon dioxide deliming. Reduced deliming costs depend on the size of the tannery, the type and cost of chemicals currently used and the means of carbon dioxide supply. The operational costs are not increased. The payback time of the investment costs is estimated to be 1 - 2 years.

Reference literature: tan/tm/35/BLC, tan/tm/03/UwHB-Abfall, tan/tm/17/Frendrup, tan/tm/16/Spain, tan/tm/09/UNIDO, tan/tm/43/World Leather November 1996, tan/tm/50/Finland.

4.3.1.2 Substitution of ammonium by organic acids

Description: Boric acid, magnesium lactate, organic acids such as lactic acid, formic acid and acetic acids, or esters of organic acids can be used to substitute ammonium agents. The advantage of substituting ammonium salts is that ammonia levels in the waste water are reduced.

The technique can be applied to both existing and new plants. Positive effects on the quality of the pelts are observed.

Main achieved emission levels: Reduction of nitrogen in the effluents.

Cross-media effects: These agents increase the COD load [tan/tm/17/Frendrup]. No data have been made available to enable a comparison of the substitution of ammonium in the effluents against a higher COD load and against the effects of the various substitutes mentioned above.

Less bating agent is subsequently needed.

Economics: The inorganic ammonium salts are cheap and effective (about DEM 10/tonne hides, 1999; this is about EUR 5/tonne hides). The organic agents are more expensive (about DEM 50 - 70 /tonne hides, 1999; this is about EUR 25 - 35/tonne hides). So the economic viability of this application must be analysed for each specific case.

Reference literature: tan/tm/28/BASF p. 1/7

4.3.2 Pickling

4.3.2.1 Optimising the float

Description: A short pickle float will reduce the salt consumption for the pickling, and reduce the water consumption and subsequently the volume of effluent generated. The float can be reduced to 50 – 60 %, which means that 0.5 - 0.6 m^3 water per tonne fleshed pelts is used. [tan/tm/09/UNIDO]. Italy reports a benchmark figure for the pickle float of 100 %, but a float volume of 50 – 80 % can be achieved. Spain reports an achievable float volume of 60 % in order to reduce salt consumption.

The technique can be applied to both existing and new plants. Some existing processing vessels may not be able to use a low-float system, such as paddles or drums with motors that do not have enough power. Also, some types of leathers are not suitable for very short float processes as they are damaged by the mechanical action.

Reference literature: tan/tm/09/UNIDO, tan/tm/58/BLC

4.3.2.2 Pickle liquor recycling

Description: Pickle liquor recycling reduces the amount of salt and effluent discharged to sewer. A suitable tank/container needs to be dedicated to the collection and storage of the pickle liquors. Before the pickle liquor can be recycled, several checks and adjustments need to be carried out. It is necessary to check and adjust the salt content and the acid content prior to recycling. If a substantive fungicide has been used (such as TCMTB), extra fungicide has to be added to ensure adequate mould protection. Also, a grease trap and a screen for filtering solids from the liquor prior to storage and re-use can enhance the number of recycling cycles.

The process requires strict analytic control by skilled personnel. A negative effect on the quality of leather, especially aniline leather, may be observed if the process is not adequately controlled and if too much mechanical action is used.

The technique can be applied to both existing and new plants. It is most appropriate where pickling and tanning are carried out in separate floats. Bovine tanneries re-use the pickle float in the tanning process (e.g. Germany and Spain). In those situations, it might be an option to recycle the exhausted chrome tanning liquor to the pickle, if high-exhaustion chrome tanning has been employed.

Main achieved emission levels: Salt savings up to 80 % are reported. The reduction of acids consumption is between 10 – 25 %, although more formic acid than sulphuric acid is saved.

Reference plant: For the reference plant in St. Croce, Italy (compare soaking in Section 4.2.1.4 and liming in Section 4.2.3.3) 50 % of water savings on hide weight are reported. Detailed data on environmental performance and economic savings are presented Section 4.2.1.4.

Reference literature: tan/tm/58/BLC, tan/tm/38/Denmark, tan/tm/16/Spain, tan/tm/09/UNIDO, tan/tm/17/Frendrup, tan/tm/43/World Leather November 1996

4.3.2.3 Re-use of chrome tanning liquors into pickle

Description: Spent liquors from the subsequent chrome tanning process can be recycled to the pickling step if the exhaustion of the chrome bath is high enough (see Section 4.3.2.2). The advantage is a reduction of the consumption and releases of salt. For further details see chrome tanning in Section 4.3.4.3.

Reference literature: tan/tm/17/Frendrup, tan/tm/28/BASF

4.3.2.4 Salt-free/reduced pickling

Description: Salt-free systems, based on non-swelling polymeric sulphonic acids are available [tan/tm/28/BASF]. Another reference [tan/tm/30/Renner] quotes the possibility of a partial substitution of chloride by using e.g., aromatic sulphonic acids.

The technique can be applied to both existing and new plants.

Main achieved emission levels: The discharge of chloride and sulphate salts is reduced to about 1 kg / t raw hide.

The exhaustion in the subsequent tanning step is enhanced.

Cross-media effects: Environmental classification of (aromatic) sulphonic acids compared to salt is not clear; certainly the COD is increased.

Reference literature: tan/tm/28/BASF, tan/tm/30/Renner, tan/tm/17/Frendrup

4.3.3 Degreasing

Emission reduction techniques for the degreasing operations are:

1. substitute the use of NPEs-based surfactants with ethoxylated alcohol-based ones
2. substitute halogenated organic solvents with non-halogenated solvents that will not contribute to AOX emissions
3. closed-loop machines (dry cleaning machines) with adequate abatement for organic solvent emissions (see for comparison Section 3.7.4.3).

There is not enough information to enable a conclusion to be drawn on whether the substitution of solvent degreasing systems with aqueous degreasing systems will result in a better environmental performance. This is because it is difficult without further information to compare the environmental impact of the use of organic solvent with that of the use of surfactants.

4.3.3.1 Aqueous degreasing of sheepskins with organic solvent and non-ionic surfactant

This traditional method of degreasing dewooled sheepskins in drums uses petroleum or white spirit in combination with a small amount of non-ionic surfactant. See Section 3.7.4.3.

The solvent degreasing wash waters contain approximately 5 – 10 % salt as well as traces of organic solvents, and the volume of waste water created during washes can vary from 300 % to 600 % based on the weight of the pickled pelts. This type of effluent can be very difficult to treat.

The amount of petroleum/white spirit can be as high as 20 % based on the lime weight. No more than 60 % petroleum is recyclable by distillation. Leakages of 20 – 40 % of the used solvent to the draining system occur and can be very dangerous. The amount of nonylphenol ethoxylates is relatively low (2 – 3 % total).

This technique, aqueous degreasing with organic solvent and surfactant, was replaced definitively in Spain ten years ago by aqueous degreasing with non-ionic surfactant. [AIICA].

Reference literature: tan/tm/38/Denmark, tan/tm/09/UNIDO, AIICA

4.3.3.2 Aqueous degreasing of sheepskins with non-ionic surfactant

Aqueous degreasing requires the use of several floats (up to 1000 % in total) of warm water (up to 60 °C), and the addition of 3 - 10 % non-ionic surfactants, depending on the surfactant that is used. This type of degreasing is used on dewooled sheepskins, see also Section 3.7.4.3.

Care should be taken that the surfactants used are easily biodegradable and do not present an unacceptable risk to the environment. Nonylphenol ethoxylates (NPEs) are still applied in tanneries across Europe when very fatty sheepskins have to be degreased. In those cases there is - to date - no substitute for NPE that can achieve a residual amount of natural fat in the pelt of 2 – 5 % (Italy).

Aqueous degreasing requires close process control and analytical checks to ensure that the level of natural grease left at the end of the degreasing process is below 5 % and the quantity of free fatty acids is lower than 1 %. Higher quantities of free fatty acids can lead to undesirable fatty spues. A fat content below 2 % in the neck area, essential for the manufacture of high quality aniline leather, is achievable with the use of NPEs (Spain).

If aqueous degreasing is carried out in a mixer, there is a danger of tangling of skins, making it harder to degrease and making the pre-tannage more uneven.

When producing water-repellent leather, care has to be taken that the surfactants are removed effectively, as the high concentrations of surfactants used may lead to some problems.

Main achieved emission levels: see Section 3.7.4.3. When the first float (1.5 - 2 l/skin) is treated separately, by breaking the emulsion of fat and surfactant by increasing the temperature to 90 ºC, 60 – 80 % of the generated COD is eliminated. When after this treatment a normal physico-chemical treatment is carried out, the obtained values (before the biological treatment) are 190 micrograms NP/l and 250 milligrams NPE/l. When this effluent is treated in a biological waste water treatment plant, values of 25 micrograms NP/l and 6 milligrams NPE/l can be achieved. Approximately 90 % of NP and 98 % of NPE can be eliminated in the biological waste water treatment plant. Considering that NP is formed as an intermediate in the degradation of NPE, the rate for NP degradation is even higher. Those data show that NP can, to a certain extent, be degraded in a dedicated waste water treatment plant.

Cross-media effects: With solvent degreasing, the grease in solvent emulsion is separated and the grease can be processed as an individual waste stream. With aqueous degreasing, a grease-in water-emulsion results which will be discharged with the rest of the effluent, thus contributing to a high COD load of the effluent. Fat emulsions can be cracked in order to segregate the fat from the waste water, thus considerably reducing the chemical oxygen demand levels as explained above.

In solvent degreasing, sealed process vessels have proved satisfactory for easy and reliable results and there appears greater tolerance to mechanical variations than with aqueous methods.

As mentioned earlier, there is not enough information to enable a conclusion to be drawn on whether the substitution of solvent degreasing with aqueous degreasing, especially when NPEs are used, will result in a better environmental performance.

Reference literature: tan/tm/58/BLC, AIICA

4.3.3.3 Optimising the use of organic solvents in dry degreasing of sheepskins

Description: Various chlorinated solvents, such as chlorinated aromatic and aliphatic compounds, are applied for degreasing wool-on sheepskins. Depending on the particular solvent or the mixture of solvents, toxicity, flammability, explosion prevention and releases to air (VOC) and soil are the major points of concern.

The dry degreasing process of wool-on skins is usually carried out in closed machines with abatement measures for air and waste water releases (e.g. activated carbon filters) and the used solvent is automatically distilled and re-used. But there will always be fugitive emissions. A certain amount of halogenated organic solvent can be recovered, but there will always remain a residue (hazardous waste) of grease, solvent and water which will always be very difficult to treat further.

The distillation can be easily performed if there is only one organic solvent applied, but it gets increasingly difficult, or even impossible, to recycle mixtures of organic solvents.

There have been some developments in the availability of chemicals to substitute for chlorinated solvents in dry degreasing but in Portugal in some cases (e.g. Australian Merino sheepskins) their performance is not good enough to be economically viable. Due to the amount of natural grease that is present in the raw skin, it is very difficult to achieve satisfactory degreasing with water-based systems. Portugal uses perchloroethylene for degreasing Merino-sheepskins. In Portugal a CRAFT project has started, with the objective of substituting the use of organic solvent degreasing for wool-on sheepskins. This is a 21-month-long project and the results are scheduled for the end of 2000. In any case the systems that are currently being used in Portugal (perchloroethylene) are run on special equipment that recycles the solvent used after it has been separated from the fat (the re-use of the recovered fat is also possible).

Main achieved emission levels: Over 80 % of organic solvent can be recovered with closed-loop systems. Residues can be collected for further processing as e.g. the production of tallow or fatliquors for the leather industry [tan/tm/09/UNIDO]. If the equipment used for degreasing is properly designed and maintained, it is possible to have either no emissions of organic solvents or very low emission levels (comments Portugal).

The technique can be applied to both existing and new plants.

Cross-media effects: Residues carrying organic solvent with fat and grease are produced. If no recycling or re-use of the contents is feasible, these residues can be incinerated. Non-halogenated solvents can be incinerated in various combustion facilities; halogenated solvents require highly sophisticated thermal treatment.

Storage and handling of halogenated and non-halogenated solvents requires special equipment and precautions for the particular agents used. These measures aim to reduce releases into air and spillage onto the ground, which causes contamination of soil and in many cases groundwater, and to provide fire and explosion protection. In particular soil and groundwater contamination found in various Member States, even at very small facilities using halogenated solvents, give rise to major environmental concerns and extremely high remediation costs.

Reference literature: tan/tm/38/Denmark, tan/tm/09/UNIDO, AIICA

4.3.3.4 Separation of sheepskin grease for re-use as technical fat

Description: It is advantageous to collect the degreasing baths separately from other liquors. The grease can be re-used in the production of technical fat. Separate treatment can also be advantageous for the waste water treatment, because grease, organic solvents, and detergents increase the COD-level.

The technique can be applied to both existing and new plants.

4.3.4 Tanning

Tanning can be performed with different tanning agents. However, about 90 % of leathers are tanned with chromium salts. Another well-known process is vegetable tanning. In the following paragraphs, techniques will be described to improve the chrome tanning process. The vegetable tanning process is covered too, but there are limited data available for this process.

In the description of the techniques, the vegetable tanning process is not seen as an alternative to the chrome tanning process for two reasons. First of all they are two completely different processes to produce different products. The second reason is the research done by Bernard Trommer and H.J. Kellert published in Leder&Häute Markt, June 1999 [tan/tm/54/Trommer]. See Annex I.1 for an English summary of this project. In this research comparing the environmental implications of different tanning methods, four representative standard processes were tested for upholstery leather on a semi-technical basis. The project concluded that:

"The environmental audit shows that the witholding or addition of a certain auxiliary material (tanning material) is not a sufficient criterion for an environmentally friendly or environmentally harmful evaluation of the product or the process. The project goes on to make it clear, that environmental improvements can never be reached in all areas (waste water, sludge, waste) at the same time. In the judgement of quality and cost, none of the tested alternatives showed advantages in comparison with the control group (chromium tanning process). Likewise no striking improvements in the effect of the tested environmental measures were recorded. With extensive experimental work, disadvantages of the alternative ways of tanning became visible that are not experienced with chromium tanning. It can be assumed in practice that chromium tanned leather, which is produced according to the 'Best Available Techniques', with the most modern processes, including all the environmentally-friendly technical measures available, may carry the designation 'environmentally beneficial'. So, for any given leather article, knowledge in headline terms of the type of tanning used is not, in itself, a reliable indicator of its biological quality. An independent investigation of the detailed technologies applied and the manufacturing conditions prevailing will also be necessary if an environmental impact assessment is to be made in addition to an assessment of hygiene, pollutants and utility value."

In this Bref, a comparison of chromium with other mineral tanning agents is not possible because the environmental impact of the latter tanning agents has not been assessed in enough detail.

The following techniques are discussed in the context of chrome tanning:

1. increasing the efficiency of chrome-tanning
2. high-exhaustion chrome tanning methods
3. recycling of spent chrome tanning liquors
4. chrome recovery through precipitation and separation
5. pre-tanning with non-chrome agents – Wet-white.

Vegetable tanning and tanning with other tanning agents are then discussed.

The following tables show emission data of chrome- and vegetable tanning. Source: tan/tm/17/Frendrup.

	Traditional technology[1]	Average unit[2]	Available technology[3]
Water volume, m³/t	4	1	0.5
Total solids, kg/t	225	175	80
Suspended solids, kg/t	7	7	7
BOD5, kg/t	3	3	3
COD, kg/t	7	7	7
TKN, kg/t	1	1	0.5
Ammonia nitrogen, kg/t	0.5	0.5	0.1
Chromium (Cr), kg/t	9	5.2	0.1
Chloride (Cl-), kg/t	70	60	28
Sulphate (SO₄--) kg/t	45	30	16
Grease and oil, kg/t	1.5[4]	1.5[4]	1.5[4]

Notes:
[1] Tanning in separate float. Long-float, high-dosage chrome tanning.
[2] Short-float chrome tanning, good management
[3] Salt-free pickling. High-exhaustion chrome tanning
[4] When fatliquor is added to the tanning liquor, the load may be higher.

Table 4.12: Waste water loads per tonne raw hide of the chrome tanning process inclusive pickling
Source: tan/tm/17/Frendrup

	Traditional technology[1]	Average unit[1]	Available technology[2]
Water volume, m³/t	5	3 - 4	3 - 4
Total solids, kg/t	200 - 300	110 - 200	65 - 100
Suspended solids, kg/t	100 - 125	10 - 15	10 - 15
BOD5,kg/t	40 - 75	40 - 75	25 - 35
COD, kg/t	120 - 220	120 - 220	70 - 110
Chloride (Cl-), kg/t	50	50	4[3]

[1] Counter-current pit technology
[2] Drum technology
[3] Salt-free pickling

Table 4.13: Rough data of waste water loads per tonne raw hide vegetable tanning (from pickling, tanning, washing and bleaching)
Source: tan/tm/17/Frendrup

4.3.4.1   Increasing the efficiency of chrome-tanning

The chrome uptake in the hides depends on many factors. Helpful measures can therefore be taken in previous process steps. For example, a thorough liming produces more groups where the chrome complex can be bound. Splitting after liming facilitates chrome penetration and reduces chemical input (see Section 4.2.4).

The next step is to ensure high efficiency in the process. The 'classic' chrome tanning carried out in long floats is characterised by poor exhaustion; 30 – 50 % of the chrome applied being lost with the waste water [tan/tm/17/Frendrup]. BLC reports that an average of 40 % of the chrome input may be discharged [tan/tm/58/BLC].

To improve the exhaustion of conventional tanning systems the following actions are relevant:

1. the chrome input must be optimised during conventional chrome tanning to reduce the possible waste
2. processing parameters, e.g. float length, pH and temperature, must be optimised to increase chrome uptake
3. short floats reduce the chrome input, combining a low chrome input with a high chrome concentration
4. allow enough time for penetration and reaction of the chrome with the substrate.

Without introducing any new chemicals or technologies, tanners can significantly improve the chrome uptake (compared to about 60 % in normal operation) [tan/tm/35/BLC]:

- 80 % chrome uptake can be achieved by altering the physical parameters (temperature rise from 20 ºC to 50 ºC, pH from 3.5 to 4.5) of the tanning operation
- up to 90 % chrome uptake by altering both physical and chemical parameters (float levels, chrome offers).

To improve control of the process parameters, (automatic) process regulation equipment has to be installed. The obvious advantages are a reduction in: the consumption of tanning agents; waste water; waste treatment and effluents.

References: tan/tm/35/BLC, tan/tm/17/Frendrup, tan/tm/58/BLC

4.3.4.2 High-exhaustion chrome tanning

Description: High-exhaustion chrome tanning recipes exist, often making use of proprietary products. There are two types of high-exhaustion systems:

1. the tanning agents are modified so that a low basicity tanning powder penetrates first into the cross section. Then a high basicity chrome powder is added and the temperature is increased.
2. there are special chrome agents (aromatic dicarbon acids, e.g. of adipin or phthalic acid, aldehyde carbon acids, e.g glyoxylic acid), which enhance the number of links available for the binding of chrome in the collagen structure.

The technique can be applied to both existing and new plants but may require the installation of pH and temperature control equipment. Furthermore, provisions need to be made to control the increase in temperature of the bath. Some leather products cannot be made with a high-exhaustion process.

Main achieved emission levels: See Table 4.13. A short float is necessary to achieve the higher exhaustion levels; these float levels may not be suitable for the production of more delicate types of leathers, which could be damaged by the high degree of mechanical action. The consumption of chrome is reduced (while the same content of chrome in the leather is achieved) by at least 10 % [tan/tm/38/Denmark]. The exhaustion depends on the process chosen and can reach 80 – 98 % (including good fixation) [tan/tm/09/UNIDO]. Italy reports a reduction of chromium content in the waste water of 50 – 80 % [tan/tm/39/Italy].

It should be noted that even if an exhaustion of the tanning liquors is reported as up to 90 %, unfixed chrome may still be released in the subsequent wet after–treatment steps. Good fixation is therefore essential.

The efficiency of retanning with chromium is generally lower than the tanning process, and exhaustion rates of retanning are generally around 60 – 70 %. If a high-exhaustion tanning

system is employed, the overall loss of chromium is generally a smaller percentage of the total chromium input.

In conventional tanning 2 – 5 kg/t raw bovine hides (8 - 12 kg/t dry goat- and sheepskins) of chrome salts are released via the spent liquors. With high-exhaustion chrome tanning this quantity can be reduced to 0.05 – 0.1 kg / t raw bovine hide.

Leaching of chrome from the tanned leather can be reduced by ensuring good fixation, e.g. use of syntans at the end of the process, and by allowing the completion of chrome tanning outside the vessel (ageing process).

As the chromium exhaustion increases, the concentration of chromium in sewage sludge and final effluent reduces.

Sodium sulphates or chlorides often dilute commercially available products. By reducing the chromium input the release of these salts is reduced at the same time.

Cross-media effects: Masking agents used in high-exhaustion chrome tanning make the precipitation of chrome hydroxide difficult. Chrome cannot be precipitated completely [tan/tm/44/Abwasser; Urhan und Knödler p. 213, tan/tm/37/Germany] if aromatic dicarboxylic acids (e.g. phthalic acid) are used.

The extraction of chrome from hydrolysates from the shaving of wet-blue hides and skins is more difficult due to the complexing substances [tan/tm/37/Germany]. On the other hand, unintended leaching of chrome from chrome leather waste is counteracted.

In the Alcanena region in Portugal there is a common chrome recycling unit that takes up all the chrome liquors produced by the tanneries in that region. In this specific case, and this may also be viable in other cases where high-exhaustion technology is applied, the chrome left to be recycled would not justify the costs of storage, transportation and the recycling process.

Reference plant: Several plants in Europe.

Economics: Savings in chrome can easily offset higher unit costs of the tanning chemicals involved [tan/tm/18/UNEP-Tan] compared to a conventional tanning process with an efficiency of 70 %.

Reference literature: tan/tm/38/Denmark, tan/tm/37/Germany, tan/tm/09/UNIDO, tan/tm/18/UNEP-Tan, tan/tm/44/Abwasser; Urhan und Knödler p. 203 - 215, tan/tm/58/BLC, tan/tm/17/Frendrup.

4.3.4.3 Recycling and re-use of chrome solutions

Description: The effect of chrome recycling on chrome discharges depends on the efficiency of the existing tanning processes, but on average 50 % of the exhausted tanning float can be recycled.

There are two options for the recycling of exhausted tanning liquors:

1. recycle the tanning liquors to pickle process
2. recycle the tanning liquors to tanning process (and the pickle liquors to the pickling).

For both options a holding tank and a screening of the solutions are required. Recycling up to 10 times before discharge is possible. Chrome liquor builds up volume (instead of discharging to environment).

Process control and monitoring are necessary for calculating and adjusting bath strength (salt content, pH, etc.) and for checking impurities.

Some changes to the tanning process might be necessary, such as reducing the amount of masking agents and salts added.

1. **Recycle the tanning liquors to pickle:** If tanning is executed in the pickle float, the exhausted tanning bath can only partly be recycled into the next batch of pickle liquor. For recycling into the pickling float the liquor is passed through a nylon screen and, after 24 hours, passed to a tank where it is mixed with the pickle acid. The hides are drummed in brine solution, then the pickle/chrome liquor is added. After the standard pickling time, the fresh chrome input is added.

2. **Recycle the tanning liquors to tanning process:** If the liquors are recycled to tannage, hides are taken out of the drums at the end of the process, allowing about 60 % of the float to be recovered. In the tanning operation, fresh chrome powder is added to the drained pickled pelts (which carry about 20 % residual float) and then the recycled liquor is added.

Quality losses may occur. The colour of the wet-blue may change and subsequently may have an impact on the dyeing operations. Impurities (protein, grease) and surfactant, masking agents and other process chemicals may build up. Careful monitoring and control are needed to limit this build-up to acceptable levels.

The techniques are simple to apply, flexible and applicable to most leather types. However, they have not been widely adopted in European tanneries due to fears about the resulting quality of the leather. Also, there seems to be a preference to increase the exhaustion of the chrome tanning process, rather than to recycle the exhaust liquor.

Recycling the tanning liquors to pickle can be applied to processes where pickle and tanning are carried out in the same float [tan/tm/35/BLC]. Where the exhaustion of the chrome tanning is in excess of 80 %, direct recycling of the exhausted chrome liquor may not be economically feasible.

The technique can be applied to both existing and new plants.

Main achieved emission levels: The efficiency of the recycling is dependent on the efficiency of the tanning process itself.

1. Recycle the tanning liquors to pickle:
On average, 50 % of the tanning float (but not the drainage water and the water from samming) can be recycled, which is equivalent to up to 20 % of the fresh chrome input. [tan/tm/35/BLC, tan/tm/17/Frendrup]

Salt carried over in the spent tan liquor allows a reduction of 40 % in salt for the brine solution.

Chrome discharge in the effluent can be reduced by 50 % (reduction of 40 – 50 % from 5.9 to 2.8 - 3.5 kg Cr / t raw hide in the waste water [tan/tm/17/Frendrup, tan/tm/18/UNEP-Tan])

2. Recycle the tanning liquors to tanning process:
The fresh chrome input can be reduced by 25 % for bovine hides and up to 50 % for sheepskins. Chrome discharge in the effluent can be reduced by 60 %.

Cross-media effects: No chrome-free pre-tanning option is possible.

When there is a common chrome recycling unit that works well and takes up all the chrome liquors produced, recycling of the liquors may not be viable.

In processes where high-exhaustion technology is not viable, recycling of the liquors can be a good alternative.

Reference plant: This option has been implemented in some tanneries in Australia and North America. This technology was used in Germany for the production of lower quality leather, but is no longer used.

Economics: Running and capital costs are low [tan/tm/17/Frendrup]. Economic feasibility will depend on the exhaustion rate of the chrome tannage and the quantity of chrome liquors generated. In general, the lower the exhaustion rate and the higher the volume of the floats, the higher the economic feasibility.

Reference literature: BLC BAT, tan/tm/17/Frendrup, tan/tm/18/UNEP-Tan

4.3.4.4 Chrome recovery through precipitation and separation

Description: Chrome can be recovered from the exhaust liquors (tanning liquors, samming water) from the conventional chrome tanning process; chromium from high-exhausting chromium salts is not recycled due to the low concentration. The chromium-containing liquors are collected in a collection tank, after which the chromium is precipitated by addition of an alkali. The precipitated chromium is separated from the supernatant, after which the chromium sludge is dissolved in concentrated sulphuric acid (for 1 kg of Cr_2O_3 as precipitate about 1.9 kg H_2SO_4 is required). The supernatant is generally discharged to the effluent. The precipitate should be re-dissolved as soon as possible, as it gets less soluble with time.

Any alkali will precipitate chrome, but the stronger the alkali, the faster the rate of coagulation. Therefore, the following precipitation options can be selected:

- sodium hydroxide or sodium carbonate (as strong alkali) will lead to a fast precipitation and voluminous sludge
- fast precipitation with additional agents like polyelectrolytes to facilitate coagulation has the advantage that only simple de-watering is necessary
- slow precipitation, e.g. magnesium oxide (as a powder, pH 8), gives a denser sludge, which allows for decanting. For 1.0 kg Cr_2O_3 in the spent liquors, 0.25 – 0.4 kg MgO, is needed depending on the basicity and masking. Another advantage of the use of MgO is that any excess addition will not cause pH to rise beyond 10, so that any sludge redissolving at higher pH levels is avoided.

Impurities and process chemicals may build up and therefore an increased level of process control is needed, and impurities may need to be destroyed after dissolving the chromium sludge. Chrome recycling may result in a slight change in the colour of the wet-blue and organic compounds can produce a greyish tint. The disadvantages are not as severe as in recycling the liquors, because a moderate concentration of organic compounds (fat, masking or high fixation auxiliaries, vegetable or synthetic tannins, small amounts of biocide) does not disturb precipitation and re-dissolving[8]. Chromium recovered in this way resembles the quality of fresh chromium, and therefore this system of chromium precipitation tends to be favoured over direct chromium recycling.

If the tanning of the grain leather is carried out with a powder, the chrome solution can be used for tanning the split [tan/tm/17/Frendrup].

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[8]   Impurities and process auxiliaries can disturb tanning and recycling: see tan/tm/17/Frendrup.

The technique is used for the treatment of effluents from the chromium tanning process, which have to be collected separately from all other effluents in the tannery. It is based on the recovery of chromium from the effluents and its recycling into the production process

The technique can be applied to both existing and new plants. It is independent of any local conditions and can be introduced in any tannery using chromium as tanning agent, although industry claims that chrome recovery may not be viable for individual plants - especially existing plants and small and medium enterprises.

From the chemical point of view, chrome recovery is a simple process with excellent environmental results, but it needs careful analytical control and it requires special equipment such as:

- a separate tank for collecting spent chrome tanning liquors
- material to analyse the chrome content, acidity and alkalinity
- a tank with stirrer and pH control for adding the right amount of alkali for the precipitation
- a sedimentation tank for chromium hydroxide settling
- a filter press for the chromium hydroxide sludge
- a tank with stirrer and heating equipment for the re-solution of the chromium hydroxide by concentrated sulphuric acid.

When a double precipitation is needed, by using fossil flour to absorb fats and other chemicals present in the spent chrome tanning liquors, more filterpresses, more chemicals, more time and more costs are involved.

Italy and Portugal each have one common chrome-recycling unit. The plant in Italy, Consorzio Recupero Cromo SpA, receives 400 - 500 m^3 exhausted floats per day from about 250 tanneries. From this input the recovery plant produces 2000 kg Cr_2O_3 per day, which is re-used in the tanneries. The tanneries mostly use a mixture of recycled and new chromium; 1 part recycled to 2 parts fresh chromium salts. The primary driver for establishing this plant was economics, because energy is saved, since neutralisation and filtration take place without the need for heat, and because chromium is recovered and re-used in the tanneries belonging to the co-operative, so there is less need to produce chromium by roasting chromite. The second reason is the environmental benefit, because chromium is removed from the sludge discharged by the centralised purification plant.

In Germany, four out of seven companies using conventional chrome salt have a chrome-recycling installation. The three companies without chrome recycling say the reason is that the high quality of leather they produce cannot be achieved with the use of recycled chromium. Tanneries using high-exhausting chromium salts do not have a chrome-recycling installation.

One of the tanneries uses the following recycling process. The chromium sulphate-containing effluent must be collected as concentrated as possible. Magnesium oxide is added and the pH is brought to 8.5 - 9. After mixing for a couple of hours and adding a polyelectrolyte, insoluble chromium hydroxide and magnesium sulphate will settle. The supernatant has a chromium concentration of about 1 - 10 mg Cr/l and has to be treated with lime milk and iron(III)chloride before it can be discharged into the sewer. The remaining sludge is dissolved with sulphuric acid, forming chromium sulphate and magnesium sulphate. After 24 hours of mixing the pH will be about 2, preventing the dissolving of magnesium sulphate. The recovered chromium sulphate has a chromium oxide content of about 20 gram Cr_2O_3/l and can be used in the tanning process for any type of leather when not more than 20 % is added, calculated on the active oxide. There are certain types of leathers (e.g. the split) that can be tanned with 100 % regenerated chromium. The driving force for this tannery to implement the chromium recycling installation has been regional legislation.

Main achieved emission levels:. Efficiencies of 95 – 98 %, 99 % and 99.9 % of chrome precipitation are reported. In the Netherlands, reported values, measured as total chrome in a daily composite sample, after sedimentation or flotation of the separate chrome-containing effluent <u>before</u> mixing, are 1 - 2 mg Cr/l. The same levels are achieved in some German tanneries (see Annex II). Elmo Calf AB in Sweden normally achieves chrome concentrations of <1 mg/l in the separated chrome-containing effluent after precipitation. The discharge to the external treatment plant after this internal measure is about 0.4 kg chrome per tonne raw hide. Most of the chrome in the discharge to the waste water comes from the post-tanning operations and these effluents are not passed through the chrome recovery unit.

Data from tanneries in the UK show chrome contents of 3000 - 6000 mg/l in the chrome liquors after tanning. Chrome precipitation can remove around 99.9 % of this chrome, which results in a concentration of chromium in the separated effluent of 3 - 5 mg/l and in a final concentration in the total effluent (due to dilution) of less than 1 mg/l. The opinion of the UK tanneries is that lower levels can only be achieved, in theory, by use of membranes, which involves additional costs.

The recovered chromium sulphate solution can be recycled into the tanning process by replacing up to 35 % of the "fresh" added chrome tanning salt [tan/tm/41/Greece, tan/tm/30/Renner].

By using the chromium recycling installation, the German reference tannery has reduced the emission of chromium from 25 % to about 1 – 2 %.

As the overall chromium utilisation ratio increases, the amount of chromium discharged to the waste water is reduced. Subsequently this results in a reduction of chromium in sewage sludge and chromium discharged to the environment. No additional waste volume is built up.

The addition of chrome tanning agent is 7 % to raw material weight. With a production capacity of 6 t/day, the total consumption of chrome tanning agent is 420 kg/day. Therefore daily savings are 126 – 147 kg chrome tanning agent. On an annual basis (250 working days/year) a total quantity of 31500 – 36750 kg of chrome tanning agent is saved.

The figures in Table 4.14 for a conventional process, apply for long floats, for good management, for short float and self-basifying agents.

Chrome balance					
	tan/tm/17/Frendrup				
kg / t raw hide	Conventional	Good management	High-exhaustion	Recycling	Recovery by precipitation
Consumption	21.5	15.5	10	12.4 – 13.1	
Leather and leather waste	13	9.6	9.6		
Waste water (including tanning, draining, samming)	7.5	5.2	0.1	2.8 – 3.5 (for total discharge)	0.5 (for total discharge)
	30 – 50 % of the Cr applied lost in waste water				
Waste water (wet after-treatments)	1	0.7	0.3		

Table 4.14: Chrome reduction applying different techniques

Cross-media effects: Chromium recovery requires the use of alkali, acids and auxiliaries. Consequently, the quantity of neutral salts discharged to the effluent is increased.

Reference plant: Several central chrome recovery installations have been constructed in European tannery conglomerations in order to benefit from economies of scale, e.g. Consorzio

Recupero Cromo SpA, in Italy. However, individual tanneries have also been able to implement chromium recovery on site, e.g. in Germany, Italy and Sweden. A full-scale facility for this technique was installed at the premises of GERMANAKOS LEATHER INDUSTRY S.A. – Athens, Greece in 1990 as a demonstration project financed by the European Commission (ACE-programme 1989), the Greek and Dutch Environment Ministries, the Hellenic Leather Centre (ELKEDE) and the company itself. Recently it has also been applied with the same good results in Indian tanneries (April 1998) as part of a project conducted by UNIDO and an Indian engineering company (SVV Engineering) at Pallavaram (Chennai).

Economics: Slow precipitation has the advantage that no investment in filtering equipment has to be made. However, slow precipitation may not always be technically possible, as fat and protein impurities may interfere with the settling of the precipitated chromium. Economic feasibility will depend on the exhaustion rate of the chrome tannage and the quantity of chrome liquors generated. In general, the lower the exhaustion rate and the higher the volume of the floats, the higher the economic feasibility.

A survey in Italy of economic costs has revealed that for a single medium-to-large tannery, the installation of all the (above-mentioned) equipment needed for carrying out chrome recovery through precipitation can cost about EUR 520000 (estimated value). The management costs should be calculated on the basis of 75 % of the working time of one technician and all the analytical controls before and after the recovery. The same survey has shown that the recovered chrome is generally used for the production of leathers that will be subjected to a quite heavy finishing and that do not need a delicate tanning process.

Based on Greek conditions (reference year 1990 - 91) the annual savings are considerable and the pay-back period is a minimum of 1.3 years and a maximum of 1.6 years. Operational and economic figures are given in Annex 1.2. Based on Indian conditions (reference year 1994) the efficiency of chromium recovery is found to be 95 – 98 %. The pay-back period is about 1 year in the case of the Indian tannery with a capacity of the chrome recovery plant of 10 m^3/day and about 1.6 years of another Indian tannery with a plant capacity of 7 m^3/day. The pay-back period for the chrome recovery plant in a tannery in Nicaragua (reference year 1995) is less than 2 years. [tan/tm/76/Nl].

Reference literature: tan/tm/41/Greece, tan/tm/24/Spain-Cr, tan/tm/39/Italy, tan/tm/17/Frendrup, tan/tm/18/UNEP-Tan, tan/tm/35/BLC, tan/tm/30/Renner, tan/tm/07/Zimpel, tan/tm/12/Ullmann, tan/tm/76/Nl.

4.3.4.5 Pre-tanning with non-chrome tanning agents – wet-white

Description: Pre-tanning changes the physical and chemical characteristics of the leather and can be used as a mechanism to improve chrome uptake or reduce the input of chrome. Certain pre-tanning recipes can be combined with non-chromium tanning agents to produce chromium-free leather. It is believed that if a pre-tannage is applied and the physical parameters for chrome tanning are well controlled (increase temperature up to 60 ºC, basify up to pH 4.2), the chrome input can be reduced from 8 to 5 % on the basis of limed weight.

Some pre-tanning agents can raise the shrinkage temperature of the collagen significantly. Pre-tanned leather can be split and shaved, thus avoiding chrome shaving and further reducing the chrome input needed per square foot of leather produced. Furthermore, pre-tanning has been reported to improve the quality of the leather, particularly with regard to grain tightness.

Pickle and pre-tanning can be combined, although pickling is not always necessary. Depending on the selection of tanning agents chosen, pre-tanning can be performed without changing the characteristics of the leather too much in order to be flexible in the choice of further processing. Pre-tanning can be followed by different tanning processes, such as chrome tanning, vegetable tanning or resins.

See Section 3.1.4. The pre-tanning agents are aluminium salts, sometimes aluminium combined with polyacrylates, glutaraldehyde derivatives, syntans, titanium salts, or colloidal silica. The minimum dosage mentioned is 1.25 % aluminium oxide or 1.0 – 1.5 % glutaraldehyde or 0.75 % titanium oxide. [tan/tm/17/Frendrup].

Zirconium has been commercially available for many years, yet it has never been widely used, mainly due to difficult application conditions.

Chrome-free pre-tanning may not be applicable if the chrome tanning effect needs to be maintained in the final product, or when the pre-tanning effect results in an unacceptable colouration of the leather. The colour of the final wet-blue can be greener, depending on the type of pre-tannage used. Problems arise because product specifications often require certain colours. The dyeing procedures then have to be adapted to the different shades of the pelt. If hides and skins are traded at this stage it is in practice difficult to select the different wet-blue shades and to perform a separate dyeing for the different shades.

To achieve the correct thickness, splitting in the wet-white condition has to be more carefully adjusted than splitting after the final tanning.

The technique can be applied to both existing and new plants. Subsequent chemical and mechanical processes require modification.

Main achieved emission levels: Pre-tanning with non-chrome agents can be used to improve the chrome up-take and reduce the chrome input, although the environmental impact of the pre-tanning agents must be carefully assessed. It is known that e.g. aluminium carries environmental risks to a higher degree than chromium, because of its higher solubility [tan/tm/17/Frendrup].

Exhaustion in subsequent chrome tanning is enhanced from 93 % to 97 %. In one case the subsequent chrome dosage was reduced from 15 kg Cr / t raw hide in conventional tanning to 6.5 kg Cr / t raw hide [tan/tm/17/Frendrup]. But the price of this improvement is the need to input pre-tanning agents.

An advantage is that only the leather needed for the final product is tanned and the input of tanning agents is therefore reduced.

The residues (or by-products, with market value) produced from splitting and shaving (shavings, dust) after this pre-tanning step are chrome-free, which in some cases is advantageous for re-use, recycling and disposal of the waste. In other cases, e.g. in the UK, the manufacturer of edible gelatine is only willing to accept chrome tanned leather. So the advantages depend on local circumstances.

The shavings and trimmings, as they are basically organic materials, have proved to have excellent value as fertiliser; equal to that of chrome tanned shavings and trimmings.

Cross-media effects: Trimmings tanned without chromium cannot be used for the manufacture of e.g. leather fibreboard, as they tend to become putrid and gluey.

For a further discussion of the cross-media effects, see Section 4.3.4.7.

Economics: The wet-white technology requires an extra process and consequently longer processing time and extra chemical costs.

Zirconium is more expensive than chrome and more difficult to monitor.

Reference literature: tan/tm/35/BLC, tan/tm/03/UwHB-Tech, tan/tm/02/HMIP, tan/tm/03/UwHB-Abfall, tan/tm/28/BASF, tan/tm/17/Frendrup

4.3.4.6 Vegetable tanning

Description: The process of vegetable tanning is well known and has applications for many different types of leather. There are several types of vegetable tanning systems, and the types of leathers produced with each system do not have characteristics comparable to chrome tanned leathers, e.g. resistance to high temperature, flexibility, etc. Some of the qualities of vegetable tanned leathers, e.g. tooling, burnishing, etc. can only be found in this type of leather.

Systems with a high degree of tanning exhaustion (~ 95 %) are available commercially. [tan/tm/17/Frendrup].

Tanning in short float
Drum tanning can be carried out using very short floats; this system allows the vegetable tanning agents to penetrate the leathers more quickly, reducing the overall tanning times. Drum processes for sole leathers are designed to be closed systems, so that very little waste liquor is discharged.

LIRITAN system
The leather is pickled and pre-tanned using sulphuric acid and polyphosphates; it is then moved into colouring pits and finally into tanning pits. The duration of the process varies from 7 to 21 days, and the discharge of tanning liquors is minimal. It is estimated that 87 % of the tanning extract input is exhausted during this process. [tan/tm/06/Europe, tan/tm/09/UNIDO, tan/tm/58/BLC].

Main achieved emission levels: See Table 4.13. The residual tanning floats are extremely low (less than 10 % of the treated pelts weight) and the chemical uptake is high. [tan/tm/06/Europe].

The vegetable tanning systems with the lowest environmental impact are the ones discharging the minimum amount of liquor, at the lower concentration of tanning material, e.g. the Liritan system. [tan/tm/58/BLC]

The poly-phenolic compound agents used in vegetable tanning contain from 60 % to 72 % of the actual tanning agents and 28 % to 40 % of non-tanning agents, for example sugar, salts, gums, insolubles. Most of the non-tanning agents are released to the waste water. The effluents contain sulphides, salts (sulphates), very high (hard) COD, high BOD, and have brown colour.

More specifically the waste water contains sulphonated phenols, which are currently not considered worth monitoring specifically. Therefore there are, except for COD and BOD, no particular emission limit parameters set.

There is no known relevant pretreatment method specifically for vegetable tanning baths to reduce the hard COD. The waste water is therefore always treated together with other individual flows and led (after buffer storage and neutralisation, if necessary) into the biological treatment.

Wastes such as splits, shavings and buffing dust can be re-used and easily disposed of as they do not contain any mineral. (See Section 4.7.1 for recycling and re-use of waste fractions).

Cross-media effects: A partial precipitation of the tanning agents has been tried by on-site treatment. This trial showed that the lime used for the neutralisation process improves the flocculation of the vegetable tanning agents during the pre-purification stage in the purification plant. Because of the high organic contamination, the volume of sludge in the waste water treatment plant is increased.

The environmental consequences of the production of tanning agents originating from rain forest trees are not clear. As far as is known, apart from Quebracho, all vegetable tannins originating from trees are sourced from renewable sources.

Reference plant: Tanning in vats without discharges is used by about 10 tanneries in Europe [tan/tm/06/Europe]. The Liritan process in South Africa.

Reference literature: tan/tm/03/UwHB-Tech, tan/tm/06/Europe, tan/tm/09/UNIDO, tan/tm/17/Frendrup, tan/tm/58/BLC.

4.3.4.7 Other tanning agents

For a discussion of the available techniques for substituting tanning agents the main environmental concerns associated with the agents are presented in Section 3.1. The effects of the discharge from alternative tanning have to be considered carefully. If account is to be taken only of the direct environmental impacts of the tanning agents used, no preference can be expressed for particular tanning agents on the strength of the currently available data.

The environmental impact of the alternatives has not yet been assessed.

Any comprehensive assessment of organic tanning agents needs to take into account not only the fate of the parent compound, but also the degradation rates, degradation products and free monomers.

Syntans and resins
Syntans and resins are also used in combination with vegetable tanning to improve the penetration of the vegetable tanning agents [tan/tm/09/UNIDO].

Alternatives are available for syntans with low phenol and low formaldehyde, for resins with low formaldehyde and for acrylic acid condensates with low acrylic acid monomer content.

There are not enough data available on the (eco-)toxicity of syntans to give a comprehensive assessment.

Aldehydes
Aldehydes are used in combination with vegetable tannins. Glutardialdehyde is a widely used chemical. Elmo Calf AB in Sweden introduced tanning by glutardialdehyde in 1999. This tannery gradually increased the amount of non-chrome tanned products and approximately 20 - 30 % of the production is glutardialdehyde tanned today. Extensive measures have been taken to monitor any negative effect in the municipal sewage treatment plant, and so far no negative effects have been noticed. But the information on the possible environmental impact is still too limited for a recommendation. Oxazolidine is used as a substitute for formaldehyde, and no data about the environmental impact of this substance are available yet.

Other mineral tannins
Aluminium, zirconium, and titanium can be used for tanning. The knowledge of the environmental impact of these metal salts is summarised in Section 3.1.4.

Aluminium offers the advantage of being inexpensive. The environmental benefits have to be balanced between a reduction of chrome against an increase of aluminium in waste water effluents and residues. The environmental risks of aluminium might be worse than those of (trivalent) chrome [tan/tm/17/Frendrup]. The environmental benefits and risks are unclear in combination with other tanning agents (aldehydes, vegetable tanning). Aluminium is under debate in various Member States. Some have set discharge limits (France 5 mg/l, Italy 1 mg/l for discharge to surface water and 2 mg/l for discharge to the sewers).

In the case of Al-tanning, due to the enhanced hardness of the leather more fat-liquor is needed (10 – 20 % increase).

Zirconium-tanned leather is white, strong and stable, though the application is difficult and the plumpness of the leather allows only restricted use. In combination with chrome or aluminium salts, this technique can reduce the input of these two metals. It is also used in combination with glutaraldehyde. The environmental risk of zirconium has not yet been accurately assessed. It is expensive.

Titanium can only be used in pre- and retanning. The environmental risk of titanium salts has not been assessed. A disadvantage for the environment is the increase of nitrogen loads in the waste water, as titanium is applied as ammonium titanyl salt. [tan/tm/17/Frendrup]

Reference plant: Elmo Calf AB, Sweden

Reference literature: tan/tm/09/UNIDO, tan/tm/17/Frendrup

4.4 Post-tanning operations

Table 4.15 shows typical and possible emissions to waste water from post-tanning operations, processing salted bovine hides. The techniques to reduce emissions are discussed in the following paragraphs.

Parameters	Conventional post-tanning processes (kg per tonne of raw hide)	Available post-tanning processes (kg per tonne of raw hide)
TS	65	30
COD	20 - 30	13
Total Nitrogen	0.8 - 1.0	-
Ammonia	0.6 - 0.8	-
Chrome	1.0	0.1 - 0.4
Chloride	2.0 - 5.0	-

Table 4.15: Emissions to waste water from post-tanning operations
Source: tan/tm/11/Nordiske Seminar, tan/tm/30/Renner, tan/tm/58/BLC

4.4.1 Chrome fixation, neutralisation and retannage

Chrome and rechroming
In the post-tanning operations, considerable amounts of organic substances (COD) and chrome may be released. The release of unfixed chrome can be as high as 1600 mg Cr/l in the combined waste water from a typical post-tanning sequence.

A reduction in chrome discharge can be obtained either using high-exhaustion chrome tanning systems or allowing the necessary ageing time for the tanned leather prior to the post-tanning processes.

Neutralisation
The use of the following salts in the neutralisation step is considered an achievable technique:

• sodium bicarbonate
• sodium formate
• sodium acetate
• borax
• neutralising syntans.

The input of the neutralising salts should be optimised to ensure that the pH of the liquor and the leathers by the end of the process are close to each other, ensuring that either no, or very little, unused salt is discharged to waste water.

The use of ammonia, ammonium salts, and salt-releasing sulphur dioxide (sodium bisulphite, sodium sulphite, sodium thiosulphate) is considered less environmentally friendly, although for the production of certain types of leathers the use of such chemicals is necessary.

Retanning
Reported achievable retanning agents are:

- synthetic materials with low free phenol/formaldehyde content (reduction in monomer content)
- easily exhausted retanning chemicals with a high affinity to the leather substrate, resulting in a reduction of retanning chemical offers, as well as a reduction in chemicals discharged to waste water
- agents with a low content of inorganic salts
- low-salt liquid retanning agents.

As for other agents applied as liquids, the advantage is easier dosage and handling, prevention of dust formation and reduction in salt. A potential disadvantage of the use of liquid formulations could be the auxiliaries contained in the formulation, such as surfactants.

Retanning agents (and fatliquoring agents) are a major source of COD from the post-tanning operations. Apart from that, water and energy consumption are important parameters for the choice of a retanning process.

Recycling of post-tanning liquors is difficult due to the wide range of different chemicals used in the various process steps.

Processing parameters, e.g. the levels of chemical inputs, the reaction time, the pH and the temperatures, must be optimised during post-tanning processing to minimise chemical wastage and environmental pollution.

4.4.2 Dyeing

Achievable techniques and technologies to reduce the impact on the environment of dyestuff and of the dying process are:

- to minimise the input of chemicals used, both dyestuff and auxiliary
- to select dyestuff and auxiliary with lower environmental impact, e.g. substitute poorly-exhausting dyestuff with high-exhausting ones, substitute dyestuff containing high levels of salts with dyestuffs containing a limited amount of salts, etc
- to avoid the use of ammonia as penetrating agent, as ammonia can be substituted completely in most cases
- to substitute powder dyestuffs with liquid ones, to reduce dust emissions.

Careful storage and disposal of chemicals is a question of compliance with good housekeeping and responsible management. Emissions during the dyeing operation can occur before, during and after the dyeing process, as dyestuff dust can be released into the air during the weighing out operation, and as the dyes are mixed prior to use. At the end of the dyeing process the spent dye bath can be discharged to the waste water treatment plant. The exhaustion of the bath discharged depends to a large extent on the type of leather, type of retannage, the type of dye, the dye concentration and the dyeing techniques employed.

Ammonia can usually be substituted completely by auxiliaries such as dye penetrators. Alternatively the penetration of the dyestuff through the substrate can be aided by thorough neutralisation using neutralising syntans, natural or synthetic anionic retanning agents prior to dyeing, a short and cold dyeing bath, better pH control of the leather cross section prior to dyeing and, if necessary, by increasing the penetration time.

The use of liquid dyes can cause the following problems;

- the price of the liquid dye, due to the manufacturing costs of dyes (i.e. solubilisation, addition of surfactants and emulsifiers, etc.)
- warehousing problems in terms of the space required for holding adequate stocks for the production of the tannery's colour range
- problems related to the stability of dyes during the time they are stocked before being used in production
- the existing dyeing processes must be adapted to the use of liquid dyes; this can lead to significant process redesigning costs.

4.4.2.1 Dyes for improving workplace safety

Liquid dyes and low-dust-producing dyes were developed to prevent health impacts by dust emissions on the workforce while handling the products. For the abatement of dust emissions see Section 4.8.

For substances that are insoluble or hardly soluble in water, auxiliary agents are added. In the case of liquid dyes this means using auxiliary chemicals to help either their solution or their dispersion in water. In choosing the auxiliaries care has to be taken particularly with regard to cross-media effects on the waste water (compare Section 4.1.1)

Liquid dyes are generally made up of the following materials:

- water and dyestuff
- diluents/fillers (chalk, syntans, polymers, etc.)
- surfactants (mainly used to aid the dispersion of non-water-soluble dyes)
- anti-foam (usually added in conjunction with a surfactant).

Information about the exact composition of a liquid dye is not generally given by the chemical manufacturer, which means it can be rather difficult to evaluate the environmental impact of the liquid dyestuff used.

4.4.2.2 Dyes not contributing to AOX

A small number of dyestuffs used in the leather industry are halogenic and can result in the emission of AOX. Where possible, halogenic dyestuffs should be replaced to avoid the release of AOX.

The use of vinyl sulphone reactive dyes is considered general practice and reduces the AOX load [tan/tm/58/BLC].

Chemicals applied in the dyeing process that have not been retained by the leather are released to the waste water. They contribute to the COD and the AOX, colour the effluents or have to be assessed as single substances due to their high potential impact. For many of the applied substances no assessment is available.

4.4.2.3 Metal-containing pigments and dyestuff

Metal-complex dyes containing metal ions such as chrome, iron, cobalt and copper are used in the leather industry for their fastness properties. Substitution of pre-metallised dyestuff is possible with the use of acid dyes, but the overall fastness properties of the leathers produced with the acid dyes will be reduced.

No comprehensive information is currently available about the impact on health and environment of metal-complex dyes, metal-free acid dyes and the respective auxiliaries.
Dyes used in finishing are mainly metal-complex dyes dissolved in organic solvent, in a mixture of solvent and water or in water alone. Changing to solvent/water-based or water-soluble dyes can reduce the use of organic solvents.

Metals such as copper, lead chromate, lead molybdate, titanium and iron are used in pigments. The use of cadmium and lead in pigments is not common in European tanneries; it should be stressed, however, that any use should be discouraged. [tan/tm/35/BLC, tan/tm/17/Frendrup, tan/tm/09/UNIDO, tan/tm/28/BASF].

Organic pigments can replace metal-complex dyes, but they have to be chosen carefully with respect to their potential impact on the environment. Organic pigments are more expensive and have a lower performance. They are therefore not to be considered a direct substitute for inorganic pigments.

4.4.2.4 Auxiliaries

Combinations of syntans and mineral tannins [tan/tm/28/BASF] are used as fixing agents, to level shades, and to increase depth of shade (compare Section 4.3.4.7). Retanning agents can also be used as auxiliaries.

4.4.3 Fatliquoring

Fatliquors can be a significant cause of waste water contamination, especially in the production of soft leathers, which require large amounts of fatliquor. Improvements can be achieved by higher exhaustion thus reducing the COD levels in the waste water.

Careful selection of the type of fatliquor used can also reduce the pollution load related either to organic solvents (solvent-based fatliquors), or to chlorinated organic compounds (chlorinated fatliquors) which increase the AOX levels.

An exhaustion of fatliquor equivalent to 90 % of the original offer can be considered achievable, together with careful selection of fatliquors not containing either organic solvents or AOX-releasing compounds. [tan/tm/58/BLC].

4.4.4 Drying

Description: Forced drying of leather is among the most energy intensive processes (apart from waste water treatment) in the tannery. Natural air-drying does not consume energy but it is not applicable under all circumstances, as it requires time and favourable climatic conditions.

Other drying techniques are hang drying or suspension drying (cabinet or tunnel), vacuum drying, toggling (cabinet, tunnel or open air), paste drying, or radio frequency/microwave drying under vacuum.

For example, a study carried out on a paste drying unit and on a hang drying unit showed that the overall thermal efficiency of the first machine was approximately 2.9 kg of steam per unit of water evaporated, whereas the second machine required approximately 2.5 kg of steam per unit of water evaporated. The poorer performance of the paste drying unit was found to be related to 30 % heat losses due to leaks, and insufficient insulation of the unit. In this case energy savings were achieved by improving the insulation of the unit, reducing heat losses and optimising the operating procedures.

Energy savings can be achieved by heat pumps incorporating recovery systems. Waste heat can be used from- and for other processes. Furthermore, low temperature drying (LTD) machines are available with reduced energy consumption, although in some cases they can lengthen the drying process (e.g. LTD drying tunnels may require all night to dry leathers, compared with 4 hours in conventional hang drying tunnels, but may have three times the capacity).

Considerable reductions in energy consumption can be achieved by optimising the mechanical dewatering processes prior to drying.

Reference literature: tan/tm/58/BLC

4.5 Finishing

4.5.1 Mechanical finishing operations

Description: Milling requires protection of the workplace from dust emissions. Leather dust contains many chemicals that have been used in processing. Investigations in tanneries have shown that exposure to dusty operations can result in higher chrome levels in the body than exposure to wet chrome tanning operations.

The techniques for dust collection are described in detail in Section 4.8.

The techniques can be applied to both existing and new plants.

Main achieved emission levels: Buffing dust concentrations vary from 0.1 mg/m³ to 30 mg/m³ depending on the equipment in place. The hazard of the dust depends mainly on its chemical composition, the particle size and the mode of contact.

Cross-media effects: Recycling of the cleaned air might save energy for workplace heating.

If a wet scrubbing system is used, slurry has to be deposited and recycling the washing water can reduce the water consumption.

The dust from filter bags can be re-used in leather fibreboard production. In most cases, however, it is landfilled.

Dust might require further treatment before depositing.

Reference literature: tan/tm/43/World Leather, October 1998, tan/tm/43/World Leather, April 1997

4.5.2 Applying a surface coat

There are fundamental differences between padding, curtain coating, roller coating, and spraying the leathers. Some of the differences are given in the following table:

Parameters	Spray line	Roller coater	Curtain coater
8 hours' throughput	2000 - 2500 sides	600 - 800 sides	1000/1200 sides
Cost of machine*)	USD 200 000 - 500 000	USD 150 000	USD 70 000 - 80 000
Level of waste	40 % - 60 %	10 %	10 %
*) USD is about equal to the euro (year 2000)			

Table 4.16: Finishing techniques
Source: [tan/tm/58/BLC]

Padding
Padding is the oldest finishing method and involves the contact application of resins or aqueous liquids via a system of brushes and pads. This method is relatively non-polluting.

Foam coating
The use of the system ceased several years ago because halogenated solvents were used as propellant. The technique is being used again, as it is now possible to produce the foam with air as foaming agent. This microfoam system can deposit 100 – 400 g/m² on the surface, making it possible to produce thick films in a single application.

The best drying system following foam coating is radio frequency drying, as overheating of leather can be avoided. Conventional drying can be applied but has to be carefully controlled.

Energy consumption is proportional to the water to be evaporated. Foam systems bring considerable energy savings, as there is 90 % less water to be evaporated.

Foam technology might not be applicable to all leather types. It is most advantageous to buffed and impregnated leathers but may not be ideal for full grain leathers and splits.

Casting / Curtain coating
Description: The leather is fed through a curtain of liquid film, which is deposited on the leather surface. The technique is used for the application of heavy finish layers only.

The technique can be applied to both existing and new plants, but requires the use of specific equipment. It can be compared to roller coating, but cannot be used as a substitute for spray coating.

Cross-media effects: This technique may be used to apply finishes which have a high organic solvent content.

Reference plant: Several plants in Europe.

Economics: Cost of the machine: USD 70 000 - 80 000 (about the same in euros)

Reference literature: tan/tm/58/BLC

Transfer coating

Description: Finishing by coating from a continuous transfer paper has been developed. It has proved successful in upgrading poor quality leathers and producing special effects. Because of the non-standard shapes of leathers the wastage of films could be as high as 30 %.

Cross-media effects: Transfer paper has to be disposed of.

Roller coating

Description: 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 cleaning of rollers to produce the desired quality. It might not be applicable to very thin leathers.

Despite the fact that research and development are ongoing, roller coating techniques are considered to be general practice, as many tanneries now use it. More specialist models allowing for hot and cold applications of oils, waxes and microfoam products are also available on the market and used in several tanneries in Europe. Latest developments are aimed at increasing the range of leathers that can be finished with roller coaters, such as full width reversed roller coaters for upholstery leathers and finishing of soft leathers.

The same conveyor/drying unit as for the spraying booth can be used.

This technique is not as flexible as spraying.

The technique can be applied to both existing and new plants.

Main achieved emission levels: A very low amount of waste (mostly cloths from cleaning) of 3 – 5 % waste of the amount of finish chemicals against up to 70 % by conventional spraying [tan/tm/17/Frendrup p. 41, tan/tm/09/UNIDO: conventional 25 – 30 %] is produced.

A considerable reduction of the releases of organic solvents and particulate is achieved.

Reference plant: In Europe 40 % of finishing operations are performed with roller coating machines [tan/tm/09/UNIDO p. 49]

Economics: Cost of the machine: USD 150000 (about the same in euros)

Reference literature: tan/tm/09/UNIDO**,** tan/tm/17/Frendrup, tan/tm/58/BLC

Spray coating

Description:
High-volume low-pressure (HVLP) spray guns [tan/tm/58/BLC, tan/tm/39/Italy]*:*
This equipment sprays with a large volume of air at low pressure. Therefore the "bounce-back" is considerably reduced compared with conventional spraying. The HVLP does not give completely satisfactory results for some articles, such as upper leather and garment leather and can be used mainly for upholstery leather.

Airless spray
In this system, the finish is ejected from the gun without air, so less drying of the vapour occurs during spraying.

Both techniques can be applied to both existing and new plants. Existing equipment can be retrofitted, but the costs and effort involved will depend on the type of systems already in place.

Main achieved emission levels: HVLP and airless spraying improve spraying efficiency up to 75 %, compared to spraying efficiency as low as 30 % for conventional spraying operations. [tan/tm/58/BLC]

Cross-media effects: Specific waste treatment has to be applied, depending on the contents of the waste. Air abatement requires energy and produces an additional waste fraction.

Due to the toxicity of organic solvents, protection of the workforce is required. The use of these techniques improves workplace conditions.

Storage and handling of organic solvents makes it necessary to protect primarily the workplace, soil and groundwater and means taking appropriate abatement measures.

Economics: Cost of the machine: USD 200 000 - 500 000 (about the same in euros).

Reference literature: tan/tm/58/BLC, tan/tm/39/Italy, tan/tm/18/UNEP-Tan, tan/tm/17/Frendrup, tan/tm/03/UwHB-Luft

Substitution of solvent-based finishing by water-based finishing
See Section 4.1.4.

4.6 Waste water abatement

Regulations in Member States (see Annex III) differentiate between indirect and direct discharge and vary emission limit values and/or environmental quality standards with regard to monitored substances, concentrations and loads for compliance. Waste water from tanneries has to be treated in compliance with the discharge limits set. Because of the variety of approaches across Member States to determine a financial charge for the discharge of effluent, the selection of waste water treatment techniques employed by tanneries or waste water treatment by off-site companies will vary.

It is important to consider the pollution load in conjunction with the production volume. Although the concentration of contaminating substances will be higher if less water is used, the treatment of the contaminants is often facilitated and/or the total amount of pollution is considerably lower.

Waste water can be treated continuously or with batch methods. Treatment of the effluents produces sludges, which are treated and disposed of according to their contamination (see Waste, p. 1).

In order to carry out effluent treatment in the most effective manner, flow segregation is useful to allow preliminary treatment of concentrated waste water streams, in particular for sulphide-bearing and chrome-containing liquors. Effluents generally contain a high organic load, which is monitored by the parameters BOD, COD and total, dissolved and suspended solids. Optimisation of segregation and combined treatment might be difficult in existing units because of high costs and depends on operational and local conditions [tan/tm/11/Nordiske Seminar].

Apart from measures for saving water, primary measures for waste water treatment in order to minimise the environmental impact are the following:

- it is common practice to oxidise sulphide-bearing effluents before mixing with acidic effluents, because at a pH lower than 9.0, the formation of toxic hydrogen sulphide gas can occur (see Section 4.2.3.4)

- because chrome precipitation is most effective if it is carried out in the separated effluent, it is common practice in the conventional chrome tanning process to segregate the chrome-bearing effluent(s) from non-chrome-bearing effluent(s). The precipitated chrome is normally recovered and recycled into the tanning process. Where segregation of flows is not possible, thorough mixing of chrome-bearing effluents and other effluent streams improves the efficiency of the effluent treatment plant because the chromium tends to precipitate out with the protein during pretreatment

- tanneries generate effluents that can vary significantly in composition. In order to cope with the high degree of fluctuation in volume and composition, effluent treatment plants need to be carefully monitored and controlled in order to optimise the efficiency of the treatment process

- the degree of on-site effluent treatment depends on the agreement with the municipal or communal effluent treatment facility. In some cases all effluent treatment may be conducted off site.

In addition to sulphide and chrome, effluents may carry contamination specific to the process step where they are generated and to the process employed.

- high salt contents are released in soaking, pickling, neutralisation and dyeing. Waste waters from unhairing & liming and deliming bear a high level of sulphide and nitrogen (total nitrogen and ammonium) and are alkaline
- surfactants can originate from any wet process step. Apart from the environmental impact, surfactants cause problems due to foam building in the waste water treatment. The use of anti-foam agents might be necessary
- biocides might be added in curing, soaking, pickling, tanning, and post-tanning operations
- solvents (halogenated and non-halogenated solvents) can originate from degreasing, dyeing, fatliquoring, (and finishing). By using halogenated solvents, AOX in the waste water is built up. AOX can also be due to the use of sodium hypochlorite in soaking and some agents used in soaking and dyeing
- complex building agents are used in tanning and post-tanning operations
- others, such as metals used in dyestuffs and finishing agents and antimony in fatliquoring, aromatic and aliphatic organic substances used as antifoaming agents, dyeing accelerators, cross-linking agents, binders etc.

4.6.1 Reduction of water consumption and process-integrated measures

The water management of a tannery depends primarily on the type of leather production carried out, and secondarily on the local conditions, i.e. the availability, quality and cost of fresh water, as well as the costs and legal requirements for waste water treatment and discharge.

The first step to efficient waste water treatment involves optimisation of water consumption and lowering the consumption of chemicals used in the process and in the waste water treatment. That will reduce both the necessary size of the waste water treatment plant and the energy consumption. Although a reduction of water consumption does not reduce the load of many

pollutants, concentrated effluents are often easier and more efficient to treat. Consequently cost reductions are achieved in many cases.

A water consumption of 40 - 50 m^3/t raw hide can be cut to 12 – 30 m^3/t (for bovine hides [tan/tm/04/Austria]), if the tannery operates efficient technical control and good housekeeping. The economic feasibility of such a change depends greatly on the cost of water consumption. In Germany there are some tanneries that use 15 - 20 m^3/t, and one tannery even reported using only 9 m^3/t (Firma Gmelich und Söhne). A tannery in the Netherlands, processing (fresh) bovine hides, uses about 20 m^3/t. For the processing of calf skins, about 40 m^3/t and sometimes more is needed.

The efficiency of water use can be enhanced by [tan/tm/18/UNEP-Tan]:

(a) increased volume control of processing water
(b) 'batch' versus 'running water' washes
(c) modifying existing equipment to use short floats
(d) using modern equipment for short floats
(e) re-use of waste water in less critical processes
(f) recycling of individual process liquors
(g) maintenance.

4.6.1.1   Increased volume control of processing water

It is found that in tanneries with poor water management, only 50 % of the water consumed is actually used in the process; the other half is lost due to extensive running water losses, overflowing vessels, leakage, continuously running pipes, and over-frequent washing of floors and drums.

Measures to be taken against inefficient use of water involve a serious worker-training programme, a clearly communicated code of practice for operators, including information about cleaning cycles, and the installation of basic technical equipment such as flow-meters and relatively simple spring valves.

4.6.1.2   'Batch' versus 'running water' washes

The consumption of water for rinsing processes varies considerably between tanneries. Running water washes, i.e. goods are run in a drum with a lattice door and continually rinsed, is one of the major sources of water wastage. The control with regards to flow rate and time necessary is minimal. Batch washes often yield a saving of over 50 % of total water. As a further advantage a great uniformity of the end-product is attained.

The use of e.g., cascading systems reduces consumption considerably. They can be applied:

– after deliming/bating
– after (chrome) tanning
– after dyeing

4.6.1.3   Modifying existing equipment to use short floats

The short-float technique yields a reduction in water consumption and processing time, savings in chemical input because of a higher effective concentration and increased mechanical action. By modifying the equipment to utilise short floats, 40 – 80 % floats instead of 100 – 250 % are achieved for certain process steps.

With a combination of batch washing and short floats, savings up to 70 % can be achieved, compared with a conventional process. Attention has to be paid, however, to the consequences for the equipment and the pelts. Short floats may increase wear on the drum bodies and the drive. Water also functions as a coolant during the process. The friction and mechanical strain on the goods are increased.

The use of drums is generally favourable to paddles or pits, which use about 300 – 1000 % floats. However, because not all the types of leather produced can be processed in drums, certain tanneries will not be able to take advantage of this option to reduce their water consumption e.g. the processing of long-wool skins must be done in paddles.

Process efficiency is achieved by optimisation of the mechanical movement, good distribution of chemicals and control of the chemical dosage, pH, and temperature. The installation of the equipment and the necessary access are also key issues to be considered for delivery of water and complete rapid removal of floats, which are essential parameters for both quality and effective use of the plant.

4.6.1.4 Using modern equipment for short floats

The installation of modern tannery machines can reduce water consumption by 50 % (compared with a conventional process) in addition to chemical savings. Depending on the cost of water, the high cost of the machines can often be justified by the water and chemical conservation and reduction of chemical input they make possible. Only minimal re-modelling may be required to allow recycling systems, as most units already achieve efficient drainage.

4.6.1.5 Re-use of waste water in less critical processes

Depending on the cleanliness of the raw materials, the liquors from the main soak can be recycled to the dirt soak. Rinsing waters from deliming and bating can also be recycled back to soaking. Part of the second lime wash may be recycled to start a new lime liquor. Lime washes together with recycle from pickle/chrome tan and some washes can be recycled to soak.

Water consumption can be reduced considerably, but residual chemicals and other contents of the rinsing water may cause difficulties in the process step to which they are recycled, or may damage the hides. The technical equipment for collecting, cleaning, and monitoring, exists, of course, but the extra effort that needs to be invested means that tanners have to be really committed to this re-use of water.

4.6.1.6 Recycling of individual process liquors

The recycling of individual process liquors is discussed in the respective chapters. See Sections 4.2.1.4, 4.2.3.3, 4.3.2.2, 4.3.2.3, 4.3.4.3 and 4.3.4.6.

4.6.1.7 Maintenance

Leaks in pipes and process vessels can account for considerable losses of water. Preventative maintenance programmes should be carried out to minimise the loss.

Apart from the deposition of solids, raw unsettled tannery waste water can cause many problems in a sewer. Calcium carbonates cause encrustation, high sulphide contents lead to corrosion and sulphates cause deterioration of concrete. It is important to use sewer material suitable for tannery waste water.

It is advantageous to keep the drainage systems for surface water on the site (rain, etc.) separated, if they are not contaminated with substances from the processes in the tannery. The prevention of such contamination involves a strict and clear separation of water used and arising from the processes and protecting handling areas from the rain.

4.6.2 Waste water treatment plant

Measures aim at the reduction of potentially harmful substances before effluents are released to the environment. The effluent treatment varies between tanneries but generally consists of a selection of the following processes:

- mechanical treatment
- physico-chemical treatment
- biological treatment and
- sludge handling.

See Annex II for figures from the common waste water treatment plants 'Cuoiodepur' and 'FIC S.p.A', both in Italy, and three examples of waste water treatment plants at individual tanneries: Firma Gmelich und Söhne, Bader GmbH & Co. and Bayern-Leder-GmbH.

The level of on-site effluent treatment required depends on the specific local situation. An advantage of the joint treatment of municipal and tannery effluents is the enhanced degradation for certain substances, e.g., ammonium, and a balancing of strongly varying effluent contents. On the other hand some substances might be degraded more effectively in a dedicated waste water treatment plant. Furthermore, the dilution of persistent substances in a communal waste water treatment plant might affect the quality of the sludge, which might limit sludge treatment options. It is also difficult to trace the particular source of persistent substances if individual discharges to sewer are not closely monitored. Some substances might interfere with the operation of the sewage treatment plant or damage the concrete.

When designing a waste water treatment plant for a tannery the following questions will need to be addressed in order to ensure optimum design and operation:

- number of hides or skins processed
- water consumption [m³/kg hide]
- capacity [m³/day] of effluent treated and potential capacity
- chemicals added in waste water treatment: type, amount kg/m³ waste water
- outline of treatment system (pretreatment, physico-chemical, biological, special treatment, sludge handling) and monitoring and control facilities
- monitoring: parameters, frequency, method
- energy consumption [W/m³ waste water]
- costs (capital, operation, chemical)
- sludge disposal / treatment option
- performance
- problems arising / limits (e.g. odour control and prevention).

An overview of the efficiency of the combination of waste water treatment measures is given in Table 4.17. The measures will be discussed in more detail in the following paragraphs.

Parameter	COD		BOD$_5$		SS		Chrome		Sulphide		N (Kjeldahl)		Sludge
% or mg/l	%	mg/l	%	mg/l	%	mg/l	%	mg/l	%	mg/l	%	mg/l	kg DS / t raw hide
PRETREATMENT													
Grease removal (dissolved air flotation)	20 - 40												
Sulphide oxidation (liming and rinsing liquors)	10									10			
Chromium precipitation								5 - 10 1 - 2[*)]					
PRIMARY TREATMENT													
Mixing + Sedimentation	25 - 35		25 - 35		50 - 70			20 - 30			25 - 35		80
Mixing + Chemical treatment + Sedimentation	50 - 65		50 - 65		80 - 90			2 - 5		2 - 10	40 - 50		150 - 200
Mixing + Chemical treatment + Flotation	55 - 75		55 - 75		80 - 95			2 - 5		2 - 5	40 - 50		150 - 200
BIOLOGICAL TREATMENT													
Primary or chemical + Extended aeration	85 - 95	200 - 400	90 - 97	20 - 60	90 - 98	20 - 50		<1		<1	50	150	130 - 150
Primary or chemical + Extended aeration with nitrification and denitrification	85 - 95	200 - 400	90 – 97	20 – 60	90 - 98	20 - 50		<1		<1	80 - 90	30 - 60	130 - 150
Primary or chemical + Aerated facultative lagooning	80 - 90	300 - 500	85 – 95	60 - 100	85 - 90	80 - 120		<1		<1	50	80	100 - 140
Anaerobic treatment (lagoon or UASB** with 66 % domestic sewage)	65 - 75	500 - 700	60 - 70	150 - 200	50 - 80	100 - 200		<2	0		20 – 30		60 - 100

These data represent typical values for tannery waste water treatment efficiency for conventional process liquors for production of finished leather from raw material.
*) Reported values in the Netherlands, measured as total chrome in a daily composite sample, after sedimentation or flotation, of the separate chrome-containing effluent <u>before</u> mixing
** Upward anaerobic sludge blanket

Table 4.17: Performance of waste water treatment plant
Source: tan/tm/43/World Leather November 1996

4.6.2.1 Mechanical treatment

Mechanical treatment includes operations for a first treatment of the raw effluent. The solid and organic content in the untreated waste water and subsequently the loads introduced in the biological stage can be reduced through primary sludge separation.

Pretreatment includes **screening** to remove coarse material, for example pieces of skin and leather fibres, which would otherwise block pipes and pumps. Such screens need regular, preferably automatic, cleaning and maintenance. The material removed is more concentrated and easier to handle. Up to 30 – 40 % of gross suspended solids (including hair and gross fats which are not in emulsion) in the raw waste stream can be removed by properly designed screens [tan/tm/18/UNEP-Tan p. 47, tan/tm/58/BLC].

Mechanical treatment may also include **skimming** of fats, grease and oils and gravity settling (sedimentation).

A preliminary settling operation for the raw waste water can remove up to 30 % COD, thus saving flocculating chemicals and reducing the overall quantity of sludge generated. [tan/tm/18/UNEP-Tan p. 47].

4.6.2.2 Physico-chemical treatment

Physico-chemical treatment involves sulphide oxidation from beamhouse effluents, chrome precipitation, flow equalisation, physico-chemical treatment for COD removal and balancing [tan/tm/03/UwHB-Abwasser p. 20].
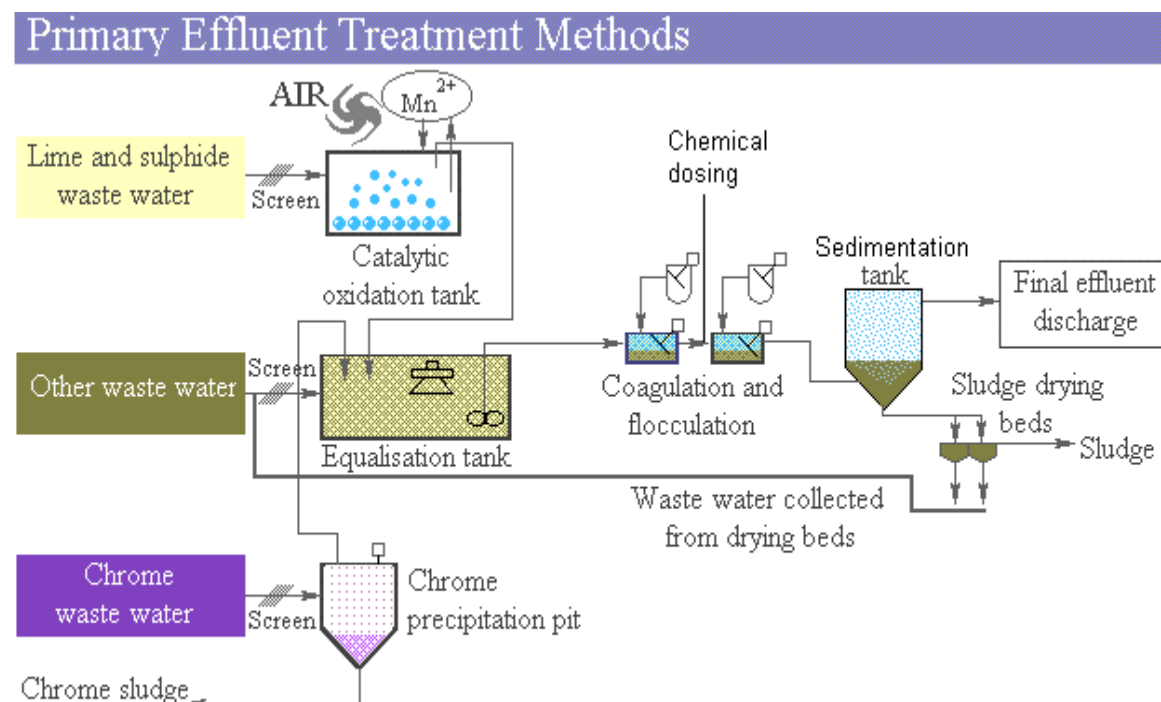
Figure 4.1: Typical scheme for physico-chemical treatment

Sulphide

Sulphides are one of the characteristic components found in the waste water of the liming and subsequent processes in the beamhouse. An accidental pH value-dependent release of hydrogen sulphide must be avoided. This might occur in mixing acidic and alkaline, sulphide-containing waste water of individual flows or possibly in the denitrification step. It is important to oxidise sulphides completely in the waste water treatment for further handling and treatment of the sludge derived from these liming effluents. Hydrogen sulphide is formed in waste water treatment by anaerobic bacteria from sulphates and the necessary precautions to eliminate H_2S from the gas must be taken.

The prevention of sulphide releases is described in Section 4.2.3.4 on the prevention of hydrogen sulphide emissions.

With flocculation and sedimentation before or after sulphide treatment, the protein-rich sludge from beamhouse operations may be re-used in agriculture. An additional advantage is the reduced sludge volume after the (on- or off-site) biological treatment.

If the sulphide-containing effluent is mixed with effluents from vegetable tanning, sulphide oxidation is possible with just a good aeration.

In sulphide treatment, odour problems due to H_2S releases to air might occur. For example, even if sulphide has previously been oxidised, de-nitrification can lead to a reformation of sulphides. Careful control of the de-nitrification can prevent this from happening and is therefore necessary. The feasibility of de-nitrification has to be studied carefully. The use of (bio-)filters might be necessary.

Precipitation of chrome

Chrome precipitation is a relatively simple technique and is more efficient if it is carried out in separated effluents after screening. The precipitation of chrome is achieved by increasing the pH to above pH 8 using alkali such as calcium hydroxide, magnesium oxide, sodium carbonate, sodium hydroxide and sodium aluminate. Chrome and other metals are precipitated as highly insoluble hydroxides. The pH value required for the precipitation depends upon the type of chrome-containing waste water to be treated.

The precipitation can be inhibited or reduced to an unsatisfactorily level by the influence of residual organic contents, masking agents, other complexing agents, fats or dyestuffs [tan/tm/44/Abwasser, Urhan und Knödler, p. 212; tan/tm/15/Reemtsma, p. 9] in the waste water.

Attention has to be paid to suspended solids (leather fibres, etc.), as chrome salts are adsorbed to the surface of the particles and colloids, thereby inhibiting precipitation to the extent that emission limit values are not met. An additional filter for filterable solids might be necessary before discharging.

Flow equalisation

Flow balancing and the combining of effluents are necessary to deal with peak flows. Balancing is best carried out after individual effluent flows have been pretreated, such as sulphide oxidation and chrome precipitation.

The effluents from various process steps vary in composition and are generated at different times during the day. In order to even out the variations in composition in effluents and achieve an efficient balancing of the effluents, the balancing tanks need to be able to hold at least one day's effluent.

Combining effluents can often lead to co-precipitation of pollutants, thus improving the efficiency of COD removal. It is essential that mixtures are well mixed, that suspended solids do not settle and aerobic conditions are maintained. Mechanical stirring devices or an air

injection system have to be installed. Air injection also encourages flocculation. A typical power requirement for mixing is 30 watts/m³ of liquid [tan/tm/18/UNEP-Tan] (Germany: 10 - 20 watts/m³).

COD removal

A substantial percentage of the COD and suspended solids can be removed after coagulation and flocculation. In order to optimise the removal, the pH of the effluent needs to be controlled to the level where coagulation and flocculation agents are most effective.

After setting the pH value and following the necessary settling period, a coagulant such as aluminium sulphate, ferrous sulphate or polymer flocculating agents can be added to the waste water. This creates a flocculate, which settles well and consists of the precipitation chemicals and organic and inorganic residual contents in the waste water, depending upon the pretreatment. If no chrome precipitation has been carried out at an earlier stage, chrome hydroxide will be formed at this stage and removed in the primary sludge. Ferrous sulphate also removes sulphides, but the disadvantages mentioned above (see sulphide page 111) have to be taken into account. Polymer flocculating enhances the efficiency of the flocculation, but also increases the volume of sludge considerably. The optimum dosage and conditions are usually established by on-site experiments.

Flotation is a method for removing suspended solids and other matter from a mixed effluent. It works on the reverse principle to sedimentation, employing fine air or gas bubbles to lift the suspended solids to the surface from where they may be removed.

The most commonly employed system is dissolved air flotation (DAF). Air is dissolved under pressure in a saturator with part of the treated effluent. When the pressure is subsequently lowered in the treatment vessel small air bubbles are released which, upon rising, carry the suspended solids to the surface. A scraping device periodically removes the surface 'blanket'.

The flotation process relies on coagulant and flocculant chemical conditioning of the feed stream, as in sedimentation, in order to enhance the solids separation process. The effluent feed may require pH adjustment, followed by dosing of a suitable coagulant. A suitable polyelectrolyte flocculant may also be required for optimum phase separation, especially of colloidal solids, and will require dosing just prior to the effluent entering the flotation tank.

4.6.2.3 Biological treatment

Effluent from tanneries after mechanical and physico-chemical treatment is generally easily biodegradable in biological treatment plants. However, small amounts of phosphate may need to be added to maintain the biological activity. Standard aerobic biological treatment plants are used, their size and abilities depending on the local situation, i.e. on-site or off-site treatment. Prolonged aeration time is important for tannery effluent treatment. Still screening analysis proves that there are still substances in the effluents that are degraded insufficiently or even newly generated.

Anaerobic treatment produces less sludge than aerobic treatment. For the anaerobic treatment of waste water effluents from beamhouse processes, a COD reduction of 40 – 62 % is reported. Biological treatment in combination with physico-chemical treatment can achieve a COD removal of up to 95 %.

The options for a biological treatment step are:

- biological filters
- activated sludge (conventional)
- activated sludge (oxidation ditch)
- lagooning (aerated, facultative or anaerobic).

Biological filters can be built as a flexible modular system, but with high BOD loads and effluents with a large amount of suspended solids, the filter beds can be clogged by the solids because, with high BOD, bacteria tend to grow very fast. This also means that frequent rinsing cycles are needed. They are not the best option to be implemented for reduction of the organic load, but they can be efficiently implemented for nitrification.

The **activated sludge** method uses the metabolic activity of micro-organisms in suspension. They convert the dissolved, biologically convertible contents into carbon dioxide and activated sludge. Other substances, such as metals, are adsorbed by the sludge.

Low-activated sludge systems, such as the 'oxidation ditch', are particularly suitable for tannery effluents. Compared to high-rate systems, the long retention time of at least 4 days and low organic loading are better able to withstand the variable character of effluent and shock loads, as well as producing a reduced quantity of sludge.

The oxidation ditch when properly operated may achieve a discharge concentration of below 20 mg/l of BOD. Energy consumption by treatment in an oxidation ditch is approximately 1 kWh/kg BOD_5 eliminated.

Conventional high-rate activated sludge treatment may be an alternative option. Oxidation takes place in a continuously aerated tank. A retention time of six to twelve hours usually suffices. The energy consumption of a conventional activated sludge plant is about 0.3 - 0.5 kWh/kg BOD_5 eliminated.

A modified extended aeration/low load activated sludge system employs a longer retention time and thus yields greater protection against shock loading. It may need retention times of one to three days, with subsequent energy input greater than 1 kWh/kg BOD_5 eliminated.

Lagoons offer a low-cost, low-maintenance solution, but with serious disadvantages, such as unpleasant odours, release of toxic substances to air, accumulation of toxic substances, disposal of accumulated material, and possible soil and groundwater contamination. Lagoons are not used in Europe.

Nitrification and denitrification

This treatment is being gradually introduced in countries with strict (ammonia) nitrogen discharge limits. Odour problems may arise in de-nitrification because of re-formation of hydrogen sulphide, due to poor management. The ammonium in the waste water originates mainly from the use of ammonium-containing agents in deliming and dyeing and from proteins released in the beamhouse.

Nitrogen can be nitrified in activated sludge systems of sufficient size and with sufficient sludge retention. Denitrification can be achieved through the creation of anoxic zones. It must be remembered here that in the presence of sulphide the denitrification may be disturbed.

In Germany, two companies process a nitrification/denitrification phase in the activated sludge system, e.g. Firma Bader. But this process is rather difficult to control and gets disturbed once in a while. When the process runs without malfunction a reduction of nitrogen of 70 % can be achieved.

Due to the difficulties in controlling this process it cannot be concidered general practice for individual plants.

4.6.2.4 Post-purification – sedimentation and sludge handling

For an overall assessment of the waste issue, both contributions to the generation of sludges have to be taken into account: first at the tannery and secondly at the (municipal or off-site) sewage treatment plant. Precipitation in the tannery extracts not only heavy metals but also organic components that might cause a high COD. In order to remove suspended solids, (vertical) sedimentation tanks or flotation are used. The separation of the activated sludge from the purified overflow is normally carried out by continuous sedimentation in a post-purification tank.

Sludge from primary sedimentation may only contain 3 – 5 % solids, and can be handled by pumping or gravity

With **sedimentation** the sludge is separated from the liquid phase by gravity settlement. It is essential to allow enough retention time prevent too much turbulence and clogging. Segregation of solids might not be complete, resulting in the carry-over of suspended solids into the discharge effluent. As a result, it is possible that certain emission limit values will be breached.

Dewatering is often practised to reduce the volume of the sludge for disposal. Sludges can be dewatered by means of filter presses, belt presses, centrifuges and thermal treatment. In most cases flocculation agents have to be added. Filter presses are capable of producing a sludge cake with up to 40 % dry solids, whereas belt presses produce a sludge cake with up to 20 – 25 % dry solids. Centrifuges are useful in attaining sludge with up to 25 – 45 % dry solids. Thermal treatment can give sludge cake with up to 90 % dry solids.

Prior to dewatering, sludge thickeners can be employed to further thicken sludges.

The energy consumption is an important factor.

Sludge is liable to decomposition during handling and storage, potentially causing a nuisance and a hazard with regard to hydrogen sulphide releases in storage and dewatering. Sludge may therefore require further treatment to abate this nuisance and hazard.

4.6.3 Special treatment

Halogenated hydrocarbons
Following gravity separation, the remaining halogenated hydrocarbons are eliminated from the waste water using a stripping and active carbon system before being passed to the drainage system. Stripping might not be efficient enough, because halogenated hydrocarbons might be absorbed by solids.

Aeration of effluents containing halogenated hydrocarbons leads to an uncontrolled, diffuse release of these substances through stripping.

Biocides, other specific organic compounds
Specially adapted biological waste water treatment can lead to a degradation of specific organic compounds such as biocides and halogenated compounds. However, these treatments require highly sophisticated process control and management. Some compounds cannot be degraded and activated carbon filtration or membrane techniques may have to be applied.

Salt
No information is currently available on techniques such as reverse osmosis and evaporation for the final treatment of high salt contents where emission limits cannot be met by implementing primary measures.

4.7 Waste management

Process-integrated measures are essential for an optimised waste treatment system. These measures are discussed in the chapters above, but end-of-pipe treatment is still necessary.

Much as for the reduction of waste water, the primary measures are:

- reduction of the input of process agents and particularly precipitation agents in waste water treatment
- separation of specific fractions of residues and different waste water streams for efficient treatment
- optimising the process and implementation recovery / re-use measures and
- reduction of the waste water to be treated.

Various solid or liquid waste fractions have to be considered. A large amount of waste is organic fractions such as hair or wool, trimmings, fleshings, splits, shavings, fats and grease. As long as these fractions are not contaminated or hardly contaminated with chemicals, recovery options can be considered that offer economic as well as environmental advantages. Recovery of proteins and fat or the production of other raw materials is feasible. The further processing can be done off site by other industries or sometimes plants used by a number of tanners or on site on a small scale. The optimum arrangement has to be found depending on the local environment and the local options available.

Many residues are currently landfilled (compare Chapter 3). This option will be restricted in the near future due to environmental legislation on a national and an EC level, as well as by decreasing landfill capacities.

4.7.1 Organic waste fractions

The main options for dealing with untanned and tanned hide and skin residues are processing at a rendering plant or other processes to separate the contents. [tan/tm/02/HMIP]

- gelatine and glue from untanned wastes can be produced; in some Member States untanned wastes are processed to produce sausage casings
- tallow recovery from raw trimmings, fleshings and splits is performed in rendering plants. Limed trimmings, fleshings and splits may need pretreatment before conversion
- fat can be separated and recycled, but this is practicable only in exceptional cases
- recovery of protein (protein hydrolysate) from e.g. splits, for conversion into fertiliser
- recovery of collagen from e.g. lime trimmings and splits. Collagen has various uses as meat and bakery product additives, in pharmaceutics and cosmetics, and as additives to rubber products
- tanned wastes can be used in leather fibreboard production.

Further treatment options for organic waste and sludges from waste water treatment are composting, recycling in agriculture, anaerobic digestion, landfill and thermal treatment. Treatment to reduce the water content may be applied. [tan/tm/03/UwHB-Stoffe]

Some treatment options are installed on-site, e.g., rendering of fleshings, but no information on emission or consumption levels are available yet.

Techniques are in use that leave open the possibility of further waste treatment. The implications for the process are discussed in the respective chapters for the process unit. Waste treatment with respect to the type of waste is summarised as follows:

Hair / wool
Options for hair saving, i.e. preventing the hair from being released via the waste water stream, are discussed in 'Hair-save technologies' (page 106). If there are no options for re-use, the hair has to be disposed of. In some cases the hair is not separated and is landfilled together with the waste water treatment sludges from unhairing effluents.

The hair residues from the unhairing step using a hair saving technology are partially destroyed. Depending on rinsing and cleaning procedures, the chemicals from the unhairing step are attached to the hair. After washing, therefore, sulphides sometimes have to be removed by oxidation. Hair residues can be compacted to reduce volume before further treatment or disposal. The options for recycling and re-use of hair are summarised in Table 4.18 [tan/tm/03/UwHB-Abfall, tan/tm/43/World Leather November 1998, tan/tm/17/Frendrup]. Hair can be also used as a fertiliser because of the nitrogen content. Hair is landfilled if there is no other outlet for the waste.

Hair
Filling material
Protein hydrolysate
Anaerobic digestion
Composting

Table 4.18: Techniques for treatment of hair

Sheep wool can be used by the textiles industry, e.g. for use in carpet manufacture.

Trimmings / fleshings / splits / shavings
Various options for further treatment of the residues are available. The choice will depend on the process used and on the contamination with process chemicals; lime, sulphides, and chrome in particular. For the re-use and recycling of residues, arrangements with other industries have to be made.

Disposal routes for trimmings, fleshings, splits, and shavings differ from tannery to tannery, and depend on the available recycling facilities and the quantity of waste generated. Furthermore, economic feasibility of recycling depends on the demand for the by-products and the cost/revenue from recycling compared to disposal routes such as landfill. For example, in the UK, a large proportion of tannery waste is landfilled because tanneries are dispersed across the country and, in comparison to landfilling, communal waste treatment plants would not be economic. The landfill cost of waste in the UK is significantly lower than in some other countries in Europe due to the wide availability of landfills in the UK. Landfilling of raw residues is not allowed in Germany.

In Italy it is economically feasible to establish communal waste treatment plants because tanneries are situated together in large numbers (pools).

Tanned waste can be processed into fertiliser. Where tanned wastes have no commercial value they are disposed of, generally to landfill. Thermal treatment of tanned waste is not carried out yet, but is being developed.

Trimmings might arise from various stages in the process (raw hides, after fleshing, after liming, after splitting and shaving, after tanning, before and after finishing) and therefore carry different contamination. Trimmings after fleshing, splits, and shavings are treated as the respective wastes from these operations. Hides that are damaged due to operating errors might be sold as a lower quality product or have to be treated as trimmings.

During the BSE situation, no UK domestic bovine by-product material has been permitted in the production of human food, animal feed, cosmetics or pharmaceuticals; all by-products from the untanned hides from animals slaughtered under the Over Thirty Month and Selective Slaughter Schemes had to be identified and handled separately, and subsequently destroyed; any animal known or suspected of suffering from BSE has been destroyed entirely, including the hides.

Raw trimmings	Tanned trimmings
Production of hide glue/gelatine, tallow	Leather fibre board production for non-finished trimmings
Animal feedstuff	Patchwork, small leather goods etc.
Anaerobic digestion	

Table 4.19: Techniques for treatment of raw trimmings and tanned trimmings

Fleshings are produced either before (green-fleshings) or after liming. The sulphide and lime content and the high pH from fleshings after liming reduce the acceptability of the residues (they are in practice often rejected due to the chemical content) and make the processing more difficult. The traditional outlet is rendering and animal glue.

Fleshings
Production of hide glue
Protein hydrolysate
Recovery of fat
Anaerobic digestion
Composting

Table 4.20: Techniques for treatment of fleshings

The **splitting** process can be performed either in limed or tanned condition (see Section 4.2.3.4). Depending where the splitting takes places within the process line, further processing is feasible.

Table 4.21 summarises the waste treatment options for untanned splits and for tanned splits together with shavings [tan/tm/11/Nordiske Seminar; tan/tm/16/Spain: composting and anaerobic treatment together with other waste fractions; tan/tm/39/Italy]. Depending on the quality, untanned splits can be used to produce hide glue, gelatine and sausage casings.

Untanned splits	Tanned splits and shavings
Processed further to leather	Leather fibre board production
Production of hide glue/gelatine	
Production of sausage casings	
Protein hydrolysate	Protein hydrolysate
Recovery of collagen	Recovery of collagen
Anaerobic digestion	
Composting	Composting

Table 4.21: Techniques for treatment of untanned and tanned splits and shavings

Shavings are produced in different sizes. Many of the recycling routes available for shavings are the same as for tanned splits. [tan/tm/03/UwHB-Abfall; tan/tm/02/HMIP].

Chrome tanned splits and shavings can be hydrolysed to produce chrome-containing sludge, fat and protein hydrolysate. Outlets have been found for the hydrolysate in various chemical and technical products. [tan/tm/03/UwHB-Abfall; tan/tm/16/Spain; tan/tm/39/Italy].

Certain tanned leather wastes are biodegradable, such as wet-white shavings and vegetable tanned shavings. This allows for a recycling route as soil improver[9] and fertiliser.

Dust
Leather dust from milling and buffing operations, is generally landfilled or treated thermally. In most cases the fine fibres contain tanning and post-tanning agents.

Fats, grease, oil
Fats, grease and oil are by-products from hides or residual process chemicals from the process steps of degreasing and post-tanning operations, particularly from fatliquoring, as that is where they are separated from waste water effluents.

Grease from sheepskin dry-degreasing can be recovered from the organic solvents and sold in the commodity market. If aqueous degreasing has been applied, either in solvent emulsion or in solvent free (using surfactants), the grease emulsions may be cracked. No market has yet been identified for the recovered grease from the aqueous degreasing process with the use of surfactants.

Grease from hides is generally separated in grease traps. This grease has no commercial value.

Fats and greases can be treated by anaerobic digestion. If these residues are not recycled and re-used, they give a good energy yield in a thermal treatment and anaerobic digestion.

Fats, grease, oil
Commodity market (grease from solvent degreasing)
Anaerobic digestion
Thermal treatment

Table 4.22: Techniques for treatment of fats, grease, and oil

Coarse material from waste water treatment
Filters or grids separate solid matter carried in the effluents before the effluents are treated. Apart from organic substances, this matter contains the chemicals used in the process. Coarse materials cannot normally be recycled because of other impurities and must be disposed of.

Sludges from waste water treatment
Different types of sludges arise from the primary (physico-chemical) and secondary (biological) treatment of effluents. Further processing depends on the contamination of the sludges and includes the following options:

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[9] Chrome tanned waste is being used to produce fertiliser in Italy, USA, and soon in France. Chrome tanned waste is also incorporated in many commercial fertilisers, also in the UK: Source: BLC.

Sludges from waste water treatment
Composting
Agriculture
Civil engineering
Anaerobic/aerobic digestion
Thermal treatment

Table 4.23: Techniques for treatment of sludges from waste water treatment

Available techniques in sludge disposal depend on the composition of the sludge and have to be assessed on a case by case basis taking into account national regulations and strategies. With regard to the re-use of sludge in agriculture, many Member States impose limits on the amount of chrome that can be applied to land; see Annex III.

4.7.2 Other residues

Other residues require further (off-site) treatment, apart from the options discussed above for recycling and re-use in the process units themselves. This includes the following wastes: salt, organic solvents and chemicals used as process chemicals, auxiliaries, or cleanser, sludges from finishing, solids from air abatement (activated carbon, sludges from wet scrubbers) and packaging material.

Salt	Salt from curing can be recovered as solid waste. Disposal is difficult, however, not allowed to landfill in many Member States and not favourable from the environmental point of view. The salt is usually released via waste water effluents. This can be a problem in areas where salinity of the effluent is a crucial criterion. Process-integrated measures relevant to liming, soaking and pickling are discussed in the chapters, which present the techniques to consider in the determination of "BAT".
Organic solvents	Organic solvents that cannot be recovered on-site need to be disposed of to external treatment plants for recycling or thermal treatment.
Chemicals	Obsolete chemicals require specific treatment, according to their content. [tan/tm/03/UwHB-Stoffe]
Finishing sludges	The sludge generated in finishing requires specific treatment, according to the content.
Sludges from wet-scrubbers	The content of the sludges from wet-scrubbers depends on the off-gas streams collected for abatement. The sludges require specific treatment, according to their content.
Other residues from air abatement	Activated carbon filters are mainly used for the abatement of organic solvents (in water and air). The filter can be regenerated by desorption several times. After exhausting the regeneration capacity, they have to be disposed of in an incineration plant.
Packaging material	Packaging material such as pallets, plastic, e.g. to cover hides for transport and containers for chemicals may be returned to the supplier for re-use. The small amount of these wastes can be disposed of, according to the contents.
Sewage and rubbish	Like any other industrial activity, tanneries will produce ordinary waste from office activities, building repairs, waste similar to household waste and sewage-type waste water. The normal municipal disposal services for such material can be used.

Table 4.24: Waste treatment and disposal for other waste fractions

4.8 Air abatement

Releases to air can arise from various process steps carrying different substances and particulates [tan/tm/02/HMIP].

Odour
Odours might arise from decomposition processes of the hides or accumulated wastes, beamhouse processes and waste water treatment plants that are poorly controlled and maintained.

Odours are not necessarily harmful or toxic, but constitute 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 putrefaction odours. It is in the interest of the tanner to prevent any damage to the hide (capital invested in the hides and skins is relatively high) from putrefaction. These odours from the raw hides can be readily avoided at source with proper storing and curing of raw hides and skins. The prevention of these odours from wastes, beamhouse and waste water treatment requires good housekeeping measures. Abatement requirements for non-toxic odours lie to a large extent within the discretion of the enforcing agency, as they cannot generally be quantified.

Odours might also stem from toxic substances, e.g., hydrogen sulphides, mercaptanes, ammonia, amines, aldehydes, ketones, alcohols or organic acids. These releases require abatement.

The releases from various process steps can be abated by primary measures discussed in the previous chapters. End-of–pipe treatment not only abates odours but at the same time removes contaminants and will be discussed in the respective paragraphs.

Organic solvents
Because of the limited applicability and effects of air abatement techniques, the best option to reduce VOC emissions is the use of water-based systems and organic solvent-saving finishing techniques.

Abatement techniques are important for the protection of the environment and for workplace safety, but it has to be remembered that they shift the problem from air to water and waste. Recovery of organic solvents should take priority over any end-of-pipe solution. It should be noted that recovery and re-use of organic solvents might only be feasible if a limited number of organic solvents are used.

Because of their health implications, solvents such as dimethylformamide, dichloromethane and, particularly, formaldehyde require high safety standards. With the reduction of organic solvent releases, the odours arising are abated.

There are various end-of-pipe abatement possibilities to reduce VOC emissions:

- wet scrubbing
- adsorption
- bio-filter
- cryogenic removal
- incineration.

Wet scrubbing is a standard technique for off-gas treatment, but dust and aerosols are mainly filtered. Water-soluble solvents (e.g., formaldehyde) are dissolved to a small extent in the scrubbing water; the majority of the solvents used in a tannery are not filtered. The solvents are not recycled but released by the effluent. Efficiencies can only be related to specific solvents, as they might vary according to solubility between 60 and 96 % [tan/tm/02/HMIP]. Waste water

and sludges arising from wet scrubbing have to be treated and then be disposed of [tan/tm/09/UNIDO].

Adsorption techniques with e.g. activated carbon only work if the concentration/volume ratio is within a certain limit and remains relatively steady while the adsorption units are charged (desorption by less loaded off-gas streams). Adsorption with activated carbon is the standard technique for the abatement of halogenated hydrocarbons. Some organic solvents can be recovered by desorption from the adsorption material. After exhaustion of the recycling capacity the adsorption material has to be disposed of. For halogenated hydrocarbons, activated carbon filters are the only means of achieving the required abatement.

Formaldehyde needs oxidation for adequate abatement. It can be oxidised to CO_2 and water by adding oxidising agents such as permanganate in the wet-scrubbing solution [tan/tm/03/UwHB-Abluft]. The use of formaldehyde as a fixing agent is not recommended. Commercial alternatives to formaldehyde are available on the market for most applications.

Among biological filter systems, bio-filters are increasingly used. Besides removing odours they can be used to oxidise organic solvents such as alcohol, ketones, ester and ethers. For reliable operation, bio-filters require careful control of the process parameters. They cannot be applied to off-gas streams where the composition changes or where concentrations are high.

Organic solvents can be removed by condensing, preferably at low temperatures (cryogenic removal). This technique requires a relatively high pollution load in the gas stream and is of only limited efficiency. The effectiveness depends on the vapour pressure of the solvents (or the mixtures). The condensate can be recycled or has to be disposed of.

Incineration (catalytic or thermal) is a reliable, but expensive, method of abating organic solvent emissions and odours. The content of organic solvent in the off-gas has to exceed a certain limit to make incineration technically possible [tan/tm/09/UNIDO].

Ammonia, hydrogen sulphide and sulphur dioxide

After all primary measures for ammonia and hydrogen sulphide reduction have been used, these substances are usually treated by good ventilation or by wet scrubbing; in the case of ammonia with acidic solution and in the case of hydrogen sulphide with alkaline solution, such as sodium hydroxide, hydrogen peroxide or sodium hypochlorite, along with sulphur dioxides.

Hydrogen sulphides released from waste water treatment can be abated by bio-filters.

Total particulate

Dust can arise not only from mechanical operations such as milling, buffing and staking but also during handling of powdery agents. Bating agents might use sawdust as a carrier. Sawdust from beech has to be substituted by different wood dust, because it is carcinogenic [tan/tm/03/UwHB-Abluft]. At these process units, air is extracted through a filter system [tan/tm/02/HMIP; tan/tm/03/UwHB-Abluft]. The parameters for assessing emissions of particulates are the concentration, the exposure time, the chemical content and the particle size.

For the most effective control of dust and to prevent fugitive emissions it is important that:

- dust is controlled at source
- dust-producing operations and machines should be grouped in the same area to rationalise dust collection
- priority is given to centralising dust collection systems. Centralised collection rather than a number of separate collectors provides lower initial and running costs, particularly in terms of energy
- dust collection systems are custom designed and built. Fans need to be purpose designed and stress relieved before dynamic balancing for low power consumption and noise levels. Ducts need to be designed for desired suction pressure at the machine hood and smooth airflow. Fan and collector pressure drops need to be carefully balanced
- the extraction of dust is supplemented with adequate room ventilation.

Dust control equipment is presented in Table 4.25

Efficient dust control equipment can reduce the dust levels to a point where no additional protective equipment needs to be used. If extra protection is necessary, it has to be ensured that dust is reduced by source extraction and general ventilation, the filters used are adequate for lung-damaging fine dust and the masks fit tightly. All dust collection systems require careful maintenance and control of efficiency.

Cyclones	Cyclones allow highly efficient collection of most coarse and fine dust and have relatively low capital and running costs. They can also be used in combination with bag filters and wet scrubbers.
Scrubbers	Scrubber systems can be Venturi scrubbers, spray scrubbers, packed static/mobile-bed scrubbers or cyclone scrubbers. The water can be recycled and the slurry has to be disposed of. Wet scrubbing is applied for particulates especially if organic solvents and/or odours have to be removed at the same time.
Bag filters	Bag filters can provide an excellent solution, the choice of type and the area of filter fabric are however, critical to the efficiency. Bag filters must have automatic cleaning devices to remove the cake-up dust from the filter fabric. Moisture has to be avoided in order not to solidify the material on the filter matrix. dust is generally landfilled or treated thermally.
Combination of collection systems	A combination of systems can improve efficiency at lower costs if it is adapted to the particular situation.
Extraction fans	Centrifugal fans are often used, but their efficiency is typically 50 % or less. This demands larger motors, higher power consumption and consequently higher capital and running costs. Fans can be a useful option in a combination of systems.

Table 4.25: Techniques for dust collection

4.9 Energy

A reduction of energy consumption focuses on the minimisation of losses, e.g. the use of heat pumps in drying, reduction of (hot) water consumption, and optimisation of energy use by enhancing efficiency (for example in drying) and in choosing the right size of machinery. Furthermore, the choice of energy source is important, e.g. fuels and renewable energy, as is consideration of energy recovery by aerobic/anaerobic digestion and thermal treatment of wastes produced in the tannery. [tan/tm/03/UwHB-Energy]

A number of possibilities for energy savings are listed below; their relevance for the individual tannery being dependent on measures already introduced and on the climate. [tan/tm/17/Frendrup].

Distribution pipes for steam and for water at a temperature above 30°C must be tight and well insulated. Not only visible steam leakages must be corrected but also the invisible parts of the system must be checked.

Steam condensate should be recovered.

The consumption of hot water must be minimised; any waste of hot water also being a waste of energy.

The use of short floats entails a slightly increased energy demand for agitating the process vessels, but this is counteracted by shorter process times.

All hot water tanks should be covered.

The cooling water from the vacuum dryer, which is not polluted, should be used in the hot water supply. 10 – 20 % of the energy consumption of the vacuum drying may be recovered in this way.

Installation of controllers for switching off hot (and cold) water valves, air exhaustion, finishing lines and light when not needed are inexpensive in relation to the savings obtainable. No water flow, machinery etc. ought to be left running without a definite purpose for more than a few minutes, and unnecessary light, ventilation etc. should be turned off during evening and night hours. No consumption without production (with the possible exception of space heating) should be the guiding principle.

By the means of heat exchangers, energy can be recovered from the waste after-treatment baths, from condensate from vacuum dryers, from evaporated water from high-frequency drying or from exhaust air from drying. Up to 75 % of waste heat from drying may be recovered.

Generation of thermal energy by the means of heat pumps is normally only economical at a price relation of

$$\frac{GJ \text{ (electric)}}{GJ \text{ (thermal)}} < 2 - 2.5$$

A system for the use of heat pumps in drying exists, developed in France [B. Vulliermet: Improvement of mass and energy balances in the tanning industry. JALCA, 1980].

Temperature and humidity during the drying need to be carefully controlled. Elimination of the greatest possible amount of water in samming may mean energy savings of 0.5 - 1 GJ/t raw hide in drying. Keeping drying temperature low and drying time and amount of exhaust air at the necessary minimum will keep heat losses to a minimum (although, consideration of leather properties will have priority).

In order to avoid energy losses for re-heating, drying installations should be run as continuously as possible. The heat capacity and heat transmission of new installations are as low as possible.

The following figures for the energy consumption of various drying methods, without and with the use of heat pumps, are found in the literature [H. Pfisterer: Energieeinsatz in der Lederindustrie, Vol 9, 1986]:

Various drying methods	MJ/kg water evaporated	
	without heat pump	with heat pump
Theoretical minimum	2.48	
Toggling	8.17	
Pasting	6.37	
Chamber drying	5.83	1.62
Vacuum drying	7.20	1.37
Through-feed drying	5.22	1.12
High-frequency drying	6.84	-

Table 4.26: Energy consumption of various drying methods

Without the use of a heat pump, the energy consumed is mainly thermal energy. The only exception is high-frequency drying, which uses electrical energy exclusively. Due to the high costs of electrical energy and to the high investment cost, this method has only gained a limited acceptance.

It is obvious that natural drying of the leather is the method with the lowest energy-consumption.

For finish drying, infrared heating is an energy-saving method.

The use of an economiser in the boiler house in order to minimise the chimney loss can be recommended when a low-sulphur fuel, especially gas, is used (otherwise corrosion problems occur). Control and maintenance of the boilers can save energy 'at source'. Other energy saving technologies for boilers are e.g:

- burners with digital combustion controls/boiler modulation controls
- flue gas economisers
- condensing economisers
- oxygen trim controls
- sequence controls
- automatic flow valves
- heat recovery from boiler blowdown
- condensate return systems
- flue shut-off dampers.

Any idle running of machinery or electromotors in general is to be avoided.

The capacity of electromotors installed should be suited to needs. For many motors, the best economy is obtained by running the motor at 75 % of maximum performance (this must be verified for individual motors). Frequency regulation of electromotors will also result in lower energy consumption.

In the case of compressors or pumps, the use of smaller units (e.g. one unit for basic requirements and a supplementary unit for peak loads) is more economical in energy usage than one big unit, due to the greater flexibility.

Compressed air is by far the most expensive form of energy. The use of compressed air is estimated at 5 m^3 per m^2 leather, corresponding to an energy consumption of 0.35 - 0.40 GJ/tonne raw hide.

In practical systems there is normally a waste of 10 – 30 %, mainly due to leakages. An overhaul of the system can often save 0.10 GJ/tonne raw hide.

Use of the waste heat from the compressor for water heating or for space heating can recover 80 – 90 % of the total energy consumption of the compressors.

Good regulation of the compressors is important, as the energy consumption of a compressor running idle or at a low performance is almost the same as for a compressor running at maximum performance.

What has been said about regulation, optimum level of performance and flexibility through small units also applies to pumping. The flow should be managed through regulation of the number of revolutions of the pumps. Any unnecessary resistance in the system must be eliminated.

The walls of spray cabinets must be kept well maintained and as tight as practically possible in order to minimise the energy loss. The velocity of exhaust air through the open area must be min. 0.5 m/s. Consequently, the loss of warm air and the energy for ventilation are proportional to the area left open (and to the running time).

It is possible to recover around 3 GJ/tonne raw hide through digesting limed fleshings and waste water sludge. Also incineration of fat from the fleshings can cover 50 – 70 % of the total demand for thermal energy. An English sheepskin tannery gets 20 % of its thermal energy consumption from incineration of sheepskin fat.

4.10 Noise, vibrations

Good practice is, in order of priority:

- the prevention of noise generation at source. Preventative maintenance and replacement of old equipment can considerably reduce the noise levels generated
- carrying out noisy operations in enclosed areas and/or using machine enclosures
- the wearing of protective equipment by personnel.

4.11 Monitoring

Standardised analysis and measurement techniques exist for **waste water** effluent parameters such as COD, BOD, SS, TKN, ammonia, total chrome, sulphides, chloride, AOX, conductivity, pH and temperature that are set in the permit for tanneries or determined by the requirements of the waste water treatment plant they discharge to.

Monitoring the water consumption will result in a better understanding of the areas where water consumption is greatest and it will identify areas for waste minimisation.

Gaseous emissions of importance are dust, VOCs, hydrogen sulphide and ammonia emissions from certain process steps and the waste water treatment plant.

Dust emissions do not require frequent monitoring if the abatement technique is operated correctly. The functioning of a dust filter can be simply monitored by measuring the pressure drop over the filter.

If organic solvents are used, regular measuring of emission concentrations and loads and the keeping of an organic solvent inventory are important.

Hydrogen sulphides and ammonia require regular monitoring and abatement.

For other gaseous emissions, specific monitoring might be required, for example if energy is generated on site by combustion plants, or waste treatment plants are installed.

The prevention of gaseous emissions in the workplace is highly relevant to the health of the workforce and to accident prevention. In particular, hydrogen sulphides, ammonia, organic solvents and dust need to be controlled.

The different **waste** fractions arising from the processes in the tannery need to be recorded according to type, amount, hazard and recycling or disposal route.

A chemical inventory is essential as part of good housekeeping practices, and is essential in good environmental management of emissions and in accident preparedness programmes (see Sections 4.1 and 5.2).

The **energy** consumption has to be recorded for electricity, heat (steam and heating), and pressurised air, particularly for the units with highest consumption such as waste water treatment and drying procedures. (See Section 5.7)

Noise requires monitoring and adequate protection measures in the workplace. Noise measurements should also take place periodically outside the tannery.

4.12 Decommissioning

When decommissioning a plant in general, all provisions and measures have to be taken into account to prevent environmental impact during and after the shutdown process. The aim is to prevent impact on the environment in general, and in particular the immediate surroundings, by activities that have to be carried out to leave the area in such a way that it can be re-used (depending on the enforcement bodies' decision on land use planning). This includes activities from the shutdown of a plant itself, the removal of buildings, equipment, residues etc. from the site, and contamination of surface waters, ground water, air or soil.

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

Thus in this document only general guidelines can be given on the possible impacts and the provisions to prevent impacts at three stages:

- what conditions in the IPPC permit for processing at a site can be set to prevent negative long-term effects on the environment during operation and after decommissioning
- what has to be taken into account consequently during operation
- what pre-requisites are to be considered for the final shut-down and what contamination might be caused.

The large quantities of raw materials and wastes handled by tanneries mean, that the prevention of soil and ground water contamination is a high priority with regards to spillage, storage, processing and final decommissioning.

Permit and operation
The conditions in the IPPC permit and operational provisions are covered to a large extent in Sections 5.1.1 on Operation and maintenance and 5.1.2. Accident prevention. Furthermore, for floors in general, not only in storage rooms, it is common practice that surfaces are used that facilitate cleaning and removal of spillage and have limited permeability. Retention tanks for process liquors, chemicals and waste water effluents, basins and drainage systems for the

collection of effluents, and storage containers for waste are mostly impermeable to prevent leakage to the soil and surface water.

End of operation

The decommissioning operations may include:

- clean-up; dismantling of installations; clean-up and demolition of buildings
- recovery, treatment and disposal of material derived from general clean-up, plant demolitions, demolition of buildings, and dismantling of environmental units
- durvey of possible contamination
- traffic due to transport and demolition activities.

The first step upon closing a production facility is a general clean-up involving: the emptying from containers and process units of liquors, chemicals and residues; draining liquors from piping and retention units; emptying storage and cleaning the equipment, storage, and buildings. The components of a plant are dismantled and sorted according to the material generated. Separating the specific waste generated in the clean-up and demolition of buildings allows for optimised recycling and disposal. The amounts of waste generated in these operations are generally large.

Residues from the general clean-up have to be sorted for further re-use, recycling, treatment or disposal similar to the residues generated during processing. Similarly, material from the dismantling or demolition of the equipment and buildings can be separated into re-usable and recyclable material and material that has to be disposed of. Good organisational management will avoid storage of material for long periods.

It is not possible to identify contamination from the clean-up and demolition that would be exclusive to tanneries. There might be amounts of hazardous waste from residues of chemicals, wastes, equipment contaminated with the chemicals and from the demolition of buildings.

Chemicals and equipment, in particular, may be sold to third parties. Any material which cannot be recycled has to be classified. It is disposed of via authorised dealers or treatment or disposal facilities.

Finally, all environmental abatement installations which might still have been needed during the dismantling of the plant, must be dismantled and disposed of.

Contamination of air may arise from inappropriate waste disposal due to spreading of dust containing infectious material or toxic substances, odours or releases of e.g., hydrogen sulphides. Such impact can, however, be readily prevented and is unlikely to have a long- term effect.

Site-specific long-term contamination in tanneries, in particular to soil (and ground water), and surface water can arise from:

- organic solvents
- oil
- chromium
- substances contained in waste
- infectious material.

Contamination from these sources might have been caused a long time ago when the possible environmental impact was not yet understood. Halogenated hydrocarbons in degreasing and other (non-halogenated) organic solvents can cause severe soil and groundwater impacts. Specifically, halogenated hydrocarbons were often handled carelessly because they do not have

high acute toxicity for humans. Waste which was inappropriately disposed of on site might have caused contamination from infectious material or process chemicals.

A survey of this possible contamination is mandatory to prevent long-term adverse effects on the environment.

Impacts on the local environment from dismantling operations and traffic are air emissions of dust from demolition and traffic on unpaved ground, combustion emissions from traffic and machines, and noise and vibrations. Measures to minimise the impact of these activities will have to be decided upon on a local basis.

5 BEST AVAILABLE TECHNIQUES

In understanding this chapter and its contents, the attention of the reader is drawn back to the preface of this document and in particular the fifth section of the preface: "How to understand and use this document". The techniques and associated emission and/or consumption levels, or ranges of levels, presented in this chapter have been assessed through an iterative process involving the following steps:

- identification of the key environmental issues for the sector; for tanneries these are waste water, solid waste, air pollution, soil protection and health and safety aspects
- examination of the techniques most relevant to address those key issues
- identification of the best environmental performance levels, on the basis of the available data in the European Union and world-wide
- examination of the conditions under which these performance levels were achieved; such as costs, cross-media effects, main driving forces involved in implementation of this techniques
- selection of the best available techniques (BAT) and the associated emission and/or consumption levels for this sector in a general sense all according to Article 2(11) and Annex IV of the Directive.

Expert judgement by the European IPPC Bureau and the relevant Technical Working Group (TWG) has played a key role in each of these steps and in the way in which the information is presented here.

On the basis of this assessment, techniques, and as far as possible emission and consumption levels associated with the use of BAT, are presented in this chapter that are considered to be appropriate to the sector as a whole and in many cases reflect current performance of some installations within the sector. Where emission or consumption levels "associated with best available techniques" are presented, this is to be understood as meaning that those levels represent the environmental performance that could be anticipated as a result of the application, in this sector, of the techniques described, bearing in mind the balance of costs and advantages inherent within the definition of BAT. However, they are neither emission nor consumption limit values and should not be understood as such. In some cases it may be technically possible to achieve better emission or consumption levels but due to the costs involved or cross-media considerations, they are not considered to be appropriate as BAT for the sector as a whole. However, such levels may be considered to be justified in more specific cases where there are special driving forces.

The emission and consumption levels associated with the use of BAT have to be seen together with any specified reference conditions (e.g. averaging periods).

The concept of "levels associated with BAT" described above is to be distinguished from the term "achievable level" used elsewhere in this document. Where a level is described as "achievable" using a particular technique or combination of techniques, this should be understood to mean that the level may be expected to be achieved over a substantial period of time in a well maintained and operated installation or process using those techniques.

Where available, data concerning costs have been given together with the description of the techniques presented in the previous chapter. These give a rough indication about the magnitude of costs involved. However, the actual cost of applying a technique will depend strongly on the specific situation regarding, for example, taxes, fees, and the technical characteristics of the installation concerned. It is not possible to evaluate such site-specific factors fully in this document. In the absence of data concerning costs, conclusions on economic viability of techniques are drawn from observations on existing installations.

It is intended that the general BAT in this chapter are a reference point against which to judge the current performance of an existing installation or to judge a proposal for a new installation. In this way they will assist in the determination of appropriate "BAT-based" conditions for the installation or in the establishment of general binding rules under Article 9(8). It is foreseen that new installations can be designed to perform at or even better than the general BAT levels presented here. It is also considered that existing installations could move towards the general BAT levels or do better, subject to the technical and economic applicability of the techniques in each case.

While the BREFs do not set legally binding standards, they are meant to give information for the guidance of industry, Member States and the public on achievable emission and consumption levels when using specified techniques. The appropriate limit values for any specific case will need to be determined taking into account the objectives of the IPPC Directive and the local considerations.

BAT summarised below is applicable to existing and new plants, unless otherwise stated. The feasibility of implementing a technique is, however, not only driven by the fact that a plant is new or existing. Other factors to be considered are e.g. disproportionate cost to smaller installations, limitations of some techniques, available space and infrastructure at a site. Such infrastructure might include sewage treatment plants, waste treatment plants and landfills.

Because of the wide variation of raw materials and product specifications in the tannery industry, it is sometimes difficult to make generalisations about BAT. Furthermore, many BAT will have an influence on the whole product line, potentially requiring process adaptations or changes. Another limit to generalisation might be set by the local environmental requirements. A detailed assessment and, finally, the choice of particular techniques can only be made on a site-by-site basis.

5.1 Management & good housekeeping

5.1.1 Operation and maintenance

Commitment of tannery management is a prerequisite for good environmental performance. Technology by itself is not sufficient; it needs to go together with good housekeeping measures.

A key to good performance is awareness of the inputs to and outputs of the process with regard to the characteristics of the materials, the quantities, and their potential environmental impacts. Criteria that ensure a better environmental performance can then be taken into account as well as technological criteria that focus on the properties of the end-product.

Reduction of spills, accidents, water wastage and chemical usage is achieved by the choice of appropriate techniques, good maintenance and operation control – by monitoring and adjusting process parameters – and good staff training.

BAT is to implement provisions for segregation of waste streams in order to allow for recycling of certain waste streams. These provisions include training of personnel.

5.1.2 Accident prevention

Chemicals used in the tannery should be stored and handled in such a way as to minimise the risk of spillages and accidents. BAT is:

- to store chemicals appropriately. Basic requirements are: separation of chemicals which could react to generate dangerous emissions; labelling and use of appropriate containers; adaptation of storage rooms and areas to provide proper ventilation and soil protection, especially for halogenated and non-halogenated organic solvents and waste containing these substances
- to implement measures such as information and training of personnel; technical provisions for safety, personal protection and organisation to minimise handling of potentially harmful agents:
  - handling and accidental spillage might lead to unforeseen chemical reactions such as, e.g, the release of sulphides etc
  - protection has to be provided against releases of harmful substances. To substitute organic solvents and other agents where possible
  - to ensure that Material Safety Data Sheets for all chemicals and preparations used and stored on site are available and easily accessible
- to provide first-aid facilities and to establish evacuation procedures
- to make contingency plans for avoiding shock loads to sewage treatment plants
- to monitor the operation of end-of-pipe abatement measures
- to have clean-up materials readily available for dealing with spillages
- to ensure efficient capture of waste water from clean-up operations
- to keep records of accidents and incidents.

5.2 Substitution of chemicals

For the substitution of chemicals, BAT is:

- to substitute less harmful chemicals for agents and auxiliaries that are known to be harmful to the environment
- to maintain an inventory of inputs and outputs, their fate in processes and releases
- to measure appropriate parameters to monitor the environmental releases
- to exercise responsible management including e.g, awareness of the chemicals applied in the process (including ready-made supplies), staff training, information and safety measures for workforce and environment.

In Table 5.1, substances to be substituted are listed in the left column. BAT substitutes are listed in the right column.

SUBSTANCE	BAT SUBSTITUTE
Biocides	• Products with the lowest environmental and toxicological impact, used at the lowest level possible e.g. sodium- or potassium-di-methyl-thiocarbamate
Halogenated organic compounds	• They can be substituted completely in almost every case. This includes substitution for soaking, degreasing, fatliquoring, dyeing agents and special post-tanning agents - Exception: the cleaning of Merino sheepskins
Organic solvents (non-halogenated) The finishing process and the degreasing of sheepskins are the major areas of relevance.	Finishing: • Aqueous-based finishing systems - Exception: if very high standards of topcoat resistance to wet-rubbing, wet-flexing and perspiration are required • Low-organic solvent-based finishing systems • Low aromatic contents Sheepskin degreasing: • The use of one organic solvent and not mixtures, to facilitate possible re-use after distillation
Surfactants APEs such as NPEs	• e.g. alcohol ethoxylates, where possible
Complexing agents EDTA and NTA	• EDDS and MGDA, where possible
Ammonium deliming agents	• Partially with carbon dioxide and/or weak organic acids
Tanning agents - Chromium - Syntans and resins	• 20 – 35 % of the fresh chrome input can be substituted by recovered chrome • products with low formaldehyde, low phenol and low acrylic acid monomer content
Dyestuffs	• De-dusted or liquid dyestuffs • High-exhausting dyes containing low amounts of salt • Substitution of ammonia by auxiliaries such as dye penetrators • Substitution of halogenic dyes by vinyl sulphone reactive dyes
Fatliquoring agents	• Free of agents building up AOX - Exception: waterproof leathers • Applied in organic solvent-free mixtures or, when not possible, low organic solvent mixtures • High-exhausting to reduce the COD as much as possible
Finishing agents for topcoats, binders (resins) and cross-linking agents	• Binders based on polymeric emulsions with low monomer content • and finishing systems
Others: - Water-repellent agents - Brominated and antimony-containing flame retardant	• Free of agents building up AOX - Exception: waterproof leathers • Applied in organic solvent-free mixtures or, when not possible, low organic solvent mixtures • Free of metal salts - Exception: waterproof leathers • Phosphate-based flame retardants

Table 5.1: BAT for the substitution of chemicals

5.3 Process-integrated BAT measures

With the implementation of BAT in the process rather than choosing an end-of-pipe abatement, improvement is gained with regard to:

- consumption of chemicals
- substitution of hazardous chemicals by less hazardous ones
- water and waste management
- emissions to air
- energy savings.

It is therefore essential in selecting BAT that the equipment used, e.g. processing vessels, the dosage of chemicals and the process control devices are also examined for their efficiency and compatibility with the above-mentioned goals. These pre-requisites are also discussed in Section 5.1.

Table 5.2: Process-integrated BAT Measures, describes BAT - where possible - for every separate process unit in a tannery. In two cases no consensus was reached in the TWG and the split view is noted at the bottom of the table.

	PROCESS UNIT	BAT is:
BEAMHOUSE	**Curing and soaking**	• To process fresh hides as far as they are available Exceptions: - When long transport time is necessary (max 8 - 12 hours for fresh, unchilled hides; 5 - 8 days if a cooling chain of 2 °C is maintained) - For certain types of end-products - Sheepskins, calf skins • To reduce the amount of salt used as far as possible.
	Unhairing & liming	• To use hair-save technology, but economics can be an issue for existing plants when re-use of the saved hair is not possible • To reduce sulphide consumption by the use of enzyme preparations; not for sheepskins • To recycle spent liquors only when processing sheepskins, which are dewoolled by painting
	Splitting	• To use lime splitting Exceptions: - When the starting material is wet blue - When a firmer leather has to be produced (e.g. shoe-leather) - When a more uniform and accurate thickness is needed in the final product • To maximise the use of split
TANYARD OPERATIONS	**Deliming and bating**	• To make a partial substitution of ammonium salts with CO_2 and/or weak organic acids
	Sheepskin degreasing	• To optimise wet degreasing using surfactants, with or without organic solvents • Closed machines with abatement for air and waste water releases when organic solvents are used to degrease skins in dry state
	Pickling	• To use partial recycling or re-use of pickle liquors **(*) split view; see below** • To use a volume of floats in the range of 50 – 60 % (based on fleshed weight) for ovine skins and bovine hides in order to reduce salt consumption
	Tanning **(**) split view; see below**	• To increase the efficiency of the chrome tanning process through careful control of pH, float, temperature, time and drumspeed, all in combination with chrome recovery through precipitation for waste water streams containing $Cr_{total} > 1$ g/l **(**)** • To use high-exhaustion tanning methods where chrome recovery is not possible **(**)** • To maximise exhaustion of the vegetable tanning liquor with counter-current (pit system) or recycling (drum tanning)
POST-TANNING OPERATIONS	**Retanning, chrome fixation and neutralisation**	• To enhance exhaustion of post-tanning treatment agents and fixation of tanning agents in the leather • To reduce the salt content of spent liquors
	Dyeing	• To enhance exhaustion of dyestuffs
	Fatliquoring	• To enhance exhaustion of fatliquor
	Drying	• To optimise mechanical dewatering prior to drying where possible
	Applying a surface coat	• To use roller coating • To use curtain coating • To use HVLP spray guns • To use airless spray guns Exception for all four above-mentioned techniques: - When very thin finishes are applied, e.g. on aniline and aniline-type leather

(*) split view on Pickling: The majority in the TWG agreed that partial recycling or re-use of pickle liquors is BAT. Experts representing one Member State and some experts representing industry in the TWG did not fully agree because in their view an exception has to be made. In their view BAT is:
• To use partial recycling or re-use of pickle liquors with an exception for high quality leathers.

(**) split view on Tanning: This BAT conclusion on chrome recovery is not fully supported by one Member State or by some experts representing industry in the TWG. Their opinion is that a separate treatment of chrome-containing liquors is not currently economically viable for a large part of the European leather industry, particularly in situations where a common specialised treatment plant is not available. In their view BAT is:
• To increase the efficiency of the chrome tanning process through careful control of pH, float, temperature, time and drumspeed
• To use chrome recovery through precipitation
    Exceptions: - When common specialised recovery plants are not available
                - When the recovered chrome cannot be recycled in order to produce high quality leathers
• To use high-exhaustion tanning methods
    Exception: - High quality leather production.

Table 5.2: Process-integrated BAT Measures

5.4 Water management and treatment

BAT for water management and treatment comprises:

- reduction of water consumption
- good housekeeping
- process-integrated measures (listed in Table 5.2) and, finally,
- effluent treatment.

Within these areas, BAT is:

GOOD HOUSE-KEEPING AND PROCESS-INTEGRATED MEASURES	To improve the matching of water flow to the requirements of the process
	To use 'batch' versus 'running water' washes
	To modify existing equipment to use short floats
	To use modern equipment for short floats
	To re-use waste water in less critical processes
	To recycle or re-use process liquors where possible (see Table 5.2)
EFFLUENT TREATMENT	To keep sulphide-containing effluent from the beamhouse separate and at high pH until the sulphide is removed. The associated emission level after treatment is 2 mg S^{2-}/l in a random sample in the separate effluent. After the sulphide is removed (on site or in a jointly used dedicated treatment plant) the effluent can be mixed. **(***) split view; see below**.
	To collect chromium-containing partial effluent (e.g. from tanning and samming) with a concentration of Cr_{total} > 1 g/l separately and send it for chrome recovery. Chrome recovery can be done on or off site **(****)**
	To treat (on or off site) chromium-containing effluent with a concentration of Cr_{total} < 1 g/l in combination with other effluent **(****)**
	To use mechanical treatment (on or off site)
	To use biological treatment (on or off site)
	To use post-purification sedimentation and sludge handling (on or off site)

(***) split view on sulphide and chromium treatment:
Industry supports the conclusion that separate treatment of sulphide-containing effluent is BAT, but in their view the mixed treatment – on site – of sulphide- and chrome-containing effluent is also BAT. The arguments are the following:
- lower costs
- less chemicals have to be used
- the technique is simple and reliable
- emission levels for the total effluent – depending on the mixing rate – of 2 mg S^{2-}/l and 1 mg Cr_{total} /l can be achieved. (e.g. if 50 % of the mixed effluent consist of the chrome-bearing effluent and 50 % of the mixed effluent consist of the sulphide-bearing effluent, emission levels for the total effluent will be 1 mg S^{2-}/l and 0.5 mg Cr_{total} /l).

(****) see split view on chrome recovery in note **(**)** on Table 5.2 **and** see split view on separate treatment in note **(***)** on this table.

Table 5.3: BAT for water management and treatment

For all the techniques mentioned in Table 5.3, it has to be decided site-specifically whether primary, secondary or even tertiary treatment is more environmentally and economically efficient on site or in a jointly used dedicated waste water treatment plant. It can also be efficient for a tannery to treat its effluent partly on site and then discharge it to a municipal sewage treatment works. The removal of particular substances from the waste water effluents e.g, biocides, halogenated organic compounds, surfactants and other process agents that need specific treatment, also has to be decided on a case-by-case basis.

5.5 Waste management and treatment

In waste management and treatment, BAT, in order of priority is:

- prevention
- reduction
- re-use
- recycling / recovery
- thermal treatment for certain types of waste.

Landfill is not BAT, although, in some cases it is the only option available.

A large amount of waste, in particular organic waste, is inherent to production in tanneries. Both organic waste fractions and other residues can be prevented and reduced to a large extent by using BAT in the process units (see Sections 5.1 and 5.3). Recycling options are numerous and carried out on site and off site. The potential for recycling should be exploited by ensuring segregation of waste. Of equal importance is commercialisation of wastes as by-products and co-operation between tanners to make recycling and re-use options economically feasible.

Waste that arises in the tannery has to be handled and stored in such a way as to avoid leaching, odour problems and emissions to air.

In Table 5.4 re-use, recycling / recovery and treatment options are given in the first column and waste fractions that can be used for the respective option are listed in the second column. BAT is to identify opportunities to implement these measures where feasible, ensuring that actions are carried through.

Re-use / recycling / recovery and treatment	Type of waste
Leather production	Splits
Leather fibre board production	Tanned wastes in general, e.g., splits, shavings, trimmings
Small leather goods etc.	Splits and tanned trimmings
Filling material, wool	Hair and wool
Gelatine and/or hide glue	Raw trimmings, green and limed fleshings and splits
Sausage casings	Untanned splits
Fat recovery	Raw trimmings, green and limed fleshings
Protein hydrolysate	Hair, raw and limed trimmings, green and limed fleshings, green, limed and tanned splits and shavings
Collagen	Limed trimmings and splits
Agriculture and fertiliser	Hair for the nitrogen content, residues from composting and anaerobic digestion, sludges from waste water treatment. The legal requirements for the application of waste to land require sophisticated waste separation and treatment of the various fractions
Composting	Hair, green and limed fleshings, green, limed and tanned splits and shavings, fats, grease and oil; sludges from waste water treatment
Anaerobic digestion	Hair, raw trimmings, green and limed fleshings, green, limed splits, fats, grease and oil; sludges from waste water treatment
Thermal treatment	Fats, grease, mixtures of non-halogenated organic solvents and oil
Recycling of organic solvents	Organic solvents (no mixtures)
Regeneration of air abatement filters	Activated carbon filters
Re-use and recycling of packaging material by feeding it back to the supplier via an appropriate recycling system	Container, pallets, plastic, cardboard

Table 5.4: BAT for waste management

5.6 Air abatement

BAT is to prevent the generation of odours through process control, maintenance and proper handling and storage of raw hides and wastes, in some cases requiring the installation of filters, e.g, at waste water treatment plants or for VOC releases.

BAT to prevent releases of e.g. hydrogen sulphides, ammonia, VOCs and dust, are mentioned in Table 5.1, Table 5.2 and/or Table 5.3. In addition, the following end-of-pipe measures are BAT for the abatement of hydrogen sulphides, ammonia and VOCs in particular:

- wet scrubbing, for example, to abate ammonia and hydrogen sulphides from deliming, pickling and dyeing
- wet scrubbing, absorption, bio-filters, cryogenic removal or incineration to abate VOC from degreasing, drying and finishing
- wet scrubbing, absorption or bio-filters to abate various releases from waste water treatment.

Techniques exist that are suitable for the abatement of a combination of releases, e.g. wet scrubbing for removal of aerosols, organic solvents and odours.

5.7 Energy

BAT is to record the energy consumption for electricity, heat (steam and heating) and compressed air, particularly for the units with the highest consumption, such as waste water treatment and drying procedures.

Operators therefore need a system for monitoring energy usage and performance. The scale of this needs to match the level of energy usage, but the following activities should be considered:

- recording actual energy usage, split by energy type and major end-uses, on a specified and appropriate regular basis (e.g. hourly, daily, weekly, etc.)
- generating energy performance indicators (historical energy performance or normalised to an indicator of production/external temperature/building occupancy etc.)
- monitoring energy performance, including mechanisms to alert the operator to significant variations from predicted energy performance
- ensuring appropriate investigative and corrective action is taken, and recorded, in response to variations
- delivering concise, appropriate and timely energy performance information to all individuals with identified responsibilities for energy management
- setting, reviewing and revising performance targets.

5.8 Decommissioning

In general, BAT for decommissioning of a tannery includes all provisions and measures that have to be taken into account to prevent environmental impact during and after the shutdown process. The aim is to prevent impact on the environment in general, and in particular the immediate surroundings, by activities that have to be carried out to leave the area in such a way that it can be re-used (depending on the enforcement bodies' decision on land use planning). This includes activities from the shutdown of a plant itself, the removal of buildings, equipment, residues etc. from the site, and contamination of surface water, groundwater, air or soil.

6 EMERGING TECHNIQUES

In this section, promising new pollution prevention and control techniques are presented that are under development. Techniques considered as emerging techniques are those currently being researched that look promising for future applications, even if they do not run at full scale in any tannery yet or there is not enough information available on full scale operations.

Information will include a description of the technique, the potential efficiency, a preliminary cost estimate, if data are already available, an assessment of the status of development, and if available, a reference [tan/tm/49/BLC-emtech].

In Table 6.1 an overview for emerging techniques considered in the document is given.

Process steps	Specific processes
Substitution of salt in curing	Flo-ice process Curing through irradiation
Unhairing & liming	Substitution of sulphides (mercaptanes, etc.)
Degreasing	Application of supercritical fluids
Tanning	Thru-blu process Iron as a tanning agent Organic tanning Vegetable tanning
Post-tanning	Research if any emerging techniques are to be included in the BREF
Finishing	Electrostatic finishing Organic solvent free finishing Substituting acrylate dilutent monomers
Membrane techniques	Application of membrane techniques in various process steps
Use of enzymes	Use of enzymes in various process steps
Waste treatment	Thermal treatment

Table 6.1: Overview for emerging techniques considered in the document

6.1 Curing

6.1.1 Short-term preservation with flo-ice

Process description
Flo-ice is produced by a cooling system which uses a 3 – 5 % brine solution to create a liquid at a temperature between 0 and –10 °C. Alternatively, the suspension of microscopic ice crystals can be made in another anti-freeze solution such as glycol. The technology is widely applied in the fish industry as a means to preserve fish. Flo-ice has been researched as a method to preserve hides and skins for short periods of time. Results of the research show that Flo-ice can preserve hides and skins up to three days at temperatures below 10 degrees when stored in a container at ambient temperature. A change in the application rate and the salt content can extend the time of preservation.

Liquid will run off after application to the hides, just as is expected when icing is carried out. However, the run off can be collected, filtered and re-used.

Environmental advantages and disadvantages
The use of flo-ice results in a reduction of salt in the effluent treatment plant, as only 3 – 5 % salt is used for preservation instead of more than 20 % in traditional salting.

The energy required to produce flo-ice is equivalent or lower compared to the energy required to produce flake ice.

Economic parameters

The process requires investment in a flo-ice generator. Costs are approximately EUR 50000 for a portable unit with a daily capacity of 10 tonnes of raw hides. Hides or skins to which flo-ice is applied need to be contained in water-tight containers.

Status of development

The use of flo-ice in the leather industry was the subject of an EU funded Life programme, which was completed in late 1997. It is not known whether this research is being exploited further for its application in the leather industry by the suppliers of the flo-ice equipment.

References

Tan/tm/53/Life

6.1.2 Curing through irradiation of hides

Process description

A Canadian invention claims that fresh hides can be sterilised by means of high speed electrons within hours after flaying. Once the hides are sterile they will retain the properties of 'fresh' green hides for up to six months. This would enable 'fresh' hides to be transported over long distances without the need for salting.

After green fleshing, hides are dipped into a solution with a low concentration of a proprietary product, which produces a strong synergism when combined with radiation. The hides are then wrung and wrapped in a thermoplastic film in which they enter the electron beam chamber. After irradiation the hides are packed in sealed boxes. The process uses the ionising form of radiation generated in an electron beam. The electrons interact with biological tissues much the same as gamma rays but differ in their penetration characteristics.

Environmental advantages and disadvantages

This method eliminates the use of salt.

Economic parameters

The process requires high capital expenditure, and needs to be installed at an abattoir.

Status of development

The patent for this process was awarded in 1993. Progress on developments after this date have not been identified.

Although it is claimed that the patented technology is available on the market and has been improved since 1992, the technology is not yet in use.

References

Irradiation curing of hides becomes a reality. Leather, September 1992, p139-145.

6.2 Unhairing and liming

6.2.1 Substitution of sulphides

Process description

The following alternatives to sulphides that are reducing agents under alkaline conditions can be used as depilatory (unhairing) agents:

- thiols
- low molecular weight amines

The hair-destroying component is an organic compound with a reducing effect. Any excess amounts of the compound not used during the unhairing process are immediately oxidised by atmospheric oxygen, so that no harmful substances are brought into the effluent.

Proprietary formulations are available on the market. It is known that these chemicals are used in tanneries outside Europe, but it is not clear how widely these agents have been adopted as alternatives to sulphides in European tanneries.

Environmental advantages and disadvantages
Reduction of sulphide in effluent. Modifications of this process exist whereby only part of the sulphide is replaced for cost reasons.

Proprietary products may contain chemicals that might be toxic to humans and aquatic life.

Economic parameters
Proprietary products are generally more expensive than traditional unhairing chemicals.

Status of development
Available on the market, though not known whether it is used as a complete replacement or partial replacement by tanneries.

6.3 Degreasing

6.3.1 Application of supercritical fluids in leather processing

Process description
Supercritical fluids begin to exhibit significant solvent properties when they are compressed to liquid-like densities and initial trials have shown that fats and oils can be extracted from animal material by this means. It may be possible that supercritical fluids offer the potential for clean, efficient, degreasing systems for use in leather production.

In addition to supercritical fluid extractions, the technique can also be used to impregnate a substrate with chemicals. Possible applications, which are being investigated, include dyeing of leather.

Environmental advantages and disadvantages
The condition required to produce supercritical CO_2 (31.1.°C and 73.8 bar) would permit extraction of skins in an untanned state, thereby eliminating the need for organic solvents and detergents. In addition there would be no waste water generated from the process and the fat would be recovered in a clean, chemically unchanged state as a commodity product. Supercritical CO_2 produces neither toxic waste nor volatile emissions, and is therefore considered environmentally acceptable.

Economic parameters
The process requires high capital expenditure, and may be prohibitively expensive in the short term.

Status of development
Research carried out on laboratory scale in several European leather research institutes.

References
Leather and supercritical fluids, G.Gavend, Industrie du Cuir, August/September 1995, p. 82-87.

6.4 Tanning

6.4.1 Thru-blu process

Process description:
This technique requires the modification of chrome complexes in order to increase the exhaustion of the chrome tanning process. Commercial, sulphur dioxide reduced, 33 % basic chromium sulphate liquor contains 11 – 15 % Cr_2O_3 which is made up of anionic, non-ionic and cationic complexes and about 10 % sodium sulphate. The exhaustion of conventional chrome tanning processes can be increased by removing the non-ionic complexes or by complexing the chrome with polymeric agents like polyamide to produce a more reactive tanning agent. The Thru-blu process is a modification of the chrome tanning process which allows for a facilitation of the absorption of the non-ionic and anionic chrome complexes, by starting the tanning at a high pH (after deliming and bating). Due to the residual acidity of the basic chrome tanning agent, the pH will drop to 3 to 4, at which level the cationic complexes are absorbed by the pelt to obtain a high chrome absorption. Since the pH drops gradually from a high level to a low level, basification and masking is not necessary. The tanning is carried out with a combination of polyamide and a chrome tanning agent.

Environmental advantages and disadvantages
The exhaustion of the thru-blu tanning process is up to 99 %. A reduction of chemical consumption is achieved as no pickling is required and no basification and masking agents are needed. Consequently, cost savings in tanning and effluent treatment can be achieved.

Status of development
The process described is covered under a pending patent application. Trials have been conducted on laboratory and small scale in New Zealand.

Reference
Minimising the environmental impact of chrome tanning: the "thrublu"
Process, DasGupta S, Journal of the Society of Leather Technologists and Chemists, Vol 82, Jan/Feb 1998, p15-21

Lasra's "Thrublu" process: Minimising the environmental impact of chrome
Tanning, DasGupta S, Leather Manufacturer, Vol 115, Dec. 1997, p. 11-13 & 23

Lasra's "Thrublu" Process: Part Two, DasGupta S, Leather Manufacturer, Jan.1998, p. 18-24 & 39

6.4.2 Iron tanning

Process description
The use of iron salts as tanning agents was reported as early as the eighteenth century. However, their application in tanning is limited due to the inherent disadvantages of the tanning process and the resulting leathers. However, research is being carried out using mixed ligand complexes of iron (II) as tanning agents. Leather has been tanned with these iron complexes on their own, and in combination with aluminium and vegetable tannins. The combination tannages resulted in leathers with shrinkage temperatures up to 89°C. Further research has also been carried out creating heterocomplexes between iron salts and tanning agents such as chromium, zirconium and aluminium. However the use of iron as tanning agents still requires further research in order to find a practical application in tanneries.

Environmental advantages and disadvantages
Not clearly defined. Heterocomplexes of tanning agents incorporating iron salts are claimed to achieve high-exhaustion of the chrome in the tanning process.

Status of development
Laboratory experiments are carried out.

References
Iron complexes as Tanning Agents, S. Balasubramanian, R. Gayathri, JALCA, Vol. 92, 1997, p. 218-224.
Investigation into Iron Tannage, C. Gaidau, F. Platon, N. Badea, Journal of the Society of Leather Technologists and Chemists, July-August 1998, No 4, Vol. 82, p. 143-146.

6.4.3 Organic tanning

Process description
The development of synthetic organic tannages is stimulated in response to market pressures and environmental regulations calling for alternatives to chrome tanning. Research is undertaken to use melamine-formaldehyde polymer resins, either on its own or in combination with vegetable tanning agents to obtain a leather which has similar properties to chrome tanned leather.

Environmental advantages and disadvantages
Alternative to chrome as a main tanning agent.

Status of development
Laboratory research undertaken by several European leather technology research organisations.

6.4.4 Vegetable tanning

Process description
Currently, no developments have been identified in this area which may classify as emerging techniques. The use of extracts with low salt concentration and rapid vegetable tanning (2 days) are already available on the market and implemented in European tanneries. Further development is hampered by the fact that there is little research being conducted in this field, due to the small market share of vegetable tanning agents.

6.5 Finishing

6.5.1 Electrostatic spraying

Process description
Powder coating is a solid system in the form of fine powders whose typical contents are resins, crosslinking agents, pigment, flow agents and other additives. It is applied on the leather and the coated leather then undergoes stoving. The powder melts and flows until a smooth film is formed. The most likely application technique for powder coating includes electrostatic spraying, fluidised bed deposition with pre-heated object and electrostatic fluidised bed deposition.

Powder coating is generally seen as unsuitable for leather because leather cannot withstand the high temperatures in the stove and because the methods for applying the powder are not applicable for leather, which is neither electrically conducive nor a good conductor of heat. However, low temperature formulations are becoming available, and some research is being carried out to develop the technique for the leather industry.

Environmental advantages and disadvantages
Elimination of organic solvent use.

Status of development
Scoping studies are being carried out.

References
Powder coating for leather finishing, J.F. Ding, M Tozan, G.E. Attenburrow, In: IULTCS Congress Proceedings, 11 - 14 September 1997, London.

6.5.2 Organic solvent-free finishing

Process description
The use of organic solvents in top coats and special effects finishes is still common in Europe. However, the range of organic solvent-free (aqueous-based) and low-solvent finishes is increasing continuously. Whereas the range of aqueous-based and low-solvent systems is considered BAT, top coat formulations which are completely free of organic solvents are not yet widely available or being used for upholstery leather for automotive and furniture use. Acrylates and polyurethanes have been identified as being particularly suitable to create organic solvent-free finishes.

A problem associated with solvent-free finishes is that the finish may form droplets on the leather due to its poor flow properties. Organic solvents reduce the surface tension of water thus giving the finish improved flow properties. Auxiliaries have been developed which improve the properties of the finish, and a number of technologies are emerging allowing for a (near) elimination of solvents in urethane dispersions and acrylic emulsions.

An example of the solvent-free finish formulations is the development of hybrid acrylic polyurethane polymers. These hybrid polymers offer the possibility of totally solvent-free finishing systems.

Whereas several solvent-free finishes are now available from a wide range of chemicals suppliers, developments are continuing to improve the technical performance of these finishes.

Environmental advantages and disadvantages
No use of VOCs and no emissions of VOCs.

Potentially toxic cross-linkers required to improve the performance of the finish.

Status of development
Several formulations are already available on the market.

References
Advances in Aqueous Polymers for Surface Coating, Leather, July 1997, p. 33-36.
The Best of Both Worlds, L. van der Heijen, Leather, October 1995, p. 28-29

6.5.3 Substituting monomers

Process description
Acrylic acid, phenol and formaldehyde are monomers that may be found in retanning agents. Chemical suppliers are developing formulations that have no presence of these monomers, though no information is available as to the state of this work. Most chemical suppliers are reluctant to disclose information about on-going research for reasons of competition.

6.6 Application of membrane techniques in various process steps

Process description

Due to the rapid development in the range and performances of membranes, and the continuous reduction of their cost, the application of membrane technology in the leather industry is being investigated by several leather institutes in Europe. Some full scale applications of ultrafiltration have now been found in tanneries such as in effluent treatment, separating oily water emulsions from aqueous degreasing processes, and recycling waste liquors from the soaking and liming processes. Also, cross-flow microfiltration has been implemented in a tannery for recycling the chrome liquor of a wool-on sheepskin tanning process.

Another particular application of membranes is the membrane bioreactor (MBR) for enhanced biological effluent treatment. The process relies on membrane filtration to effectively separate the biomass instead of conventional settling, thus enabling a process to operate at much higher mixed liquor concentrations (up to 20 - 40 g/l MLSS). The MBR can be fitted with a hollow fibre membrane to supply bubbles of dissolved oxygen to the biological treatment plant in a highly efficient manner.

Three tanneries in Europe operate MBR systems in order to concentrate the activated sludge to increase effectivity and reduce volume. They are: Jules V. Paermentier, Oeselgem, Belgium; Lederfabriek P. Driesen, Dongen, Netherlands; Bayern-Leder GmbH & Co KG, Neutraubling, Germany.

The principal reason for using this system is to meet discharge limits by reducing suspended solids, COD and BOD levels. The system can also reduce levels of specific substances that might be a problem - such as chromium or insecticide residues.

This system is a secondary treatment: it is particularly relevant where discharges are direct to the aquatic environment; it is less relevant where discharge is to sewer.

Despite the above-mentioned applications of membranes, many of these systems are still not fully technically proven for further adaptation. Further research is now being carried out to investigate the economic and technical feasibility of several membranes for the following applications:

- recovery and recycling of spent tannery liquors, in particular lime-sulphide liquors
- recovery of oils and recycling of surfactants from aqueous degreasing
- application of dynamically-formed membranes for treating 'difficult' effluents, in particular for reducing colour, toxins, hard COD and fine suspended solids
- enhanced biological effluent treatment using membranes for biomass filtration and oxygenation, including inoculation with specialist micro-organisms for the degradation of persistant organic compounds.

Environmental advantages and disadvantages

Up to 80 % reduced chemical and water consumption and effluent generation when applied for the recycling of process liquors. When applied for the treatment of effluent, enhanced performance whilst minimising sludge generation.

Economic parameters

Capital costs and energy consumption may be high.

Status of development

Research is on-going on pilot-plant and full-scale basis in several countries in Europe and elsewhere.

References
Membrane Technologies for the Treatment of Tannery Residual Floats, M. Aloy and B. Vulliermet, Journal of Society of Leather Technologists and Chemists, Vol. 82, 1998.
Membrane technologies and the leather industry. S. Barefield and F. Turan, World Leather, Vol. 10, Nov. 1997.
Integration of ultrafiltration into unhairing and degreasing operations. A. Cassano, E. Drioli and R. Molinari, Journal of Society of Leather Technologists and Chemists, Vol. 82, 1998.
Weitergehende biologische Behandlung von Gerbereiabwasser einschliesslich Kreislaufführung des Brauchwassers, Institut für Siedlungswasserbau, Wassergüte- und Abfallwirschaft der Universität Stuttgart, Professor Dr. Ing. Kh Krauth, Dipl. Ing. K.F. Staab, Dezember 1999

6.7 Use of enzymes in various process steps

Process description
The use of neutral and alkaline stable enzymes in tanneries is common in soaking, unhairing, and bating. Further research has been carried out to develop an application for lipases in the degreasing of sheepskins, though their use has not been fully exploited due to technical limitations.

Research is currently being carried out in the following areas:

- application of cellulase type enzymes to degrade dung present on hides and skins
- application of specific protease and keratinease enzymes which can be used to develop a sulphide-free unhairing process
- application of lipases in the post-soaking stage after unhairing and fleshing to disperse and remove natural lipid
- application of acid active lipase and protease enzymes in pickling and wet blue stage to re-bate and degrease hides and skins.

Environmental advantages and disadvantages
Enzymes can be utilised as powerful biological catalysts to replace or reduce the amount of chemicals required in processing leather. Also, the use of enzymes may reduce the pollution load of effluent, for example when enzymes are used for a hair-save process. Enzymes are not persistent and can be readily inactivated and biodegraded. As an example, the use of proteolytic enzymes during unhairing has been demonstrated to reduce the input of sodium sulphide by as much as 50 %. The use of lipases for degreasing would eliminate the need to apply organic solvents in the degreasing process (solvent degreasing) or the use of pre-tanning agents and surfactants (aqueous degreasing).

Economic parameters
Enzymes may be expensive, though they can potentially be applied in all existing processes.

Status of development
The main problems associated with the application of enzymes in various process steps are:

- a lack of product knowledge on specific enzymes and innovative applications
- a lack of sufficiently pure preparations
- a limitation in the activity range of currently used enzymes, especially with regard to the pH
- a risk of damaging the valuable grain enamel
- enzymes are expensive and their benefits can be difficult to quantify.

6.8 Waste treatment

6.8.1 Thermal treatment

Thermal treatment involves pyrolysis or incineration. Up to now incineration (pilot) plants are installed off-site only. Incineration at low temperatures and low oxygen prevents the oxidation of trivalent to hexavalent chrome. The chrome found in the ash can be recycled in the metallurgic industry. A pilot plant exists in Denmark, but has been closed down. In autumn 2000 a plant of this kind was put into use in a Norwegian tannery.

7 CONCLUDING REMARKS

7.1 Timing of the work

The work on this BAT Reference document started with a kick-off meeting on 5 and 6 February 1998. Two drafts were issued to the Technical Working Group (TWG) for consultation. The first draft of Chapters 1 to 6 was sent out for consultation in January 1999. There was then a break of about three months in the writing because of a change of BREF author. The second draft was issued in June 2000 and the work concluded with a second TWG meeting on 20 - 22 November 2000. After the second TWG meeting there were short consultation periods on the revised Chapters 1 to 6 and on the new Chapter 7 Concluding remarks, the Glossary and the Executive Summary. After this the final redrafting took place.

7.2 Sources of information

Many reports from industry, authorities and suppliers have been used as sources of information in the drafting of this BREF. Of these documents tm/09/Unido, tm/17/Frendrup and tm/03/BLC can be considered as general building blocks for the first draft. Chapter 6 (Emerging Techniques) is mainly based on information from the BLC Leather Technology Centre Ltd.

For the second draft, tm/58/BLC, tm/17/Frendrup and of course the comments made on the first draft were the main sources. Other information submitted was more focused on a particular environmental issue, where the emphasis was largely on chrome tanning versus vegetable tanning and waste water conditions and treatment.

Most of the information submitted was focused on the tanning process in general; very little detailed information was made available on the performance of techniques to be considered in the determination of BAT, especially on achieved emission and consumption levels and on economics.

7.3 Level of consensus

This BREF has the support of most of the TWG members, although on three BAT conclusions the following split views had to be noted:

1. The majority in the TWG agreed that partial recycling or re-use of pickle liquors is BAT, but experts representing one Member State, and some experts representing industry in the TWG, did not fully agree. In their view BAT is to use partial recycling or re-use of pickle liquors with an exception for high quality leathers.

2. Experts representing one Member State and some experts representing industry do not fully support this BAT conclusion on chrome recovery. Their opinion is that a separate treatment of chrome-containing liquors is not currently economically viable for a large part of the European leather industry, particularly in situations where a common specialised treatment plant is not available.

3. Industry supports the conclusion that separate treatment of sulphide-containing effluent is BAT, but in their view also the mixed treatment –- on site – of sulphide- and chrome-containing effluent is BAT.

Another issue worth noting is the difference in opinion between authorities and industry about the toxicity of chromium (III) salts used in the tanning industry. While industry takes the view that the chromium (III) tanning agent is not toxic and can be compared with table salt, the authorities' opinion is that chromium (III) should be considered toxic, especially for aquatic life. Both opinions are supported by the references used for writing this document.

7.4 Recommendations for future work

Very little was exchanged in the way of data and information on the current emission and consumption levels and on the performance of techniques to be considered in the determination of BAT, especially on the achievable emission and consumption levels and on economics. For future BREF reviews, all TWG members and interested parties should continue, or start, to collect these data for all tanning processes and tanning agents. The data should be expressed as concentrations as well as loads and, where appropriate, in relation to the amount of input and/or output material.

Information on reference plants and actual performance data are scarce; for the revision of this document the missing information should be provided. Apart from data missing in general, as mentioned above, specific areas where data and information are missing are the following:

- the quantity of chrome-contaminated and chrome-free wastes and sludges from waste water treatment
- a description of techniques, together with their performance and the costs, such as reverse osmosis and evaporation for the final treatment of high salt contents where emission limits cannot be met by implementing primary measures
- the possibilities and performances of substitutes for:
  - (heavy) metal-free dyeing agents
  - sodium chloride (for curing)
  - sulphide unhairing agents
  - pickling agents
- an actual decommissioning of a tannery
- the environmental performance of solvent degreasing systems and aqueous degreasing systems
- the source, amount and type of residues in wastes from ovine skins and salted and fresh bovine hides. A clear reference to the state of the hide or skin, e.g. green, salted, etc and the humidity of the waste (especially for sludge) is important. It would also be helpful to know what the destination of the waste is
- the amounts and types of substances emitted to air. The data need to be collected on the emitted air before and after treatment, to ascertain the efficiency of the abatement technique
- on energy, to ascertain the consumption ratios in different process units in e.g. mechanical operations and process machinery, drying, heating, warm water supply, light, waste water treatment and other abatements and to get an idea of losses from e.g., air exchange, waste heat, warm water effluents and inadequate equipment
- comprehensive emission and consumption data for all mineral tanning agents used, such as chrome, aluminium and zirconium, together with information on the environmental impact of all these tanning agents
- on dyeing agents, components usually monitored by summary parameters, e.g. chlorinated organic compounds (AOX), surfactants and aromatics or for the colour of the effluent
- on finishing operations data on air emissions, waste water, waste and energy consumption, but also on solvent-free finishes. This TWG suggested inviting coating manufacturers to address the issue of the application of very thin layers with high efficiency-sprayers.

Some research projects are going to be carried out or are being carried out at the moment. For example in the Netherlands a kind of Life Cycle Analysis, only on a smaller scale, will be carried out. The purpose of this project is to compare the environmental aspects of tanning with chromium salt with those of other mineral tanning agents such as aluminium, zirconium and titanium. In another project in Italy, the use of membrane techniques to achieve maximum recovery from the final liquor in vegetable tanning is being investigated.

In order to verify the environmental impact of chemicals, a method for benchmarking chemicals is currently being developed in the Netherlands. This benchmarking method will probably be part of the horizontal Bref on cross-media and economics.

This TWG recommends that, when this BREF is reviewed, consideration be given to adopting a sectoral approach (bovine/ovine/sheepskin etc.) by reference to the end-product. The advice is to start the review in 2004 or 2005.

7.5 Suggested topics for future R&D projects

The following topics might be considered for future Research and Development projects:

Water and sludge:
- the development of advanced waste water treatment units, leading to open or closed-loop recycling of water
- NPEs are used in degreasing sheepskins because, to date no alternative has been found with equal performance in degreasing very fatty sheepskins. Further research is necessary to find a suitable substitute
- when the use of NPEs is the only option, research on monitoring and reducing the level of NPEs in the waste water is necessary
- the feasibility of implementing a de-nitrification step in an individual waste water treatment has to be studied carefully because de-nitrification can lead to a re-formation of sulphides and therefore needs close control and proper management
- when salted hides or skins are processed, the high amount of salt in the waste water is a problem. Research on abatement techniques to remove salt in a cost-effective way is necessary. The removal of sulphates should also be considered
- enzymatic deliming for ovine and bovine skins and hides, in order to avoid sodium sulphide consumption, which can be considered the main COD pollutant of the leather processing
- the reduction, re-use and treatment of sludge from tannery effluent treatment plants.

Solid waste:
- the prevention, re-use and valorisation of waste (e.g. collagen and keratines), e.g. by biotechnology
- thermal treatment of leather waste.

Air:
- the reduction of odour emissions
- development of techniques for the use of high transfer efficiency spraying equipment in the application of very thin finishing layers to aniline leather.

Soil:
- assessment of the long-term environmental impact of contaminated sites on, e.g. groundwater
- development of remediation technologies for contaminated sites.

The EC is launching and supporting, through its RTD programmes, a series of projects dealing with clean technologies, emerging effluent treatment and recycling technologies and management strategies. Potentially these projects could provide a useful contribution to future BREF reviews. Readers are therefore invited to inform the EIPPCB of any research results which are relevant to the scope of this document (see also the preface of this document).

REFERENCES

Tan/tm/1/HMIP	Pollution Control in the Treatment and Processing of Animal and Vegetable Matter. DoE Report No: DoE/HMIP/PR/93/058, 1993	Her Majesty's Inspectorate of Pollution, department of the Environment UK (by Bradbury LTD)	1993
Tan/tm/2/UK guidance	Chief Inspectors's Guidance to Inspectors - Processing of Animal Hides and Skins, Process Guidance Note IPR 6/7, 1995	HMIP – Her Majesty's Inspectorate of Pollution -UK	1995
Tan/tm/3/UwHB	Umwelthandbuch für die ledererzeugenden Betriebe, Hans Andres, November 1995, draft version		1995
Tan/tm/4/Austria	BAT – Documentation of Tanneries & Leather factories in Austria	Hans Andres	1997
Tan/tm/5/Austria BK	Branchenkonzept für die ledererzeugenden Betriebe Österreichs, Arbeitsgemeinschaft Lederwirtschaft (ARGELE), Bundeskammer der gewerblichen Wirtschaft, Bundesministerium für Umwelt, Jugend und Familie	Umweltbundesamt	1992
Tan/tm/6/Europe	European BAT documentation OE 013868/LR/sh		1992
Tan/tm/7/Zimpel	Industrielle und gewerbliche Abwassereinleitung in öffentliche Abwasseranlagen	Jörg Zimpel et.al.	1997
Tan/tm/8/ TEGEWA	Zur Nomenklatur der Textilhilfmittel, Leder- und Pelzhilfsmittel, Papierhilfmittel und Tenside	TEGEWA, Verband der Textilhilfsmittel-, Lederhilfs	1987
Tan/tm/9/ UNIDO	Low Waste Technology Suitable For Tanneries in Developing Economies	Higham, R.D.	1994
Tan/tm/10/ UNIDO/UNEP	Audit and Reduction Manual for Industrial Emissions and Wastes	UNIDO - UNEP	1991
Tan/tm/11/Nordiske Seminar	Possibilities for a Reduction of the Pollution Load from Tanneries	Rydin, S.; Frendrup, W.	1993
Tan/tm/12/Ullmann	Leather	Heidemann, E.	
Tan/tm/13/ Ullmann-fur	Furs	Nungesser, T.	

References

Tan/tm/14/ Germany-dyes	Textilfärberei und Farbstoffe	Ebner, G.; Schelz, D. Springer-Berlin Heidelberg	1989
Tan/tm/15/ Reemtsma	Wirkung einer anaerob-aeroben biologischen Behandlung auf gelöste organische Stoffe in Gerbereiabwasser	Reemtsma, T.	1994
Tan/tm/16/ Spain	Aplicaciones del Manual Media a Sectores Industriales - Sector de Curtidos de Pieles Animales	various	1997
Tan/tm/17/Frendrup	Willy Frendrup: Practical Possibilities for Cleaner Production in Leather Processing	Danish Technological Institute	1999
Tan/tm/18/ UNEP-Tan	Tanneries and the Environment (Technical Guide)		1991
Tan/tm/19/	Textilhilfsmittel	Heimann, S. et al.	
Tan/tm/20/	Procedure for the Evaluation of Substances and Preparations in the Context of the Pollution of Surface Waters Act	Niebeek, G.	1997
Tan/tm/21/	Biocides in Cooling Water Systems (final report)	CES (UK)	1994
Tan/tm/22/	The Evaluation of Substances and Preparations in the Context of the Pollution of Surface Waters Act	Benschop, P.	1997
Tan/tm/23/ PANORAMA	Panorama of EU Industry	DG III Industry and Eurostat	1997
Tan/tm/24/Spain-Cr	La recuperación del cromo de los baños de curtición, Recrisa: Una realidad	López Sivera, E.	1988
Tan/tm/25/	Estabilización del Pelo Recuperado de las Pieles Vacunas y sus Aplicaciones	A.I.I.C.A (E)	1988
Tan/tm/26/	Información Técnica	A.I.I.C.A. (E)	1988
Tan/tm/27/Finland	The Finnish Background Report for the EC Documentation of BAT for Tanning Industry	Kustula, V.; Salo, H.; Witick, A.; Kaunismaa, P.	1998
Tan/tm/28/BASF	The ecological aspects of leather manufacture	BASF	1997
Tan/tm/29/UBA	Recycling von Gerbereiabwasser	UBA (D)	1994

Tan/tm/30/Renner	Abwasser aus der Zellstoffindustrie und der Lederherstellung	Renner, G.	1995
Tan/tm/31/	Environmental Contaminants Encyclopedia Chromium (In General) Entry	Irwin, R.J.;	1997
Tan/tm/32/	Environmental Contaminants Encyclopedia Chromium III (Trivalent Chromium) Entry	Irwin, R.J.	1997
Tan/tm/33/	Environmental Contaminants Encyclopedia Chromium VI (Hexavalent Chromium) Entry	Irwin, R.J.	1997
Tan/tm/34/	Umweltbeeinträchtigende Stoffe im Abwasser der Leder-, der Pelzveredlungs- und der Lederfaserwerkstoffindustrie	Pauckner, W.; Rein, E.; Herfeld, H.P.	1988
Tan/tm/35/BLC	BAT in Tanneries (draft)	BLC Leather Technology Center by Scheijgrond, J.W.	
Tan/tm/36/UK	Current Practices in UK Tanneries		1998
Tan/tm/37/Germany	Stand der Technik der Lederherstellung in Deutschland (State of the art and future processes in German tanneries)	UBA (D)	1997
Tan/tm/38/Denmark	Preliminary Danish contribution to the draft BAT notes on tanneries	Friis, J	1998
Tan/tm/39/Italy	Italian BAT Contribution	Stazione Sperimentale (I)	1998
Tan/tm/40/Portugal	Resposta ao questionário da DG Industria	APIC (P)	1998
Tan/tm/41/Greece	candidate BAT from Greece	Tsotsos, D.	1998
Tan/tm/42/Unido-Mass	Mass Balance in Leather Processing	Buljan, J.; Reich, G.; Ludvik, J.	1998
Tan/tm/43/World Leather	Various articles of World Leather 1996/97/98	Sources/authors are mentioned as a foot-note in the document	1996, 1997, 1998
Tan/tm/44/Abwasser	Various articles of various authors in: Sfb 193-Biologische Abwasser-reinigung 5, p. 159-243	Authors are mentioned as a footnote in the document	1995
Tan/tm/45/Leather	Various articles of "Leather Technology"	Sources/authors are mentioned as a foot-note in the document	1998

References

Tan/tm/46/FAO	Wold Statistical Compendium for Raw Hides and Skins, Leather and Leather Footwear 1979 - 1997	Food & Agricultural Organisation of the UN, Rome	1998
Tan/tm/47/	Dissolved Organics in Tannery Waste waters and their Alterattion by a Combined Anaerobic and Aerobic Treatment	Reemtsma, T.; Jekel, M.	1997
Tan/tm/48/	Microbial Transformations and Biological Effects of Fungicide-Derived Benzothiazoles Determined in Industrial Waste water	Reemtsma, T.; Fiehn, O.; Kalnowski, G.; Jekel, M.	1995
Tan/tm/49/BLC-emtech	Emerging Techniques for Tanneries	Scheijgrond, J.-W.	1998
Tan/tm/50	BAT Candidate for tanning Industry: Deliming Using Carbon Dioxide. Origin: University of Jyväskylä (SF).	Kustula,V; Weaver, A.	1998
Tan/tm/51	Pollution Control in the Treatment and Processing of Animal and Vegetable Matter. DoE, 1993	Bradbury ltd	1993
Tan/tm/52/Handbook	Leather Poducers' Association (UK)	Sharphouse, J.H.	1971
Tan/tm/53	Demonstration project for the extensive introduction of clean technologies, conservation of raw materials and optimisation of production processes in tanneries - final report	BLC Leather Technology Centre (UK)	1997
Tan/tm/54	Ökologischer Vergleich verschiedener Gerbarten (Wissenschaft & Technik)	Trommer, B.; Kellert, H.-J.	1999
Tan/tm/55/EPA	Air Emissions and Control Technology for Leather Tanning and Finishing Operations US EPA	Mitsch, B.F.; Howle, R.H.; McClintok, S.C.	1993
Tan/tm/56	Sperimentazione Prodotti Chimici in Fase Acquosa nella Rifinizione delle Pelli	CO.VI.AM. Concercie Vicentine per l'Ambiente	1999
Tan/tm/57	R&D of new technologies for: hides mechanical dehairing; production of stabilised hides after deliming/bating phase	Hellenic Leather Center S.A.	1999

Tan/tm/58/BLC	BLC Information Document -No 200- Best Available Technologies	R.P. Pearson, M.D. Maguire, R.J.Bowden	1999
Tan/tm/59	Lederfabricage	RIVM, RIZA (NL)	1995
Tan/tm/60	Lederindustrie	InfoMil (NL)	1996
Tan/tm/61	Untersuchungen zum Einsatz von Konservierungsmitteln in der Chromgerbung und ihrer quantitativen Verteilung im Wet-blue. Das Leder, Heft 9	Hauber, C.; Germann, H.-P.	1996
Tan/tm/62	Maßnahmen zur Vermeidung, Verminderung und verwertung von Reststoffen aus der Lederindustrie, Pelzveredlung und Lederfaserstoffherstellung	Umweltministerium	1995
Tan/tm/63	Zur Nomenklatur der Textilhilfmittel, Leder- und Pelzhilfsmittel, Papierhilfmittel und Tenside	TEGEWA, Verband der Textilhilfsmittel-, Lederhilfs	1987
Tan/tm/64/LAWA	Stellungnahme der LAWA zu Kapitel 4 des BREF-Entwurfs	Lindemann, Zimpel	1999
Tan/tm/65/Ohio	Flame Resistance of Leather	Kadir Donmez, W.E. Kallenberger	1992
Tan/tm/66/	Assessment of Procedures for Reducing VOC Emissions from Leather Finishing Operations; Information Document ID-162.	D.R. Corning, N.J. Cory, F. Turan	
Tan/tm/67	La toxicité des effluents de tannerie e mégisserie; Technique-Technology	Michel Aloy; Arlette Vulliermet, CTC	1993
Tan/tm/68	Ermittlung der Lösungsmittelemission bei der Leder-zurichtung; Das Leder nr.40	G. Schmid, W. Pauckner	1989
Tan/tm/69	Teilstrombehandlung sulfid- und chromhaltiger Gerbereiabwässer; Das Leder nr.5	G. Renner, H.P. Germann	1995
Tan/tm/70	Aufbereitung von Salzlake aus der Hautkonservierung	Prof.Dr.Ing. Ch. Mostofizadeh	
Tan/tm/71	Wasserseitige Emission aus der lederherstellenden Industrie	Lindemann, Zimpel	2000
Tan/tm/72	Verschiedene Unterlagen über Komplexbildner	Authors: various	

References

Tan/tm/73	Abwasserreinigung der Firma Bayern-Leder-GMBH & Co.	I-T-G Ingenieurgemeinschaft für Umwelttechnologie W. Genest	1997
Tan/tm/74	Information of reference tanneries in Germany		2000
Tan/tm/75	Centralized plant for the recovery of basic chromium sulfate from tannery effluent, Italy	E.C. Directorate-General for Energy	1982
Tan/tm/76/Nl	Information about chrome recovery Installations in India and Nicaragua	Several authors, source: Netherlands	1994-1995
Tan/tm/77/Reich	Ökologische Aspekte wichtiger Gerbverfahren	Reich, G.	2000
IARC	Monographs on the evaluation of the carcinogenic risk of chemicals to humans: wood, leather and some associated industries		
Stern, 1987	Mortality of chrome leather tannery workers and its chemical exposures in tanneries' Scand J. Work Environ Health, 13, 108 - 117	Stern F.B. et al	1987
Pippard, 1985	Mortality of tanners', British Journal of Industrial Medicine, 42, 285 - 287	Pippard E.C. et al	1985
Chattopadhyay, 2000	The Environmental Impact of Waste Chromium of Tannery Agglomerates in the East Calcutta Wetland Ecosystem, 84, 94 - 100	Chattopadhyay B. et al	2000
Rutland, 1991	Environmental Computability of Chromium-containing Tannery and Other Leather Product Wastes at Land Disposal Sites, JALCA, 86, 346 - 375	Rutland F.	1991
Donmez, 1989	Soil Leachate: Determination of Hexavalent Chromium', JALCA, 86, 110 - 121	Donmez L.H. & Kallenberger W.E.	1989
Font, 1998	Waste Management Research 16:2, 139-149	R. Font, V. Gomis, J. Fernandez & M.C. Sabater.	1998
Slooff, 1989	Basisdocument Chroom, rapport nr. 758701001 Rijksinstituut voor volksgezondheid en milieuhygiene Bilthoven	W. Slooff, R.F.M.J. Clevens, J.A. Janus, P. van der Poel (eds.)	1989

GLOSSARY

Abbreviations and chemical formulae used in the document	
Al	Aluminium
AOX	Adsorbable Organic Halogen (X): The total concentration in milligrams per litre, expressed as chlorine, of all halogen compounds (except fluorine) present in a sample of water that are capable of being adsorbed on activated carbon
APE	Alkyl Phenol Ethoxylates
BAT	Best Available Techniques
BOD	Biochemical Oxygen Demand: a measure of the oxygen consumed by bacteria to biochemically oxidise organic substances present in water to carbon dioxide and water. The higher the organic load, the larger the amount of oxygen consumed. As a result, with high organic concentrations in the effluent, the amount of oxygen in water may be reduced below acceptable levels for aquatic life. BOD tests are carried out at 20 °C in dilute solution and the amount of oxygen consumed is determined after 5, 7, 20 or, less commonly, 30 days. The corresponding parameters are called BOD_5, BOD_7, BOD_{20} and BOD_{30}. The unit of measurement is mg O_2/l
BREF	BAT Reference Document
Bronopol	2-bromo-2-nitro-propane-1,3-diol
BSE	Bovine Spongiform Encephalopathy
CFC	Chlorofluorohydrocarbons
CH_2Cl_2	Dichloromethane or methylene chloride
Cl^-	Chloride
CO_2	Carbon dioxide
COD	Chemical Oxygen Demand: The amount of potassium dichromate, expressed as oxygen, required to chemically oxidize at approximately 150 °C substances contained in waste water. The unit of measurement is mg O_2/l or mg O_2/g of substance
Cr	Chromium
Cr_2O_3	Chromic oxide
Cu	Copper
DAF	Dissolved Air Flotation
DEM	German Mark
DDT	An organochlorine pesticide which has been banned in most European countries. The isomer used as pesticide is: p,p'-DDT 1,1,1-trichloro-2,2-bis(4-chlorophenyl)ethane
DG	Directorate General (of the European Commission)
DS	Dry Solids
DSP	Di-sodium phthalates
DTPA	Diethylene-triamine-penta-acetate
EC	European Commission
EC_{50}	Effect Concentration: The concentration at which effects are observed in 50 % of the test population after administering a single dose. Effects include the immobilization of daphnia, inhibition of growth, cell division or biomass production, or the production of chlorophyll by algae

EDDS	Ethylene-diamine-di-succinate
EDTA	Ethylene-diamine-tetra-acetate
EU	European Union
EUR	Euro (currency)
H_2O_2	Hydrogen peroxide
H_2S	Hydrogen sulphide
H_2SO_4	Sulphuric acid
HCH	Hexachlorocyclohexane (pesticide)
HVLP	High Volume Low Pressure
IPPC	Integrated Pollution Prevention and Control
ITL	Italian Lire
IUE	International Environment Commission
LAS	Linear alkylated benzenesulphonacids
LC_{50}	Lethal Concentration: The lowest concentration of a substance in water or ambient air in milligrams per litre sufficient to cause death in 50 % of the test population within a defined period (e.g. 96 hours for fish, 48 hours for daphnia)
LD_{50}	Lethal Dose: The lowest dose of a substance administered to species such as mice or rats sufficient to cause death in 50 % of the test population within a defined period (no more than 14 days), expressed in milligrams of test substance per kilogram of body weight
LOEC	Lowest Observed Effect Concentration: The lowest experimentally determined concentration of a test substance at which adverse effects can be observed
LTD	Low-Temperature Drying
MBR	Membrane Bioreactor
MGDA	Methyl-glycine-di-acetate
MgO	Magnesium oxide
Mn	Manganese
MS	Member States (of the European Union)
MLSS	Mixed Liquor Suspended Solids
MBT	Methylene bis-thiocyanate
N-tot	Total nitrogen
NaHS	Sodium hydrogen sulphide
Na_2S	Sodium sulphide
NH_3	Ammonia
NH_4 -N	Ammonium nitrogen
NOAC	No Observed Acute effect Concentration
NOEC	No Observed Effect Concentration:
NP	Nonylphenol
NPE	Nonylphenol ethoxylates
NTA	Nitrilo-tri-acetate
P	Phosphorus
PAH	Poly-aromatic hydrocarbons
PCDD/F	Polychlorinated dibenzodioxins / polychlorinated dibenzofurans
PCP	Pentachlorophenol
PDTA	Propylene-diamine-tetra-acetate
pH	The measure of acidity or alkalinity of a chemical solution, from 0 to 14. Anything neutral has a pH of 7. Acids have a pH less than 7, bases (alkaline) greater than 7
QAC	Quaternary Ammonium Compound
S^{2-}	Sulphide

SMEs	Small and Medium Sized Enterprises
SO$_4$$^{2-}$	Sulphate
SS	Suspended Solids
TCMTB	Thiocyanomethylthiobenzothiazole
TDS	Total Dissolved Solids
THP	Tetrakis (hydroxymethyl) phosphonium compound
TKN	Total Kjeldahl Nitrogen. The Kjeldahl technique is used to determine fixed nitrogen in organic and inorganic materials
TOC	Total Organic Carbon
TS	Total Solids
TWG	Technical Working Group
UK	United Kingdom
USA	United States of America
USD	United States Dollar
USSR	Union of Soviet Socialist Republics
VOC	Volatile Organic Compound
Zr	Zirconium

Units			
°C	degree Celsius	**m**	metre
cm	centimetre	**m^2**	square metre
d	day	**m^3**	cubic metre
g	gram	**mg**	milligram
GJ	Gigajoule	**MJ**	Megajoule
h	hour	**mm**	millimetre
ha	hectare	**Nm^3**	Normal cubic metre (m^3 at 273K, 101.3kPa, dry)
J	Joule	**s**	second
K	Kelvin	**sq ft**	square foot = 0.092 m^2
kg	kilogram	**t**	metric tonne (1000kg)
kPa	kiloPascal	**t/d**	tonnes per day
kWh	kilowatt hour	**t/yr**	tonnes per year
		yr	year

Technical terms commonly used in the tanning industry	
Aniline leather	A leather that has been coloured with aniline dyestuffs only, with little or no finishing' to obtain a 'natural' leather look
Bating	The manufacturing step which follows liming and precedes pickling. The purpose of bating is to clear the grain, reduce swelling, peptize fibres and remove protein degradation products
Beamhouse/Limeyard	That portion of the tannery where the hides are washed, limed, fleshed and unhaired, when necessary, prior to the tanning process
Bovine	Of or from ox, cow, calf and buffalo
Brining	Curing hides by washing and soaking in a concentrated salt solution
Buffing	Abrasive treatment of the leather surface. If it is carried out on the flesh side, a "suede" leather is obtained. If it is carried out on the grain side, a corrected grain or a nubuck leather is obtained
Calf skin	The skin of a young immature bovine animal not exceeding a certain weight

Collagen	The principal fibrous protein in the corium of a hide or skin that, on tanning, gives leather
Conditioning	Introduces controlled amounts of moisture to the dried leather, giving it a varying degree of softness
Crust leather	Leather which has simply been dried after tanning, retanning and dyeing, without a further finishing process
Curing	Preventing the degradation of hides and skins from the time they are flayed in the abattoir until the processes in the beamhouse are started
Degreasing	Eliminating, as far as possible, the natural grease in the skin
Deliming	Removing the lime from hides coming from the beamhouse before tanning, by the action of inorganic or organic acids or salts of these acids
Dewooling	Separating the wool from the sheepskins
Drum	A cylindrical closed container rotating on an axis
Dyeing	Giving the desired colour by treatment with natural or synthetic dyestuff
Fatliquoring	Incorporating fat into the leather in order to give it flexibility and impermeability
Fellmongeries	Tanneries working on goatskins and sheepskins
Finishing	a) Mechanical finishing operations to improve the appearance and the feel of the leather e.g.: conditioning, staking, buffing, dry milling, polishing, plating/embossing b) Applying a pigmented or a fixing surface coat to the leather
Fleshing	Eliminating sub-cutaneous tissue, fat and flesh adhering to the hide, by the mechanical action of a cylinder equipped with cutting blades
Fleshings	Pieces of sub-cutaneous tissue, fat and flesh separated from the hide during fleshing
Float (liquor)	A solution containing reagents required for a specific action, in which the skins, hides and leathers are immersed
Grain	Can mean: a) the outer, or hair side, of a hide or skin that has been split into layers or b) the pattern visible on the outer surface of a hide or skin after the hair or wool has been removed
Green fleshing	Fleshing done prior to liming and unhairing
Hide	The pelt of a large animal, such as cow and horse
Leather	Is a general term for hide or skin which still retains its original fibrous structure more or less intact, and which has been treated so as to be non-putrescible
Length of (liquor) float	Volume of a float expressed as a percentage relative to the weight of the skins, hides or leathers
Limed hide or skin	Hide or skin obtained after elimination of hair, epidermis and sub-cutaenous tissue. This is the name given to hides and skins after liming
Lime fleshing	Fleshing done after the liming and unhairing
Liming	Is the process which causes a controlled alkaline hydrolysis of the collagen in order to remove the hair or wool, epidermis and sub-cutaenous tissue and thus to give a certain flexibility to the leather
Mineral tanning	The tanning process where the tanning agents are mineral salts such as those of aluminium, chrome or zirconium
Neutralisation	Bringing the tanned hides to a pH suitable for the process of retanning, dyeing and fatliquoring
Ovine	Of or from sheep
Painting	Unhairing the skin by the action of a paste (the painting lime) applied on the flesh side. The painting lime is made of water, lime, sodium sulphide and a thickening agent

Pickled pelt	The hide or skin after pickling and able to be sold at this stage
Pickling	The process that follows bating, whereby the skin or hide is immersed in a brine and acid solution to bring it to an acid condition
Plating/embossing	Flattening or printing a pattern into the leather
Retanning	Subjecting a skin or hide, which has been first more or less completely tanned by one process or one kind or blend of tanning materials, to a second tanning process involving similar or, more usually, different tanning materials
Rinsing	Is the process carried out after each particular treatment and effected by continuous inflow and outflow of water in a treatment apparatus. Usually it is not carried out because of the high water consumption
Shavings	Leather particles obtained during thickness levelling on leather with the help of a cylinder equipped with cutting blades
Soaking	First process in the manufacture of leather, to rehydrate and wash the hides
Skin	The pelt of a small animal, such as calf (calf skin), pig (pigskin), sheep (sheepskin) etc.
Split	Part obtained by splitting the hides and skins horizontally
Splitting	The horizontal splitting of hides and skins into a grain layer and, if the hide is thick enough, a flesh layer. Splitting is carried out on splitting machines, fitted with a band knife. Splitting can be done in the limed condition or in the tanned condition
Staking	Softening and stretching of leather
Tanning	In this process the collagen fibre is stabilised by the tanning agents so that the hide or skin is no longer susceptible to putrefaction or rotting
Trimming	Cutting off some of the edges of the hides and skins, such as legs, tails, face, udders etc. This process is generally carried out during the sorting process, but is also done in other stages in the tanning process
Trimmings	The residues arising from trimming the hides and skins
Upholstery leather	This is a general term for leather processed for use for furniture, aircrafts, buses and cars
Vat	A tank
Vegetable tanning	The tanning process with exclusively vegetable tanning agents, which are leached from wood, barks, leaves, roots etc.
Wet-blue	A hide or skin which has been subjected to the usual beamhouse processes, has been chrome-tanned, therefore turned blue, and left wet. It may be stored or exported in this state
Wet-white	Is a term for a hide or skin which has been subject to the usual beamhouse processes and has been (pre-) tanned with non-chrome agents and therefore turned white

Sources: tan/tm/18/Unido, tan/tm/28/Basf, tan/tm/6/Europe, Ullmann

ANNEX I: REFERENCES / DETAILED DATA

I.1 Environmental comparison of different ways of tanning

This text is an unofficial translation made by the EIPPCB on July 28, 1999. It is the translation of Section 5 of the article: **"Ökologischer Vergleich verschiedener Garbarten"** by Bernard Trommer and H.J. Kellert. Forschungsinstitut für Leder- und Kunstledertechnologie gGmbH, Freiberg, Deutschland.
Source: [tan/tm/59/Trommer] Leder&Häute Markt, Juni 1999.

Summary:

For an environmental comparison of different ways of tanning, four representative standard processes were tested for upholstery leather manufacture on a semi-technical scale.
As a comparison and control group, conventional chromium tanning served as Technology I. Technology II represented the wet-white processes using synthetic tanning agents. Technology III represented combination tanning based on pre-tanning with glutardialdehyde and chromium re-tanning. For technology IV a vegetable tanning process with Mimosa (wattle) extract was used. To compare the tanning types, more than 100 environmental, technical, economic and quality parameters were experimentally determined and evaluated. The results of this comparison can be summarised as follows:

Technology I proved to be efficient and cost-effective and caused a comparatively small load in waste water, sludge and waste per produced leather surface. The leather quality stood out significantly against the other technologies. A number of possible techniques for the recovery and recycling of production residues were investigated. A disadvantage of technology I is the contamination of the sludge with chromium and the associated problems for agricultural use, combustion or landfill.

Technology II caused the smallest salt load in the waste water of all technologies. Heavy metals and sludge did not appear to be a problem. The general organic load (BOD, COD) was clearly higher than that from the control group. The aquatic toxicity of the raw waste water was particularly high in the post-tanning/wet finishing. Significant environmental nuisances were caused by substances characterised by the parameters phenol index and aldehydes. The leather quality was unsatisfactory for some parameters. The leather showed the lowest contraction temperature. For the disposal of the leather waste thermal processes are mainly used. High leachate values may mean that agricultural use and normal landfilling are not possible. Compared with the control group no existing practical solutions were found for the recovery of the leather waste.

Technology III is a compromise between chromium tanning and alternative technologies and needs the least reagents, but it uses more process water than the control group. The raw waste water of the post-tanning/wet finishing contained the least aquatic toxicity of all the tested wet finishing liquor-baths. The leather quality was satisfactory. The contraction temperature came the nearest to the control group. Technology III provided splits (after tanning) with acceptable leachate values. For the disposal of the leather waste, landfilling, thermal treatment and agricultural use appeared to be feasible options. The possibilities for the recycling of leather waste are as unclear as with technology II. Significant, compared with the other processes, was the organic load by aldehydes.

Technology IV caused the highest costs of tanning chemicals, was the most expensive technology (water consumption, process time), and produced by far the highest loads in waste water, sludge and leather waste. The leather quality clearly dropped compared to the other processes. All raw waste water was organically highly loaded, according to the sum parameters. In the waste water treatment the sludge problem was particularly notable compared with the

other technologies. Also the leachate of the splits (after tanning) showed critical values. This technology has the advantages of the absence of heavy metals in the leather, waste water, sludge and waste as well as the possibility of using the leather waste as a raw material for new products. Agricultural use and the possibility of thermal treatment of all the waste are also possitive indicators. During waste water treatment with the activated sludge process, positive synergistic effects occurred in nitrification with the combined treatment of Beamhouse- and tanning- waste water.

The environmental audit shows that the witholding or addition of a certain auxiliary material (tanning material) is not a sufficient criterion for an environmentally friendly or environmentally harmful evaluation of the product or the process. The project goes on to make it clear that environmental improvements can never be reached in all areas (waste water, sludge, waste) at the same time. In the judgement of quality and cost, none of the tested alternatives showed advantages in comparison with the control group (chromium tanning process). Likewise no striking improvements in the effect of the tested environmental measures were recorded. With extensive experimental work, disadvantages of the alternative ways of tanning became visible that are not experienced with chromium tanning. It can be assumed in practice that chromium tanned leather, which is produced according to the "Best Available Techniques ", with the most modern processes, including all the environmentally-friendly technical measures available, may carry the designation 'environmentally beneficial'. So, for any given leather article, knowledge in headline terms of the type of tanning used is not, in itself, a reliable indicator of its biological quality. An independent investigation of the detailed technologies applied and the manufacturing conditions prevailing will also be necessary if an environmental impact assessment is to be made in addition to an assessment of hygiene, pollutants and utility value.

I.2. Chrome recovery technique
[tan/tm41/Greece]

Introduction

A technique has been successfully applied in a Greek tannery which can be considered as a candidate BAT due to its simplicity and attractive environmental performance.

It is independent of any local conditions and can be introduced in any tannery using chromium as tanning agent. It is based on the recovery of chromium from the effluents and its recycling into the production process.

Applicability

This technique has being installed on full-scale at the premises of GERMANAKOS LEATHER INDUSTRY S.A. - Athens, Greece in 1990 as a demonstration project financed by European Commission (ACE-programme 1989), the Greek and the Dutch Ministry of Environment, the Hellenic Leather Center (ELKEDE) and the company itself. Know-how has been provided by the Dutch research institute TNO-Waalwijk, which had developed this technique on a pilot scale and acted as technical consultant/project leader during project's implementation.

The technique is used for the treatment of effluents from the chromium tanning process, which have to be separately collected from all other effluents in the tannery.

It is a simple method with excellent environmental results and acceptable investment/operational costs.

Recently it has also been applied with the same good results in Indian tanneries (April 1998) in the framework of a project conducted by UNIDO and an Indian engineering company (SVV Engineering) at Pallavaram (Madras).

Description of the technique

After chrome tanning, liquors are collected in a pit, on the top of which a sieve is installed for the removal of coarse particles. After the collection has finished (batch process), the liquors are transferred from the pit into a treatment tank where MgO is added under continuous stirring (3 - 5 hours), in order to transform soluble $Cr\ 3\pm$ salts to settleable $Cr(OH)_3$- sludge.

After sedimentation of $Cr(OH)_3$ overnight, the clear supernatant is decanted through a pipe into the sewerage network of the tannery. The sludge is then mixed (1 - 2 hours) with H_2SO_4 and the recovered chromium sulphate solution can be recycled into the tanning process by replacing up to 35 % of the "fresh" added chrome tanning salt without any negative impact on the final leather quality.

Right after pickling, the recycled chrome liquor is added from the storage tank into the tanning drum through the hollow axle, whereas the additional amount of "fresh" chrome tanning salt is added through the drum's door.

Technical characteristics of the recycling system

Item	Function	Characteristics
gutter	collection of liquors from tanning drums	fiberglass / polyester, movable
pit	storage of collected liquors	concrete
sieve	sieving of coarse particles	stainless steel with holes (mesh size: 10 mm)
feedpump	feeding treatment tank from pit, feeding storage tank from treatment tank	Mohno type
treatment tank	recovery of chromium sulfate solution (settling - redissolving)	reinforced fiberglass polyester, with mechanical stirrer (80 rpm) – flexible decantation pipe
storage tank	storage of recovered chromium solution	reinforced fiberglass polyester
dosing unit	automatic dosing of conc.sulphuric acid	Small tank with dosing pump (4 l/min)

Chemical analysis - quantitative data

Waste water quantity (batch)	8 - 9 m^3
MgO	65 kg
H_2SO_4 (98 %)	58 l
pH	3.5 - 4.0
Cr – conc.of tanning effluents	4000 - 4500 mg/l
Cr – conc. of treated tanning effluents	0.6 - 2.0 mg/l
Cr – conc. of recycled Cr - solution	25 - 45 g/l
pH of recycled Cr - solution	1.8 - 3.0

Ph-vsicochemical background

The recycling of chrome from tanning liquors is based on the principle of precipitation as $Cr(OH)_3$ and redissolving with H_2SO_4.

Cr is transferred into insoluble $Cr(OH)_3$ by raising pH up to 9 with the addition of an alkali. In this process pH control is essential and sludge volume and settling time are related to the type of alkali. The precipitation with MgO gives a low sludge volume (8 %) and a short settling time (1 hour). As a consequence, filtration / dewatering of sludge is avoided, so that the clear supernatant can be simply decanted.

Another advantage of the use of MgO is that any excess addition will not cause pH raising beyond 10, so that any sludge redissolving at higher pH level is avoided.

Environmental performance

Emission value for trivalent chromium is set in Greece at a level of maximum 2 mg/l. Lower values (0.5 mg/1) are set for hexavelent chromium which is currently not applied in Greek tanneries.

A removal efficiency of 99 % has been achieved by applying the chrome recycling system, so that the initial concentration of 4500 mg/l of the separated Cr - tanning effluents can be reduced to 45 mg/l, which after mixing with the other effluents meets the desired level of 2 mg/l.

Monitoring requirements

Due to the fact that this technique is focusing entirely on Cr 3+ reduction, monitoring effluent analysis is limited to the supervision of the Cr 3+ - content of the supernatant. During treatment (addition of MgO) pH - control is needed, in order to maintain optimum flocculation / settling conditions of the $Cr(OH)_3$ - sludge.

Economical evaluation

The addition of chrome tanning agent is 7 % to raw material weight. By a usual production capacity of 6 tonne/day, the total consumption of chrome tanning agent is 420 kg/day.

Taking into consideration that an average quantity of 30 – 35 % of "fresh" chrome can be replaced by the recycled solution, daily savings are 126 - 147 kg. On annual basis (250 working days/year) a total quantity of 31500 - 36750 kg of chrome tanning agent is saved.

The actual operational data are as follows

frequency of treatment	125 batches/year (1 batch/ 2 days)
labour	750 hours/year (6 hours/ 2 days)
energy	12500 kWh/year
MgO	8125 kg/year
H_2SO_4	7250 kg/year

Based on Greek conditions (reference year: 1990 - 91) the economical figures are as follows:

Investment Costs (tanks, pump etc.)   7200000 Gdrs
Running Costs / year
labour (1450 Gdrs/hour)   1087500 Gdrs
energy (21 Gdrs/Kwh)   262500 Gdrs
MgO (46 Gdrs/kg)   373750 Gdrs
H_2SO_4 (17 Gdrs/l)   123250 Gdrs
Total   1847000 Gdrs

Annual savings of chrome tanning agent
(200 Gdrs/kg Salchromo F40)   6300000 - 7350000 Gdrs
Net savings
(annual savings - running costs)   4453000 - 5503000 Gdrs / year
Pay-back period   1.6 (max.) – 1.3 (min.) years

References

- TNO - Institute, Waalwijk, The Netherlands: A survey of the TNO-system for the reduction of the quantity and the polluting load of tannery waste water (1980)

- Report of the Commission of E.U. concerning the project ACE 88/GR 004/A 21 (16.7.92)

- Advertising leaflet of SVV Engineering Industries Hosur - 635136, Tamilnadu, India (project nr. MS/IND/90/244)

I.3. Input/output overview for Elmo Calf AB, Sweden

Table: Input/output overview for Elmo Calf AB per tonne raw hide treated, year 1999.

Annual production	11700 tonne raw hide 2.4 million m^2 finished products, (automotive and furniture use)
	Discharge per tonne raw hide
Water (discharge to the municipal sewage treatment plant)	20 m^3 COD 270 kg BOD$_7$ 120 kg Chrome 0.4 kg Sulphide 0.02 kg Total nitrogen 12.3 kg
Chemicals	470 kg
Energy	11.3 GJ - Electric energy 3.0 GJ - Thermal energy 8.3 GJ
Air	VOC 3.6 kg NH$_3$ 0.7 - 1.0 kg H$_2$S 0.05 kg
Waste	Hair 0.2 kg Untanned 360 kg Tanned 140 kg Sludge from treatment plant 185 kg dry matter (42.6 % dry matter content)
Outlet from treated water (municipal sewage treatment plant with more then 90 % of the load coming from Elmo Calf AB)	COD 27 kg BOD$_7$ 3 kg Chrome 0.007 kg Chrome reduction in average 98.5 % Total nitrogen 9.4 kg

ANNEX II: WASTE WATER TREATMENT PLANTS
II.1 Bader GmbH & Co., Ichenhausen

II.2. Firma Gmelich und Söhne, Grossbottwar. Conventional tanning of bovine hides to upholstery leather

Air　　MnSO$_4$ - salt

Beamhouse → High pH Sewage → **Sump** → **Sulphide oxidation** → *Sample point* | Sulphide < 2 mg/l → **Public Sewer to municipal wwtp**

float ca. 2/3

Pickling/ tanning → Concentrated chromium sewage → **Sump** → **Chromium Precipitation** → **Chromium Recovery** → Supernatant

float ca. 1/20

Chrome sludge　　　　discontinuous

Final clasification (Sedimentation)

Chrome-containing sewage

Retanning dying fatliquoring finishing → **Screen** → **Buffer or equalitation tank** → Lime　FeCl$_3$　Flocculant → **Neutralisation (Precipitation)** → **Final clarification (Sedimentation)** → Effluent <1 mg/l Chrom(total) → **Sewer to municipal wwtp**

float ca. 1/3

Sludge conditioning ⟶ **Sludge filter press** ⟶ re-use

Filtrate

⟶ **Waste water treatment**　⋯⋯▸ **Sludge treatment**

II.3. Bayern-Leder-GmbH, Neutraubling

unhairing
rinse-water
pickling
soaking
finishing

350 m³/d, pH 12.5

Screen 3 mm

Fat for recycling

Clarifier with scraper (40 m³/h)

Sludge

Sulphide oxidation + Buffer

v1 = 500 m³
v2 = 300 m³
v3 = 130 m³

Exhaust air

$MnSO_4/O_2$

Acid/CO_2

De-foamer

H_2O_2

Exhausted air

Biofilter

High speed settler 30 m³/h

Sludge

Phosphorsalt

< 2 mg $^{S^{2-}}$/l

NaOH

De-foamer

670 m³ Membrane bioreactor 20 g/l TS

Excess sludge

Buffer

v1 = 58 m³
v2 = 58 m³

Polymer

Filtrate to Sulphide oxidation

Belt Filter Press

Sludge ca. 5 - 7 t/d

Lime

Agriculture/ Composting

dyeing
rinse-water
fatliquoring
tanning
re-tanning

230 m³/d, pH 4 - 9

Chromiumflocs filtration 300 Mikron

Landfill

pH adjustment pH = 10 56 m³ basin

Chromium precipitation 175 m³

High speed settler 20 m³/h + dosage + scraper

Supernatant

Cr < 1 mg/l

Recessed plate Filter press

Chromium sludge disposal

Discharge to Municipal WW treatment plant

II.4. Cuoiodepur, Pisa, Italy

WWTP, Cuoiodepur, Pisa, Italy

1. Fine grid/screen
2. Pre-accumulation
3. Pump
4. Primary settling tank
5. Equalisation basin, accumulator for oxidising sulphide
6. Pump
7. pH monitor
8. Physical-chemical treatment
9. Flocculation
10. Physical-chemical settling tank
11. Denitrifacation basin
12. Nitrification tank
13. Denitrification-nitrification recycle
14-15 Biological treatment
16. Pump
17. pH monitor
18. Flocculation
19. Calamity-basin
20. pH monitor
22. Primary sludge extraction
23. Physical-chemical sludge extraction
24. Biological sludge extraction and recycle
25. Sludge thickener
26. Sludge thickener
27. Belt press room
28. Filter press room
29. Storage silos for de-watered sludges
30. Internal recycle
31. Municipal waste water storage
32. Ventilation room
34. Odour abatement towers
35. Odour abatement towers
36. Autoclave
38. Emergency storage area for emergency sludge

Primary treatment

Final chemical-phisical treatment

Chemical-phisical treatment

Sludge treatment

Biological treatment

II.5. FIC, S.p.A., Arzignano, Italy

WWTP, FIC, S.p.A., Arzignano, Italy

1. Screen
2. Primary settling tank
3. Equalisation basin
4. Pump
5. Primary settling tank
6. Pre-denitrification
7. Oxidation-nitrification
8. Recycling of aereated mixture
9. Floatation
10. Final sedimentation
11. Flocculation

12. Sludge thickener
13. Belt press
14. Second belt press
15. Second belt press
16. Storage for dewatered sludges
17. Dryer
18. Cogeneration
19. Packaging in big bags
10. Disposal/landfill

1 C   Screen
2 C   Primary settling tank
7 C   Oxisation
10 C Final sedimentation

ANNEX III: LEGAL FRAMEWORK IN MEMBER STATES

Comparison of discharge standards for tannery waste waters for several countries [tan/tm18/Unido]

Parameter (mg/l unless other)	Austria	Brazil	Denmark	France	Germany	Hungary	India	Italy	Japan	Netherlands	Switzerland	UK	USA
pH units	6.5 - 8.5	5.0 - 9.0	6.5 - 8.5	5.5 - 8.5	6.5 - 8.5	5.0 - 10.0	5.5 - 9.0	5.5 - 9.5	5.0 - 4.0	6.5 - 9	6.5 - 8.5	6.0 - 9.0	6.0 - 9.0
Temperature ºC	30	40	30	30	<30		30	25		30			
BOD$_5$	25	60		40 - 200	25**		30	40	160	10	20	20 - 130	40
COD	200				250***	50 - 150	250	160	160				
Susp. solids			30	30 - 100			100	80	300	10 - 30	20	30 - 50	60
Sulphide	0.1	1.0	2.0	2.0	2.0*	0.01 - 5	2.0	1.0			0.1		
Chrome (III)				1.0		2.0 - 5.0	2.0				2.0	2.0 - 5.0	
Chrome (VI)	0.1			0.1	0.5*	0.5 - 1.0		0.2			0.1	0.1	
Chrome total	1.0		0.2		1.0*			2.0	2	0.16			1.0
Chloride								1200		200 - 400	200		4000
Sulphate			300				1000	1000		100 - 200			
Ammonia			2.0	15 - 80	10	2.0 - 3.0		15				100	
TKN			5.0	10 - 60						10			
AOX	0.5				0.5								
Oil/grease		20	5			8 - 50		20	50		20		

* in separate effluent, before mixing with effluent from other processes in the tannery. In case of combined treatment the limit is lower according to the mixing rate
** 25 or reduction by 97.5 %
*** 250 or reduction by at least 90 %

Comparison of discharge standards for sewer systems for several countries [tan/tm18/Unido]

Parameter (mg/l unless other)	Austria	Brazil	Denmark	France	Germany	Hungary	Italy	Netherlands	New Zealand	Switzerland	UK	USA
pH units	6.0 - 9.5	5.0 - 9.0	6.5 - 9.0	6.5 - 9.0		6.5 - 10.0	5.5 - 9.5	6.5 - 10.0	6.0 - 9.0	6.0 - 9.5	6.0 - 10.0	6.0 - 10.0
Temperature ºC	30	40	35	30	<35			30	55	40	40	
BOD$_5$	no limits			1000	no limits		250	no limits				
COD	no limits				no limits		500			3000 - 6000		
Susp. solids				500		75	200	100 - 200		500 - 1000		
Sulphide	2.0	5.0			2.0*	1.0	2.0	2.0	1.0 - 5.0	1.0	5.0	24
Chrome (III)		5.0				5.0				2.0	10 - 20	8 - 19
Chrome (VI)	0.1				0.5*	1.0	0.2	0.0				
Chrome total	3.0		2.0		1.0*		4.0	2.0	5.0 - 50			
Chloride							1200	600				
Sulphate						400	1000	300		300	1000 - 1200	
Ammonia						200	30					
TKN					no limits							
Oil/grease		100			100	60	40	20 - 200				

* in separate effluent, before mixing with effluent from other processes in the tannery. In case of combined treatment the limit is lower according to the mixing rate

Comparison of sludge re-use standards in several countries [tan/tm18/Unido]

Parameter	Belgium	Denmark	England & Wales	France	Germany	Holland	Norway	Sweden	Switzerland	USA
Maximum permissible soil concentration (mg Cr/kg)	150	100	600	150	100	100*				
Maximum permissible sludge concentration (mg Cr/kg DS)	500	100		2000	900	500	200	150	1000	1000
Suggested annual loading limit for Cr (kg/ha/yr)	2.0			6.0	2.0	1.0	0.4	1.0	2.5	20 - 120
Maximum recommended metal loading (kg/ha)			1000	360	210	100	4			100 - 600
Maximum sludge solids loading (t/ha)					167	200		5 in 20	5 yrs	
Suggested maximum annual sludge solids application		1.5		3.0	1.7	2 (arable) 1 (grass)		2	1	2.5 (t/ha)
Minimal application period (years)		20	30		100	100		10	5	
Minimal soil pH			6.5**	6.0						6.0

* Varies according to clay content, eg 50 + (2 x% clay) = max. permissible soil Cr concentration
** The pH quoted is for arable land; for grassland, minimal pH is 6.0