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## SCOPE

This BREF for the tanning of hides and skins covers the following activities within the scope of Annex I to Directive 2010/75/EU:

- activities specified in Section 6.3: *Tanning of hides and skins where the treatment capacity exceeds 12 tonnes of finished products per day*
- activities specified in Section 6.11: *Independently operated treatment of waste water not covered by Directive 91/271/EEC and discharged by an installation undertaking activities covered under Section 6.3 above.*

In particular, this document covers the following processes and activities: core processes in the tanning of hides and skins and the associated activities. In deciding which processes to include in the BREF, the ordinary definition of 'tanning' as 'leather making' has been used. This includes all or any part of the process starting from a raw hide or skin and ending with a piece of the material called leather. For clarity, the word 'tanning' is used within this BREF only in the technical sense used within the industry, i.e. as meaning that stage of the leather making process at which collagen fibres are stabilised by tanning agents.

The scope of the BREF is restricted to the processing of material of ovine and bovine origin, as the production capacities of plants using other types of raw material are far below the threshold value in the Directive.

Other reference documents which are relevant for the sector covered in this document are the following:

Reference document	Subject
Energy Efficiency (ENE)	General energy efficiency
Economics and Cross-Media Effects (ECM)	Economics and cross-media effects of techniques
General Principles of Monitoring (MON)	Emissions and consumption monitoring
Emissions from storage (EFS)	Emissions from tanks, pipework and stored chemicals
Waste Incineration (WI)	Waste Incineration
Waste Treatments Industries (WT)	Waste Treatment

The scope of the BREF does not include matters that only concern safety in the workplace or the safety of products because these matters are not covered by the Directive. They are discussed only where they affect matters within the scope of the Directive.



# 1 GENERAL INFORMATION ON THE STRUCTURE OF THE INDUSTRY

The leather making 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. Preserving hides and skins by tanning and performing various steps of preparation and finishing, generates a final product with specific properties: stability, appearance, water resistance, temperature resistance, elasticity and permeability for perspiration and air, etc.

Leather is a material used in the manufacture of a variety of products, for which it is often the major material input. These include shoes, clothing, leather goods, furniture, upholstery for cars, boats and aircraft, and many other items in daily use. These different applications require different types of leather.

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

Most of the basic stages of leather making are still the same, but the industry has undergone important changes and with respect to environmental protection, major improvements have been made.

Provisions for pollution control, waste minimisation and disposal, the correct use of chemicals, and accident prevention are essential for minimising the potential impact on air, water, and soil from the processing of hides and skins.

The solutions for better environmental performance are frequently complex and have to be assessed with regard to their overall costs and benefits. Changing techniques may have potential impacts on other process units and techniques need to be selected which achieve the best environmental outcome, from the process considered as a whole. Best available techniques will be balanced against these criteria and may therefore involve changes within process units as well as end-of-pipe abatement techniques.

Sophisticated treatment and processing techniques play an important part in achieving improved competitiveness and environmental performance. Competent operation and regular maintenance are as essential as the choice of technique. This includes good management decisions/practices; education and supervision of the workforce; and the monitoring of processes and environmental performance.

## 1.1 Overall production in Europe and worldwide

The production of raw hides and skins depends on animal population and the slaughter rate and is related mainly to meat consumption. On a global scale, significant cattle populations are to be found in China, the US, Brazil, Argentina, India, Russia and the EU. Sheep and lamb skins originate predominantly in China, New Zealand, Australia, the Near East and the EU.

Cattle kept in Europe and in countries with similar systems of animal husbandry generally suffer less skin damage than those kept under herding or ranching systems. Their hides are said to offer a higher yield of useful leather for this reason. European sourced hides are unlikely to be contaminated by banned pesticides.

While EU hides and skins are increasingly exported, EU tanners face barriers to the access of raw materials from some third countries. Export taxes and export-restrictions on raw hides and skins and on the intermediate material 'wet blue', constitute trade barriers. Only about 40 % of the globally available hides and skins enter the free international market, with consequent problems of dual pricing of raw materials, price volatility on open markets, and relative scarcity of raw material.

The main centres for raw skin production do not necessarily coincide with the major leather production centres, thus indicating the necessity of proper storage and means of transport. Typically, raw hides and skins are traded in the salted condition, or (increasingly) as intermediate products, particularly as 'wet blue' for bovine hides and the pickled condition for ovine skins.

While developing countries hold over 78 % of the world bovine herd they together produce about 64 % of the number of hides, or 57 % of total output by weight. With respect to sheepskins, developing countries account for about 65 % of the global number of skins produced.

The trend in the trading of bovine hides and skins is that developing countries change from being net exporters to being net importers, reflecting an expansion in tannery capacity, especially in the Far East and in Latin America. As a result, the position of developed countries has changed. The EU became a net exporter of raw bovine hides in 2004.

As regards sheepskins, developing countries became net importers in the mid-nineties. Europe became a net exporter of raw sheepskins in 2002.

The origin of EU imports is presented in Table 1.1.

Table 1.1: Raw hides and skins: top 10 EU suppliers

	2006		2007		2008		2009		2010		Growth (%)
	Value (million EUR)	Share (%)	Value (million EUR)	Share (%)	Value (million EUR)	Share (%)	Value (million EUR)	Share (%)	Value (million EUR)	Share (%)	2006 to 2010
<b>Total</b>	<b>482</b>	<b>100.0</b>	<b>484</b>	<b>100.0</b>	<b>394</b>	<b>100.0</b>	<b>276</b>	<b>100.0</b>	<b>424</b>	<b>100.0</b>	<b>-12.0</b>
US	85	17.7	77	15.9	69	17.6	42	15.1	74	17.4	-13.4
Switzerland	33	6.9	33	6.8	31	7.8	24	8.7	38	9.0	14.9
Bosnia and Herzegovina	37	7.8	34	7.0	27	6.8	17	6.0	36	8.5	-3.4
Iran	33	6.8	44	9.1	44	11.1	33	11.9	36	8.4	9.9
South Africa	29	6.0	36	7.5	32	8.2	22	8.1	30	7.1	4.2
Australia	34	7.1	38	7.8	29	7.3	21	7.6	28	6.7	-17.2
New Zealand	43	8.9	32	6.7	32	8.2	26	9.2	28	6.6	-35.2
Norway	15	3.1	14	2.8	15	3.8	9	3.1	16	3.7	5.1
Belarus	4	0.8	3	0.6	1	0.2	6	2.0	13	3.2	232.6
Serbia	6	1.3	6	1.3	5	1.3	5	2.0	11	2.6	79.9

*Source:* [ 164, Eurostat 2012 ].

EU imports of raw hides and skins have fallen significantly since the turn of the millennium. Raw bovine hide imports fell by 64.9 % from 353 575.3 tonnes in 2000 to about 124 200 tonnes in 2007. For sheep skins, the fall was close to 38 % and the quantities involved are well below those in the bovine sector. In 2007, less than 42 400 tonnes entered the EU. A similar scenario applies to goatskins and other raw skins.

The US remains the EU's top supplier of raw hides and skins with a share of more than 15 % in value terms of all extra-EU imports.

Apart from the EU, the major leather production centres in the world (on the basis of 2008 figures) are found in Mexico, Argentina, Brazil, South Korea, China, India, and Pakistan.

The global output of heavy leather increased in the mid-nineties. The principal production regions are the Near East and Far East. The output of heavy leather continued to decline in developed regions.

The EU's share of 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 6.0 million tonnes of raw hides on a wet salted basis were processed to yield about 522 600 tonnes of heavy leather and about 1185 million square metres of light leather, including split leather. In comparison, Europe produced about 71 700 tonnes of heavy leather and about 230 million square metres of light leather. For goat and sheep skins, worldwide 646 800 tonnes of raw skins on a dry basis were converted into almost 438 million square metres of sheep and goat leather. The light leather production from goat and sheep skins in Europe yielded approximately 82 million square metres. All figures represent an average of the years 2001 to 2003 [98, COTANCE 2008].

With a positive trade balance in 2005 of EUR 584 million in finished leather, the EU leather industry is successfully resisting the gradual increase in imports in quantitative terms. The EU is still the world's largest supplier of leather in the international marketplace. Italy still represents around 15 % of the world's leather production and about 60 % of Europe's total. Exports account for some 40 to 90 % of the leather making 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. The top markets for the European tanners are presented in Table 1.2



Table 1.2: Top markets for European tanners for finished leather

	2006		2007		2008		2009		2010		Growth (%)
	Value (million EUR)	Share (%)	Value (million EUR)	Share (%)	Value (million EUR)	Share (%)	Value (million EUR)	Share (%)	Value (million EUR)	Share (%)	2006 to 2010
<b>Total</b>	<b>2 634</b>	<b>100.0</b>	<b>2 737</b>	<b>100.0</b>	<b>2 487</b>	<b>100.0</b>	<b>2 009</b>	<b>100.0</b>	<b>2 495</b>	<b>100.0</b>	<b>-5.3</b>
Hong Kong	677	25.7	616	22.5	534	21.5	438	21.8	563	22.6	-16.8
China	293	11.1	369	13.5	317	12.8	291	14.5	363	14.5	23.6
Tunisia	150	5.7	180	6.6	183	7.4	166	8.3	186	7.4	23.5
US	279	10.6	239	8.7	205	8.2	121	6.0	169	6.8	-39.2
Croatia	61	2.3	136	5.0	147	5.9	106	5.3	98	3.9	59.0
India	88	3.4	96	3.5	95	3.8	81	4.1	96	3.8	8.2
Turkey	127	4.8	122	4.5	83	3.3	59	2.9	79	3.2	-37.7
Vietnam	49	1.9	61	2.2	68	2.7	60	3.0	79	3.2	60.5
South Korea	79	3.0	65	2.4	55	2.2	60	3.0	73	2.9	-7.6
Morocco	52	2.0	55	2.0	60	2.4	61	3.0	73	2.9	40.4

*Source:* [ 164, Eurostat 2012 ].

## 1.2 Distribution of the EU leather 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 together with France, Germany, Portugal, and the UK accounts for most of the balance of the EU leather industry.

In 2007, Italy alone accounted for about 60 % of the production in the EU and 15 % on a worldwide basis [98, COTANCE 2008]. Italy has about 1415 tanneries, Spain about 140, France 62, and Germany 30. Production units in Italy are generally smaller than in the other countries. In the Nordic countries, leather making was a major industry, but only a few tanneries remain. In 2007, there was one tannery in Denmark, with four in Sweden, and approximately nine of importance in Finland [90, Tanneries 2008].

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 (Santa Croce sull'Arno and Ponte a Egola with 615 companies), Vicenza (Arzignano, Zermeghedo and Montebello Vicentino with about 465 companies), Avellino (Solofra), Naples (about 193 companies) and Lombardy (Turbigio, Castano Primo with about 70 companies) most of the EU leather sector's operators are concentrated.

Santa Croce and Arzignano are the centres of bovine leather making 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 (in Vic and Igualada near Barcelona), and about 35 % in Valencia, Murcia and Madrid. In Portugal, about 85 companies are concentrated in Lisbon and the Tagus Valley Region (Alcanena), and in the Northern Region (Porto) there are about 15 companies. In Greece, there are smaller leather producing regions in Thessaloniki, Crete, and Athens. There are similar smaller centres of production in the Midi-Pyrénées in France.

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

Despite the progressive enlargement of the EU to 27 members, the total number of tanneries continues to decline. While in 1998 there were still over 3 000 tanneries in the EU-15 and about 50 000 workers, the leather sector has shrunk to fewer than 3 000 enterprises and fewer than 50 000 people including the new Member States. Over the last decade, the leather sector has lost a further third of its industrial capacity and a third of its work force. Most of the loss in industrial capacity has been in Northern European countries. Germany and the United Kingdom have suffered a particularly sharp decline in the number of tanneries. Southern European countries like Italy and Spain are now also losing enterprises in the leather sector.

Tanneries in Europe are small- and medium-sized enterprises (SMEs) and 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.

Hides and skins are imported in a raw state (wet-salted or dry-salted) or as partly processed products, for example wet blues. An increase in the use of imported intermediate materials means that certain steps of the leather-making process are transferred to other countries, particularly to third world countries. From the environmental point of view, this development has two consequences. First, environmentally important process steps such as those carried out in the beamhouse and tanning are transferred to other countries, leading to 'pollution creep'. Secondly, particular agents which are restricted or prohibited within the EU, might be applied and could appear in the effluents of finishing plants.

**Structure of the European Leather Industry in 2007**

The distribution of leather manufacturing in European countries in 2007 is shown in Table 1.3.

**Table 1.3: Structure of the European leather industry, 2007**

Country	Employees	Companies	Turnover (thousand EUR)	Exports (%)	Production (thousand m <sup>2</sup> )	
					Cattle/calf ( <sup>1</sup> )	Sheep/goat ( <sup>2</sup> )
Belgium	124	1	21 742	94.70	492	
Finland	147	12	19 000	80.00		
France	1721	62	296 000	41.00	3490	3247
Germany ( <sup>3</sup> )	2125	30	440 000	60.00	12 000	500
Greece ( <sup>4</sup> )	476	68				
Hungary	65	3	4 200	67.20		
Italy	17 175	1496	5 435 578	67.00	126 742	40 603
Netherlands ( <sup>3</sup> )	380	15	85 000	75.00	3500 ( <sup>1</sup> )	
Portugal						
Slovenia						
Spain	3 974	140	851 407	39.90	20 950	11 792
Sweden	430	4	76 500	90.00	2400	80
UK	1300	25	220 000	75.00	3890	2170
Lithuania ( <sup>3</sup> )	200	4	15 000	90.00	750	
Bulgaria		19				
<b>EU Total</b>	<b>28 117</b>	<b>1879</b>	<b>7 464 427</b>	<b>70.90</b>	<b>170 714</b>	<b>58 392</b>
Norway	102	2	19 000	95.00	431	
Switzerland						
<b>EU + EFTA Total</b>	<b>28 219</b>	<b>1881</b>	<b>7 483 427</b>		<b>171 145</b>	<b>58 392</b>

(<sup>1</sup>) Including buffalo leather and other leather made of hides.  
(<sup>2</sup>) Including pig leather and other leather made of skins.  
(<sup>3</sup>) Provisional figures.  
(<sup>4</sup>) In volume: estimated by Cotance.  
Source: [98, COTANCE 2008].

Demand for leather depends on a multitude of factors, including how it is perceived by consumers. Price plays a fundamental role, particularly in the middle and lower end of the market.

EU tanners now adjust 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 (e.g. automotive leather) or innovations in fashion. The transition from quantity to quality has swept through much of Western Europe's leather industry during the last decades and is still ongoing.

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 17 % of EU tanners' output, and the leather goods sector, 13 %. These ratios vary widely from one member state to another. Northern European countries (Sweden, Germany, Austria, and the UK) have become important suppliers of upholstery leathers for the automotive and aircraft industries. Furniture upholstery leather is produced in a number of countries (Sweden, Germany, Austria, Netherlands, Italy,

Spain, Poland, and Slovakia). The production of leather for leather goods manufacture is also widely dispersed across Europe (Italy, Spain, Portugal, Finland, Bulgaria, and Greece).

The relative proportions of European leather used in the most important manufacturing sectors are shown in Table 1.4.

**Table 1.4: Destination of European leather output**

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

Leather making is a raw materials- and capital-intensive industry. Raw materials account for 50 to 70 % of production costs, labour 7 to 15 %, chemicals about 10 % and energy 3 %. EU tanners' environmental costs are estimated at about 5 % of their turnover [22, DG III 1997]. The remaining 5 to 15 % are other production costs. These figures refer to Europe in general [90, Tanneries 2008].

The innovations in the leather industry related to environmental performance are usually focused on chemicals rather than on machines. The most obvious changes during the 21st century have been in the finishing of leather, specifically the change to water-based finishes as 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 high performance finishing chemicals, reasonably high quality leather can be manufactured even from hides and skins with natural defects. High quality aniline leather requires comparatively little finishing but it is necessary to use faultless hides or skins as raw material.

The high cost of raw materials makes it risky to experiment with unproven technological solutions and can be a barrier against investment. Investment in environmental improvement 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 adapted 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 leather industry

Environmental concerns in a tannery include the prevention and control of emissions to water, air, and soil. A range of process chemicals is used, some of which may require special treatment in the effluent.

The environmental effects that have to be taken into account in any tannery 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, the 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.

Table 3.1 in Section 3.2 contains a detailed list of raw materials and the more important auxiliaries used, the releases to waste water and air, and the residues for each process step. Figure 2.4 in Section 2.6.1 illustrates process inputs and liquid effluent streams.

About 20 – 25 % of raw (salted) bovine hide weight is transformed into leather; for sheep or goat skins, this range is 12 – 15 %, based on salted raw skins. When sole leather is produced, the proportion is approximately 65 %.

Some of the organic material which is not transformed into product may be recovered as useful by-products, but the rest will be solid residues or a contaminant of the liquid effluent. The processing of 1 tonne of raw hides generates approximately 600 kg of solids and 15 – 50 m<sup>3</sup> of effluent containing about 250 kg COD and 100 kg BOD [9, UNIDO-UNEP 1991]. About 500 kg of process chemicals are added. The quantities and qualities of emissions and waste produced by tanneries strongly depend on the type of leather being produced, the source of hides and skins, and the techniques applied. Figure 3.1 in Section 3.2 gives an input/output overview for the leather making process.

Of all world tanneries, 80 – 90 % use chromium(III) salts in their tanning processes. Chromium(III) is not listed in Annex X of the Water Framework Directive 2000/60/EC following its amendment by the Directive 2008/105/EC on Priority Substances. Tannery wastes containing chromium(III) 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.

Chromium(VI) is not used in tanning [87, EURAR 21508 2005]. For reasons of product safety, tanners in Europe employ specific precautions to prevent the oxidation of chromium(III) to chromium(VI) in the leather during manufacture [85, Hauber and Knödler 2008]. The substitution of chromium tanning agents has been limited because no alternative has been found which provides leathers with the same qualities. Some users, particularly vehicle manufacturers, demand the use of alternative tanning agents on leathers supplied to them. In a number of Member States, monitoring of chromium(VI) in tannery waste waters is carried out, either by the permitting authority or by the operator. The levels of chromium(VI) found have all been insignificant, or below the level of detection.

Most of the steps of a tannery's operations are performed in water. Consequently, waste water is one of the major concerns in tanneries. The characteristics of (untreated) waste water are a high chemical and biochemical oxygen demand, and a high salt and process chemical content. The data have to be interpreted in the context of the processed hide weight and concentrations have to be discussed with regard to the loads. Large variations in concentrations may occur due to different water consumption and process types [90, Tanneries 2008].

Tanneries in Europe usually discharge their waste water effluents to large waste water treatment plants, which are either urban waste water treatment plants or plants operated for large leather making clusters. Few tanneries discharge directly to surface water. Most tanneries discharging

to sewer systems have some form of on-site effluent treatment installed, ranging from pretreatment to biological treatment.

Overall, European bovine tanners are estimated to generate 400 000 tonnes of sludge per year and around the same amount of other solid residues with a moisture content between 40 % and 80 %. In general terms, the solids produced during the primary treatment of tannery effluent amount to 5 to 10 % of the total volume of effluent treated. 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 that generated by primary treatment alone. Most tanneries will dewater their sludge to reduce the volume of sludge for disposal. Typically, dewatered sludge has 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 sludge.

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

For many residues, further reuse and recycling options exist. The viability of reuse options depends not only on the composition but also on the price of alternative raw materials and the quantities produced, as well as the cost of transport to interested users.

In some Member States, the landfilling of wastes with high organic content is now subject to more restriction than it was in the past, mainly due to the implementation of waste and landfill legislation. However, landfilling is still a legal option for many of these waste fractions in several Member States and in some cases the only available disposal route. The legislation had a considerable impact on trends to increase reusing and recycling versus landfilling. Member States were required to establish a national strategy for the reduction of biodegradable waste going to landfills. These strategies included reduction measures by means of, in particular, recycling, composting, biogas production, or materials or energy recovery and have affected tanneries all over Europe.

More than 80 % of tanneries in Europe discharge their effluent to public sewers. The main exceptions are those parts of Italy and Spain, where the tanneries are in clusters connected to common effluent treatment plants. Further sludge will be generated in urban waste water treatment plants that treat tannery effluents in combination with other industrial and domestic effluents. No data are available on the amount of additional sludge that is generated as a result of the treatment of tannery wastes in urban waste water treatment plants.

Waste disposal routes for waste water treatment sludges differ in all Member States and are strongly dependent on the local disposal facilities and the acceptability of applying sludge to agricultural land.

Air emissions can be toxic and/or may contain odorous substances, e.g. sulphides, ammonia, organic solvents, particulates, and standard gas emissions from energy supply and other incineration processes. The emission of organic solvents has been regulated by laws implementing the Solvent Emissions Directive, now replaced by Chapter V of the IED.

Emissions of toxic substances such as sulphides, ammonia and many organic solvents may reach levels requiring rigorous ventilation of the workplace [17, UNEP 1991]. Leather dust from mechanical operations and powdered dyestuffs can also require special ventilation arrangements. The odour from substances such as sulphides, thioles, and organic solvents and odour from putrefaction may constitute a major problem.

For ambient air quality, emissions of VOCs, NH<sub>3</sub>, sulphides, and emissions from incineration processes for power supply are relevant. For the incineration of waste from tanneries, further toxic releases (chromium(VI), PCDD/F due to halogenated organic compounds, PAHs) have to be taken into consideration.

Soil and possibly groundwater can be affected directly by the activities of a tannery, particularly from accidental releases of process chemicals and wastes.

Tannery operators are required to comply with Regulation (EC) No. 1069/2009, which lays down animal and public health, rules for the collection, transport, storage, handling, processing, and use or disposal of animal by-products. Animal by-products from non-member countries, including hides and skins, may only be imported subject to a system of approval prescribed in the Regulation.









## 2.2 Beamhouse (or limeyard) operations

The operations carried out in that part of the plant known as the beamhouse or limeyard are often carried out in the same processing vessels, with changes of float and chemicals. In modern practice the vessels are either mixers (see Figure 2.2) or drums (see Figure 2.3).



Figure 2.2: A mixer or inclined processor

### 2.2.1 Soaking

Soaking is carried out to allow hides and skins to reabsorb any water which may have been lost after flaying, in the curing process, or during transport. Soaking also cleans the hides and skins (removal of dung, blood, dirt, etc.) and removes interfibrillary material.

The soaking methods used 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. The duration of soaking can range from several hours to a few days.

Putrefying bacteria can thrive during soaking and biocides may be added to curtail their activity. Depending on the type of raw materials being soaked, other additives may be used, such as surfactants and enzyme preparations.

### 2.2.2 Unhairing and liming of bovine hides

The aim of unhairing and liming is to remove the hair, epidermis, and to some degree, the interfibrillary proteins, and to prepare the hide or skin for the removal of adhering flesh and fat by the fleshing process.

Hair removal is performed by chemical and mechanical means. The keratinous material (hair, hair roots, epidermis) and fat are traditionally eliminated from the pelts mainly with sulphides ( $\text{NaHS}$  or  $\text{Na}_2\text{S}$ ) and lime. Alternatives to inorganic sulphides include organic sulphur compounds such as thioles or sodium thioglycolate in combination with strong alkali. Enzymatic preparations are sometimes added to improve the performance of the process.

After liming in a tannery recognised as a 'technical plant' by the competent authority, the hides or skins are no longer subject to animal by-products controls.















The retanned, dyed, and fatliquored leather is usually washed before being piled onto a 'horse' to 'age' (letting the fat migrate from the surface to the interior of the material).

### **2.4.6 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, 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.

## 2.5 Dry finishing operations

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 as required for the end use, including:

- extensibility
- break
- light and perspiration fastness
- water vapour permeability, and
- water resistance.

Generally, finishing operations can be divided into mechanical finishing processes and coating.

### 2.5.1 Mechanical finishing processes

A wide range of mechanical finishing processes may be carried out to improve the appearance and the feel of the leather. The following list of operations includes commonly used mechanical finishing processes:

- 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 (flattening);
- embossing a pattern into the leather surface.

These operations may be carried out before or after applying a coat, or between the applications of coatings. The list is not exhaustive and many other processes exist for special leathers such as sole leathers, wool-on skins, and special effects leathers.

### 2.5.2 Applying a surface coat

The purpose of applying a surface coat is:

- to provide protection from contaminants (water, oil, soiling);
- to provide colour;
- 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;
- curtain coating, which is passing the leather through a curtain of finishing material;
- roller coating, which is the application of finishing mix by a roller;
- transfer coating, which is the transfer of a film/foil onto leather previously treated with an adhesive.

## 2.6 Abatement of potential releases to the environment

The main releases from tanneries are waste water, solid residues, and odours. Treatment may be required before release, as detailed below.

### 2.6.1 Waste water streams

Tanneries generate effluents that are typically high in organic and inorganic pollutants. Since tanneries employ a sequence of batch processes, and use a wide range of raw materials, their effluent is complex in nature, with variations in characteristics from time to time, process to process and tannery to tannery. The main inputs and the effluents which might be produced are shown schematically in Figure 2.4.

Tannery effluents may be treated fully on site, to meet standards specified for discharges to surface waters, or they may be discharged untreated for treatment elsewhere. In some tanneries, part of the treatment is carried out on site, with the remainder undertaken off site. Off-site treatment may be undertaken in specialist treatment works serving clusters of tanneries, or in sewage treatment works serving the locality.

The waste water treatment strategies employed by tanneries are so varied that it is difficult to generalise, but most employ a selection of the methods listed in Table 2.1.

**Table 2.1: Effluent treatment methods used by tanneries**

<b>Mechanical pretreatment</b>	Consists of skimming of fats, oil and grease, and gravity settling (sedimentation).
<b>Physico-chemical treatment</b>	Includes oxidation, precipitation, sedimentation, flotation, equalising flows and neutralisation. It is mainly performed to remove organic matter, sulphide from beamhouse effluents and chromium(III) from tanning and post-tanning operations.
<b>Biological treatment</b>	By bio-aeration or percolating filter. The high organic content is reduced. A nitrification/denitrification step is being introduced in countries with strict nitrogen discharge limits.
<b>Sedimentation</b>	Secondary sedimentation is used to separate sludge from the purified overflow. The primary sludge that 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 generally applied to reduce the volume of sludge for disposal. This is mostly done by mechanical equipment such as filter presses or centrifuges, sometimes followed by a drying process. Prior to dewatering, sludge thickeners can be employed to thicken further sludges.

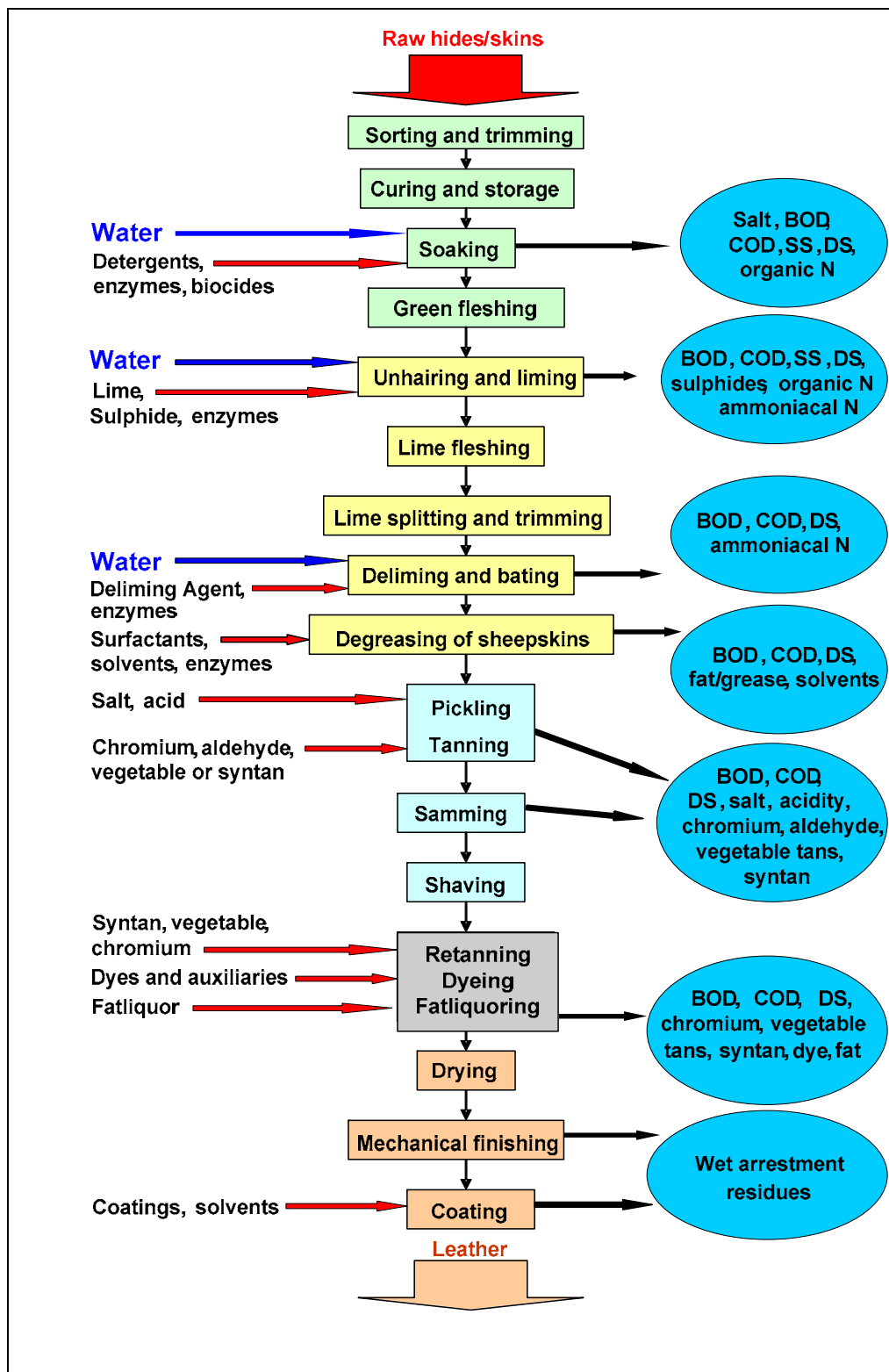


Figure 2.4: Main inputs and aqueous effluents

## 2.6.2 By-products and wastes

Only 20 – 25 % of the weight of the raw hide or skin is processed to leather. The exact percentage depends on the animal species and product specification. The rest of the weight plus the unused fraction of the process chemicals either is discharged in the waste water or arises as a residue at some point in the process. Residues from tanneries can be by-products, non-hazardous waste or hazardous waste

The European Commission has established a harmonised list of wastes (Commission Decision 2000/532/EC). The part of the list which describes tannery wastes is shown in Table 2.2.

**Table 2.2: European waste list**

Waste list code no.	Waste description
<b>04 01</b>	<b>Wastes from the leather and fur industry</b>
04 01 01	Fleshings and lime split waste
04 01 02	Liming waste
04 01 03 <sup>(1)</sup>	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
<sup>(1)</sup> Hazardous wastes for the purposes of Council Directive 91/689/EEC.	

No distinction is made in the waste list between green fleshings and limed fleshings. Such a distinction may be made in the application of Regulation (EC) No. 1069/2009 on animal by-products (ABP). Provided that the tannery is recognised by the competent authority as a 'technical plant', materials which have been limed are no longer subject to the requirements of the ABP Regulation.

Residues 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 processes other than finishing, solids from air abatement, packaging material, and others [3, Andres 1995]. The type of waste and the amounts of waste vary significantly according to the processes used for leather production and for waste water treatment.

Some residues, such as fleshings, lime splits, grease, shavings, and trimmings, may be sold or given away as raw materials to other industry sectors. Some of the wastes may be treated on site to facilitate reuse or disposal. Such treatments could include dewatering, compacting, 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 and odours.



The local availability of industries which can use tannery residues, is a major determinant of the options available to any particular tannery, as is the local availability of treatment and disposal facilities.

Possible arisings of co-products, by-products and wastes are shown schematically in Figure 2.5.

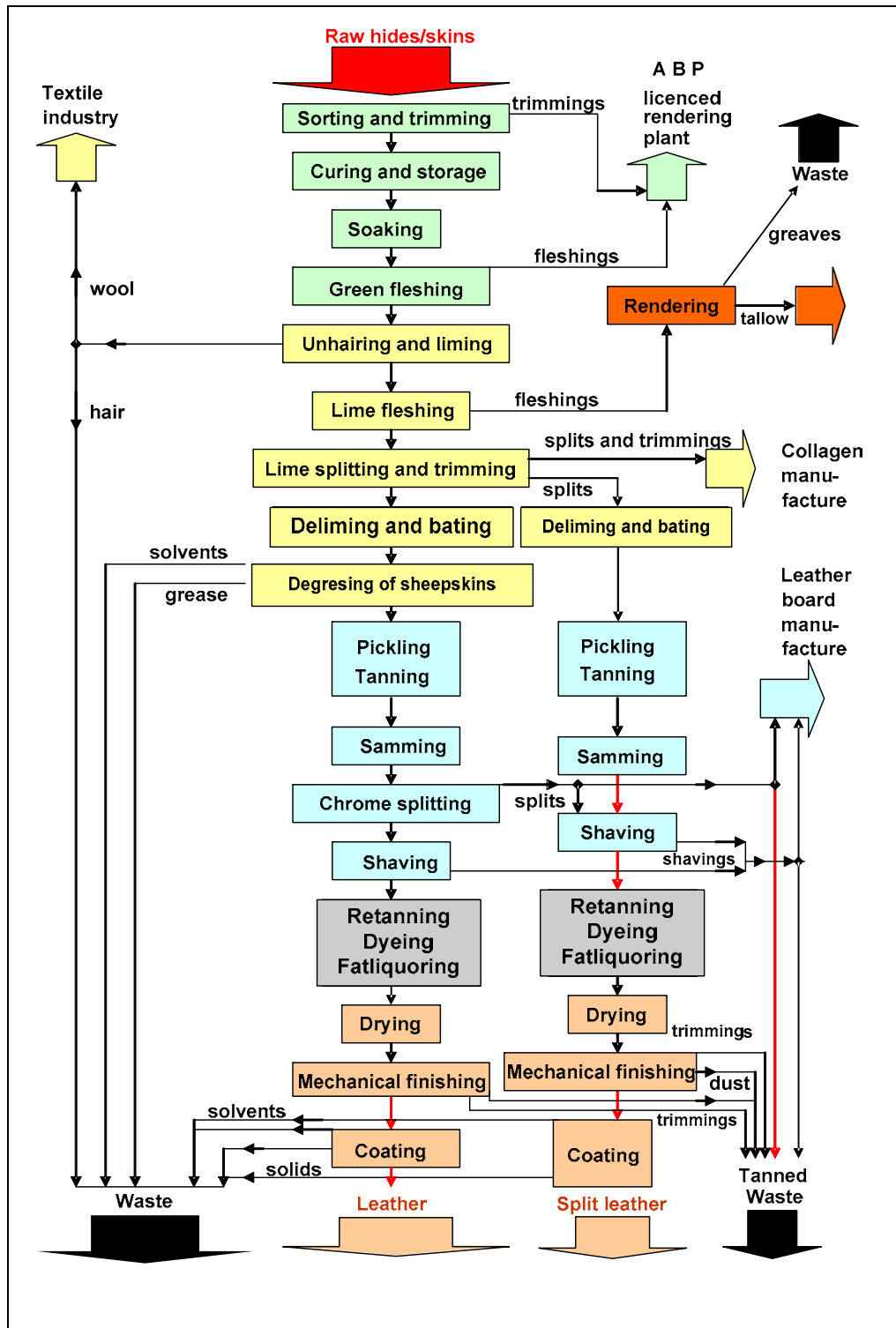


Figure 2.5: Possible arisings of co-products, by-products, and wastes

### 2.6.3 Air emissions

Compared to emissions to water, air emissions occur generally in relatively small quantities. Traditionally tanneries have been associated with odour rather than any other air emissions, although the emissions of organic solvents have been a major problem. Modern tanneries should not have significant odour emission problems. Whether a tannery has the following air emissions depends on the type of processes employed:

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

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

#### **Airborne particulate emissions**

The majority of particulate matter emissions arise from the dry processes, such as milling, and buffing. Spray mist arises from spray finishing. These emissions can be abated by using filters.

Enclosed dosing equipment, process chemicals in liquid form and soluble packaging are all used to curtail dust emissions, but their main effect is on dust levels within the workplace.

#### **Organic solvents**

The principal source of organic solvent emissions in tanneries is the coating process. Examples of solvents that are used are butyl acetate, ethyl acetate, acetone, methyl isobutyl ketone and methyl ethyl ketone. The consumption of organic solvents can be reduced by the introduction of water-borne coating materials, as well as modern methods of application, such as improved spraying techniques and roller coating. Tanneries employing solvent-based degreasing processes for sheepskins also have organic solvent emissions requiring special abatement.

#### **Hydrogen sulphide**

Hydrogen sulphide gas is both toxic in relatively low concentrations and odorous in miniscule concentrations.

Hydrogen sulphide can be released during the handling or treatment of effluent streams that contain high concentrations of sulphide, such as the effluent streams from the unhairing process step. Under alkaline conditions, sulphides remain largely in solution, but when the pH of the solution drops below 9.5, hydrogen sulphide evolves from the effluent: the lower the pH the higher the rate of evolution.

For this reason alkaline and acidic liquors should be handled separately in the tannery. They should also be treated separately in the effluent treatment plant until the sulphide has been fully oxidised, unless the mixing is undertaken in an enclosed vessel with air extraction through a scrubber.

Hydrogen sulphide can be released during the delimiting and pickling processes. The addition of small quantities of oxidising compounds (such as hydrogen peroxide or sodium bisulphite) can reduce the amount of hydrogen sulphide being released during delimiting. Optimisation of washing processes in order to remove sulphide before delimiting and pickling will also reduce the emissions.

Local exhaust ventilation from processing areas (with exhaust treatment) may be necessary to control fugitive releases.

Hydrogen sulphide may also be formed by anaerobic bacteria from sulphates during waste water treatment, and sludge storage and dewatering operations. Hydrogen sulphide can also be formed in the sewer system, and in waste disposal sites taking tannery wastes

### **Ammonia**

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

### **Odour**

Odours from tanneries can be a major cause of complaints depending on the location of the tannery. They are generated during several of the processes which collectively turn hides and skins into finished leather, and from the wastes and effluents from those processes.

Both odour emissions and deterioration of the raw material stocks can be controlled by the correct curing and storage of hides and skins and rigorous stock rotation. Cool and dry conditions should be maintained in storage facilities for salted materials and doors should remain closed. Temperature-controlled storage is required for unsalted hides.

In addition to hydrogen sulphide and ammonia, there are characteristic mixtures of organic compounds which are noticeable (even more noticeable when hydrogen sulphide and ammonia are controlled) during each stage of the process.

Tannery buildings require good ventilation for safety reasons, due to the potential for hydrogen sulphide and ammonia releases. Air extracted from some areas may need treatment.

In tanneries with on-site treatment plants for liquid effluents, these are usually the largest source of odour emissions. Oxidation of substances in solution involves bringing air (or oxygen) into intimate contact with the liquid. This also means that odorous compounds can pass from the liquid into the air.

Odorous air can be treated in a biofilter. Because these are biological systems, the concentrations of both ammonia and hydrogen sulphide must be controlled and a chemically dosed scrubber may be necessary as a pretreatment (or substitute).

### **Other air emissions**

Sulphur dioxide emissions might occur during bleaching.

Where energy is obtained from waste incineration, the requirements of laws implementing what is now Chapter IV of the Directive must be followed.

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## 3 CURRENT EMISSION AND CONSUMPTION LEVELS

### 3.1 Introduction

This chapter gives information as to the typical emission 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 emission and consumption 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.

Figures are given for the performances of both conventional tanneries and advanced plants. Throughout the document, the term 'conventional' will refer to tanneries that have not adopted measures to reduce their environmental impact and 'advanced' will refer to tanneries that have done so. The techniques to consider in the determination of BAT will be presented in Chapter 4.

## 3.2 Inputs and outputs

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 has the potential to contaminate soil and groundwater. The use of certain techniques for production processes and abatement may result in some cross-media effects.

The main releases of waste water originate from wet processing in the beamhouse, the tanyard, and the post-tanning operations.

The potential releases to air are:

- gaseous emissions from wet processing and effluent treatment
- particulate matter from dry-finishing, and
- solvent vapours from the degreasing of sheepskins and from coating.

The main solid outputs from leather making arise from fleshing, splitting, and shaving. Some of these solid outputs may be sold as raw materials to other industry sectors. A further solid output is the sludge from effluent treatment (where carried out on site).

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

The raw materials used by the European tanneries, which are dealt with in this document, are bovine or ovine. They originate from EU and non-EU countries. Hides and skins may arrive in a dried, salted, or fresh condition. Plants carrying out only part of the process may receive materials in a pickled, wet blue/wet white or crust state.

Figure 3.1 provides a rough overview of the input and output flows in a tannery running a conventional process. Figure 3.2 gives an input/output overview from an advanced tannery producing upholstery leather. The tannery has its own waste water treatment plant.

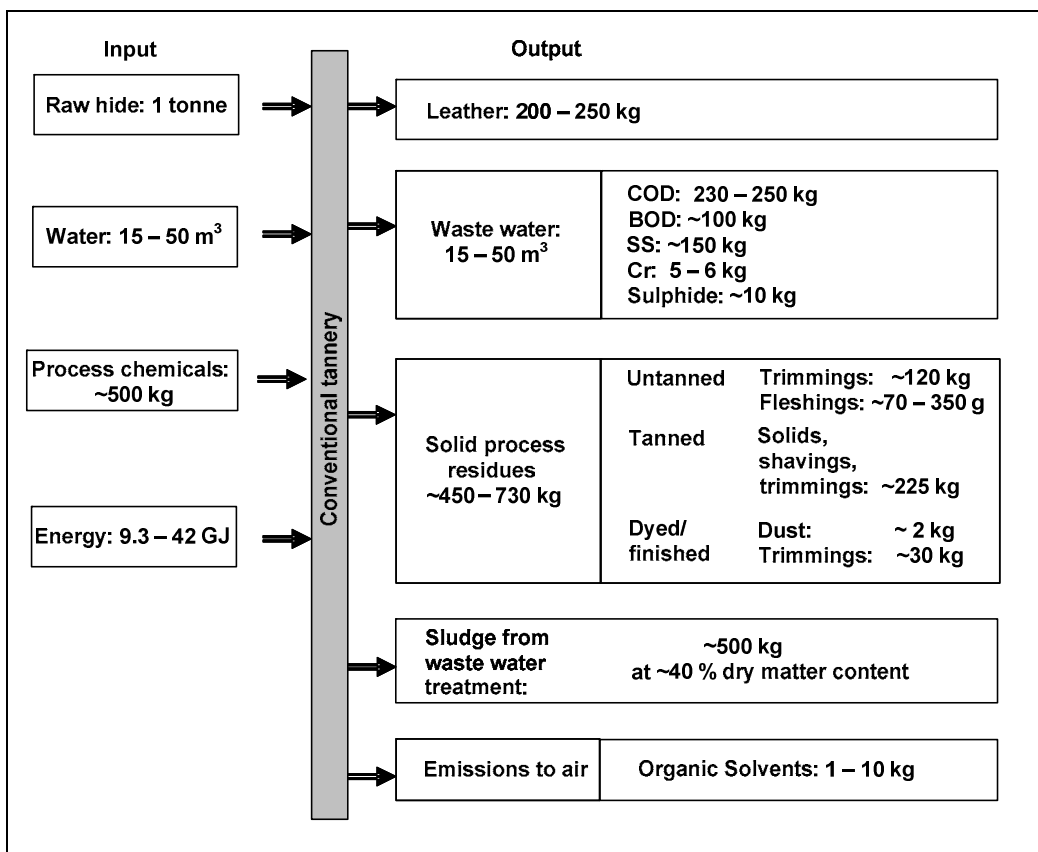


Figure 3.1: Input/output overview for a conventional (chrome-tanning) process for bovine salted hides per tonne of raw hide treated

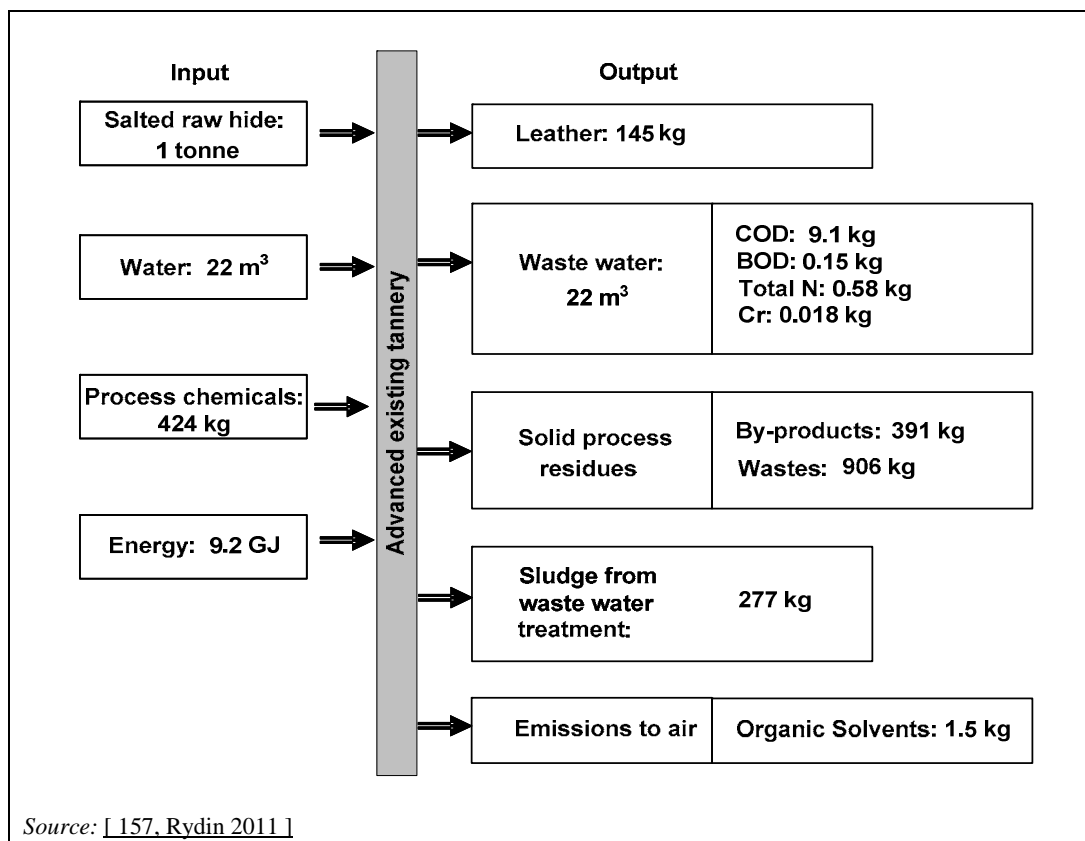


Figure 3.2: Input/output overview from an advanced existing tannery for bovine salted hides per tonne of raw hide treated, producing upholstery leather (some chromium tanned)

Table 3.1 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 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.

A discussion in more detail of the input chemicals, the most important auxiliaries, the emissions to waste water and air, and the residues for each process is contained in Section 3.9. Particular advantages or problems in a process unit are indicated, 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 3.1, the most commonly found sequence is presented.



Table 3.1: Steps in the tannery showing the main emissions and consumptions

Process unit	Inputs	Waste water	Waste	Air emissions	Remarks
<b>Hide and skin storage and beamhouse operations</b>					
<b>Trimming</b>			<ul style="list-style-type: none"> <li>Parts of the raw hides (trimmings)</li> </ul>		
<b>Curing and storage</b>	<ul style="list-style-type: none"> <li>Salt</li> <li>Energy for cooling/drying</li> <li>Biocides</li> </ul>	<ul style="list-style-type: none"> <li>Small volumes of highly concentrated exudate of similar composition to those from soaking</li> </ul>	<ul style="list-style-type: none"> <li>Salt</li> </ul>	<ul style="list-style-type: none"> <li>Odour</li> </ul>	<ul style="list-style-type: none"> <li>Noise from refrigeration</li> </ul>
<b>Soaking</b>	<ul style="list-style-type: none"> <li>Water</li> <li>Alkali</li> <li>Sodium hypo-chlorite</li> <li>Wetting agents, surfactants, enzymes</li> <li>Biocides</li> </ul>	<ul style="list-style-type: none"> <li>BOD, COD, SS, DS from soluble proteins, dung, blood etc.</li> <li>Salts</li> <li>Organic nitrogen</li> <li>AOX</li> <li>Emulsifiers, surfactants, biocides</li> </ul>			<ul style="list-style-type: none"> <li>Waste water released in soaking and residues depend on the curing method used</li> </ul>
<b>Fleshing <sup>(1)</sup></b>	<ul style="list-style-type: none"> <li>(Cold) water</li> </ul>	<ul style="list-style-type: none"> <li>BOD, COD, SS, DS from fat, grease</li> </ul>	<ul style="list-style-type: none"> <li>Fat, connective tissue, lime</li> </ul>		<ul style="list-style-type: none"> <li>Contamination depends on choice of green fleshing or lime fleshing, blood is found in green fleshing</li> </ul>
<b>Liming and unhairing</b>	<ul style="list-style-type: none"> <li>Water</li> <li>Lime, alkali sulphides</li> <li>Thioalcohols</li> <li>Enzymes</li> <li>Surfactants</li> </ul>	<ul style="list-style-type: none"> <li>Sulphides,</li> <li>BOD, COD, SS, DS (emulsified and saponified fat, protein, degradation products from hair)</li> <li>Lime</li> <li>High pH</li> <li>Organic nitrogen, NH<sub>4</sub>-N</li> <li>Biocides</li> </ul>	<ul style="list-style-type: none"> <li>Hair</li> <li>Sludge from liming effluents (waste water treatment)</li> </ul>	<ul style="list-style-type: none"> <li>Sulphides</li> <li>Odour</li> </ul>	<ul style="list-style-type: none"> <li>Noise and vibration</li> </ul>
<b>Rinsing after unhairing</b>	<ul style="list-style-type: none"> <li>Water</li> </ul>	<ul style="list-style-type: none"> <li>Same as for liming and unhairing</li> </ul>			
<b>Splitting <sup>(2)</sup></b>	<ul style="list-style-type: none"> <li>Water</li> </ul>	<ul style="list-style-type: none"> <li>Same as for liming</li> </ul>	<ul style="list-style-type: none"> <li>Lime split (flesh-side)</li> <li>Trimmings</li> </ul>		<ul style="list-style-type: none"> <li>Problems in waste fractions: pH ~ 12 and sulphides</li> <li>Splitting in tanned condition</li> <li>Noise and vibration</li> </ul>

Process unit	Inputs	Waste water	Waste	Air emissions	Remarks
<b>Tanyard operations</b>					
<b>Delimiting/bating</b>	<ul style="list-style-type: none"> <li>• Ammonium salts</li> <li>• Organic and inorganic acids and their salts</li> <li>• Carbon dioxide</li> <li>• Enzymes</li> <li>• Water</li> </ul>	<ul style="list-style-type: none"> <li>• BOD, COD, SS, DS from epidermis, skin and pigment residues, degradation products and excess bating agents</li> <li>• NH<sub>4</sub>-N</li> <li>• Sulphides</li> <li>• Calcium salts (mainly sulphates)</li> <li>• AOX</li> </ul>		<ul style="list-style-type: none"> <li>• NH<sub>3</sub></li> <li>• H<sub>2</sub>S</li> <li>• Dust from bating agents</li> </ul>	<ul style="list-style-type: none"> <li>• NH<sub>4</sub>-N depends on delimiting method</li> <li>• Prior treatment using H<sub>2</sub>O<sub>2</sub> or (Sodium bisulphite to oxidise the sulphides)</li> <li>• Dust emission from bating agents depend on the agents and the method in which they are applied</li> <li>• Noise and vibration</li> </ul>
<b>Rinsing</b>	<ul style="list-style-type: none"> <li>• Water</li> </ul>	<ul style="list-style-type: none"> <li>• As from delimiting/bating</li> </ul>			
<b>Degreasing</b>	<ul style="list-style-type: none"> <li>• Surfactants and water</li> <li>• Organic solvents</li> </ul>	<ul style="list-style-type: none"> <li>• BOD, COD, SS, DS</li> <li>• Organic compounds (fat, solvents)</li> <li>• Surfactants</li> </ul>	<ul style="list-style-type: none"> <li>• Distillation residues</li> <li>• Waste water treatment residues</li> </ul>		<ul style="list-style-type: none"> <li>• Chlorinated/non-chlorinated hydrocarbons</li> <li>• Workplace conditions for VOCs</li> </ul>
<b>Pickling</b>	<ul style="list-style-type: none"> <li>• Water</li> <li>• Organic and inorganic acids</li> <li>• Salt</li> <li>• Fungicides</li> </ul>	<ul style="list-style-type: none"> <li>• BOD, COD, SS, DS</li> <li>• Salt</li> <li>• Acidity</li> <li>• Fungicides</li> </ul>		<ul style="list-style-type: none"> <li>• Hydrogen sulphide</li> <li>• Acid fumes</li> <li>• Odour</li> </ul>	<ul style="list-style-type: none"> <li>• Fungicides</li> <li>• Addition of some hydrogen peroxide may be necessary</li> </ul>
<b>Tanning</b>	<ul style="list-style-type: none"> <li>• Water</li> <li>• Tanning agents</li> <li>• Organic and inorganic acids, salt</li> <li>• Basifying salts</li> <li>• Fungicides</li> <li>• Complexing agents</li> </ul>	<ul style="list-style-type: none"> <li>• Contents according to tanning process</li> <li>• SS, DS, BOD, COD, acidity</li> <li>• Complexing agents</li> <li>• Fungicides</li> </ul>	<ul style="list-style-type: none"> <li>• Hides due to operating errors</li> <li>• Tanning liquors containing residues of tanning agents</li> </ul>		<ul style="list-style-type: none"> <li>• Toxicity of tanning agents (aldehydes)</li> <li>• Complexing agents: masking agents, sequestering agents for water treatment</li> <li>• Noise and vibration</li> </ul>
<b>Rinsing</b>	<ul style="list-style-type: none"> <li>• Water</li> </ul>	<ul style="list-style-type: none"> <li>• Same as for tanning</li> </ul>	<ul style="list-style-type: none"> <li>• Tanning agents</li> </ul>		
<b>Draining, samming and setting</b>		<ul style="list-style-type: none"> <li>• Same as for tanning</li> </ul>	<ul style="list-style-type: none"> <li>• Tanning agents</li> </ul>		<ul style="list-style-type: none"> <li>• Noise, as in all mechanical processes</li> </ul>
<b>Splitting and Post Tanning</b>					
<b>Splitting &amp; Shaving</b>			<ul style="list-style-type: none"> <li>• Split and shavings</li> <li>• Trimmings</li> </ul>	<ul style="list-style-type: none"> <li>• Particulate matter if dry shaving is performed</li> </ul>	<ul style="list-style-type: none"> <li>• Noise, as in all mechanical processes</li> <li>• Content of the residues depending on tanning techniques</li> </ul>

Process unit	Inputs	Waste water	Waste	Air emissions	Remarks
<b>Rinsing</b>	<ul style="list-style-type: none"> <li>• Water</li> </ul>	<ul style="list-style-type: none"> <li>• Leather fibres from shaving</li> </ul>			
<b>Neutralisation</b>	<ul style="list-style-type: none"> <li>• Water</li> <li>• Organic and inorganic acids, alkali salt</li> <li>• Neutralising tanning agents</li> </ul>	<ul style="list-style-type: none"> <li>• DS, SS, BOD, COD</li> <li>• Rest of tanning agents</li> </ul>		<ul style="list-style-type: none"> <li>• Ammonia can be released into the air</li> </ul>	
<b>Rinsing</b>	<ul style="list-style-type: none"> <li>• Water</li> </ul>	<ul style="list-style-type: none"> <li>• Same as for neutralisation</li> </ul>			
<b>Retanning</b>	<ul style="list-style-type: none"> <li>• Water</li> <li>• Tanning agents (possibly different agents from those used in tanning)</li> <li>• Organic and inorganic acids, salt</li> <li>• Basifying salts</li> <li>• Complexing agents</li> </ul>	<ul style="list-style-type: none"> <li>• Contents according to retanning process used.</li> <li>• SS, DS, BOD, COD, acidity</li> <li>• Complexing agents</li> </ul>	<ul style="list-style-type: none"> <li>• Hides due to operating errors</li> <li>• Retanning liquors containing residues of retanning agents</li> </ul>		<ul style="list-style-type: none"> <li>• Toxicity of tanning agents (aldehydes)</li> <li>• Complexing agents: masking agents, sequestering agents for water treatment</li> <li>• Noise and vibration</li> </ul>
<b>Bleaching</b>	<ul style="list-style-type: none"> <li>• Water</li> <li>• Organic and inorganic acids, alkali salt</li> </ul>	<ul style="list-style-type: none"> <li>• Organic load (BOD, COD)</li> <li>• Others, depending on the agents used</li> </ul>		<ul style="list-style-type: none"> <li>• Sulphur dioxide</li> </ul>	
<b>Dyeing</b>	<ul style="list-style-type: none"> <li>• Dyestuff</li> <li>• Ammonia</li> <li>• Organic solvents</li> <li>• Auxiliaries: surfactants, chlorinated organic compounds</li> <li>• Water</li> </ul>	<ul style="list-style-type: none"> <li>• High colour</li> <li>• Organic solvents</li> <li>• Dyeing agents</li> <li>• AOX</li> </ul>	<ul style="list-style-type: none"> <li>• Residues of chemicals</li> <li>• Dyeing agents</li> </ul>	<ul style="list-style-type: none"> <li>• NH<sub>3</sub></li> <li>• Phenols</li> </ul>	
<b>Rinsing</b>	<ul style="list-style-type: none"> <li>• water</li> </ul>	<ul style="list-style-type: none"> <li>• Same as for dyeing</li> </ul>			

Process unit	Inputs	Waste water	Waste	Air emissions	Remarks
<b>Fatliquoring</b>	<ul style="list-style-type: none"> <li>• Synthetics-mineral-based oils</li> <li>• (Sulphonated) animal, vegetable oil fish oil</li> <li>• Chlorinated organic compounds</li> <li>• Surfactants</li> <li>• Other auxiliaries</li> <li>• Water</li> </ul>	<ul style="list-style-type: none"> <li>• High oil</li> <li>• Chlorinated organic compounds (AOX)</li> <li>• Surfactants</li> </ul>			<ul style="list-style-type: none"> <li>• Chlorinated organic compounds (AOX)</li> <li>• Surfactants</li> <li>• Toxicity of auxiliaries</li> </ul>
<b>Finishing</b>					
<b>Staking/other mechanical operations</b>			<ul style="list-style-type: none"> <li>• Particulate matter</li> </ul>		<ul style="list-style-type: none"> <li>• Other mechanical operations like polishing, embossing, plating, rolling, etc.</li> <li>• Noise, as in all mechanical processes</li> </ul>
<b>Drying</b>	<ul style="list-style-type: none"> <li>• Energy</li> <li>• Biocides</li> </ul>			<ul style="list-style-type: none"> <li>• Heat</li> <li>• Acid fumes</li> </ul>	<ul style="list-style-type: none"> <li>• Moth protection for wool-on sheepskins, fungicides for crust, noise and vibration</li> </ul>
<b>Milling/buffing</b>			<ul style="list-style-type: none"> <li>• Particulate matter</li> </ul>	<ul style="list-style-type: none"> <li>• Particulate matter</li> </ul>	<ul style="list-style-type: none"> <li>• Noise, as in all mechanical processes</li> </ul>
<b>Coating</b>	<ul style="list-style-type: none"> <li>• Lacquers (solvent based)</li> <li>• Lacquers (water based)</li> <li>• Binders and cross-linking agents</li> <li>• Auxiliaries</li> <li>• Water</li> </ul>	<ul style="list-style-type: none"> <li>• Finishing agents in water or in aqueous solutions (organic solvents, heavy metals)</li> <li>• Auxiliaries</li> </ul>	<ul style="list-style-type: none"> <li>• Residues from chemicals,</li> <li>• Sludges from finishing agents (over-spray, etc.)</li> </ul>	<ul style="list-style-type: none"> <li>• organic solvent use and release: aerosols</li> <li>• Formaldehyde as fixing agent</li> </ul>	<ul style="list-style-type: none"> <li>• Workplace protection</li> <li>• Toxicity and health effects of water-based agents and organic solvents, binders, cross-linking agents, and auxiliaries</li> </ul>
<b>Trimming</b>			<ul style="list-style-type: none"> <li>• final trimmings</li> </ul>		<ul style="list-style-type: none"> <li>• With or without finish</li> </ul>
<b>Abatement</b>					
<b>Air treatment</b>	<ul style="list-style-type: none"> <li>• Filter matrices</li> <li>• Water, acidic and basic agents for wet-scrubbers</li> </ul>	<ul style="list-style-type: none"> <li>• Waste water from wet-scrubbers</li> </ul>	<ul style="list-style-type: none"> <li>• Sludges from waste water from wet-scrubbers</li> <li>• Filter materials</li> <li>• Particulate matter</li> </ul>	<ul style="list-style-type: none"> <li>• Non-abated emissions</li> </ul>	<ul style="list-style-type: none"> <li>• Depending on the method of air abatement for various effluent streams</li> </ul>

Process unit	Inputs	Waste water	Waste	Air emissions	Remarks
<b>Waste water treatment</b>	<ul style="list-style-type: none"> <li>• Energy</li> <li>• Precipitation agents</li> <li>• Other treatment agents (flocculation, etc.)</li> </ul>		<ul style="list-style-type: none"> <li>• Sludges</li> <li>• Coarse material</li> <li>• Filter materials (e.g. from special treatment)</li> </ul>	<ul style="list-style-type: none"> <li>• According to waste water stream and process (e.g. sulphides, ammonia, odour)</li> </ul>	<ul style="list-style-type: none"> <li>• Depending on the method of waste water abatement for various effluent streams</li> </ul>
<b>Waste treatment</b>	<ul style="list-style-type: none"> <li>• Energy</li> <li>• Other treatment agents according to process</li> </ul>	<ul style="list-style-type: none"> <li>• According to waste fraction and process</li> </ul>	<ul style="list-style-type: none"> <li>• According to waste fraction and process</li> </ul>	<ul style="list-style-type: none"> <li>• According to waste fraction and process</li> </ul>	<ul style="list-style-type: none"> <li>• Depending on the method of waste water abatement for various effluent streams</li> </ul>
<p><sup>(1)</sup> Fleshing can be performed before or after liming resulting in different releases.  <sup>(2)</sup> Splitting can be performed with limed or tanned hides and skins resulting in different releases.</p>					

### 3.3 Chemicals

The amount of chemicals used varies significantly with the specification of the final product, the pelts treated and the process chosen. Figures for the 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 variation is in the amount of tanning agents used. Table 3.2 gives an example of overall consumption levels. [10, Rydin and Frendrup 1993].

**Table 3.2: Main and auxiliary process chemicals for a conventional process for salted, bovine hides**

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

Besides the main process chemicals, a great variety of substances 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, bioaccumulation, 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 compositions of the products, so tanneries may have to seek additional information from the chemical suppliers in order to determine the environmental impact of the products they use. 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 the factors listed below:

- 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, some can react in the process or some 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, the waste and the 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.

Information about chemicals and their safe use should be provided to tanneries as part of the European chemical legislation (REACH). REACH is the name of the Community Regulation on chemicals and their safe use (EC 1907/2006). It deals with the registration, evaluation, authorisation and restriction of chemical substances. Manufacturers and importers of chemicals are required to gather information on the properties of their chemical substances, which will allow their safe handling, and to register the information in a central database run by the European Chemical Agency (ECHA) in Helsinki. REACH entered into force on 1 June 2007, but the REACH provisions are being phased-in over an 11-year period which started in 2007.

### 3.3.1 Salt

Common salt (sodium chloride) is found in tannery effluents principally from the soaking and tanning processes. It arises in soaking if salted or brine-cured hides or skins are being processed. It appears in effluent from the tanyard due to the use of salt in pickling. Being highly soluble and stable, it is unaffected by conventional waste water treatment.

Salt loads in effluents from various stages of processing are illustrated in Figure 3.3.

The discharge of salt into the freshwater environment has a significant effect on both animal and plant life, with most freshwater species unable to tolerate even relatively low concentrations of salt in the water. The problem is increased in areas where fresh water is scarce, and the concentration of salt in the water body is greater. 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 type of surface water which receives the ultimate discharge from the tannery or the sewage treatment plant taking its effluent. Where the ultimate discharge is to the sea or an estuary, the impact may be small enough to ignore.

Where waste water is used to irrigate land, the impact of the salt content on the land has to be assessed.

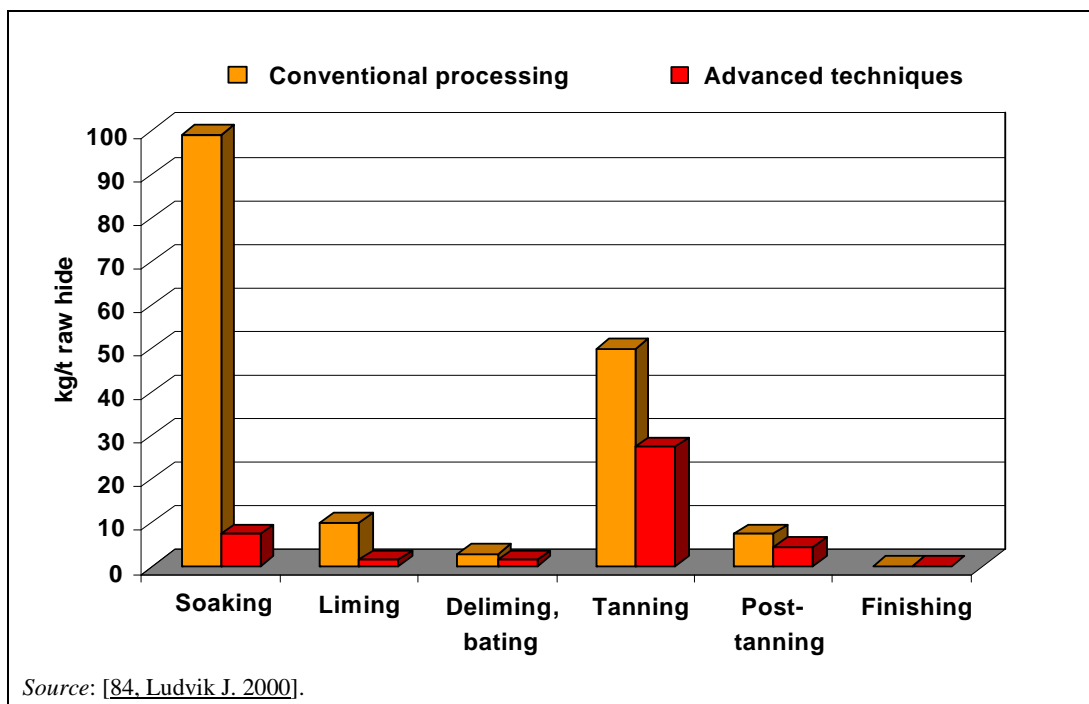


Figure 3.3: Comparison of the mean chloride loads

### 3.3.2 Sulphates

The main source of sulphate from tanneries is the delimiting process. Other relevant processes in relation to the discharge of sulphate are tanning and post-tanning processes. Sulphates are formed during the oxidation of sulphides in the waste water.

Sulphates originate from the use of ammonium sulphate, sulphuric acid or products with a high (sodium) sulphate content. Many process chemicals contain sodium sulphate. For example, chrome tanning powders contain high levels of sodium sulphate, as do many synthetic retanning agents.

Sulphate loads in effluents from various stages of processing are illustrated in Figure 3.4.



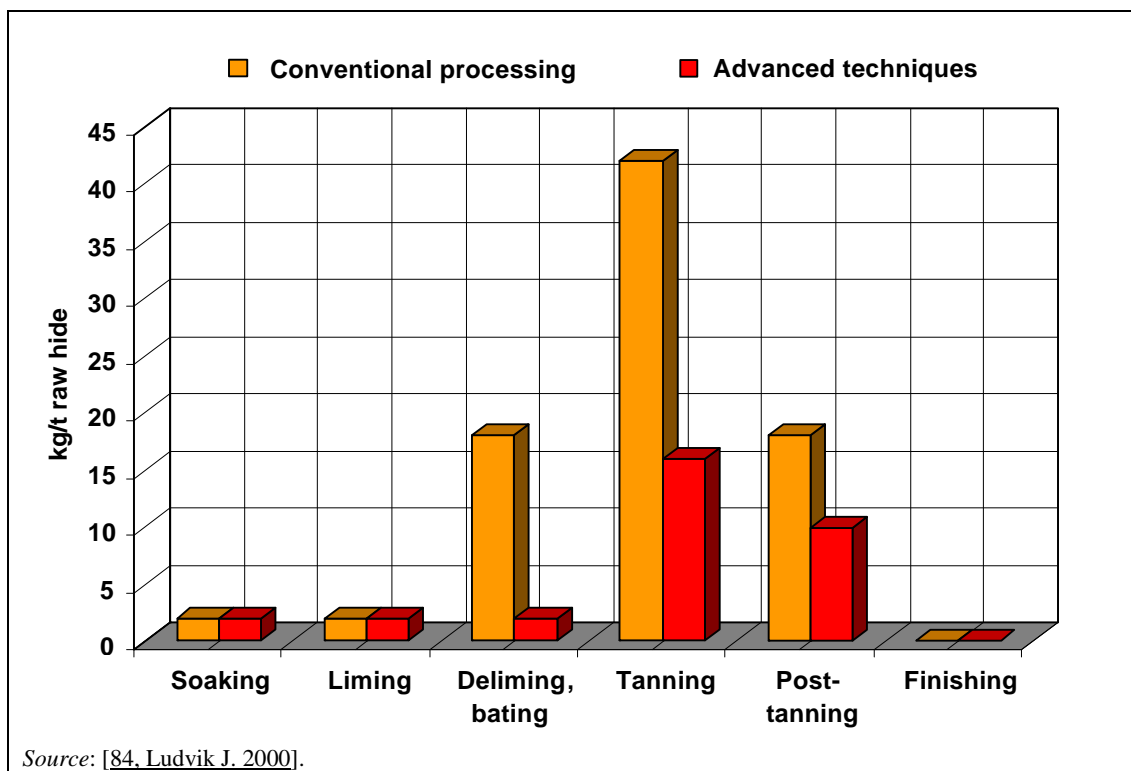


Figure 3.4: Comparison of the mean sulphate loads

### 3.3.3 Sulphides

The sulphide content in tannery effluents is due to the use of sodium sulphide and sodium hydrosulphide, (and the breakdown of hair) in the unhairing process. Sulphide loads in effluents from various stages of processing are illustrated in Figure 3.5.

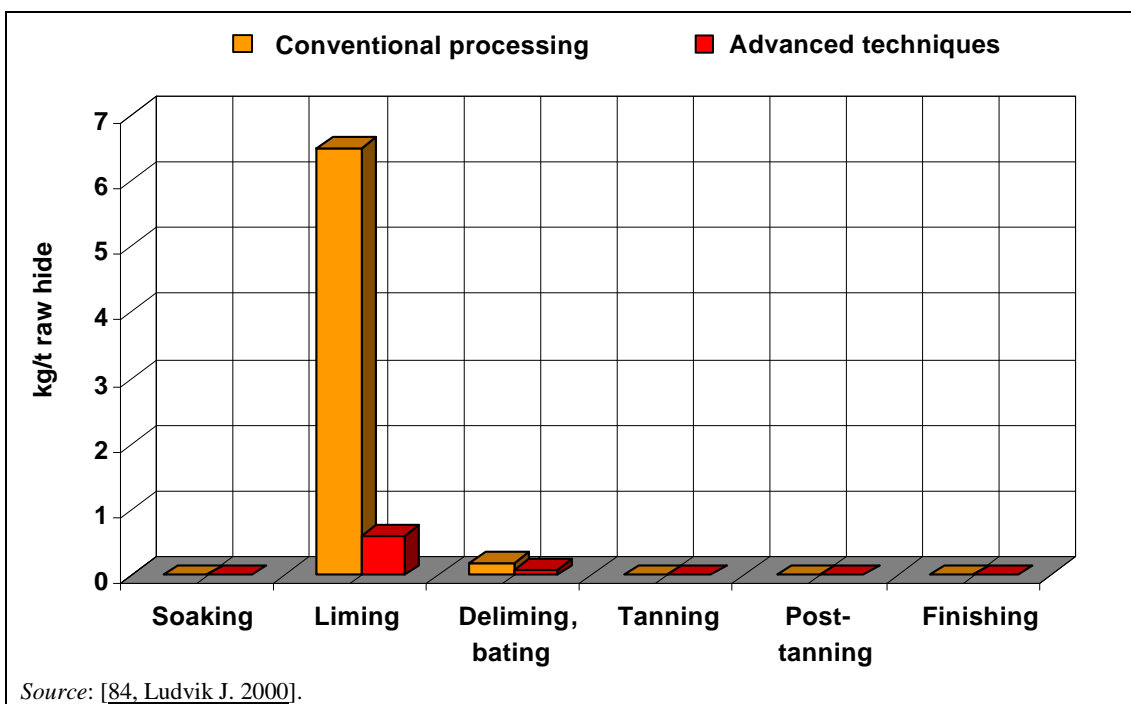


Figure 3.5: Comparison of the mean sulphide loads

Under alkaline conditions, sulphides remain largely in solution. When the pH of the effluent drops below 9.5, hydrogen sulphide evolves from the effluent: the lower the pH, the higher the rate of evolution. Hydrogen sulphide can give rise to a severe odour problem, since it can be detected by the human nose in very low concentrations.

At concentrations above 100 ppm, hydrogen sulphide cannot be detected by smell and can be lethal. For these reasons, parts of tanneries need effective ventilation. The extracted air may need to be treated to remove hydrogen sulphide.

There is also a risk of the formation of hydrogen sulphide under anaerobic conditions in waste waters containing sulphate, due to the action of sulphur-reducing bacteria.

Aliphatic thiols may be used as auxiliaries in the unhairing process. They are also built by the degradation of proteins containing sulphur 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.

### 3.3.4 Nitrogen

Several components of tannery waste waters contain nitrogenous compounds. The major sources are ammonium salts, used for delimiting, and the breakdown products of proteins removed from hides and skins during liming and unhairing.

Ammoniacal nitrogen can be converted to nitrates during biological waste water treatment. A similar process can occur (more slowly) in natural waters.

The discharge of nitrogen compounds to natural waters should be avoided, and is likely to be subject to legal restrictions. This is because:

- ammoniacal nitrogen is toxic to aquatic life;
- unnatural concentrations of nitrates are one of the causes of eutrophication;
- the breakdown of nitrogenous compounds causes a high oxygen demand;
- nitrates in drinking water have harmful effects, especially in very young children.

#### 3.3.4.1 Ammonium

The main source of ammonium in the waste water from tanneries is the delimiting process. Ammonium loads in effluents from various stages of processing are illustrated in Figure 3.6.

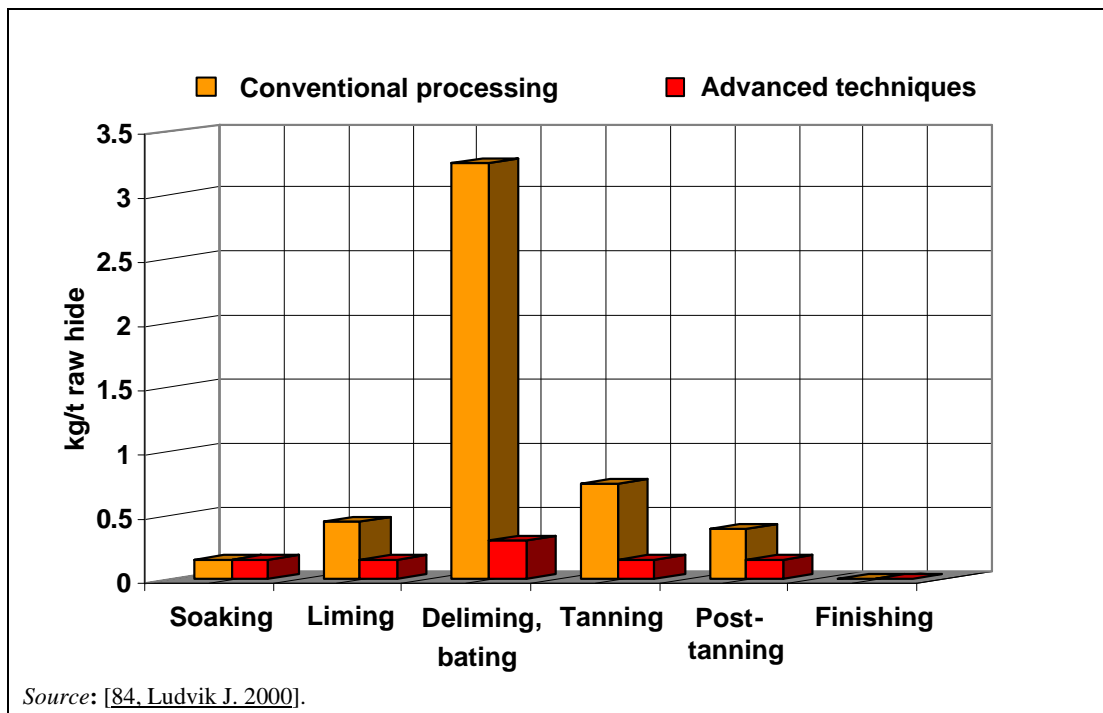


Figure 3.6: Comparison of the mean ammonium loads

### 3.3.4.2 Total Kjeldahl nitrogen

The main source of the nitrogen compounds in effluents from tanneries is the liming process. Other important processes in relation to discharge of nitrogen are soaking, delimiting and the post-tanning processes. Nitrogen loads in effluents from various stages of processing are illustrated in Figure 3.7 measured as total Kjeldahl nitrogen (TKN).

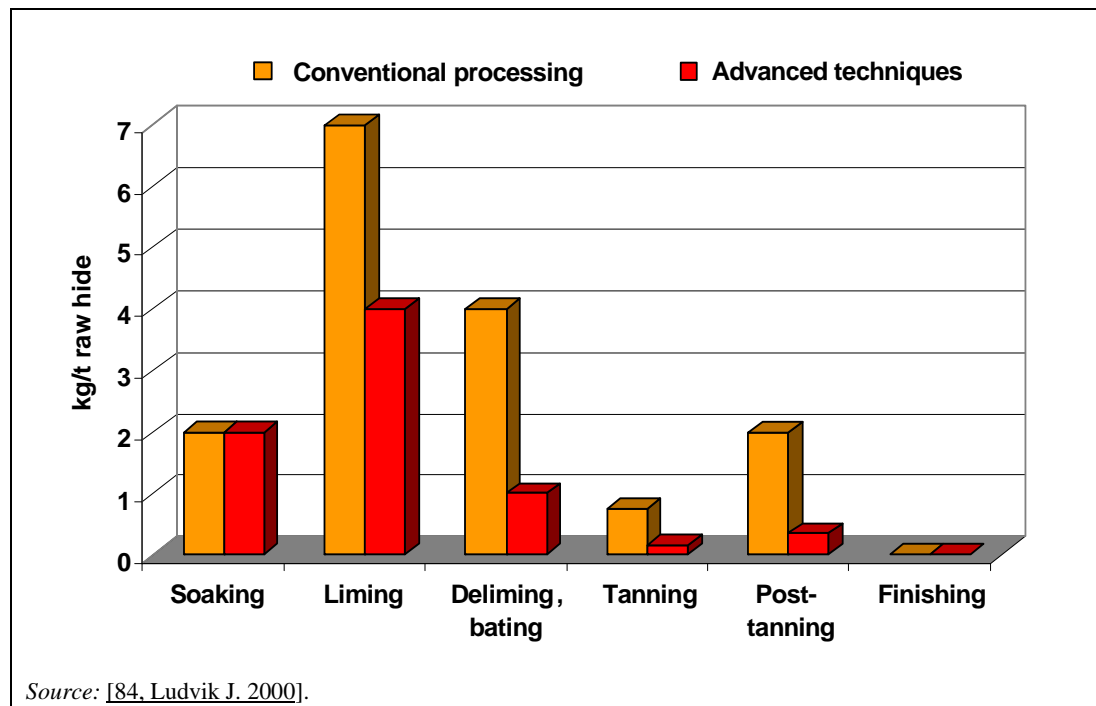


Figure 3.7: Comparison of the mean TKN loads

### 3.3.5 Tanning agents

#### 3.3.5.1 Chromium(III) salts

The main source of chromium in water effluents is the tanning process, but effluents from the post-tanning processes will also contain chromium when chromium retanning is applied. Smaller amounts of chromium arise as a result of leaching of chromium during the wet process steps which follow chromium tanning or retanning. Chromium loads in effluents from various stages of processing are illustrated in Figure 3.8.

The tanning properties of chromium(III) salts were discovered at the end of the nineteenth century. Since that time their use has increased, so that over 80 % of the leather produced now is 'chrome tanned'.

The strength of a chromium tanning liquor may be expressed as a percentage by weight of chromium or as chromium(III) oxide, but these substances are too insoluble for tanning purposes. Chromium(III) sulphate ( $\text{Cr}_2\text{SO}_4$ ) is dissolved in water, producing a solution containing chromium(III) hydroxide sulphate ( $\text{Cr}(\text{OH})\text{SO}_4$ ) [50, Sharpshouse 1983].

Chromium(III) salts in the environment have low availability and mobility. In natural waters, they are adsorbed onto particulate matter or form insoluble polynucleate complexes. Most chromium(III) released into water is deposited in sediment. Reported levels in surface waters in Europe vary between less than 0.01 and 43.3  $\mu\text{g}$  per litre, with a median level of 0.38  $\mu\text{g}$  per litre [112, Santonen et al. 2009].

The United Kingdom and Ireland have both adopted 4.7  $\mu\text{g}$  per litre as a long-term environmental quality standard for chromium(III) in inland surface waters, with a short-term standard of 32  $\mu\text{g}$  per litre.

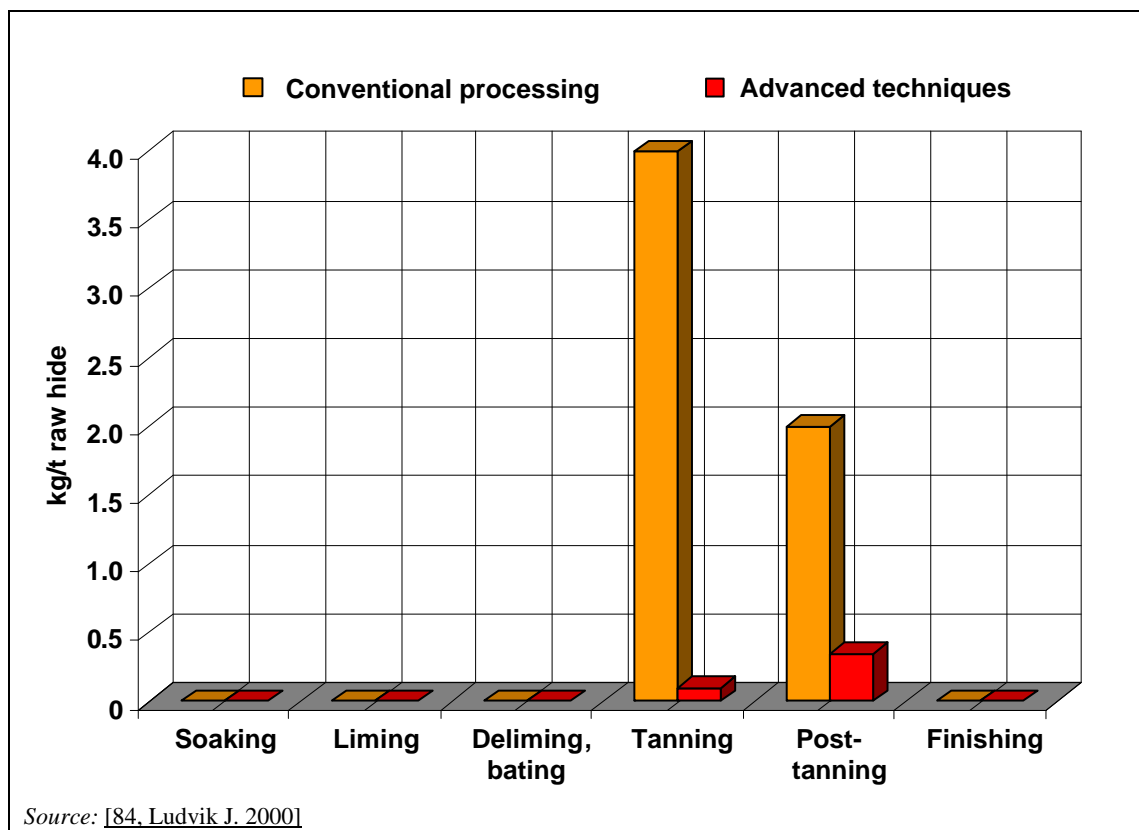


Figure 3.8: Comparison of the mean chromium loads

France is implementing a 'Strategy to reduce discharges of dangerous substances from tanneries into the aquatic environment', which includes chromium(III).

A concise international chemical assessment document is being prepared for chromium(III) under the auspices of the WHO and other international bodies [112, Santonen et al. 2009].

### 3.3.5.2 Vegetable extracts

Other tanning agents such as vegetable tanning agents, syntans, and aldehydes have the potential to cause damage to surface waters. Problems arise due to their low biodegradability and their toxicity to aquatic life.

**Vegetable tanning agents** are polyphenolic compounds. Vegetable tannins may be classified as:

- hydrolysable pyrogallol (myrobalan, oak, sumac, chestnut, etc.); or
- 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. Conversely, the concentration of tanning agents in waste water is below the concentration used for the process and is likely to contain their oxidation products [122, Zywicki et al 2002].

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 3.9.4.3.2).

### 3.3.5.3 Syntans and other synthetic organic compounds

**Syntans, resins, and polyacrylates** are agents used alternatively or in addition to chromium and vegetable tannins.

Syntans are sulphonated condensation products of hydroxyl-substituted aromatic compounds (phenol, cresol or naphthalene) with formaldehyde and often with amides [27, BASF 1997] [2, HMIP 1995]. There is a wide variety of syntans, some of which are hardly biodegradable, whereas others are easily biodegradable. Syntans with low levels of free phenols, and therefore with a lower impact on the environment, are available commercially.

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 [14, Reemtsma 1994]. It is expected that these substances are not retained in the sewage treatment plants 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.

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 [8, Higham 1994].

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 [27, BASF 1997].

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. Acrylic acids and the condensates are anaerobically and aerobically biodegradable [14, Reemtsma 1994].

### 3.3.5.4 Aldehydes

Glutaraldehyde is the most commonly used aldehyde tanning agent. Aldehydes react completely with the proteins found both in the hides/skins and in the effluents. Therefore, they normally do not create an environmental problem during treatment of tannery waste water. However the precipitation of chromium during effluent treatment is affected if aldehydes are present in the effluent stream.

Glutaraldehyde has bactericidal effects and is therefore also used as a disinfectant. Glutaraldehyde is only degraded to a limited extent, has high toxicity and may influence biological treatment negatively if the concentration is high. For safety reasons, glutaraldehyde is mainly used in the form of a modified glutaraldehyde product in the leather industry in Europe.

### 3.3.6 Organic solvents

Organic solvents are mainly used in the coating of leather. Other organic solvents are used in the degreasing of sheepskins.

Solvents are usually categorised 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.

Table 3.5 shows some of the organic solvents used in finishing operations in tanneries and Table 3.3 gives similar information for the degreasing of sheepskins.

Releases from processes, and the handling and storage of solvent materials may require special ventilation arrangements for the protection of the workforce. Explosion and fire hazards also require special protection measures. Organic solvents are mainly released to air, but they also occur in waste water effluents. Solid wastes containing organic solvents are usually classified as hazardous waste.

**Table 3.3: Organic solvents used in the degreasing of sheepskins**

Degreasing of pickled pelts	Degreasing of dry leather
Paraffin (kerosene)	Trichloroethene
White spirit	Tetrachloroethane
	2-butoxyethanol
	2-ethoxyethanol
	Chlorobenzene
	Hexachlorobenzene

The storage and use 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, but their substitution by non-halogenated compounds may require additional safety precautions to be taken.

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 current Chapter V of Industrial Emissions Directive (and formerly the VOC Solvents Emissions Directive), taken steps towards a total phasing-out of the use of these halogenated substances.

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 [41, Various 1998]. 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.

Tetrachloroethene, chlorobenzene and hexachlorobenzene are examples of halogenated organic solvents used in degreasing sheepskins and pigskins.

The Solvents Emissions Directive 1999/13/EC sets limits on the emissions of volatile organic solvents from certain activities and installations. These limits are now specified in Chapter V and Annex VII of Directive 2010/75/EU. Leather coating where the organic solvent consumption is more than 10 tonnes per year is an activity to which limits are set. The implementation of this legislation has had a direct impact on the use of volatile organic compounds in the finishing process in tanneries. The emission limits which apply to the coating of leather are shown in Table 3.4. For the purposes of Chapter V, solvents used in an activity are said to be consumed unless they are recovered for reuse.

**Table 3.4: Solvent emission limits for leather coating**

Annex VII of Directive 2010/75/EU Activity No. 13	Annual solvent consumption in tonnes	ELV g of solvent emitted per m <sup>2</sup> of product produced
For leather-coating activities in furnishing and particular leather goods used as small consumer goods like bags, belts, wallets, etc.	> 10	150
Other coating of leather (medium use)	10 – 25	85
Other coating of leather (high use)	> 25	75

The treatment of the exhaust air, in order to eliminate or recover its content of organic solvents, has generally been shown to be impracticable or at least prohibitively expensive. The main reasons for this are the mixture of solvents used and the large fluctuations of their concentrations in the exhaust air. The concentration varies from 100 to several thousand milligrams per cubic metre during the finishing operations. The extractions of the finishing

booth have a flow that may reach 10 000 or 20 000 m<sup>3</sup>/hour for one finishing line. Considering these emission characteristics, the arrestment techniques which can be applied are limited.

Equipment for wet scrubbing of the exhaust air has become a standard installation in modern spraying units in order to eliminate dust particles and aerosols. A wet scrubber of this type does however only eliminate a minor part of the solvent content of the air. Solvents soluble in water are preferentially arrested.

Abatement techniques such as activated carbon filters are feasible but not standard in tanneries [57, Bles et. al. 1995].

**Table 3.5: Organic solvents used in finishing**

Substance <sup>(1)</sup>	Systematic name	CAS No.	EC No.
<b>Alcohols</b>			
Methyl alcohol	Methanol	67 – 56 – 1	200 – 659 – 6
Ethyl alcohol	Ethanol	64 – 17 – 5	200 – 578 – 6
n-Propylalcohol	Propan-1-ol	71 – 23 – 8	200 – 746 – 9
Isopropyl alcohol	Propan-2-ol	67 – 63 – 0	200 – 661 – 7
n-Butyl alcohol	Butan-1-ol	71 – 36 – 3	200 – 751 – 6
Di-acetone alcohol	4-hydroxy-4-methyl-pentan-2-one	123 – 42 – 2	204 – 626 – 7
<b>Glycol Ethers</b>			
	2-Ethoxyethanol	110 – 80 – 5	203 – 804 – 1
	2-Butoxyethanol	111 – 76 – 2	203 – 905 – 0
	2-Ethoxyethyl acetate	111 – 15 – 9	203 – 839 – 2
Butyl glycol acetate	2-Butoxyethyl acetate	112 – 07 – 2	203 – 933 – 3
	1-Methoxy-2-Propanol	107 – 98 – 2	203 – 539 – 1
	1-Methoxy-2-Propyl acetate	108 – 65 – 6	203 – 603 – 9
<sup>(1)</sup> The listed substances are the ones commonly used by large tanneries under the scope of this BREF. Other substances (hydrocarbons, ketones, and esters) might be used in smaller tanneries with special production.			

Untreated organic solvent emissions from the finishing process can vary between 100 and 3500 mg per m<sup>3</sup> in conventional processes. 50 % of measurable emissions arise from spray-finishing machines, 50 % from dryers. Fugitive emissions to the air and solvents in wastes account for the rest of solvent consumption.

The industry sector as a whole has considerably reduced its solvent use. For example, the solvent use per square metre of leather produced in the Arzignano district in Italy was reduced to below 50 g by 2005, see Figure 3.9.



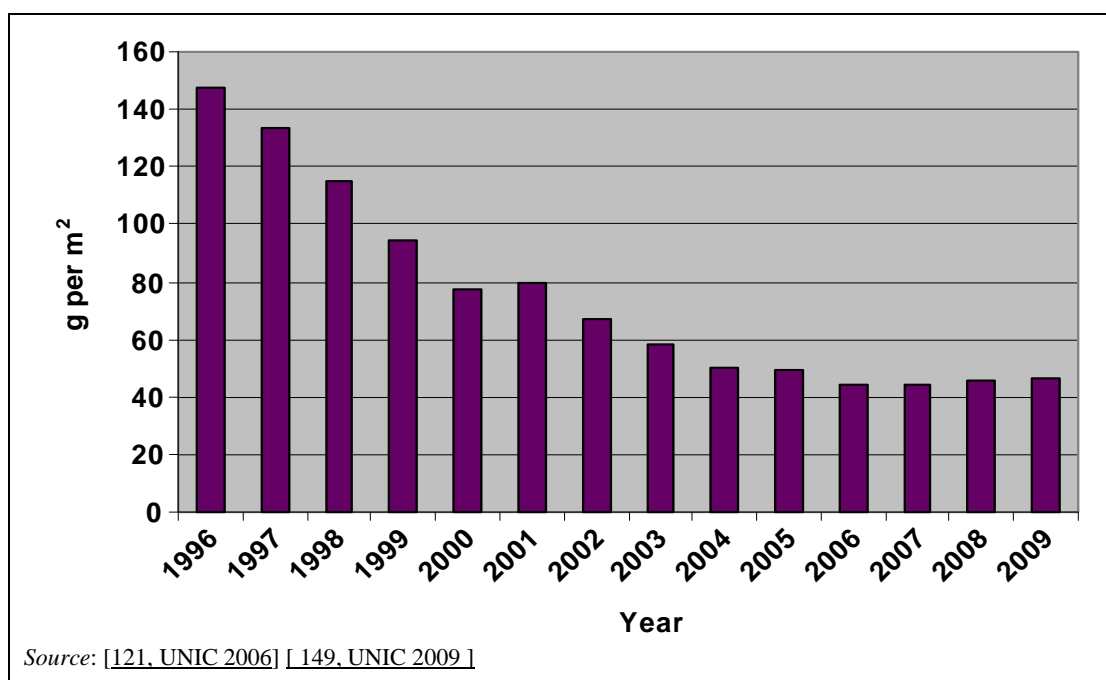


Figure 3.9: Solvent consumption in the Arzignano district

Table 3.6 shows a comparison of the average of VOC emissions and emission concentrations between the several types of finishes from a survey in the Netherlands [57, Bles et. al. 1995].

Table 3.6: Comparison of VOC emissions from different types of finishes

Coating material	Organic solvent content	Emission (kg/h)	Emission concentration (g/m <sup>3</sup> )
Solvent-based finish	> 75 %	50	3
Water-based finish	10 – 75 %	5	0.3
Solvent-free finish	< 10 %	<1	

For emissions to water, non-volatile brominated and chlorinated compounds are often analysed as 'adsorbable organic halogens' (AOX). In some Member States, emission limit values for these parameters are applied because many organic halogen compounds are acutely or chronically toxic. However, the AOX value in itself does not state whether the effluent is toxic or not but is an indication that toxic substances may be present. The organic halogen content of waste water is sometimes measured as EOX (extractable organic halogens).

### 3.3.7 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 facilitate the dispersion of oils in water.

**Non-ionic surfactants**, such as alkoxyates, 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 polyethoxyates.

The use of nonylphenol and nonylphenol ethoxyate (NPE) in leather manufacturing has been severely restricted by laws implementing a succession of EU Directives, most recently the

REACH Directive. The degreasing of sheepskins is now mainly carried out using ethoxylated alcohols. Aliphatic polyethoxylates are used as substitutes for NPEs. They do not break down to produce phenols. They were not detectable in the waste water of a tannery in which they were in use [45, Reemtsma and Jekel 1997].

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 are possible.

Linear alkylated benzenesulphonic acids (LAS) are well assessed because they are broadly applied in household detergents. Linear alkylbenzene sulphonates are readily biodegradable [11, Heidemann 2000], and are being used in tanneries. There are other surfactants, such as sulphonated polyphenols, that are used only in industry and that are found in effluents of tanneries. They are far less understood, but it is known that they are not biodegradable and have a higher mobility than LAS [14, Reemtsma 1994].

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

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

### 3.3.8 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) oils 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 methyl ester sulphonates).

Chlorinated hydrocarbons of chain length C16-30 (chlorinated alkanes) may also be applied [6, Europa 1992]. Chlorinated organic compounds increase the AOX and might even exceed existing emission limit values. In principle, these substances can 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 biomass of the bacteria. [14, Reemtsma 1994].

Lime carbohydrates, natural and synthetic mucilaginous substances and preparations thereof (stuffing agents) [61, TEGEWA 1987] are added to the preparation.

### 3.3.9 Other post-tanning agents

In order to correct the hydrophilic properties of the leather, following the use of surfactants, or to impregnate the pelts in order to achieve waterproof properties, natural, mineral, or synthetic fatty substances, polymers, poly-condensates, poly-addition products, metallic acid complexing compounds, silicon derivatives, and perfluorinated organic compounds are used.

Impregnation with substances may be carried out at this stage to improve the wearing properties and abrasion resistance of the leather and for some uses, its oil-repelling, anti-electrostatic, gas permeability, or flame-retardant properties.

Oil-repellent agents and agents to reduce the permeability to 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 [61, TEGEWA 1987].

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

Emissions to waste water from the fatliquoring agents and the impregnating agents may be significant. Besides increasing the COD and BOD in the waste water, chlorinated fatliquors will contribute to AOX in the waste water.

**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 ethylenediaminetetraacetate (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. 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 chromium in the waste water treatment. Certain phthalates, such as di-sodium phthalates (DSP), are also used as masking agents in chrome tanning.

### 3.3.10 Dyes and dyeing auxiliaries

#### 3.3.10.1 Dyes

Even small amounts of dyestuff in the effluent stream can discolour the waste water effluents. In general, dye levels of 10 ppm or higher in the waste water are visible to the eye. Many dyestuffs are hard to biodegrade (increasing COD, BOD, and SS) and in a few cases some dyes could contribute to the AOX levels in the waste water effluents [113, Puentener 1998].

The number of dyestuffs used by a tannery to colour the leather varies with the range of its products, and the extent to which the use of those products follow fashions. Because each tannery can use a wide variety of dyestuffs, these chemicals have to be discussed as groups of substances, for example anionic and cationic dyestuffs.

Around 98 % of leather dyes on the market for drum application are dyes which fix using the ionic interaction between the anionic sulphonate group of the dye and the cationic amine group of the collagen.

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 the high pH and temperature required for their application. The use of basic dyes is also limited.

Dyes are normally applied to leather as aqueous solutions.

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

Azo dyes are the largest group of synthetic dyes in terms of their diversity and their consumption. The REACH regulation forbids the use of those azo dyes that (by reductive cleavage of one or more azo groups) may release any of 22 aromatic amines specified in Appendix 8 of Annex XVII of the regulation. The use of azo colourant specified in Appendix 9 of Annex XVII of the regulation is also forbidden. The azo dyes identified as such are no longer available for use.

Metal complex dyes consist of a central metal ion and one or two azo ligands. The central ion can be iron, chromium, copper, or cobalt for leather dyes. Metal complex dyes containing lead and cadmium are no longer used in Europe.

Fixing agents are added to minimise the release of dyes by the leather produced. Metal complex dyes have a special use for leather dyeing. The chromium, cobalt, copper and iron organic complex dyes are used to achieve good light-fastness of the leather and also to achieve special colours.

Experiments have shown that metal-complex dyes do not impair the compostability of chromium-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 [113, Puentener 1998].

Vegetable dyes are extracts of logwood, redwood, 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.

### 3.3.10.2 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); or
- wetting agents (auxiliaries) can be divided into anionic (e.g. alkyl-sulphates, alkane-sulphonates, alkyl aryl sulphonates), non-ionic (e.g. phosphoric acid esters), and cationic (e.g. alkyl aryl amine polyglycol ethers, amine derivatives, betains, polyamine condensates).

**Sequestering agents** to be added to the water can be divided into the following groups: nitrilo-tri-acetate (NTA), ethylenediamine tetra acetate (EDTA), polyphosphate (calgon), carboxylic acids.

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

**Antifoaming agents** are low foaming 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, or using bleaching syntans or using a combination of the two.

### 3.3.11 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-metallised dyes.

Pigments form the most significant colouring agents used in leather finishing. Both organic and inorganic pigments are used. Inorganic pigments include iron oxides, titanium dioxide and carbon black. [27, BASF 1997]. The use of inorganic pigments containing lead and chromate has been prohibited by legislation implementing amendments to Directives 67/548/EEC and 76/769/EEC on dangerous substances.

#### Auxiliaries

For dispersion of the pigments in various organic solvents and/or water, surface-active substances may be added. The preparations can also 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 polymer chains in the finishing material, and reduce the water solubility of the compounds. The following cross-linking agents may be used:

- Polyisocyanates (for both base- and top-coats), applied for polyurethane finishes.
- Carbodiimides, for polyurethane base- and top-coats.
- Aziridines, which are highly toxic and, for this reason, they have been replaced by polyaziridines, which are less toxic and can be used for base-coats and top-coats.
- Epoxies, which can only be used for top-coats.
- Formaldehyde, for casein and protein finishes.
- Ethyleneimine-based cross-linking agents, for top-finishes. Ethyleneimine 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, isopropanol).

### 3.3.12 Biocides

Biocides can be applied in various tannery processes to protect the substrate against microbial attack. Generally, biocides are included in most liquid chemical formulations such as dyes, fatliquors and casein finishes. Clearly, all biocides are potentially toxic since they are designed to kill certain life forms.

The biocides used in tanneries can be divided into two main categories: **bactericides and fungicides**.

**Bactericides** are used mainly at the beginning of the leather-making process, when hides and skins are more vulnerable to microbial degradation, e.g. curing and soaking. Commercial biocide preparations may contain a mixture of biocides.

The quaternary ammonium compound didecyldimethylammonium chloride is one of the most frequently used active ingredients against bacteria. It is added at a rate of between 0.03 and 0.1 % of hide weight.

Other compounds used in soaking have a broader activity spectrum, including activity against fungi. Examples are:

- Sodium dimethyldithiocarbamate
- N-hydroxymethyl-N-methyldithiocarbamate
- Tetrahydro-3,5-dimethyl-2H-1,3,5-thiadiazine-2-thione
- 2-Thiocyanomethylthiobenzothiazole (TCMTB).

These materials are added at rates of between 0.02 and 0.1 % by weight.

Dilution by effluents from other stages of processing reduces the concentration sufficiently to prevent adverse effects on biological effluent treatment. Most of the residues are destroyed in the reducing conditions in tannery effluents before treatment [120, Hauber 2005].

**Fungicides** are typically used from the pickling stage to the drying stage, because the pH conditions in these processes are more conducive to mould growth. Pickled sheepskins must contain fungicides to protect them from mould growth during transport and storage [2, HMIP 1995], [9, UNIDO-UNEP 1991]. Finished leather may also be susceptible to mould growth if not properly dried and when stored under high humidity conditions.

Fungicides are used for the preservation of wet tanned intermediates like wet blue and wet white that are stored or transported over long distances before the completion of processing. Active substances like o-phenylphenol (OPP), p-chloro-m-cresole (CMK), n-octylisothiazolinone (OIT) and thiocyanomethylthiobenzothiazole (TCMTB) are available.

Two active substances are often combined in commercial products to maximise both the efficacy and the range of fungal species controlled. From the very small range of products available, the use of organic halogen compounds, e.g. CMK cannot always be avoided.

For the effective preservation of wet blue by CMK or OPP at least 580/280 mg/kg has been recommended and for preservation by OIT 80 mg/kg. Wet white is more susceptible to mould than wet blue. Levels of >1 500 mg/kg CMK, >1 200 mg/kg OPP and >600 mg/kg TCMTB were found to be satisfactory but OIT at 400 – 500 mg/kg was ineffective. [ 85, Hauber and Knödler 2008 ]

### 3.3.13 Pesticides

Raw hides and skins may contain pesticides that are applied to the animal to protect it from disease during its life. Pesticides are used in farm animal husbandry to deal with ectoparasites. Different pesticides can be used on sheep and cattle. They can remain in the hide or skin for some time and can be introduced into the float from this source.

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 manufacturing 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 but they may be imported through raw hides from non-EU states. The European Commission has regulated the discharge of biocides through 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 imported skins. Arsenic is still used for animal treatment in some parts of the world.

## 3.4 Water & waste water

### 3.4.1 Water Consumption

Water consumption consists of two main components: process water, and technical water needed for, cleaning, energy generation, waste water treatment, and sanitary purposes. The last is estimated to account for about a fifth of the total water consumption [40, Buljan et al. 1998]. Process water consumption varies greatly between tanneries, depending on the processes involved, the raw material used, and the manufactured products. Water consumption is higher in the early process stages than in finishing. A difference can also arise due to more or less stringent water reduction measures, e.g. in rinsing steps.

A cumulative table of water use in the different process stages (as measured by waste water discharges) is given in Table 3.7. [16, Frendrup 1999] [84, Ludvik J. 2000] [99, IUE 2006] These figures are for tanneries which have not taken steps to reduce water consumption and should be compared to Table 4.2.

**Table 3.7: Water consumption in process stages (conventional processing)**

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

The water used may be obtained from rivers, mains supplies or from company-owned sources. Initiatives to reduce water consumption depend strongly on the source of the water supply and on the costs of waste water treatment.

### 3.4.2 Waste Water

The most commonly monitored parameters for setting the requirements for waste water effluents are chemical oxygen demand (COD), biochemical oxygen demand (BOD<sub>5</sub>), suspended solids (SS), total nitrogen (N-tot), total Kjeldahl nitrogen (TKN), ammoniacal nitrogen (NH<sub>4</sub>-N), phosphorus (P<sub>total</sub>), sulphide (S<sup>2-</sup>), chromium (total), grease and fat content, pH and temperature. Chlorides (Cl<sup>-</sup>), sulphates (SO<sub>4</sub><sup>2-</sup>), total dissolved solids (TDS), adsorbable organic halogenated compounds (AOX), surfactants, pesticides, phenols and fish toxicity are not as common. The composition of water effluents varies greatly between tanneries.

Chemical oxygen demand can be regarded as a broad measure of the strength of the effluent. It might be expected that those tanneries which use the least water would produce the strongest effluent. COD per cubic metre of waste water is plotted against water use per tonne of raw hides or skins in Figure 3.10, for a small number of tanneries for which data are available [101, France 2008], [90, Tanneries 2008]. The expected correlation is indicated by the 'approximate fit' line. Two of the tanneries are able to control both water use and effluent strength and their data appear below the correlation line.



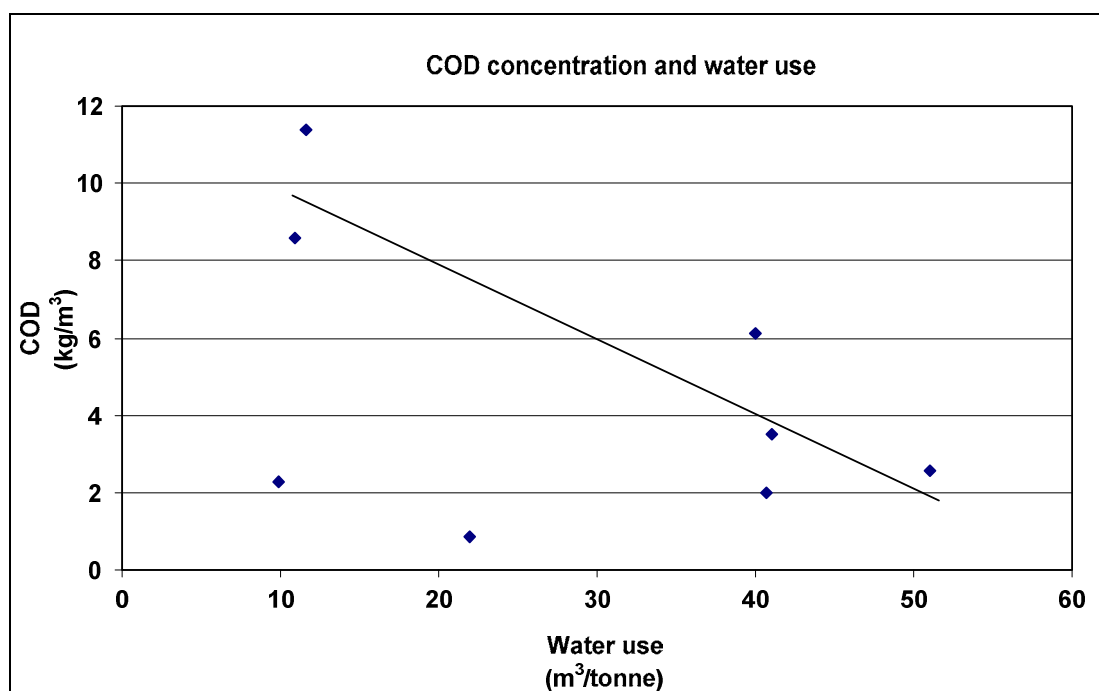


Figure 3.10: Chemical oxygen demand against water use

It is estimated that effective utilisation of process chemicals leads to a take up into the final product of about 15 %, implying that 85 % enters either the waste or waste water streams. [40, Buljan et al. 1998].

The pollution loads in waste water likely to arise at various stages of leather production are shown in Table 3.8. The loads are described in amounts per unit of production rather than concentration so as to remove the effects caused by differing water use rates. The loads to be expected from goatskin processing are approximately the same as for bovine hides on a weight basis.

About 75 % of the BOD and COD load is produced in the beamhouse, with the main load coming from unhairing without hair saving [10, Rydin and Frendrup 1993]. A significant proportion of the COD (about 45 %) and BOD (about 50 %) load stems from liming/unhairing [17, UNEP 1991]. Liming /unhairing is also the main generator of SS (about 60 %). In total the beamhouse emissions contribute about 90 % of total SS.

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.

Table 3.8: Pollution loads from tannery processes

Salted bovine hides (or goatskins)											
Parameter	Water consumption	COD	BOD <sub>5</sub>	Suspended solids	Cr <sup>3+</sup>	S <sup>2-</sup>	TKN	Cl <sup>-</sup>	SO <sub>4</sub> <sup>2-</sup>	Grease	TDS
Amount per tonne of raw hide	m <sup>3</sup>	kg	kg	kg	kg	kg	kg	kg	kg	kg	kg
Beamhouse (soaking to bating)	7 – 25	120 – 160	40 – 60	70 – 120		2 – 9	9 – 14	120 – 150	5 – 20	5 – 8	200 – 300
Tanning operations	1 – 3	10 – 20	3 – 7	5 – 10	2 – 5		0 – 1	20 – 60	30 – 50	1 – 2	60 – 120
Post-tanning	4 – 8	15 – 40	5 – 15	10 – 20	1 – 2		1 – 2	5 – 10	10 – 40	3 – 8	40 – 100
Finishing	0 – 1	0 – 10	0 – 4	0 – 5							
<b>TOTAL</b>	<b>12 – 37</b>	<b>145 – 230</b>	<b>48 – 86</b>	<b>85 – 155</b>	<b>3 – 7</b>	<b>2 – 9</b>	<b>10 – 17</b>	<b>145 – 220</b>	<b>45 – 110</b>	<b>9 – 18</b>	<b>300 – 520</b>
Sheepskins (wet-salted)											
Parameter	Water	COD	BOD <sub>5</sub>	S.S.	Cr <sup>3+</sup>	S <sup>2-</sup>	TKN	Cl <sup>-</sup>	SO <sub>4</sub> <sup>2-</sup>	Grease	
Amount per skin	Litres	g	g	g	g	g	g	g	g	g	
Beamhouse	65 – 150	250 – 600	100 – 260	150 – 300		6 – 20	15 – 30	150 – 400	5 – 40		
Degreasing-tanning	30 – 100	50 – 300	20 – 100	15 – 30	8 – 12		4 – 10	40 – 200	30 – 50	40 – 150	
Post-tanning	15 – 35	30 – 100	15 – 35	10 – 20	1 – 3		2 – 4	20 – 40	10 – 20		
Finishing	0 – 10	0 – 5	0 – 2	0 – 2							
<b>TOTAL</b>	<b>110 – 295</b>	<b>330 – 1005</b>	<b>135 – 397</b>	<b>175 – 352</b>	<b>9 – 15</b>	<b>6 – 20</b>	<b>21 – 44</b>	<b>210 – 640</b>	<b>45 – 110</b>	<b>40 – 150</b>	
Wool on Sheepskins											
Parameter	Water	COD	BOD <sub>5</sub>	Suspended solids	Cr <sup>3+</sup>	S <sup>2-</sup>	TKN	Cl <sup>-</sup>	SO <sub>4</sub> <sup>2-</sup>	Grease	TDS
Amount per skin	Litres	g	g	g	g	g	g	g	g	g	kg
Beamhouse	160 – 240	550 – 1100	150 – 1000	100			16	400			600
Tanning operations	40 – 70	150 – 300	45 – 250	15	15		2	460		40 – 150	650
Dyeing operations	75 – 100	80	25 – 50	80	5		3	50			270
Finishing											
<b>TOTAL</b>	<b>275 – 410</b>	<b>780 – 1500</b>	<b>220 – 1300</b>	<b>195</b>	<b>20</b>		<b>21</b>	<b>910</b>		<b>40 – 150</b>	<b>1520</b>

Source: [99, IUE 2006]

The concentration of pollutants in the waste water discharges from the wet process steps is a measure of the environmental efficiency of the leather making process itself, in putting process chemicals into the product and not into the effluent. These are important data, allowing a common point of reference for both those plants using on-site treatment and those using off-site treatment.

A number of authors have produced data on the outputs expected from the wet processing stages. The IUE produced the data shown in Table 3.8 on the basis of tannery practices throughout the world. These data allow comparisons to be made of the emissions likely to arise from the processing of bovine and other raw materials. They do not distinguish the emissions which are likely to arise in the production of leather for different purposes.

Lower figures are put forward by Frendrup [16, Frendrup 1999], see Table 3.9 and by Ludvik [84, Ludvik J. 2000], see Table 3.10.

**Table 3.9: Waste water loads (before treatment) per tonne of raw hide achieved by good practice**

	Unit	Soaking	Unhairing	Deliming- bating	Pickling- tanning	Wet after treatments	Various	Total
Water consumption	(m <sup>3</sup> /t)	2	5	2.5	0.5	2	3	15
Total solids	(kg/t)	35	70	20	80	30	10	245
Suspended solids	(kg/t)	10	19	6	7	7	1	50
BOD	(kg/t)	12	20	5	3	6	0	46
COD	(kg/t)	23	45	12	8	13	1	102
Total Kjeldahl Nitrogen	(kg/t)	2	2.5	1.1	0.5	0.1	0	6.2
Ammonia nitrogen	(kg/t)	0	0.3	0.2	0.1	0.1	0	0.7
Sulphide	(kg/t)		0.7	0.03				0.7
Chromium	(kg/t)				0.1	0.15		0.25
Chloride	(kg/t)	5	3	1	28	3	2	42
Sulphate	(kg/t)			2	16	4	1	23
Grease and oil	(kg/t)			5	1.5	2	0.1	8
<i>Source: [16, Frendrup 1999].</i>								

Table 3.10: Waste water loads (before treatment) per tonne of raw hide achieved by good practice

	Chemical oxygen demand	Biochemical oxygen demand (5 day)	Suspended solids	Chromium as Cr <sup>3+</sup>	Sulphide as S <sup>2-</sup>	Total Kjeldahl nitrogen	Chloride as Cl <sup>-</sup>	Sulphate as SO <sub>4</sub> <sup>2-</sup>
Process step	kg per tonne of raw hide							
Beamhouse (soaking to bating)	79 – 110	28 – 42	33 – 55	0	0.4 – 0.8	4.6 – 7.5	7 – 14	3 – 6
Tanning operations	7 – 11	2 – 4	1 – 2	0.05 – 0.1	0	0.1 – 0.2	20 – 35	10 – 22
Post-tanning (wet finishing)	10 – 12	3 – 5	1 – 2	0.1 – 0.4	0	0.2 – 0.5	3 – 6	4 – 9
Total	96 – 133	33 – 51	35 – 59	0.15 – 0.5	0.4 – 0.8	4.9 – 8.2	30 – 55	17 – 37
<i>Source : [ 84, Ludvik J. 2000 ].</i>								

Data were collected from operating European tanneries in 2008 and 2011, which are shown in Table 3.11. These figures include the emissions from all the process stages carried out at the particular installation.

Table 3.11: Waste water loads from tanneries, before treatment

	Bovine tannery, vegetable	Sheepskin tannery, fellmonger, starting from wet-blue	Bovine tannery, shoe upper leather	Bovine tannery, upholstery	Bovine tannery, upholstery from fresh hides	Bovine tannery (70-75% salted and 25-30% fresh)	Pigskin tannery	Wet-blue production from elk skins	Austria
Water consumption (m <sup>3</sup> /t)	40	7	15	15 – 23	13 – 14		85	10	15 – 20
COD (kg/t)	245	98			133	92 – 94 <sup>(1)</sup>	740	465	90 – 100
BOD <sub>5</sub> (kg/t)	52		54.7				406	167	45 – 50
Suspended solids (SS) (kg/t)	49	13						290	
Chromium (kg/t)		0.6	0.6			4.5 - 4.7		2.4	
TKN (kg/t)	14.4		8.0		10	9.7 – 10		36.7	
Total nitrogen (kg/t)									5 – 10
Chloride (kg/t)	229				44	120 – 124			
Sulphate (kg/t)			27		10	55 – 57			
Sulphide (kg/t)			1.2					8.9	
Phosphate (kg/t)	1.96		0.5					0.07	
<sup>(1)</sup> Filtered sample									
Source: [ 90, Tanneries 2008 ] [ 156, Austria 2011 ].									

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 chromium salts and acids (pH about 4). Vegetable tanning increases the COD and possibly the phenol concentration. 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.

The mean input and output concentrations in 2007 for some waste water treatment plants in Europe are shown in Table 3.12. These include data from two common treatment plants in Italy which are described below.

The common treatment plant operated by F.I.C. S.p.A. is in the Arzignano area of Italy. In this plant 30000 m<sup>3</sup> per day of waste water from 160 tanneries and 150 other industrial activities, and 10000 m<sup>3</sup> per day of urban waste water are treated. The plant produces 90000 tonnes of sludge per year with a water content of 65 %. After the sludge has been treated in a belt press and plate press, a thermal treatment process dries the sludge to a water content of 10 %. This dried sludge is landfilled. Alternative disposal routes (such as different types of thermal treatment, including gasification) are being investigated.

Cuoioedepur is another common treatment plant in Santa Croce in Italy with a capacity to treat 5 000 m<sup>3</sup> of urban waste water per day together with the waste water from 150 tanneries (5 000 m<sup>3</sup> per day). 95 % of the tanneries discharging to this plant use vegetable tannins. It is a modern plant and totally covered; air is removed through a scrubber reducing the concentration of H<sub>2</sub>S to 0.4 ppm (the Italian standard is 5 ppm). The sludge produced is dried to a water content of 15 – 20 % (about 30 000 tonnes per year based on 85 % dry matter) with the aim of using it as a fertiliser. In 2008, it was reported to be used in landscaping works. [90, Tanneries 2008].

**Table 3.12: Input and output concentrations in 2007 for some waste water treatment plants in Europe**

WWTP No.	Water (m <sup>3</sup> /d)	COD (mg/l)	BOD <sub>5</sub> (mg/l)	SS (mg/l)	TKN (mg/l)	S <sup>2-</sup> (mg/l)	Cr <sup>3+</sup> (mg/l)	Cl <sup>-</sup> (mg/l)	SO <sub>4</sub> <sup>2-</sup> (mg/l)	
<b>Tannery effluent treatment plants</b>										
<b>1</b>	Influent	1250	9800	4133		320		6.6		
	Effluent	1250	567	13		23		0.21		
<b>4</b>	Influent	700	5425			425	184		1841	770
	Effluent	700	251			120				
<b>Common effluent treatment plants</b>										
<b>2</b>	Influent	40 000	5189	2350	2410	459	47	87	2616	1761
	Effluent		93	< 5	11	8	<DL <sup>(1)</sup>	0.29	1577	1373
<b>3</b>	Influent	10 000	12 000 – 14 000	3500	5709		127	19	7091	1850
	Effluent		120 – 150	0 – 20	0 – 20		<DL	0	3000 – 4500	900 – 1500
<sup>(1)</sup> DL=detection limit. Source: [90, Tanneries 2008].										

Table 3.13 below gives data on the waste water loads likely to arise from a vegetable tanning process [35, UBA 1997].

Table 3.13: Example of effluent composition of a vegetable tanning process

Manufacture of vegetable tanned leather chemicals used, composition and volume of effluents						
Effluent No.	Chemicals used, effluent constituents	A) Starp and russet upper leather (e.g. belts, handbags, suitcases)		B) Sole leather		
		Operation	Flow (m <sup>3</sup> /t)	Operation	Flow (m <sup>3</sup> /t)	COD (% load)
1	Alkali, wetting agents, biocides, dung, blood, soluble protein, curing salt, AOX	Preliminary soaking	~ 15	Soaking	6 – 8	~ 50%
2	Lime, Na-sulphite, Na-hydrogen sulphide, residual protein from hair and skin, fat, degradation products	(Soaking) liming		Liming		
3	Ammonium sulphate, oxalates, CO <sub>2</sub> , citrates, enzymes; epidermis, hair and pigment residues, non-collagenic proteins, soluble lime salts	Deliming, bating, washing		Deliming, bating		
4	Vegetable and synthetic tanning agents (A: ca. 20% tanning agent/pelt weight; B: c. 25-30% tanning agent/pelt weight); leather fibres, organic degradation products	Pit tanning ( <sup>1</sup> ) (removal of contents at 4-6 week intervals)	~ 8	Pit tanning (removal of contents at 2 – 6 month intervals)	~ 2	~ 50%
5		Dripping, washing, samming		Washing samming		
6	Greasing agents, emulsifiers, leather fibres	Fatliquoring	1 – 2			
7	Vegetable and synthetic tanning agents, dyes, fat, emulsifiers, leather fibres	Retanning, dyeing, greasing, washing, samming	~ 5			
Global			Σ 15 – 30		Σ ~ 10	

Manufacture of vegetable tanned leather chemicals used, composition and volume of effluents						
Effluent No.	Chemicals used, effluent constituents		A) Starp and russet upper leather (e.g. belts, handbags, suitcases)		B) Sole leather	
			Operation	Flow (m <sup>3</sup> /t)	Operation	Flow (m <sup>3</sup> /t)
	COD	kg/t	~ 150		COD ~ 100 kg/t	
	mg/l	5 000 – 10 000		10 000 – 12 000 mg/l		

(<sup>1</sup>) Drum tanning used in split manufacture; here, the volume of waste water is ~1 m<sup>3</sup>/tonne raw hides; COD: up to 10 000 mg/l; BOD<sub>5</sub>: up to 3 000 mg/l.

### 3.4.2.1 Suspended solids

The main source of suspended solids in the effluents from tanneries is the liming process, as shown in Figure 3.11.

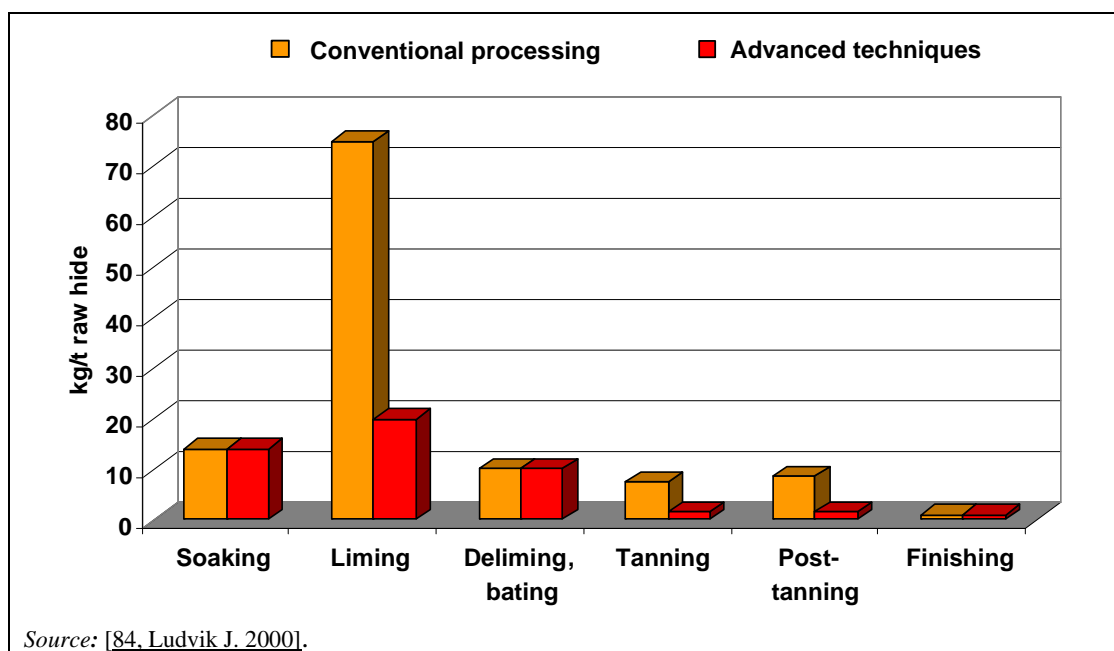


Figure 3.11: Comparison of mean suspended solid loads

### 3.4.2.2 COD

The main source of COD from tanneries is the liming process as shown in Figure 3.12. Approximately 50 % of the COD arises from this source. Soaking and the operations carried out post-tanning are also important sources.



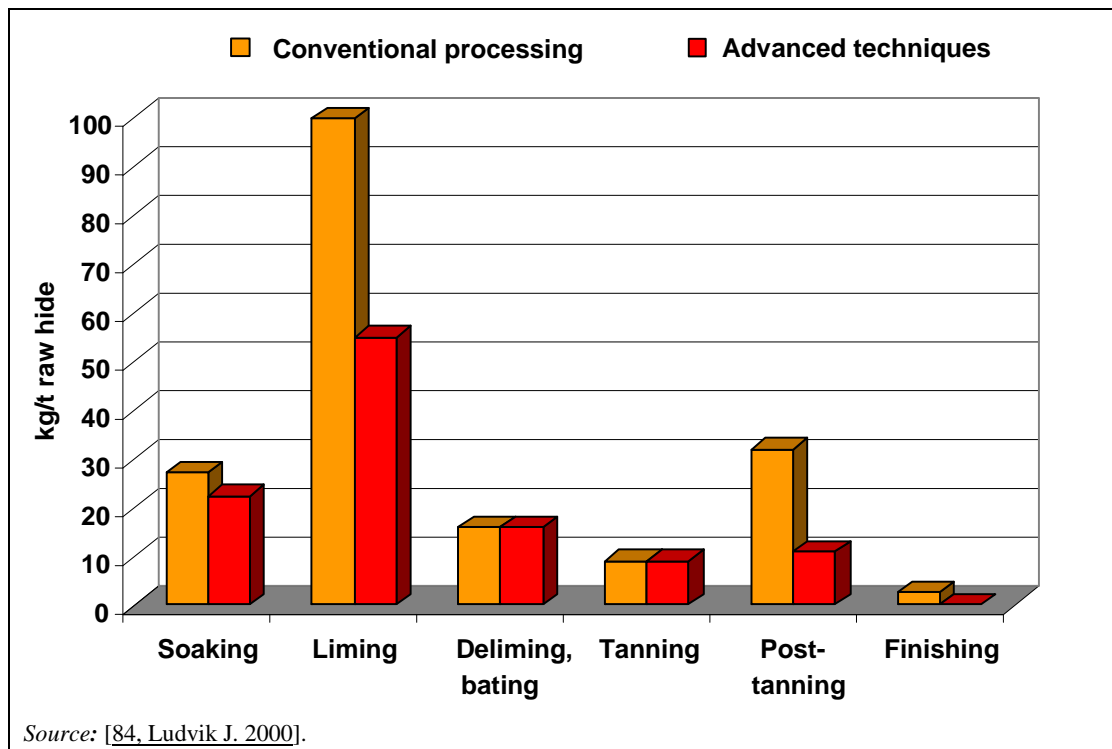


Figure 3.12: Comparison of mean COD loads

### 3.4.2.3 BOD

The main source of BOD from tanneries is the liming process and approximately 50 % of the BOD arises from this process. Soaking and the operations carried out post-tanning are also important sources.

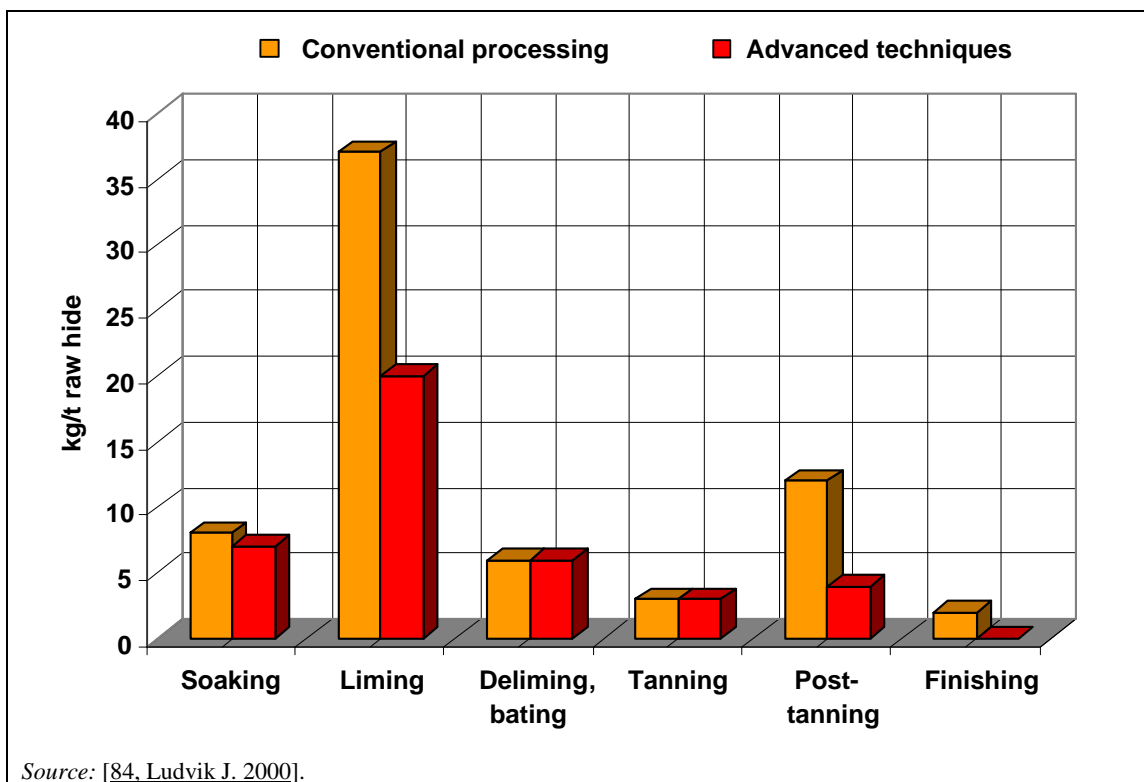


Figure 3.13: Comparison of the mean BOD loads

### 3.5 By-products and wastes

Fully processed grain-side leather comprises (very approximately) 20 % of the weight of the raw hides used in its production. In practice, the proportion varies, depending on the type of leather processed, the source of hides or skins and the techniques applied.

Some tanneries produce (and market) by-products such as lower specification leathers. A number of uses for tannery residues have been found in the past, and some may still be available. Tanneries produce also wastes for which there is no use and for which a disposal route must be found.

Directive 2008/98/CE and the laws implementing it contain definitions of waste which include some tannery residues. The established uses of these residues must be described as waste recycling for legal purposes.

Table 2.2 shows the categories of tannery wastes included in the European Waste List.

Table 3.14 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. The option chosen by a tannery will depend to a very high degree on the local availability of treatment or disposal facilities.

Table 3.14: Residues and wastes, their recycling and disposal

Process unit	Type of waste	Contents	Further treatment/disposal/recycling
<b>Trimming</b>	<ul style="list-style-type: none"> <li>Parts of the raw hides (trimmings)</li> </ul>	<ul style="list-style-type: none"> <li>Collagen, hair, fat, connective tissue, blood</li> </ul>	<ul style="list-style-type: none"> <li>Production of hide glue</li> <li>Animal feed stuff <sup>(1)</sup></li> <li>Biogas</li> <li>Thermal treatment</li> <li>Landfill <sup>(1)</sup></li> </ul>
<b>Curing</b>	<ul style="list-style-type: none"> <li>Solid salt</li> <li>Brine</li> </ul>	<ul style="list-style-type: none"> <li>NaCl and possibly biocides</li> </ul>	<ul style="list-style-type: none"> <li>Reuse (problems with infectious material on salt)</li> <li>Landfill <sup>(1)</sup></li> </ul>
<b>(Green) fleshing</b>	<ul style="list-style-type: none"> <li>Green fleshings</li> </ul>	<ul style="list-style-type: none"> <li>Fat, blood, meaty scraps</li> </ul>	<ul style="list-style-type: none"> <li>Production of hide glue</li> <li>Recovery of fat</li> <li>Composting</li> <li>Biogas</li> <li>Landfill <sup>(1)</sup></li> </ul>
<b>Liming and unhairing</b>	<ul style="list-style-type: none"> <li>Hair/wool</li> </ul>	<ul style="list-style-type: none"> <li>Keratin-rich material</li> </ul>	<ul style="list-style-type: none"> <li>Wool is sold</li> <li>Reuse as filling material</li> <li>Production of lanolin from sheep wool</li> <li>Fertiliser/agriculture/animal feedstuff</li> <li>Composting</li> <li>Biogas</li> <li>Landfill <sup>(1)</sup></li> </ul>
<b>(Lime) fleshing</b>	<ul style="list-style-type: none"> <li>Fleshings</li> </ul>	<ul style="list-style-type: none"> <li>Fat, meaty scraps</li> <li>Liming and unhairing chemicals</li> </ul>	<ul style="list-style-type: none"> <li>Production of hide glue/gelatine protein hydrolysate</li> <li>Recovery of fat (fleshings only)</li> <li>Composting</li> <li>Biogas</li> <li>Landfill <sup>(1)</sup></li> </ul>
<b>Lime splitting</b>	<ul style="list-style-type: none"> <li>Lime split (flesh-side)</li> </ul>	<ul style="list-style-type: none"> <li>Collagen plus liming and unhairing chemicals</li> </ul>	<ul style="list-style-type: none"> <li>Splits can be tanned to produce split leather</li> <li>Production of hide glue/gelatine</li> <li>Protein hydrolysate</li> <li>Sausage casings and other collagen products</li> </ul>
<b>Solvent degreasing</b>	<ul style="list-style-type: none"> <li>Distillation residues</li> </ul>	<ul style="list-style-type: none"> <li>Organic solvents and fat</li> </ul>	<ul style="list-style-type: none"> <li>Recycling of organic solvents</li> <li>Reuse of fats</li> <li>Thermal treatment of non-halogenated-organic-solvent-containing waste</li> <li>Recovery of fat using acid cracking for possible use in the cosmetic industry</li> <li>Low pH waste waters to be treated</li> </ul>
<b>Aqueous degreasing</b>	<ul style="list-style-type: none"> <li>Waste water treatment residues</li> </ul>	<ul style="list-style-type: none"> <li>Surfactants</li> <li>Emulsified and non emulsified fat</li> <li>Pretanning agent residues (e.g. aldehyde)</li> </ul>	
<b>Tanning/retanning</b>	<ul style="list-style-type: none"> <li>Tanning liquors</li> </ul>	<ul style="list-style-type: none"> <li>For chemical composition of agents, see Section 3.3.5</li> </ul>	<ul style="list-style-type: none"> <li>Recovery of chromium in tanning liquors</li> </ul>
<b>Tanned splitting</b>	<ul style="list-style-type: none"> <li>Tanned split</li> </ul>	<ul style="list-style-type: none"> <li>Leather material of inconsistent thickness and no 'grain' surface</li> </ul>	<ul style="list-style-type: none"> <li>Split leather</li> <li>Leather fibreboard production</li> <li>Protein hydrolysate</li> <li>Composting</li> <li>Agriculture</li> </ul>

Process unit	Type of waste	Contents	Further treatment/disposal/recycling
			<ul style="list-style-type: none"> <li>• Thermal treatment</li> <li>• Landfill <sup>(1)</sup></li> </ul>
<b>Shaving and final trimming</b>	<ul style="list-style-type: none"> <li>• Shavings,</li> <li>• Trimmings</li> </ul>	<ul style="list-style-type: none"> <li>• Organic matter with tanning chemicals</li> </ul>	<ul style="list-style-type: none"> <li>• Leather fibreboard production</li> <li>• Protein hydrolysate</li> <li>• Composting</li> <li>• Agriculture</li> <li>• Thermal treatment</li> <li>• Landfill <sup>(1)</sup></li> </ul>
<b>Fatliquoring</b>	<ul style="list-style-type: none"> <li>• Obsolete chemicals</li> </ul>	<ul style="list-style-type: none"> <li>• For chemical composition of agents, see Section 3.3.8</li> </ul>	<ul style="list-style-type: none"> <li>• Disposal of chemicals according to their characteristics</li> </ul>
<b>Dyeing</b>		<ul style="list-style-type: none"> <li>• For chemical composition of agents, see Section 3.3.10</li> </ul>	
<b>Milling/buffing</b>	<ul style="list-style-type: none"> <li>• Particulate matter</li> </ul>	<ul style="list-style-type: none"> <li>• Organic matter with contents according to tanning</li> </ul>	<ul style="list-style-type: none"> <li>• Landfill <sup>(1)</sup></li> <li>• Thermal treatment</li> <li>• Filler for plastics</li> </ul>
<b>Finishing (coating)</b>	<ul style="list-style-type: none"> <li>• Residues from finishes,</li> <li>• Sludges from finishing agents (over-spray, etc.)</li> </ul>	<ul style="list-style-type: none"> <li>• For chemical composition of agents, see Section 3.3.11</li> <li>• Solvents</li> <li>• Heavy metals</li> </ul>	<ul style="list-style-type: none"> <li>• Landfill <sup>(1)</sup></li> <li>• Thermal treatment</li> </ul>
<b>Trimming (final)</b>	<ul style="list-style-type: none"> <li>• Trimmings with or without finish</li> </ul>	<ul style="list-style-type: none"> <li>• Leather with contents according to tanning and finishing</li> </ul>	<ul style="list-style-type: none"> <li>• Leather fibreboard production for not lacquered</li> <li>• Trimmings other reuse (patchwork, small leather goods, etc.)</li> <li>• Landfill <sup>(1)</sup></li> <li>• Thermal treatment</li> </ul>
<b>Air treatment</b>	<ul style="list-style-type: none"> <li>• Depending on the abatement techniques: activated carbon, sludges from wet-scrubbers, filter dust etc.</li> </ul>	<ul style="list-style-type: none"> <li>• Depending on the off-gas stream</li> </ul>	<ul style="list-style-type: none"> <li>• Recovery of organic compounds (e.g. solvents)</li> <li>• Thermal treatment</li> <li>• Landfill <sup>(1)</sup></li> </ul>
<b>Waste water treatment</b>	<ul style="list-style-type: none"> <li>• Sludge from waste water treatment</li> </ul>	<ul style="list-style-type: none"> <li>• Depending on the separation of waste water streams</li> </ul>	<ul style="list-style-type: none"> <li>• Use in agriculture</li> <li>• Composting</li> <li>• Biogas</li> <li>• Landfill <sup>(1)</sup></li> <li>• Thermal treatment</li> </ul>
<b>Waste treatment</b>	<ul style="list-style-type: none"> <li>• Residues from on-site waste treatment</li> </ul>	<ul style="list-style-type: none"> <li>• Greaves from rendering, residues from anaerobic or aerobic digestion</li> </ul>	<ul style="list-style-type: none"> <li>• Use in agriculture</li> <li>• Landfill</li> <li>• Thermal treatment</li> </ul>
<b>Packaging</b>	<ul style="list-style-type: none"> <li>• Pallets</li> <li>• Paper</li> <li>• Plastics</li> <li>• Containers for chemicals</li> </ul>		<ul style="list-style-type: none"> <li>• Recycling</li> <li>• Landfill <sup>(1)</sup></li> <li>• Thermal treatment</li> </ul>
<b>Other</b>	<ul style="list-style-type: none"> <li>• Obsolete chemicals</li> <li>• Scrap metal and defunct equipment</li> </ul>		<ul style="list-style-type: none"> <li>• Recycling</li> <li>• Landfill <sup>(1)</sup></li> <li>• Thermal treatment</li> </ul>

<sup>(1)</sup> Legal restrictions apply.

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

Apart from the summary of waste treatment options summarised in Table 3.14, recycling, reuse and disposal of all waste fractions will be discussed in detail in Chapter 4.

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

Data for the percentage of various waste fractions with respect to the total waste production for salted bovine hides has been compiled from various sources [17, UNEP 1991], [4, Andres 1997] [8, Higham 1994], [10, Rydin and Frendrup 1993], and are shown in Table 3.15.

**Table 3.15: Proportion of organic residues generated during leather production from salted bovine hides.**

Residue	Mean amount of residue per unit of raw hide weight
	kg/t
Trimmings from raw hides	20 – 50
Lime fleshing	100 – 400
Lime split <sup>(1)</sup> and pelt trimmings	100 – 200
(Chromium) shavings <sup>(1)</sup>	200 – 300
(Chromium) split <sup>(1)</sup>	
(Chromium) leather trimmings	
Buffing dust	2 – 10
Finishing chemicals	5
Sludge from waste water treatment	400 – 500
Packaging	15
<sup>(1)</sup> Amount depending on whether splitting is undertaken in the limed or tanned condition.	

Other waste fractions not shown in Table 3.15 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.

### 3.5.1 Hair and 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 3.14). The majority of tanneries still 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.

### 3.5.2 Trimmings/fleshings/splits/shavings/particulate matter

The residues arising from the initial trimming of the raw hides are pieces of the raw hides, which carry curing agents and possibly biocides.

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 3.14.

Trimmings from later stages in the process, such as after tanning, post-tanning or finishing can be reused in the production of leather fibreboard (if they are not lacquered) [35, UBA 1997]. Trimmings that are not recovered or reused are a waste for which a disposal route must be found.

The figures for the amount of trimmings from raw salted bovine hides range from 2 % [10, Rydin and Frendrup 1993] to 5 % [16, Frendrup 1999]. If trimmings after lime splitting are included, the amount is estimated to be about 12 % [4, Andres 1997]. 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.

The average composition of fleshings calculated from data collected from 6 German tanneries between 1994 and 2006 are shown in Table 3.16.

**Table 3.16: Composition of Fleshings**

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

Fleshings and non-tanned splits 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 liming or after tanning. The flesh side of the split hide or skin, 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 particulate matter from milling and buffing contain the tanning chemicals. Any further reuse and treatment depends on the particular chemical composition. Some information from Germany on the composition and properties of tanned residues is shown in Table 3.17.

**Table 3.17: Composition of chromium tanned residues**

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

### 3.5.3 Sludges from waste water treatment

Waste water treatment sludges can arise from the treatment of tannery effluent on site or off site. 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. 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 in Italian tanneries is shown in Table 3.18. The figures are percentages of sludge from a biological treatment plant after dewatering.

Table 3.18: Composition of waste water treatment sludges in Italy

Parameter	Min. %	Max. %
Water content	55	75
Organic matter	40	75
Inorganic matter	25	60
Organic carbon	21	38
Ammonium	0.1	1.6
Nitrogen (organic)	1.3	7.0
Substance extractable with CH <sub>2</sub> Cl <sub>2</sub>	0.06	0.4
Phosphorous	0.01	0.06
Chromium(III)	0.8	5.0
Aluminium	0	5.0
Iron	0.6	12
Calcium	1.0	15
Sulphur (total)	0.7	7.0
<i>Source: [37, Italy 1998].</i>		

The composition of sludges from the treatment of chromium-bearing waste water in Germany is summarised in Table 3.19, and the composition of the eluate in Table 3.20.

The availability of disposal routes for sludges is decreasing overall. The availability of particular disposal routes also differs markedly between Member States.



Table 3.19: Composition of chromium-containing sludges in the original substance in Germany

Parameter in the original substance	Unit	Chemical-physical treatment of the segregated stream (precipitation)	Chemical-physical treatment of the combined streams (precipitation)	Biological precipitation of the segregated streams
Loss on ignition	%	34 – 70 mean 46	40 – 75	41 – 80 mean 50
TOC TOC-bio (62 days)	%	6.5 – 18.3 16.9	7 – 23 17.8	4.5 – 28 11.8
C total	%	15.7 – 28 mean 20.2	22 – 27 mean 24.3	12.8 – 26.8 mean 19.1
Extractable lipoph. substances	%	0.1 – 7.2 mean 3.0	4.1	1.4 – 6.8 mean 4.7
Fermentation test GB 21 <sup>(1)</sup>	NL/kg	28.4	161.9	26.0
Biological activity AT4	mg/g	3.3		
Calorific value	kJ/kg	3600 – 7100	9700	3200 – 11000 mean 8750
Soluble substances	%	0.2 – 3.9 mean 2.1		3.4
AOX <sup>(1)</sup>	mg/kg	25 – 85	15 – 25	30 – 290 mean 120
Chromium total <sup>(1)</sup>	mg/kg	6000 – 170 000 mean 100 000	5000 – 20 000 mean 10 000	5000 – 60 000 mean 15 000
As <sup>(1)</sup>	mg/kg	ND – 0.9	1 – 42 mean 25	0.8
Pb <sup>(1)</sup>	mg/kg	ND – 24 mean 5.2	25 – 60	5 – 35 mean 16
Cd <sup>(1)</sup>	mg/kg	ND – 0.1	ND – 0.3 mean 0.2	ND – 0.3 mean 0.2
Cu <sup>(1)</sup>	mg/kg	10 – 25 mean 16	20 – 35	40 – 120 mean 70
Ni <sup>(1)</sup>	mg/kg	5 – 25 mean 15	35 – 50 mean 41	5 – 25 mean 13
Hg <sup>(1)</sup>	mg/kg	0.2 – 1.1 mean 0.5	0.1 – 0.15	ND – 0.1
Zn <sup>(1)</sup>	mg/kg	100 – 200	90 – 200	100 – 250 mean 170
Cyanide l.f. <sup>(1)</sup>	mg/kg	<0.01	<0.01	<0.1
Al <sub>2</sub> O <sub>3</sub> (%)	%	0.5 – 40	0.3 – 1	0.2 – 1
Fe <sub>2</sub> O <sub>3</sub> (%)	%	0.4 – 10	10 – 15	0.5 – 5
CaO (%)	%	4 – 35 mean 15	15 – 25 mean 21	13 – 25 mean 19
MgO (%)	%	3 – 27	1 – 3	0 – 5

NB: ND = not detectable.  
<sup>(1)</sup> Related to dry matter (DM).  
Source: [ 85, Hauber and Knödler 2008 ].

Table 3.20: Eluate of chromium-containing sludges from tannery installations in Germany

Parameter in the original substance	Unit	Chemical-physical treatment of the segregated stream (precipitation)	Chemical-physical treatment of the combined streams (precipitation)	Biological precipitation of the segregated streams
pH	-	8 – 11.5	7.5 – 8.5	7.3 – 10.5
Conductivity	µS/cm	1500 – 8000 mean 4350	2000 – 5500	1500 – 8500 mean 4000
TOC	mg/l	65 – 500 mean 270	220	200 – 1000 mean 500
Total phenolics	mg/l	ND – 3.5 mean 1.1	4 – 5	0.01 – 1.5 mean 0.3
Fluoride	mg/l	ND – 2.8 mean 0.9		ND – 0.1
NH <sub>4</sub> -N	mg/l	0.3 – 70 mean 24		
AOX	mg/l	0.02 – 0.9 mean 0.25		0.01 – 0.19 mean 0.08
Cr <sub>total</sub>	mg/l	ND – 0.5 mean 0.11	0.2	ND – 0.7 mean 0.21
Cr(VI)	mg/l	ND – 0.45 mean 0.06	ND – 0.05	ND – 0.05
Volatile cyanide	mg/l	ND – 0.05 mean 0.001	ND – 0.05	0.001 – 0.06
As	mg/l	ND – 0.002 mean 0.0005	0.003	0.001 – 0.007 mean 0.003
Pb	mg/l	ND – 0.08 mean 0.01	ND	ND – 0.5 mean 0.1
Cd	mg/l	ND ND	0.0001	ND – 0.002 0.001
Cu	mg/l	ND – 0.05 mean 0.02	ND	ND – 0.01 mean 0.005
Ni	mg/l	ND – 0.09 mean 0.02	0.07	ND – 0.15 mean 0.04
Hg	mg/l	ND – 0.00015 mean 0.00004	ND – 0.001	ND – 0.001 mean 0.0003
Zn	mg/l	ND – 0.08 mean 0.02	ND	ND – 4.5 mean 1.0

NB: ND = not detectable.  
Source: [ 85, Hauber and Knödler 2008 ].

Although disposal is usually carried out outside the control of the tannery operator, the cost of that disposal has an economic impact. Another effect on tannery operations is that the pretreatment of wastes to facilitate their disposal may be carried out on site. In extreme cases, process changes may be required to alter the type or quantity of waste produced.

### 3.5.3.1 Landfilling of sludge

Landfilling of sludges has become difficult, partly because the availability of landfills is diminishing, but mainly because legislation implementing the Landfill Directive (99/31/EC) is being applied.

Member States may choose to specify limits on the total organic carbon content of wastes for landfill disposal. For example, a limit of 5 % has been specified by Austria, and between 1 and 6 % by Germany. Without pretreatment, sludges from biological waste water treatment plants do not meet these limits.

Underground storage of wastes in mine workings is included within the scope of the Landfill Directive. Member States may make limited exceptions for the underground storage of certain wastes.

An advantage of landfill disposal for sludges from tannery waste water treatment is that the chromium remains in the form of chromium(III) hydroxide, which is barely soluble. Conversion of chromium(III) to chromium(VI) in the interior of a landfill could not be detected [ 85, Hauber and Knödler 2008 ].

### 3.5.3.2 Landfilling with pretreatment

Anaerobic digestion is a pretreatment method applied to sludges from sewage treatment plants to prepare them for landfilling. Its use on similar materials from a tannery causes problems. Under anaerobic conditions, some species of bacteria reduce sulphate to sulphide. This results in hydrogen sulphide production. A pretreatment to remove sulphur compounds is necessary before anaerobic digestion can be applied to sludges from beamhouse or mixed effluents. Anaerobic digestion alone will not achieve a sufficient reduction to meet the TOC limit for landfill disposal that has been applied in some Member States.

Composting is another waste treatment method to prepare wastes for landfill disposal. In its simplest form it consists of spreading waste in thin strips to encourage aerobic decomposition. Some reduction in the organic matter content is achieved. Some tannery sludges are unsuitable for this treatment because of odour production.

Mechanical-biological treatment is a more rigorous pretreatment method. Some facilities in Germany have been able to treat tannery wastes. The proportion of chromium-bearing sludges has to be limited to 5 % of the input materials to the biological stage, and the time has to be extended by 10 – 20 %. Acid dosing of the exhaust air scrubbers is required to deal with ammonia emissions [ 85, Hauber and Knödler 2008 ].

### 3.5.3.3 Application of sludge and anaerobic digestates in agriculture

Although the application of sludge to land is generally an 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, might be necessary.

Laws implementing Directive 1986/278/EEC set limits for the concentrations of several heavy metals in sludge, but not for chromium in any form, and limits for the amounts of heavy metals which may be added to the soil in sludge.

In the UK, certain wastes treated by anaerobic digestion are exempted from subsequent control under waste legislation, so as to allow their use in agriculture and horticulture. Wastes included in Chapter 4 of the European Waste List are specifically excluded from the exemption. Some operators of anaerobic digestion plants may be reluctant to accept tannery wastes for this reason.

### 3.5.3.4 Thermal treatment of sludge

Incineration, gasification, or pyrolysis of sludges as a means of disposal, whilst recovering energy from waste is currently being investigated (see also Section 6.9.1).

The ash from the process still has to be disposed of, but this is more easily achieved than with untreated sludges.

For wastes containing chromium, a two-stage incinerator with a starved air primary chamber is required, to avoid the oxidation of chromium(III) to chromium(VI) [126, Bowden W. 2003]. Laws implementing Directive 2000/76/EEC on waste incineration (now Chapter IV of Directive 2010/75/EC) require that the temperature of gases in the secondary combustion chamber be held above 1123 K (850 °C) for a minimum of 2 seconds, to ensure the destruction of dioxins and furans. Comprehensive monitoring of the emissions is also prescribed. The cost of compliance raises the economic threshold for incineration.

### 3.5.4 Other waste fractions

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

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

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

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

**Finishing sludges** can contain hazardous substances depending on the finishes used. They can be treated physico-chemically or thermally or they may have to be disposed of as hazardous waste.

**Activated carbon filters** from air emissions abatement can be regenerated several times; final disposal is by thermal treatment or landfill. Leather dust can be thermally treated or it can be disposed of as a waste. Dust may also be compacted before disposal to facilitate handling. Sludges from wet-scrubbers are a waste for which a disposal route must be found.

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

Table 3.21 presents figures for the different disposal routes for other wastes. The principal practicable disposal routes are highlighted for each waste fraction (compare with Table 3.14).

**Table 3.21: Treatment and disposal routes for various wastes in Member States**

Disposal	Salt	Organic solvents	Chemicals	Fats from degreasing	Pigment sludges	Air abatement	Waste treatment	Packaging material
Reuse within process	x	x						x
Reuse in agriculture							x	
Physical/chemical treatment	x			x		x <sup>(1)</sup>		
Thermal treatment		x	x				x	x
Other reuse/recycling		x	x	x <sup>(2)</sup>				x
Back to supplier								x
Landfill	x <sup>(3)</sup>	x <sup>(3)</sup>	x <sup>(3)</sup>	x <sup>(3)</sup>	x	x	x	x

(<sup>1</sup>) Regeneration of activated carbon.  
(<sup>2</sup>) Recovery of organic solvent and fat.  
(<sup>3</sup>) Landfilling might still be allowed in some Member States.

### 3.6 Airborne emissions

For emissions to the air, data are only available for VOCs 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 their use is not standard practice 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.

Emissions into the workplace are generally outside the scope of this reference document. The ventilation of the workplace for safety reasons may however result in their being released to the environment.

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

Emissions from on-site incineration processes are controlled by laws implementing Directive 2000/76/EEC on waste incineration (now Chapter IV of Directive 2010/75/EC). A separate BREF document has been published for incineration [119, EC 2006].

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 use and emissions of VOCs from leather coating are regulated under laws implementing Directive 1999/13/EC on Solvent Emissions (now Chapter V of Directive 2010/75/EC).

Some general information on the control of emissions from coating using solvents is included in the BREF entitled 'Surface Treatment Using Organic Solvents' [139, [European Commission2007](#)]; information specific to leather coating is not included.

### 3.7 Energy

Energy consumption in tanneries depends mainly on the following factors:

- the production methods, and the capacity and size of equipment
- the age and sophistication of electric motor controls
- the amount of mechanical handling used to move hides and skins
- the drying methods used
- heat losses from process vessels and from buildings
- air exchange rates to meet workplace safety conditions
- types of waste water treatment on site
- types of waste treatment and recovery of energy from waste on site.

Heat losses may be mitigated by thermal insulation, but may be exacerbated by a low external temperature. A high moisture content in the air may increase the energy consumed in drying. Energy use data from one climatic zone may not be an accurate guide to what may be achieved in another.

The age and efficiency of the combustion equipment and boiler plant will determine the proportion of the energy of fuel which is made available as thermal energy in the tannery. A larger central boiler may be more efficient, but if operations are dispersed on a large site, heat losses from pipework may eliminate the gains. Such considerations are not confined to tanneries and are covered more fully in the BREF document for energy efficiency (ENE) [109, EC 2008].

**Table 3.22: Consumption of thermal and electrical energy**

Energy input	Use	% of overall consumption
<b>Thermal energy</b>	• Drying	32 – 34
	• Hot water	32 – 34
	• Space heating	17 – 20
<b>Electric energy</b>	• Machinery and process vessels	9 – 12
	• Compressed air	1.5 – 3
	• Light	1.5 – 3
<i>Source: [3, Andres 1995] [16, Frendrup 1999].</i>		

Table 3.22 gives an indication of energy consumption by type of energy input. The proportions can vary greatly between tanneries. For example, mechanical handling can be undertaken by fork lift trucks powered by internal combustion engines or by electrically powered conveyors. For this reason, the total energy input to the leather making process is a better comparator.

It is necessary that data be compared for the same stages of the leather making process. Ideally, energy use should be monitored and reported separately for each process stage, and it is known that some of the most energy-efficient tanneries do so.

Where more detailed data for energy use are available it is important that comparisons between tanneries be made on the same basis. For example, 'effluent treatment' may or may not include biological treatment, which can account for more than 50 % of the total energy consumption in the treatment of tannery effluent.

### 3.8 Noise and vibration

Some mechanical operations are the source of noise problems. Proper design and maintenance should reduce noise to acceptable levels.

Possible sources of noise audible outside the tannery include:

- drums and mixers
- pumps for water or liquid effluents and for circulating reagents in scrubbers
- fans for air extraction and aeration
- air compressors
- refrigeration, ice making or chiller units (including those of parked delivery vehicles)
- building panels actuated by vibration
- on-site power generation units or standby generators
- deliveries of compressed gases.



## 3.9 Typical emissions and consumptions from process units

This section discusses each of the process units used in the tannery. Overviews of the expected emission levels are given in Table 3.8. This information is indicative and not prescriptive. Variations may occur depending on the types of raw materials used and the types of products produced. Emission levels in connection with the use of techniques to consider in the determination of BAT are given in Chapter 4.

### 3.9.1 Trimming

Hides and skins may be trimmed in the tannery upon receipt. This generates trimmings that must be disposed of in compliance with EU Regulation 1069/2009 as animal by-products. Where hides and skins have not been preserved for long-term storage, trimmings are putrescible.

### 3.9.2 Curing

#### Consumptions

Hides and skins are brought from slaughterhouses to tanneries either directly or through hide markets, hide merchants and even other tanneries. The raw material has to be transported from the slaughterhouse to the tannery or from the slaughterhouse 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 of hides and skins in transit that cannot be processed immediately. The choice depends mainly on the period of time envisaged for preservation.

**Long-term preservation** methods are:

- salting
- brining
- drying
- 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 raw stock. 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 US 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 % hide weight for brine curing), p-dichlorobenzene, sodium silicofluoride, and borax. More

commonly known biocides such as boric acid and sodium metabisulphite might occasionally be used as preservatives.

Skins originating from countries with very hot climates may have been dried or dry-salted. Dry and dry-salted skins may contain insecticides such as pyrethrum and permethrin, which are added either to the raw material or to the salt to keep insects away from the edible 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) [37, Italy 1998].

**Short-term preservation** methods are:

- ice
- refrigerated storage
- biocides.

One of the short-term preservation methods is cooling. If the time between flaying and processing in the tannery is no more than 5 – 8 days, it is possible to cool the hides and skins, after draining the blood, to a temperature of 2 °C. 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 of processing fresh hides, the use of salt is avoided. However it 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 °C is maintained), for certain types of end-products and when processing sheepskins and/or calfskins.

In general, there are no biocides used in the preservation of raw bovine hides in Europe. Biocides that were used in the past included PCPs, DDT, HCH and other environmentally damaging substances. 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 EU. Furthermore, hides and skins could contain traces of biocides because of animal treatment with these substances prior to slaughtering.

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

### **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 reuse waste salt as this would increase the risk of contamination with salt-tolerant bacteria.

### **3.9.3 Beamhouse operations**

The range of processes carried out in the beamhouse (or limeyard) prepares the hides and skins for tanning. Substances removed from the hide or skin and the residues of processing chemicals contribute to the emissions to water of a tannery. The range of emission levels is summarised in Table 3.23 and Table 3.24.

**Table 3.23: Waste water loads from processing dry goatskins and sheepskins**

Dry goatskins and sheepskins	COD (kg/t)	S <sup>2-</sup> (kg/t)	NH <sub>4</sub> <sup>+</sup> (kg/t)	Cl <sup>-</sup> (kg/t)
Soaking				60 – 200
Liming/unhairing	200 – 350	10 – 25		
Deliming	15 – 30		6 – 12	
<i>Source: [37, Italy 1998].</i>				

**Table 3.24: Emissions to waste water from the beamhouse process, from the manufacture of chrome leather from bovine hides**

Bovine hides	COD (kg/t)	S <sup>2-</sup> (kg/t)	NH <sub>4</sub> <sup>+</sup> (kg/t)	Cl <sup>-</sup> (kg/t)
Soaking				60 – 200
Liming/unhairing	80 – 100	5 – 12		
Deliming	8 – 10		5 – 10	
<i>Source: [37, Italy 1998].</i>				

### 3.9.3.1 Soaking

#### Consumptions

The 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. Sheepskins generally require more water in wet processing than hides, because of the nature of the wool. In most tanneries, the soaking is repeated 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 and the production of foul odours. The biocides are added particularly if the soaking is performed at an elevated temperature, at a rate of about 0.1 % of the hide weight. [50, Sharphouse 1983].

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 [10, Rydin and Frendrup 1993] is added, although the latter might cause problems with AOX in the waste water effluents. Alternatively, weak acids such as formic acid or sodium bisulphite can be used. Generally, biocides, alkali, e.g. caustic soda or sodium carbonate, surfactants and enzymes are added each in amounts of less than 1 % of the weight of the salted hides and skins.

#### Emissions

The soak liquor is discharged to the waste water treatment plant. The effluent contains soluble proteins like albumin and proteolytic and other bacteria. Suspended matters like dirt, dung, and blood washed from the hides and skins are discharged in the soak liquor, which results in a high COD loading of the effluent.

If the hides and skins were preserved, the effluent contains most of the salt and biocides which were on the hides. The salinity of the soak liquor varies from 11 200 to 23 600 mg/l (as Cl). Soak liquors undergo putrefaction very rapidly since they contain a large amount of impurities and have a favourable pH for the growth of the bacteria. The BOD of the soak liquor is usually

between 1100 and 4930 mg per litre. The quantity of soak liquor discharged will be 250 and 400 litres per 100 kg of hide or skin tanned. The BOD load per 100 kg of hide processed is between 0.41 to 2.48 kg.

The substances added in the soaking operation are largely contained in the soak liquor. These substances include biocides, surfactants, and organic solvents. As organic substances, they contribute 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.

Table 3.25 shows the range of concentrations of types of pollutants that may be found in the effluent from the soaking process. The actual loads and concentrations of pollutants vary widely from tannery to tannery depending on the raw materials used, the process operated and the specifications of the products.

**Table 3.25: Emission loads from conventional soaking**

Pollutants in waste water	Present	Emission loads from conventional soaking of salted bovine hides, in kg per tonne raw hide			
Total solids	Always				160
Suspended solids	Always	15		15	15
COD	Always	40		30 – 50	27
BOD	Always	8 – 10		8 – 10	10
Chloride	Often	200 ± 50	60 – 200	200 ± 50	85
Biocides	Often				
Detergents	Often				
Enzymes	Sometimes				
<i>Source: [10, Rydin and Frendrup 1993] [37, Italy 1998] [56, Pearson et al. 1999] [16, Frendrup 1999].</i>					

Sixty percent of tannery chloride originates from the 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 [8, Higham 1994], [10, Rydin and Frendrup 1993].

Further possible problems are odours due to putrefaction and releases of hydrogen sulphide and ammonia [15, Spain 1997].

### 3.9.3.2 Liming and unhairing

The environmental impact from the liming and unhairing of hides and skins will vary depending on the incoming raw material. There are components which, in any case, have to be eliminated from the hide (hair, fat, non-collagenous proteins, mucopolysaccharides, etc.). Normally, a maximum of 240 kg hide substance out of 1100 kg fresh weight or 1000 kg salted weight (as bought by the tanneries) can be used as leather; the remaining parts are waste or by-products. Factors which influence the specific amount of these components are species and breed of the animal, hair length, fat content and thickness of the hide, and hide cleanliness.

### Consumptions

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<sub>2</sub>S (or plus NaHS). Water consumption, including the rinsing afterwards, is considerable (almost a quarter of overall consumption in the tannery).

Other tanneries use thiols, mercaptoethanoates, amines or enzyme preparations to substitute for some or all of the sodium sulphide.

Sodium hydroxide, sodium carbonate and calcium chloride can also be used as 'sharpening' agents [50, Sharpouse 1983].

The concentration of chemicals varies greatly depending on the type of raw stock processed. For example, small calfskins will require higher chemical concentrations to achieve successful hair removal. A broad range of percentages (based on the raw material weight) of water and chemicals used during processing is shown in Table 3.26.

**Table 3.26: Water and chemical use in processing**

Water (including washes)	150 – 3000 %
Hydrated Lime	3 – 6 %
Sulphides	1 – 5 %
Amines	0.2 – 1 %
Enzymes	0.5 – 1 %
<i>Source: [56, Pearson et al. 1999].</i>	

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

Table 3.27 and Table 3.28 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 stated.

Table 3.27: Waste water load of liming-unhairing process

Typical waste water loads per tonne raw (soaked) hides: liming/unhairing			
Parameter	Unit	Conventional technology Hair-dissolving process, carried out with high quantities of chemicals (5 % lime, 1.6 % S <sup>2-</sup> )	Average process Hair-dissolving process with good chemicals economy (2 % lime, 0.8 % S <sup>2-</sup> )
Water volume	m <sup>3</sup>	12	9
Total solids	kg	187	150
Suspended solids	kg	93	66
BOD <sub>5</sub>	kg	50	40
COD	kg	130	100
Total Kjeldahl nitrogen (TKN)	kg	5.8	5.8
Ammonia nitrogen	kg	0.4	0.4
Sulphide (S <sup>-</sup> )	kg	8.5	5
Chloride (Cl <sup>-</sup> )	kg	15	15
Grease and oil	kg	5	5

Source: [16, Frendrup 1999].

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.

Table 3.28: Waste water load of conventional liming and unhairing process

Raw material	COD (kg/t)	S <sup>2-</sup> (kg/t)
Bovine hides	80 – 100	5 – 12
Dry goat skins and sheepskins	200 – 350	10 – 25

Source: [37, Italy 1998]

The effluents of liming and unhairing are characterised by their high alkalinity, their high sulphide content and their 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 [10, Rydin and Frendrup 1993]. 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 stem from liming and unhairing [16, Frendrup 1999].

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 effluent containing sulphide with acidic effluent. Low emissions of sulphides might even arise if no agents containing sulphide are used, because some degradation products from keratin are alkyl sulphides. Thiols, which are added or are formed by the degradation of sulphur containing proteins, are found in waste water effluents. Some are highly volatile, so might cause an odour problem in the waste water treatment and may need abatement measures [14, Reemtsma 1994]. If the sulphide solution is alkaline, 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 acidic.

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

### 3.9.3.3 Painting and pulling of sheepskins

#### Consumptions

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 polyacrylates.

Some tanneries in Spain spray the flesh side of sheepskins with a paint which does not contain lime.

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 but with the difference that there is a carryover 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 from this process are recycled.

#### Emissions

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

### 3.9.3.4 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 wool scourers.

#### 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.

### 3.9.3.5 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.

Fleshing is a mechanical process and involves cutting away the non-hide tissue from the flesh side of the hide or skin. If the fleshing has not already been carried out in the slaughterhouse, it can be carried out before or directly after liming. Fleshing after liming is traditionally the preferred practice, as the hide or skin is easier to flesh and to split in the swollen condition.

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 the fleshing of hides and skins, other than sawdust that operators may use to get a better grip of the slippery hides. The fleshing machines generally use water to wash away the fleshings.

### **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 fleshings may be putrescible, or subject to legal control under the Animal By-products Regulation. These factors determine the availability of disposal routes for the fleshings. The disposal route for fleshings also depends on the local availability of treatment facilities. In some Member States, fleshings can be landfilled normally after treatment, such as digestion or composting. Often fleshings will be sold for the production of, e.g. hide glue, or for fat recovery. A traditional outlet is rendering.

### **3.9.3.6 Splitting**

#### **Consumptions**

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 the splitting is carried out, the fewer chemicals and the less water will be used to process the hides and skins. However, tanneries do not always split in the limed stage for technical reasons or because of 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 to 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 can 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.



### 3.9.3.7 Deliming and bating

#### Consumptions

In order to reduce the alkalinity and remove the calcium from the limed hides, a combination of washes and delimiting agents is used. Generally, the calcium held on the surface of the hides can be removed through washing. Adding delimiting salts, such as ammonium chloride or ammonium sulphate and organic ammonium salts can further reduce the pH [27, BASF 1997] [27, BASF 1997]. The amount added is about 2 – 3 % of the weight of raw hides [15, Spain 1997], [16, Frendrup 1999], while a use of 2.5 – 4 % has also been reported [56, Pearson et al. 1999].

Carbon dioxide can also be injected into the float as a full or partial replacement for ammonium salts. The amount of CO<sub>2</sub> ranges between 1 and 2.2 %, [16, Frendrup 1999], while Finland reports a typical carbon dioxide consumption of 0.75 – 1.5 % (of the weight) [48, Kustula, V et al. 1998]. When thick hides are processed, delimiting with CO<sub>2</sub> reaches its limits and ammonium compounds or organic or inorganic auxiliaries (e.g. boric acid) are added to aid the speed of the delimiting process [16, Frendrup 1999].

For both types of process, about 200 % of the raw hide weight of water is necessary. Further alternative delimiting agents, which may be used on their own or in combination with traditional delimiting salts, include organic acids and sodium bisulphite. Auxiliary surfactants are added at the rate of 0.2 % of weight of raw hide [15, Spain 1997].

Bating enzymes sold for tannery use contain only 1 – 5 % of either pancreatic or bacterial enzymes (active ingredient). The remaining 95 – 99 % of bating agents consists of inert carriers (wood flour, kaolin) and salts (ammonium chloride in most cases) [56, Pearson et al. 1999].

#### 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<sub>2</sub> delimiting (and in pickling).

When using ammonium salts for delimiting, the ammonium reacts with the alkaline liquors to form ammonia gas, which is released to air. Good ventilation is necessary.

Furthermore, the ammonium salts contribute to a large extent to the total NH<sub>4</sub>-N released [16, Frendrup 1999]. 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/denitrification in a waste water treatment plant.

If carbon dioxide (CO<sub>2</sub>) is used as a delimiting agent to completely or partly substitute ammonium, the reduction of ammonium in the waste water is considerable (see Table 3.29).

A comparison of the emission levels from the delimiting and bating operation using either ammonium salts or carbon dioxide is shown in Table 3.29

**Table 3.29: Emissions in waste water from delimiting and bating**

Emissions to waste water from delimiting and bating in kg per tonne of raw hide	Ammonium salts	CO <sub>2</sub>
BOD	3 <sup>(1)</sup>	3 <sup>(1)</sup>
COD	6 <sup>(1)</sup>	6 <sup>(1)</sup>
TS	45 <sup>(2)</sup>	30 <sup>(1)</sup>
TKN	5 <sup>(1)</sup>	1.5 <sup>(1)</sup>
NH <sub>4</sub> -N	4.1 <sup>(1)</sup>	0.1 <sup>(1)</sup> – 0.2 <sup>(2)</sup>
<sup>(1)</sup> Rydin and Frendrup, 1993. <sup>(2)</sup> Frendrup, 1999. Source: [10, Rydin and Frendrup 1993] [16, Frendrup 1999].		

### 3.9.4 Tanyard operations

#### 3.9.4.1 Pickling

##### Consumptions

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 in 2008 were 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 first 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 [29, Renner 1995], [17, UNEP 1991]. A wide variety of commercial fungicides is on the market, e.g. TCMTB, thiobenzothiazole and p-chlorometacresol. Fungicides are typically applied in low quantities, up to 0.2 % of the weight of the pelts. The use of certain biocides will be restricted by the implementation of Directive 98/8/EC, from 2010. The active substances that may be used by the leather industry will be those mentioned in Annex I of this Directive.

##### Emissions

Effluent from pickling is acidic (pH as low as 2) and very high in salt concentration. Pickling liquors are second only to soaking liquors as a source of salinity in the tannery effluent.

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 hydrogen peroxide or sodium metabisulphite to the float can prevent these emissions.

### 3.9.4.2 Degreasing

#### Consumptions and 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 [ 24, AIICA 1988 ] [37, Italy 1998]

- degreasing in an aqueous medium with organic solvent and non-ionic surfactant
- degreasing in an aqueous medium with non-ionic surfactant
- degreasing in an organic solvent medium.

#### 1. Degreasing in an aqueous medium with organic solvent and surfactant

This 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 Baumé) and small amounts of non-ionic surfactant. The need to use salted water for washing (4 – 5 % sodium chloride) can be avoided if the skins are previously neutralised. The amount of petroleum/white spirit used in this process can be as high as 20 % based on the lime weight.

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 consequently 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.

#### 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 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. Depending on the surfactant used, the amount needed is in the range of 3 – 10 % to achieve a fat residue in the pelts of 2 – 5 % [37, Italy 1998].

There are some variations according to the specific characteristics of the skins, the fat content and its nature. Usually a certain pretanning is required to increase the shrinkage temperature. This enables the fat to emulsify and to flow easily when its melting point is too high. The shrinkage temperature of the skins must be at least 20 °C higher than the operation degreasing temperature, which can be up to 60 °C [16, Frendrup 1999]. Pretanning agents that could be used (1 – 3 %), include glutaraldehyde, aluminium sulphate, or syntans [16, Frendrup 1999].

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.

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.

### Emissions

The amount of water in the whole degreasing process (main float and further washes) is about 8 – 10 l/skin. The first float (1.5 – 2 l/skin) is treated separately, as the fat and surfactant content (7 – 9 %) is much higher than the rest. Treatment consists of breaking the emulsion of fat and surfactant by increasing the temperature to 90 °C. 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.

### 3. Dry degreasing in an organic solvent medium

This is applied by extraction at an intermediate temperature directly in the solvent, usually trichloroethene or tetrachloroethene. 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 at the crust stage to equalise the residual fat and to ensure a steady dyeing in further operations. The degreasing is carried out in closed machines; the used solvent is automatically distilled and reused. The distillation is quite effective, although never complete. [24, A.I.I.C.A 1988].

As the technique uses solvent alone, the pelts have to be in a dry state otherwise the solvent cannot come into contact with the fat. Moreover, since 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 is only used when aqueous degreasing is not possible or not efficient enough and has to be completed by degreasing in the dry state [24, A.I.I.C.A 1988]. Possible cases are wool-on sheepskins, very fatty skins (domestic English, Australian, etc.) and fatty wet blue imported as such [37, Italy 1998].

### Emissions

The residual fat retains a considerable amount of the chlorinated solvent [24, A.I.I.C.A 1988]. Also the waste water contains chlorinated solvent which can be removed by using activated carbon.

### 3.9.4.3 Tanning

#### Consumptions

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 types of tannage shown in Table 3.30 can be used in a tannery.

**Table 3.30: Type of tannage, main tanning agents, and auxiliaries**

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

For the tanning process, a large variety of chemicals is necessary and only a part of these chemicals is 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 chromium, 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 synton tannins by the formation of water-insoluble compounds. These products are mainly aluminium or manganese salt, albuminous materials, usually cationic organic compounds containing nitrogen 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.

#### 3.9.4.3.1 Mineral tanning

Although tanning with chromium agents was introduced only about 100 years ago, this is the most commonly used procedure. The main tanning agent is a basic sulphate complex of trivalent chromium. 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 chromium salts are mostly added as a powder with offers between 8 and 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 25 % of active tanning material (2 – 3 % measured as Cr<sub>2</sub>O<sub>3</sub>) and 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  $\text{Cr}^{3+}$ ) are sometimes introduced. Masking increases the precipitation point of the complex. The amount of masking agent can vary from 0.5 to 1.0 % [56, Pearson et al. 1999].

In a conventional tanning process, between 60 and 80 % [56, Pearson et al. 1999] [50, Sharpshouse 1983] of the chromium oxide may be fixed on the leather, the remainder being left in the water phase. Several options exist to reduce the releases of chromium into the environment from this process step. Further chromium releases occur from the subsequent steps in the tannery either because the chromium is not totally fixed in the hides and skins and is washed off, or because more chromium 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 chromium, a mixture of salts, complexing agents, natural grease, and traces of fungicide.

In Table 3.31, the consumption of water and main effluent parameters for liquors from chrome tanning are summarised from various references.

**Table 3.31: Water consumption and emissions to waste water from pickling and chrome tanning per tonne of raw hide**

Liquors	Drain	$\text{Cr}^{3+}$ salts in spent liquors	Salt (Cl)	TDS	SS	BOD	COD	TKN	$\text{NH}_4\text{-N}$
m <sup>3</sup> per tonne of raw hide	m <sup>3</sup> per tonne of raw hide	kg per tonne of raw hide	kg per tonne of raw hide	kg per tonne of raw hide	kg per tonne of raw hide	kg per tonne of raw hide	kg per tonne of raw hide	kg per tonne of raw hide	kg per tonne of raw hide
0.2	0.3 – 0.5	5 – 10	30 – 100	~ 175	~ 5	~ 3	~ 14	~ 1	~ 0.5
<i>Source:</i> [7, Zimpel 1997] [56, Pearson et al. 1999] [11, Heidemann 2000] [29, Renner 1995] [56, Pearson et al. 1999] [11, Heidemann 2000]									

High exhaustion methods of chromium tanning can reduce the chromium content of waste water by as much as 95 %. Residual floats can have a chromium content of about 0.5 to 1 kg per tonne of raw hide processed [8, Higham 1994].

Besides chromium, some tanning, retanning or pretanning is done using aluminium, zirconium, and titanium. Aluminium, zirconium and titanium cannot be used as substitutes for chromium in the tanning process, as the leathers tanned with chromium 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 pretanning [2, HMIP 1995] [3, Andres 1995]. Occasionally aluminium is used in chrome tanning to increase the uptake of chromium [11, Heidemann 2000], 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 [16, Frendrup 1999]. For a reduction of chromium, the dosage could be ~ 1.5 % Cr<sub>2</sub>O<sub>3</sub> (~12 kg/t raw hide) and 0.25 % aluminium oxide.

Aluminium salts can also be combined with aldehydes; such as glutaraldehyde. 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 type of glutaraldehyde used is a modified glutaraldehyde, which is considered much safer.

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

Zirconium sulphate is mostly used as tanning material. Using zirconium as a tanning agent, a lower pH (1.3 – 1.5) than for chrome tanning is initially 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 pretannage with formaldehyde or as a retannage for chrome leather in combination with aluminium or chromium salts [8, Higham 1994].

Titanium salts are excellent pretanning and retanning agents and they can be used successfully in combination with other mineral tanning agents [56, Pearson et al. 1999]. 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.

#### 3.9.4.3.2 Vegetable tanning

##### Consumptions

The plant extracts applied for vegetable tanning are either polyphenolic compounds (condensed vegetable tannins) or esters of glucose and gallic acid (hydrolysable vegetable tannins), which are leached (with water) from wood, barks, leaves, roots, and other plant material [56, Pearson et al. 1999] [3, Andres 1995] [16, Frendrup 1999].

The most commonly used vegetable tannin extracts are:

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

Three techniques of vegetable tanning can be distinguished:

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

Another principle is based on the Liritan system, whereby the pelts are pretanned using Calgon (sodium hexametaphosphate) and they are subsequently tanned in the same strength liquor [56, Pearson et al. 1999].

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

The countercurrent system uses a series of pits in which hides are successively immersed in tanning liquors which vary from 'nearly exhausted' to freshly prepared. As liquors lose strength, they are pumped to earlier stages of the process. Deliming acids may be formed in the nearly exhausted liquors by fermentation but may be supplemented by adding acid [50, Sharphouse 1983].

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 opportunity to use depleted 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 resistance to mechanical action. After this process, full penetration of vegetable tannins can take place in a drum [56, Pearson et al. 1999]. This tanning system is capable of tanning medium/heavy weight leathers in five days.

In sole leather, about 350 – 500 kg of tanning extracts 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 pretanning, shaving and splitting stages.

Depending on the type of vegetable tanning employed, vegetable-tanned leather can be used for shoe soles, shoe uppers, harnesses, saddles, belts, leather goods, clothing, 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 220 kg/tonne hide). Some of this load consists of materials of low biodegradability, or 'hard COD'. A further problem may be the colour and phenolic compounds of these effluents.

There is no specific pretreatment method for vegetable tanning liquors to reduce the hard COD. The waste water is therefore always treated together with other effluent streams and taken (after buffer storage and neutralisation, if necessary) into biological treatment.

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

Materials such as splits, shavings and buffing dust can be reused and easily disposed of, as they do not contain any minerals (see Section 4.11.1 for the recycling and reuse of these materials).



Apart from quebracho, all vegetable tannins originating from trees are obtained from renewable sources. An increase in the use of vegetable tannins might cause consumption to exceed this supply. See also Section 6.3.1.

### 3.9.4.3.3 Other organic tanning

#### Syntans, resins, and polyacrylates

Synthetic tanning agents (syntans) were developed as substitutes for vegetable tannins [16, Frendrup 1999]. Some syntans are tanning agents in their own right. Others are used in pretanning and retanning (e.g. acrylic polymers, sulphonated phenol formaldehyde and naphthalene formaldehyde), some are used as auxiliaries to induce certain leather properties (e.g. urea formaldehyde and melamine resins).

Depending on the combination with other tanning methods, 1 – 15 % of the pelt weight of syntans is applied [4, Andres 1997] [17, UNEP 1991].

Syntans and resins are also used in combination with vegetable tanning to improve the penetration of the vegetable tanning agents [8, Higham 1994].

Modern formulations of syntans are available with a low phenol and low formaldehyde content, as are resins with a low formaldehyde content, and acrylic acid condensates with a low acrylic acid monomer content.

#### 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.

#### Aldehydes

Some aldehydes are used as tanning agents [16, Frendrup 1999]. Glutaraldehyde and modified glutaraldehydes are used for pretanning and retanning. They are also used as tanning agents, producing leather with distinct properties (very soft and full, yellowish with high wash and sweat resistance) for special purposes, e.g. golf gloves or wooskin bedspreads for hospitals.

Formaldehyde is not used 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 pretanning to accelerate vegetable tanning and to fix hairs of fur and sheep wool [11, Heidemann 2000].

#### Emissions

Glutaraldehyde is generally fully exhausted in the tanning 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 the excess cod oil and washing with sodium carbonate, they may be subject to some after-treatments, such as dyeing. In an alternative, a pretanning step with glutaraldehyde is performed, before the cod oil is applied to the hides and with warm air blowing into the vessel. [3, Andres 1995]

#### 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.

### 3.9.4.4 Draining and 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 m<sup>3</sup> of effluent per tonne limed hide can be generated [7, Zimpel 1997].

### 3.9.4.5 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 known as shavings, which typically constitutes between 2 and 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 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 and dust 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 4.10)

## 3.9.5 Post-tanning operations

The output to the water medium from post-tanning operations arises principally from the retanning and fatliquoring processes.

Table 3.32 shows emissions to waste water from post-tanning operations, in an advanced tannery processing salted bovine hides.

Table 3.32: Emissions to waste water from post-tanning operations

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

Large differences can be noted between the COD discharges from the post-tanning operations of some plants. These occur because the post-tanning operations are designed to give particular properties to the final leather for various uses. The COD discharge from the production of upholstery leather is usually higher than that from the production of upper leather.

Fungicides have to be used in tanning with glutaraldehyde, in doses higher than those required for chromium tanning. A proportion of these materials will appear in the effluent from post-tanning processes.

### 3.9.5.1 Neutralisation

#### Consumption

Neutralising agents are mildly basic. The following neutralising agents can be used:

- sodium carbonate, sodium bicarbonate, and ammonium bicarbonate
- sodium bisulphite, sodium metabisulphite, and sodium thiosulphate
- ammonia
- sodium tetraborate (borax)
- sodium formate, calcium formate, and 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.

### 3.9.5.2 Retanning

#### Consumption

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.

#### Emissions

The main environmental problems stem from: high COD from incomplete exhaustion of retanning agents; the non-tannins contained in vegetable tanning agents; and residual monomers contained in syntans and polymeric tanning agents. Chromium is emitted in the effluent from chromium retanning and from the retanning of chromium-tanned leather. There may also be emissions of inorganic salts originating from syntans.

### 3.9.5.3 Stripping and bleaching

#### Consumption

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 chromium(III) to chromium(VI) in the leather.

### **3.9.5.4 Dyeing**

#### **Consumption**

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 a central metal ion and one or two azo dye ligands. The central ion can be iron, chromium, nickel, copper and cobalt. It is assumed that metal complex dyes containing lead and cadmium are no longer used in Europe [91, Suppliers 2008].

Vegetable dyes are extracts of logwood, redwood, 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, other chemicals are used as, e.g. wetting agents [61, TEGEWA 1987] levelling agents, bleaching agents, shade intensifiers, and 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.

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

The exhaustion of the liquor 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.

A limited number of dyes contain one or two chlorine atoms in the structure (for leather dyes other halogens will normally not be used). As an example, one dye supplier markets around 80 dyes for drum application, and of these only six dyes have chlorine in their molecular structure (7 – 8 % molecular weight of the dyes). These dyes are not produced in large quantities. On a weight basis the sale of dyes containing chlorine for this supplier is around 2 – 3 %. [91, Suppliers 2008].

Dyes in the 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.

### 3.9.5.5 Fatliquoring

#### Consumption

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 and 15 % based on shaved weight, with shoe uppers requiring less fatliquor than upholstery [17, UNEP 1991] [4, Andres 1997] [8, Higham 1994]. 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. Many fatliquors are produced from unsaturated oils or aliphatic hydrocarbons and they may be sulphochlorinated before they can be emulsified in water.

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 [11, Heidemann 2000]. The wet leather is treated in a drum with a warm mixture of molten fat also containing 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 and carbohydrates as well as natural and synthetic mucilaginous substances and preparations thereof [61, TEGEWA 1987].

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 properties.

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 (see Table 3.33). 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 contribute to the AOX load.

**Table 3.33: Emissions to waste water from conventional post-tanning operations**

Emissions to waste water from conventional post-tanning operations	Emissions per unit of raw hide (kg/t)
TS	65
SS	7
BOD	14
COD	20 – 30
N-tot	0.8 – 1
NH <sub>4</sub> <sup>+</sup>	0.6 – 0.8
Cr	1
Cl <sup>-</sup>	2 – 5

*Source: [10, Rydin and Frendrup 1993] [29, Renner 1995].*

### 3.9.5.6 Application of flame-retardants

Leather can rarely be considered a flammable material. The application of flame-retardants is therefore restricted to particular applications such as leather in aircraft seats, train seats or facilities in public buildings. In exceptional cases, safety shoes and safety gloves are treated with flame-retardants.

The main chemical classes of flame-retardants are listed below:

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

Brominated flame-retardants (BFRs) have been added to consumer products including leather for several decades, as they are efficient flame-retardants even in low concentrations. However, during recent years (information from 2008) they have attracted renewed attention because of environmental and health concerns. As a consequence, some flame-retardants belonging to polybrominated diphenyl ethers (BDE), such as penta- and octa-BDE, were banned for use in the European Union in 2003 (Directive 2003/11/EC). Other organic bromine compounds are subject to careful examination in EU risk assessments.

### 3.9.5.7 Drying

#### Consumption

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 out 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 make the grain side adhere 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. Some tanneries have installed low temperature drying and vacuum drying systems to improve the area yield of the leathers produced, and to save energy. Energy saving efforts mainly concentrates on insulating pipes and drying equipment and controlling the temperature and humidity of the air.

### 3.9.6 Finishing

#### 3.9.6.1 Mechanical finishing operations

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 is chrome tanned, a high chromium content. The dust from milling and buffing is exhausted from the workplace. The techniques for dust collection and abatement are described in detail in Section 4.10.

Buffing dust concentrations vary from 0.1 to 30 mg/m<sup>3</sup> depending on the equipment in place. The hazard of the particulate matter depends mainly on its chemical composition, the particle size and the mode of contact.

In some tanneries, particulate matter is compacted and briquetted, after being collected by various systems (see Section 4.10). These residues are wastes for which a use or disposal route must be found. If a wet scrubbing system is used, the slurry produced is a waste for disposal. Recycling the washing water can reduce the water consumption [41, Various 1998] [91, Suppliers 2008].

Mechanical finishing operations create noise, and consume energy. Dust extraction systems contribute to both of these parameters. Recycling of the cleaned air might save energy for workplace heating.

#### 3.9.6.2 Coating

The different types of finishing processes were mentioned in Section 2.5.2.

Padding can be carried out manually or by machine. This operation has a relatively low throughput, and is labour intensive. 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 minimise emissions into the working environment. Extracted air may require treatment to reduce particulate and organic solvent emissions.

A comparison between finishing techniques is shown in Table 3.34.

**Table 3.34: Finishing techniques efficiency compared**

Parameters	Spray line	Roller coater	Curtain coater
<b>8 hour throughput</b>	2000 – 2500 sides	600 – 800 sides	1000 – 1200 sides
<b>Level of waste</b>	40 % – 60 %	10 %	10 %
<i>Source: [56, Pearson et al. 1999].</i>			

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. In assessing the VOC emissions, a distinction has to be made between the applied solvents according to their toxicity. Formaldehyde, for example, is used for fixing protein finishes (and ironing wool-on sheepskins) [17, UNEP 1991]. It is carcinogenic and requires special precautions. Provisions for organic solvent recycling include a careful selection of organic solvents; otherwise recycling can be impossible (see Section 4.10.2).

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 top-coat. Quantities of surface coats applied to leather range from 0.2 g/m<sup>2</sup> for sole leather up to 400 g/m<sup>2</sup> for heavily finished leathers, such as corrected grain, pigmented splits and oily leathers. The main finishing coats and their components are shown in Table 3.35.

**Table 3.35: Finishing coats: main components and additives**

Type of coat	Main components	Additives
<b>Base coats</b>	Water/organic solvent	Waxes
	Pigments/dyes	Surfactants
	Resins	Thickening agents
		Fillers
<b>Intermediate coats</b>	Water/organic solvent	Waxes
	Pigments/dyes	Thickening agents
	Resins	Fillers
<b>Top coats</b>	Water/organic solvent	Waxes
	Solvent-based lacquers	Silicon-based agents
	Water-based lacquers	Matting agents
	Binders	Cross linkers

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 [3, Andres 1995] [11, Heidemann 2000].

Processes such as padding, plating or ironing are done to achieve the desired final appearance (see Section 2.5). 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 3.3.6) is the emission of volatile organic compounds (VOCs) released during and after the coating process. The release of VOCs requires special abatement techniques [3, Andres 1995]. 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.

There is a marked variation in the use of solvents between the finishing of leather for different uses, and between individual producers within those sub-sectors. Solvent use by producers of leather for furniture and for vehicle and aircraft seating is shown in Figure 3.14. The reduction in solvent use in the production of different types of leather is shown in Figure 3.15.

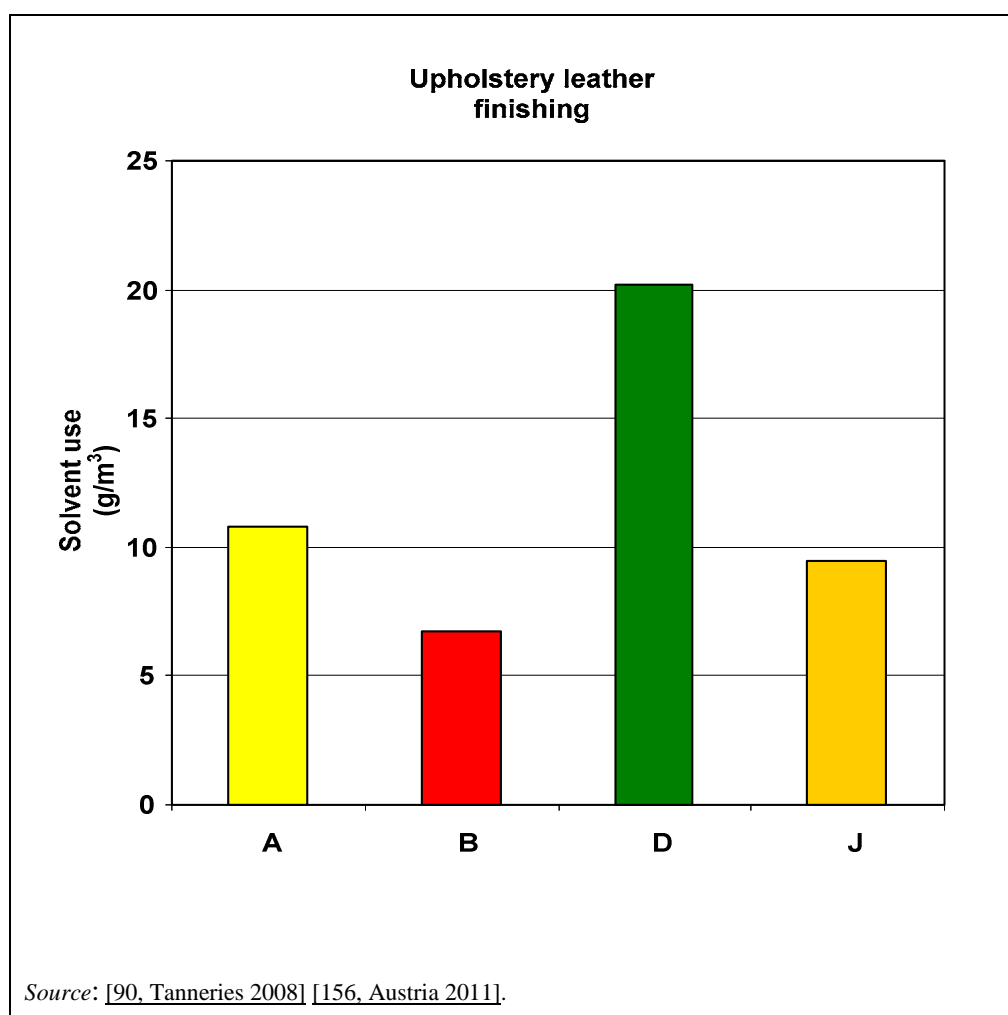
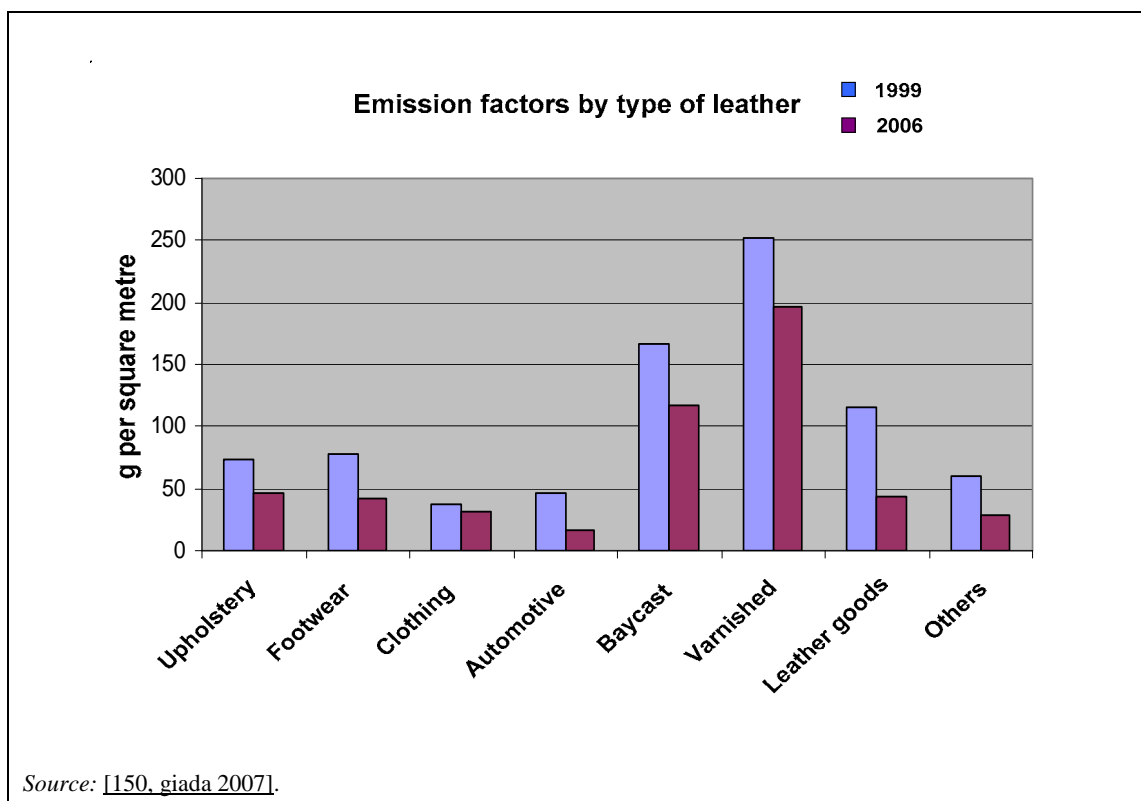


Figure 3.14: Solvent use in finishing leather for furniture and vehicle and aircraft interiors



**Figure 3.15:** Solvent use in finishing leather for various purposes

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 filtration. These residues are disposed of in appropriate incineration plants [7, Zimpel 1997]. Organic solvents may be recovered and reused 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 leather goods manufacturers, is collected for reuse or is landfilled.

Water-based finishes exist which have low or near-zero concentrations of organic solvents. Water-based finishes require longer drying periods than organic solvent-based systems.

#### Further finishing operations

Wool-on skins of lambs and sheep can be sheared to obtain special effects [11, Heidemann 2000].

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.

### 3.9.7 Waste water treatment

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 chromium-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 depend on operational and local conditions [10, Rydin and Frendrup 1993].

The level of effluent treatment required depends on the specific local situation. The pollution load generated by the tannery must be reduced at some stage before its discharge to the water environment to a level acceptable for such discharges. This level will be set to ensure that environmental quality standards are met in the receiving water, as required by laws implementing the Water Framework Directive (2000/60/EC).

An advantage of the joint treatment of urban 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 can be treated more effectively in a dedicated waste water treatment plant.

#### 3.9.7.1 Prohibited substances in waste water

Biocides may be used in the curing, soaking, pickling, tanning, and post-tanning processes. The residues of pesticides used to treat live animals may remain in the hides and skins after slaughter.

Biocides are subject to regulation (i.e. Biocide Products Directive 98/8/EC). Formulations of these biocides will need to be registered nationally prior to use. In all cases, only approved biocides may be used and special attention needs to be paid to the conditions for product use. It is anticipated that only a limited number of biocides will be supported for the leather industry.

The European Commission has regulated the discharge of some biocides and pesticides (DDT, hexachlorohexane, 'drins') through EC Directive 2006/11/EC on Pollution caused by certain dangerous substances discharged into the aquatic environment of the Community. The discharges of some of these compounds and others such as naphthalene are also regulated by the Water Framework Directive 2000/60/CE (they are identified by Directive 2008/105/EC as 'priority substances' for the aquatic environment and their discharges have to be reduced or stopped).

Biocides and pesticides that are prohibited in Europe may be imported with hides and skins from countries where their use continues.

Some prohibited substances, notably organochlorine compounds, are stable enough to survive waste water treatment processes.



## 4 TECHNIQUES TO CONSIDER IN THE DETERMINATION OF BAT

This chapter describes techniques (or combinations thereof), and associated monitoring, considered to have the potential for achieving a high level of environmental protection in the activities within the scope of this document. The techniques described will include both the technology used and the way in which the installations are designed, built, maintained, operated and decommissioned.

It covers environmental management systems, process-integrated techniques and end-of-pipe measures. Waste prevention and management, including waste minimisation and recycling procedures are also considered, as well as techniques that reduce the consumption of raw materials, water and energy by optimising use and reuse. The techniques described also cover measures used to prevent or to limit the environmental consequences of accidents and incidents, as well as site remediation measures. They also cover measures taken to prevent or reduce pollution under other than normal operating conditions (such as start-up and shutdown operations, leaks, malfunctions, momentary stoppages and the definitive cessation of operations).

Annex III to the Directive lists a number of criteria for determining BAT, and the information within this chapter will address these considerations. As far as possible, the standard structure in Table 4.1 is used to outline the information on each technique, to enable a comparison of techniques and the assessment against the definition of BAT in the Directive.

This chapter does not necessarily provide an exhaustive list of techniques which could be applied in the sector. Other techniques may exist, or may be developed, which could be considered in the determination of BAT for an individual installation.

**Table 4.1: Information for each technique**

<b>Headings within the sections</b>
Description
Technical description
Achieved environmental benefits
Environmental performance and operational data
Cross-media effects
Technical considerations relevant to applicability
Economics
Driving force for implementation
Example plants
Reference literature

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 technique is only as effective as its operation, maintenance and upkeep allows it to be. Advanced techniques often require 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 less hazardous 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.

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 to get a cleaner waste water effluent, with the advantage of in some cases usable hair or in other cases an additional waste product.

The costs of raw materials, water, energy, process auxiliaries, 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. However, not every measure that has to be taken to ensure adequate environmental protection can be expected to pay back on the microeconomic scale of a tannery.

## 4.1 Environmental management systems

### Description

A formal system to demonstrate compliance with environmental objectives.

### Technical description

The Directive defines 'techniques' (under the definition of 'best available techniques') as 'both the technology used and the way in which the installation is designed, built, maintained, operated and decommissioned'.

In this respect, an environmental management system (EMS) is a technique allowing operators of installations to address environmental issues in a systematic and demonstrable way. EMSs are most effective and efficient where they form an inherent part of the overall management and operation of an installation.

An EMS focuses the attention of the operator on the environmental performance of the installation; in particular through the application of clear operating procedures for both normal and other than normal operating conditions, and by setting out the associated lines of responsibility.

For installations to which the Directive applies an environmental management system (EMS) is a tool that operators can use to address these issues in a systematic and demonstrable way. EMSs are most effective and efficient where they form an inherent part of the overall management and operation of an installation. The cycle is an iterative dynamic model, where the completion of one cycle flows into the beginning of the next (see Figure 4.1).

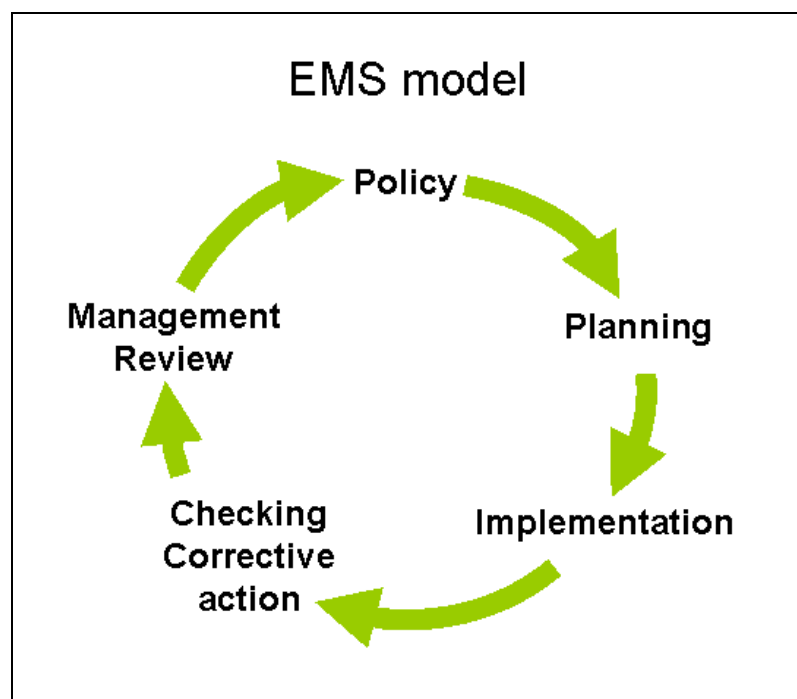


Figure 4.1: Continuous improvement in an EMS model

An EMS can take the form of a standardised or non-standardised ('customised') system. Implementation and adherence to an internationally accepted standardised system, such as EN ISO 14001:2004, can give higher credibility to the EMS especially when subjected to a properly performed external verification. EMAS provides additional credibility due to the interaction with the public through the environmental statement and the mechanism to ensure compliance with the applicable environmental legislation. However, non-standardised systems

can, in principle, be equally effective provided that they are properly designed and implemented.

While both standardised systems (EN ISO 14001:2004 or EMAS) and non-standardised systems apply in principle to **organisations**, this document takes a narrower approach, not including all activities of an organisation, e.g. with regard to their products and services, due to the fact that the Directive only regulates **installations/plants**.

An EMS can contain the following components:

1. commitment of management, including senior management;
2. definition of an environmental policy that includes the continuous improvement of the installation by the management;
3. planning and establishing the necessary procedures, objectives and targets, in conjunction with financial planning and investment;
4. implementation and operation of procedures paying particular attention to:
  - (a) structure and responsibility
  - (b) training, awareness and competence
  - (c) communication
  - (d) employee involvement
  - (e) documentation
  - (f) efficient process control
  - (g) maintenance programmes
  - (h) emergency preparedness and response
  - (i) safeguarding compliance with environmental legislation;
5. checking performance and taking corrective action paying particular attention to:
  - (a) monitoring and measurement (see also the Reference Document on the General Principles of Monitoring) [110, EC 2003].
  - (b) corrective and preventive action
  - (c) maintenance of records
  - (d) independent (where practicable) internal and external auditing in order to determine whether or not the EMS conforms to planned arrangements and has been properly implemented and maintained.
6. review of the EMS and its continuing suitability, adequacy and effectiveness by senior management;
7. preparation of a regular environmental statement;
8. validation by certification body or external EMS verifier;
9. following the development of cleaner technologies;
10. consideration for the environmental impacts from the eventual decommissioning of the installation at the stage of designing a new plant, and throughout its operating life;
11. application of sectoral benchmarking on a regular basis.

### **Achieved environmental benefits**

An EMS typically promotes and supports the continuous improvement of the environmental performance of the installation. If the installation already has a good overall environmental performance, an EMS helps the operator to maintain the high performance level.

### **Environmental performance and operational data**

EMSs have been implemented in both new and existing installations. The introduction of environmental management systems have also been a demand from customers in some sectors such as leather users in the auto industry.



**Cross-media effects**

None reported. The systematic analysis of the initial environmental impacts and scope for improvements in the context of the EMS set the basis for assessing the best solutions for all environmental media.

**Technical considerations relevant to applicability**

The components described above can typically be applied to all installations within the scope of this document. The scope (e.g. level of detail) and nature of the EMS (e.g. standardised or non-standardised) will be related to the nature, scale and complexity of the installation, and the range of environmental impacts it may have.

**Economics**

It is difficult to determine accurately the costs and economic benefits of introducing and maintaining a good EMS. There are also economic benefits that are the result of using an EMS and these vary widely from sector to sector.

External costs relating to verification of the system can be estimated from guidance issued by the International Accreditation Forum [[148, IAF 2010](#)].

**Driving forces for implementation**

The driving forces for the implementation of an EMS include:

- improved environmental performance;
- improved insight into the environmental aspects of the company which can be used to fulfil the environmental requirements of customers, regulatory authorities, banks, insurance companies or other stakeholders (e.g. people living or working in the vicinity of the installation);
- improved basis for decision-making;
- improved motivation of personnel (e.g. managers can have confidence that environmental impacts are controlled and employees can feel that they are working for an environmentally responsible company);
- additional opportunities for operational cost reduction and product quality improvement
- improved company image;
- reduced liability, insurance and non-compliance costs.

**Example plants**

EMSs are applied in a number of installations throughout the EU.

**Reference literature**

- EMAS Regulation (EC) No 1221/2009 [[143, Reg. 1221/ 2009](#)].
- DG Environment EMAS website [[145, DG Environment 2010](#)].
- EN ISO 14001:2004:
  - ISO 14000 family of standards website: [[146, ISO 2004](#)].
  - ISO 14000 technical committee: [[147, ISO 2010](#)].

## 4.2 Substitution of substances

Responsible management by the tanner requires awareness of substances and their fate in and after the process. Information available from suppliers, primarily in workplace safety data sheets may not cover the environmental risks. The REACH regulations introduce a requirement that suppliers shall provide information on environmental risks, but their implementation for all substances used in a tannery may take some time.

Additional substitutions are discussed in:

- Sections 4.5.5.1 and 4.5.5.2 for deliming agents
- Section 4.7.5 for nitrogenous compounds in post-tanning phases
- Section 4.8.2 for finishing solvents.

### 4.2.1 Substitution of octylphenol and nonylphenol ethoxylates

#### Description

Use of linear alcohol ethoxylates instead of alkylphenol ethoxylates in the aqueous degreasing of sheepskins.

#### Technical description

Surfactants are used in many different processes throughout the tannery, e.g. soaking, liming, degreasing of sheepskins, tanning and dyeing. Nonylphenol ethoxylate (NPE) surfactants were used in the leather industry in the past. NPEs can be degraded to smaller chain NPEs and nonylphenol, both of which are toxic. The European Union carried out an extensive risk assessment of nonylphenol which concluded that nonylphenol displays an endocrine-disrupting activity [89, EU RAR nonylphenol 2002].

The use of NPE in leather processing is now restricted under the REACH regulation. Its use is banned except for (a) activities with no release to waste water or (b) 'systems with special treatment where the process water is pretreated to remove the organic fraction completely prior to biological waste water treatment (degreasing of sheepskins)' specified in point 46 of Annex XVII of the regulation. In sheepskin processing, a closed loop cycle is adopted in order to avoid discharges of octylphenol and nonylphenol ethoxylates. Good housekeeping techniques help to achieve general emissions reduction (for water management see Section 4.3.2).

The main alternatives in the degreasing of sheepskins are linear alcohol ethoxylates with different chain lengths and ethoxylation degrees. These compounds show a much lower toxicity than NPE and can be degraded to non-toxic compounds [85, Hauber and Knödler 2008]. The efficacy of C<sub>10</sub> linear alcohol ethoxylate as a degreasing agent is comparable to that of NPE. In this application a nanophase with very low surface energy is formed that is converted into a macroemulsion.

A process for recovery of the surfactant and fat by solvent distillation using heptane and ethanol has been demonstrated on a pilot scale [132, AIICA 2005]. The best recovery rate found was 75 %.

Possible differences in their effectiveness have to be taken into account in case of the need for a change in the quantity used. Each one of the aliphatic ethoxylated alcohols has distinct properties, so that the process design differs depending on the material chosen.

#### Achieved environmental benefits

Lower toxicity in water, easier biological degradation. No toxic bioaccumulable degradation products.

**Environmental performance and operational data**

The products are commercially available from a number of chemical suppliers. The operational data will depend on the type of production.

The need for pretreatment to remove the organic fraction completely prior to biological waste water treatment is removed.

**Cross-media effects**

None reported.

**Technical considerations relevant to applicability**

Linear alcohol ethoxylates may substitute alkylphenol ethoxylates (APE) in all their applications in the leather industry.

**Economics**

The costs of linear alcohol ethoxylates can be compared to those of APE. Higher costs are possible if the substitution requires higher concentrations of the surfactant to achieve the same effect.

**Driving force for implementation**

Legislation restricting the use of NPEs, now incorporated into REACH.

**Example plants**

Many tanneries, both inside and outside the EU, use linear alcohol ethoxylates instead of APE during leather manufacturing.

**Reference literature**

[ 85, Hauber and Knödler 2008 ] [91, Suppliers 2008] [132, AIICA 2005].

**4.2.2 Substitution of halogenated organic compounds****4.2.2.1 Substitution of halogenated organic compounds in degreasing****Description**

Possibilities exist for replacing halogenated organic compounds either by using non-halogenated solvents or by changing over to an aqueous degreasing system.

**Technical description**

Linear alkyl polyglycol ethers, carboxylates, alkyl ether sulphates and alkyl sulphate can be used instead of halogenated solvents. 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 to curtail 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 solvent degreasing systems can be minimised by the use of closed cycle machines.

**Achieved environmental benefits**

Reduction or elimination of emissions of halogenated solvents.

**Cross-media effects**

The substitution of halogenated 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.

Wastes consisting of greasy residues (at a rate of 10 – 20 % of pickled weight), organic solvents and the filters from the abatement of emissions of organic solvents to the air present a disposal problem.

### **Driving force for implementation**

Emissions of halogenated organic solvents to the air, and of adsorbable organic halogens (AOX) in aqueous effluents are already subject to restrictions. Further restrictions are likely. In Germany, laws restrict the use of halogenated organic solvents in degreasing to tetrachloroethene and dichloromethane only. German laws also specify the construction and operation of closed cycle degreasing machines.

### **Reference literature**

[8, Higham 1994] [62, Lindemann 1999].

## **4.2.2.2 Substitution of halogenated organic compounds in fatliquors**

### **Description**

Use of fatliquors which do not contain halogenated compounds.

### **Technical description**

Fatliquors are available that do not require stabilisation by organic solvents (and therefore do not contribute to the AOX) and perform with improved exhaustion for example fish oils.

Short-chain and middle-chain chlorinated alkanes in fatliquors can now be replaced e.g. by fatliquoring polymers based on methacrylates; or by silicone oils or modified silicone oils.

For special applications, no substitute has yet been found for long-chain chlorinated alkanes.

### **Achieved environmental benefits**

Reduction of the concentration of halogenated organic compounds in the effluent.

### **Driving force for implementation**

The use of AOX-free fatliquors is triggered essentially by AOX emission limits.

The use of preparations containing more than 1% of chlorinated alkanes of chain length C<sub>10</sub> to C<sub>13</sub> is banned in the fatliquoring of leather (REACH Annex XVII point 42).

### **Reference literature**

[4, Andres 1997] [8, Higham 1994] [27, BASF 1997] [85, Hauber and Knödler 2008].

## **4.2.2.3 Substitution or optimisation of halogenated organic compounds in water-, soil- and oil-repellent agents**

### **Description**

Use of water-repellent agents, oil-repellent agents, and soil-repellent agents, which do not contain halogenated organic compounds. When a complete substitution is not possible, optimised fluorocarbon resins in combined finishes for water-, soil- and oil-repellent leather are used to reduce the release of halogenated organic compounds.

### **Technical description**

Like fatliquors, these agents can also contain organic solvents and organic halogenated compounds.

For leather requiring only a water-repellent finish, halogen-free water-repellent agents with a different chemical basis are used depending on the specified finish requirements, e.g. paraffin formulations, polysiloxanes, modified melamine resins or polyurethanes. For combined water-, soil- and oil-repellent finishing of leather, in most cases fluorocarbon resins are still used.

Fluorocarbon resins are used because of their very good water-, soil- and oil-repellency and high permanence of the repellency effect. A typical aqueous formulation contains 20 – 30 % active polymer compound with 20 – 50 % fluorine in the polymer.

In the past, unintended by-products from the production of these fluorocarbon resins, for example perfluorooctane sulphonates (PFOS) and perfluorooctanoic acid (PFOA), caused concern in view of health and environment considerations. These fluorocarbon resins are currently replaceable by optimised fluorocarbon resins based on raw materials with a chain length of four (C4) or six (C6) rather than a chain length of eight (C8). The shorter chain fluorocarbon resins are more favourably assessed toxicologically, although they are as stable in the environment. Consequently, preventative measures are also applicable for optimised fluorocarbon resins, in order that their release into the environment be minimised by the use of controlled application processes with high exhaustion, as well as the retention and controlled disposal of segregated liquor residues, if no recycling is possible.

#### **Achieved environmental benefits**

The use of halogen-free agents can result in a decrease of the COD and the elimination of halogenated compounds from the effluent. Optimised fluorocarbon resins reduce the emissions of PFOS and PFOA and their precursor compounds into the environment.

#### **Environmental performance and operational data**

The water-repellent agents available which do not contain organic solvents minimise the emission of organo-halogenated contaminants. The process parameters correspond to those used for conventional leather application processes.

#### **Cross-media effects**

The use of agents with a different formulation may lead to the release of different chemicals into the environment.

Perfluorinated chemicals, in principle, exhibit high persistence, i.e. they can remain in the environment for long periods. Optimised short-chain fluorinated substances have a better toxicological and environmental profile; however, their possible release into the environment through leather applications cannot be completely estimated. In any case, emissions can be minimised by optimising the exhaustion and retention of the residual liquors.

#### **Technical considerations relevant to applicability**

The use of oleophobic and hydrophobic agents based on fluorocarbon resins is still required for some applications, particularly when anti-soiling and water-repellent properties are required at the same time.

If the specified requirements for the leather include, e.g.:

- very high water repellency, or water pressure resistance
- combined soil, oil, and chemical repellency
- resistance to abrasion
- suitability for lamination,

then these requirements can only be achieved at this point in time by using fluorocarbon resins. Alternative fluorine-free products for these fields of application do not exist at present.

### **Driving force for implementation**

Emissions of halogenated organic solvents to the air and of adsorbable organic halogens (AOX) to water are already subject to restrictions. Further restrictions are likely.

Within the European Union, restrictions on the use of products with a PFOS content greater than 0.005% were introduced in 2006. The participating countries of the Stockholm Convention on Persistent Organic Pollutants (POP) have listed PFOS and heralded the start of a worldwide restriction on PFOS and corresponding products.

### **Reference literature**

[ 85, Hauber and Knödler 2008 ] [ 163, TEGEWA 2012 ].

### **4.2.2.4 Substitution of halogenated organic compounds in flame-retardants**

#### **Description**

Use of flame-retardants which do not contain halogenated organic compounds.

#### **Technical description**

Alternatives to brominated flame-retardants exist for the leather industry. Firm leather with a dense fibre interweaving is more flame resistant than other leather types. Therefore, flame resistance is possible by applying appropriate syntans and the addition of melamine resins in the retanning process, as well as by selecting suitable fatliquors. Furthermore, the application of, e.g. ammonium bromide leads to a flame-retardant effect that is sufficient for some applications.

Inorganic phosphorus compounds (such as ammonium polyphosphate) could be considered an alternative to brominated flame-retardants.

Silicon polymer products used in finishing can confer some fire resistance, in that they burn to leave a residue of silica (SiO<sub>2</sub>) which protects the leather beneath.

#### **Achieved environmental benefits**

The environmental benefit is a reduced concentration of brominated compounds in the effluent.

#### **Environmental performance and operational data**

Operational data will depend on the desired properties of the end-product.

#### **Cross-media effects**

No cross-media effects are known.

#### **Technical considerations relevant to applicability**

The technique can be applied to both new and existing installations.

For some types of leather the affinity to the leather is insufficient and for some applications the flame-retardant effect is insufficient.

The flame proofing of some types of waterproof leather may still require the use of halogenated chemicals.

#### **Economics**

The economics will be case-specific and will depend on the price of the chemicals and their substitutes and the amount needed for the process.

### **Driving force for implementation**

The main driving force is to reduce the concentration of halogenated compounds in the effluents with the main developments being made by the chemical suppliers to the industry.

**Example plants**

A large number of installations in Europe.

**Reference literature**

[ 85, Hauber and Knödler 2008 ].

### 4.2.3 Eliminating pesticides from the raw material (hides/skins)

**Description**

Selection of materials free from persistent pesticides which are resistant to effluent treatments.

**Technical description**

To prevent the arrival of materials contaminated by banned pesticides and biocides in the tannery it is possible either:

- to source hides and skins only from Europe and countries with similar regulatory regimes for pesticides; or
- to use supply chain contracts specifying that only hides or skins free from these materials shall be supplied.

**Achieved environmental benefits**

Prevention of the discharge of pesticide residues in tannery effluent.

**Technical considerations relevant to applicability**

May not be practical for all tanneries.

**Economics**

Will involve analytical costs.

**Driving force for implementation**

If neither of these methods is possible or effective; regulators are likely to include ELVs for these compounds in permits, calculated to protect receiving waters.

### 4.2.4 Use of approved biocides

**Description**

Biocides are subject to special regulation (i.e. Biocide Products Directive 98/8/EC, upcoming Biocides Regulation <sup>(1)</sup>).

**Technical description**

Biocides may be used in the curing, soaking, pickling, tanning and post-tanning processes. Formulations of these biocides will need to be nationally authorised prior to use. In all cases, only approved biocides, or biocides still allowed in the EU because they are part of the EU review programme, should be used and special attention needs to be paid to the conditions for product use. It is anticipated that only a limited number of biocides will be supported for the leather industry.

According to the upcoming Biocide Regulation, which will apply from 1 September 2013 with a transitional period for some provisions, rules are laid down for the following areas, also relevant to the leather production:

<sup>(1)</sup> [http://ec.europa.eu/prelex/detail\\_dossier\\_real.cfm?CL=en&DosId=198337](http://ec.europa.eu/prelex/detail_dossier_real.cfm?CL=en&DosId=198337)

- the establishment at the EU level of a list of active substances which may be used in biocidal products;
- the granting of an authorisation to biocidal products;
- the mutual recognition of authorisations within the EU, so as to reduce the administrative burden on producers;
- the making available on the market and the use of biocidal products within one or more Member States or the EU;
- the placing on the market of treated articles: articles incorporating pest control chemicals, e.g. leather treated with biocides, may no longer be treated with unauthorised chemicals and must be labelled under the conditions specified in the Regulation. These obligations apply to all articles treated with biocidal products on the EU market, including imported ones.

### **Achieved environmental benefits**

Prevention of the discharge of those biocides that are not considered acceptable for use in the EU.

## **4.2.5 Substitution of complexing agents**

### **Description**

Use of complexing agents that do not contain EDTA or NTA.

### **Technical description**

Complexing agents such as EDTA (ethylenediaminetetraacetate) and NTA (nitrilotri-acetate), are used as sequestering agents. Apart from impeding the waste water treatment, complexing agents have an adverse impact on the environment.

EDTA poses a particular hazard because of its long life in the environment. NTA is more easily biodegradable but its use is undesirable.

Polyphosphate-based and phosphonate-based products can be used instead of EDTA and NTA in the dyeing or the pretanning to wet white.

### **Achieved environmental benefits**

The substitution of these substances is environmentally beneficial. EDTA is poorly biodegradable and may increase the discharge of chromium in the waste water by re-mobilising it from the sludge during effluent treatment. [ 85, Hauber and Knödler 2008 ].

### **Cross-media effects**

None known.

### **Technical considerations relevant to applicability**

Complexing agents such as EDTA or NTA cannot yet be completely eliminated from the wet finishing process, particularly for the avoidance of iron stains. The substitution of EDTA and NTA in other processes such as dyeing or pretanning of wet white is possible.

### **Driving force for implementation**

Environmental reasons are the main driver for implementation.

### **Example plants**

Use of EDTA and NTA has ceased in Germany.

### **Reference literature**

[85, Hauber and Knödler 2008][129, IARC 1998].



## 4.3 Reduction of water consumption

### 4.3.1 Rainwater management

#### Description

The management of rainwater so as to minimise the amount of rainwater which comes into contact with process materials and which therefore requires treatment as a process effluent.

#### Technical description

The amount of rainwater which falls onto a tannery site will vary according to the weather pattern for the locality, but its management involves some more general considerations.

It is good practice for rainwater falling on the roofs of the buildings to be collected separately from the process effluent so as to reduce the volume of water requiring treatment. It may be useful to store it for use in process operations or cleaning.

A further reduction in the volume of water to be treated can be obtained if rainwater falling onto paved yard areas which cannot become contaminated with materials from the process is also diverted away from the process effluent stream. This rainwater may be less suitable for use as a water source. These yard areas can be defined as those protected from contamination or the inflow of contaminated water by permanent physical barriers.

Rainwater from paved yard areas in which spills of process liquids or chemicals are likely to occur is collected as a process effluent. It is good practice to design operations so that the yard area used is as small as possible, so as to minimise the amount of rainwater collected. Effluent treatment arrangements are designed to cope with rainwater from this source.

Where an appropriate system of environmental management (see Section 4.1) is in place, a further reduction of the yard area permanently drained to the process effluent stream can be achieved. This involves the drainage of identified paved areas where spillages are 'possible but unusual'. Rainwater from these areas can be directed away from the process effluent stream in normal circumstances but with equipment available to divert contaminated water into the process effluent stream in the event of an accident.

#### Achieved environmental benefits

The technique can achieve a reduction of the volume of water to be dealt with as process effluent, a reduction of the risk of overwhelming effluent treatment equipment in periods of heavy rain, and control of the risk of spillages being washed into surface waters.

#### Environmental performance and operational data

If roof water is to be used as a water source, rainwater separators may be needed.

#### Technical considerations relevant to applicability

The technique can be applied in new or reconstructed plants, or plants where the drainage system is being renovated.

#### Economics

Effluent treatment costs can be reduced.

#### Driving force for implementation

Reduction of the volume of water to be dealt with as process effluent.

#### Example plants

Several plants in the tannery sector.

### 4.3.2 Process water management

#### Description

Good process water management is achieved by determining the optimum quantity required for each process step and introducing the correct quantity using simple measuring equipment. Batch washing involves washing of hides and skins during processing by introducing the required quantity of clean water into the processing vessel and using the action of the vessel to achieve the required agitation, as opposed to using the agitation provided by the inflow and outflow of large quantities of water.

#### Technical description

The first step to efficient process water management 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, physico-chemical treatment of concentrated effluents is more efficient. Consequently, cost reductions are achieved in many cases, but the biological treatment stages may become more difficult.

Process efficiency is achieved by optimisation of the mechanical movement, good distribution of chemicals and control of the chemical dosage, pH, and temperature, which are essential parameters for both quality and effective use of the plant. The installation of the equipment and the necessary access are also key issues to consider for the delivery of water and complete rapid removal of floats.

The efficiency of water use can be enhanced by: increased volume control of processing water; 'batch' versus 'running water' washes; use of short floats; and an effective preventive and corrective maintenance programme. These measures are described below.

a. **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 cleaning 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.

b. **'Batch' versus 'running water' washes**

The consumption of water for rinsing processes varies considerably between tanneries. Running water washes are 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.

c. **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 of 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 better than 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.

d. **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 remodelling may be required to allow recycling systems, as most units already achieve efficient drainage.

e. **An effective preventive and corrective maintenance programme**

Leaks in pipes and process vessels can account for considerable losses of water. Preventative maintenance programmes can prevent losses from occurring while corrective maintenance can minimise the loss.

**Achieved environmental benefits**

A water consumption of approximately 12 – 25 m<sup>3</sup>/t (for bovine hides) can be achieved if the tannery operates efficient technical control and good housekeeping. The economic feasibility of a change in consumption to this level depends greatly on the cost of water consumption. In Germany, some tanneries use 15 – 20 m<sup>3</sup>/t. A tannery in the Netherlands, processing (fresh) bovine hides, uses about 20 m<sup>3</sup>/t. For the processing of calfskins, about 40 m<sup>3</sup>/t and sometimes more is needed.

Economising in the use of water does not in itself reduce the pollution load, but nevertheless it has a number of beneficial effects: the saving of energy as a consequence of saving hot water; an improved uptake of chemicals and consequently savings of chemicals result from the use of shorter floats: the use of batch washing makes better control possible. Additionally and importantly, the lower effluent volume makes it possible to construct a waste water treatment plant with smaller capacity in the physico chemical stages, or to increase the efficacy of physico-chemical treatment in an existing treatment plant.

**Environmental performance and operational data**

The minimum levels to which water consumption in individual processing operations may be reduced is summarised in Table 4.2. Care is required in processing at these levels to avoid product damage by abrasion.

**Table 4.2: Minimum water consumption in individual processing operations**

Process stage	Waste water discharge
	m <sup>3</sup> per tonne of raw hide
Soaking	2
Liming	4.5
Deliming, bating	2
Tanning	0.5
Post-tanning	3
Finishing	0
Total	12
<i>Source</i> : [84, Ludvik J. 2000].	

In addition to the water required for individual processing operations, a certain amount of water is used in pasting/vacuum dryers, for cleaning, or for sanitary and similar purposes. The

minimum volume required is 2–3 m<sup>3</sup> per tonne raw hide under conditions of very good housekeeping. A further 2 to 3 m<sup>3</sup> of water per tonne will be required for the processing of salted hides (see Section 4.4.1.1).

Rates of water use in some operational tanneries processing bovine hides are illustrated in Figure 4.2. Data refer to example plants located in seven different Member States, producing either wet blue or finished leather from bovine raw hides.

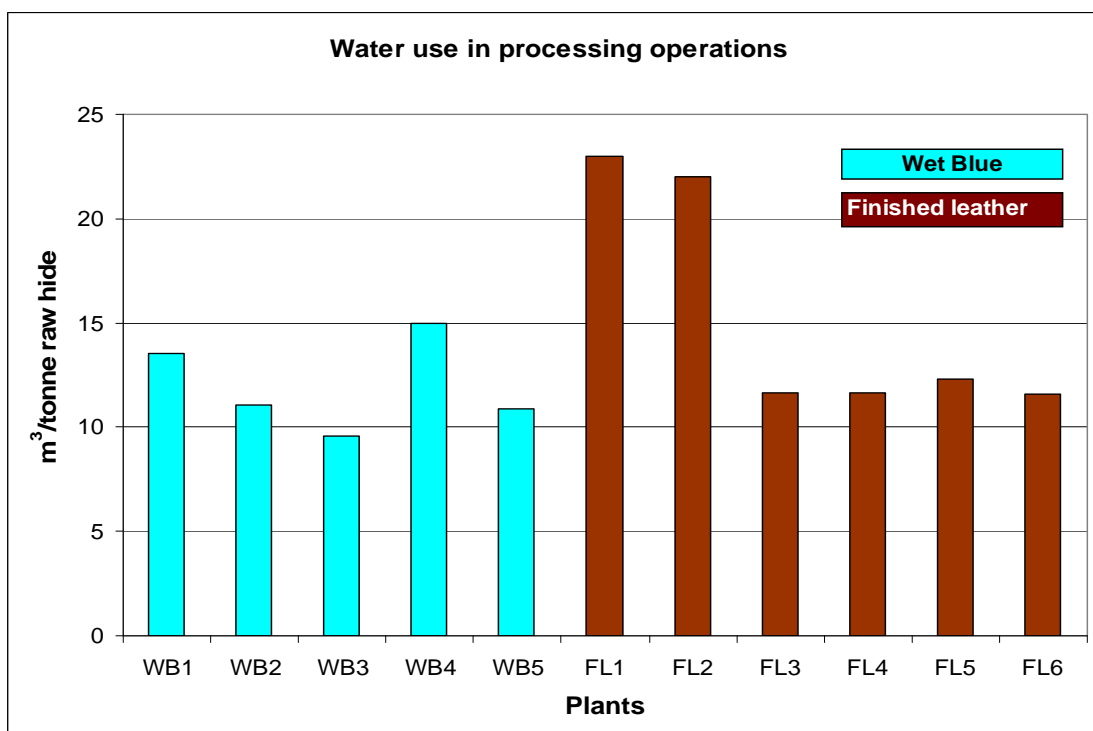


Figure 4.2: Examples of water use in processing of wet blue and finished leather

There are few data available on the levels to which water use in the processing of sheepskins can be reduced by good practice. There are data from the IUE, see Table 3.8, but lower levels have been submitted [152, Spain 2010]. These are combined in Table 4.3 below for the processing of wet salted sheepskins, from which the wool is removed during processing. Much larger volumes are used in processing wool-on sheepskins.

Table 4.3: Water consumption in the processing of wet salted sheepskins (wool removed during processing)

Process stages	Water consumption litres per skin monthly mean
Raw to pickle	65 to 80
Pickle to wet blue	30 to 55
Post tanning steps	15 to 45
<b>Total</b>	<b>110 to 180</b>

#### Technical considerations relevant to applicability

These techniques to reduce water consumption can be implemented by both new and existing installations. The use of short floats requires either new equipment or the modifying of existing equipment.

**Economics**

An efficient control of water consumption will require the investment of an automated dosage system for water. The investment cost will be around EUR 10 000 for an automatic water dosing system controlling the water dosage to 5 – 8 drums [91, Suppliers 2008].

**Driving force for implementation**

The main driving force is to reduce an excessive use of water and thereby reduce the cost of water consumption. Another driver for an increased control of the water use (and use of chemicals) are that an increased control of process conditions such as water dosage, chemical dosage, pH and temperature control will lead to an improvement of the product quality. Better process control and quality control result in fewer faults and consequently less reprocessing (savings of water, chemicals, and energy).

**Example plants**

Many plants in Europe are using the techniques to reduce their water consumption.

**Reference literature**

[84, Ludvik J. 2000] [16, Frendrup 1999] [17, UNEP 1991] [4, Andres 1997].

**4.3.3 Reuse of individual floats or treated waste water**

Depending on the cleanliness of the raw materials, the liquors from the main soak can be recycled to the dirt soak. Rinsing waters from delimiting (but not those containing bating enzymes) 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 recycled water from pickle/chrome tan and some washes can be recycled back to the 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 reuse of water.

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 rendering [33, BLC 1995].

The recycling of individual process liquors is discussed in Sections 4.3.3.1 and 4.6.3.3.

**4.3.3.1 Reuse of treated waste water in soaking and liming processes****Description**

Treatment and storage of waste water for use in the early stages of processing.

**Technical description**

For reuse, the water from tanning and dyeing is treated in a sedimentator and utilised for soaking in the liming drum and as rinse water after liming.

The acidic waste water from tanning, retanning, dyeing and fatliquoring is treated mechanically and is subsequently alkalised and sedimented with the addition of polyelectrolytes and metal salts. The water thus treated is used in soaking. The rinse water from before delimiting is reused for the first rinse stage after liming.

The second rinse water after liming is stored, sedimented and temperature-controlled in a tank and is used the next day as the first rinse.

Due to high organic and sulphide loading, the first rinse has to be treated and cannot be reused in the process.

### **Achieved environmental benefits**

A saving of approximately 20 % of total water consumption can be achieved by applying this water recirculation technique.

### **Environmental performance and operational data**

Through this measure the reference company was able to reduce freshwater consumption in soaking and liming by 60 %.

Comparative operational data before and after introduction of the measure are shown in Table 4.4 (values refer to the overall process).

**Table 4.4: Operational data for reuse of treated water in soaking and liming**

<b>Parameter</b>	<b>Without water recirculation</b>	<b>With water recirculation</b>
Waste water	~ 12 m <sup>3</sup> per tonne of raw hide	~ 9.5 m <sup>3</sup> per tonne of raw hide
Energy	6.3 GJ per tonne of raw hide	6.3 GJ per tonne of raw hide
Chemicals	~ 450 kg per tonne of raw hide	~ 450 kg per tonne of raw hide
<i>Source: [114, Germany 2010].</i>		

### **Cross-media effects**

A build-up of the salt content, an increase in temperature, and problems arising during biological treatment of the effluent.

### **Technical considerations relevant to applicability**

Can be used in both new and existing installations. The reference company with 90 employees produces high-quality upper leather for shoes in a full-stage process extending from soaking to finishing. The introduction of this measure at the company led to no loss in quality.

### **Economics**

Investment costs: EUR 298 000. Cost savings: approx. EUR 40 000 per year. The measure was supported with a EUR 100 000 subsidy under the funding programme 'Ecological and sustainable water resources management initiative of North Rhine-Westphalia'.

### **Driving force for implementation**

Reducing water consumption for economic and environmental purposes.

### **Example plant**

Josef Heinen GmbH & Co. Kg, Wegberg.

### **Reference literature**

[114, Germany 2010] [115, U and Nat Nordrhein Westfalen 2008].

## 4.4 Curing and storage

The hides and skins bought by tanners are putrescible materials. If allowed to decompose they produce foul odours. Decomposition damages the raw material, of particular concern when high specification leathers are being produced. Correct curing and rigorous stock rotation eliminate decomposition odours.

### 4.4.1.1 Cooling and processing of fresh hides and skins

#### Description

Hides are not preserved by salting. Either short delivery times or temperature control are used to prevent deterioration.

#### Technical description

Chilling the hides and 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 °C, has been used for many years, e.g. in Australia. If the refrigeration temperature is reduced to 2 °C, hides and skins can be stored for three weeks without suffering damage. The temperatures to which hides and skins should be chilled depend on the required duration of preservation.

There are advantages of processing cooled hides, which include:

- under normal circumstances, there is no salt in the waste water from 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;
- reduced soaking time.

Salt facilitates the elimination of some proteins and therefore some salt is added during the soaking process; enzymes can be used instead of salt to remove proteins.

#### Achieved environmental benefits

A reduction of nearly 100 % of salt in the effluent from soaking is achieved.

#### Environmental performance and operational data

Rapid post-mortem cooling is essential for the successful use of the technique. Cooling of the hides and skins 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<sub>2</sub> snow;
- by using refrigerated storage units.

The following information comes from a reference tannery. 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 of up to 3 hours driving time, no cooling at all is considered 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 only applicable if the slaughterhouse (and any hide dealer involved) has a cold storage facility where the hides are stored at a temperature of +2 °C 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.

There are, however, several restrictions when using short-term preservation methods.

- The slaughterhouse must be relatively close to the tannery.
- The raw material must be processed almost immediately (depending on the chilling method, between one and twenty days). Contingency arrangements for curing excess material at the tannery may be necessary.
- 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.
- It may still be necessary to use some cured material to smooth out the pattern of deliveries.
- It is more difficult to form homogeneous batches due to the limited time available before processing.

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.

Some of the above-mentioned options depend strongly on the local conditions, and good management of the input stock of the raw hides.

The amount of water used in processing fresh hides is 2 to 3 m<sup>3</sup> per tonne less than that used for processing salted hides [ 16, Frendrup 1999 ] [ 152, Spain 2010 ].

Depending on the existing national legislation on food hygiene, there may be better reuse options for the wastes generated in trimming and fleshing.

### **Cross-media effects**

Cooling and chilling require energy.

It is reported from the Netherlands and elsewhere that more biocides are needed when processing fresh hides.

Noise from engine-powered refrigeration units may cause problems when run overnight at some installations. Arrangements to provide electrical supplies for delivery trucks are necessary in these circumstances.

### **Technical considerations relevant to applicability**

The technique can be applied by both new and existing installations. Applicability is limited by the availability of fresh hides or skins.

### **Economics**

The reference tannery's transport costs vary between EUR 0.015 and 0.03 per kg, depending on the distance. The cost of an ice-making machine is not as high as the capital investment required



for chilling units and cold stores. The technique is considered economically viable when the cooling chain is no longer than 2 days.

Carbon dioxide cooling meets the needs of small slaughterhouses. 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.

**Driving force for implementation**

A major driving force for processing fresh hides in tanneries is the need to reduce the discharge of salt to the waste water.

**Example plants**

A high number of tanneries in Europe use fresh hides as raw material. The number of tanneries using fresh hides is increasing due to increased environmental pressure.

**Reference literature**

[56, Pearson et al. 1999] [16, Frentrup 1999] [90, Tanneries 2008]

## 4.5 Beamhouse or Limeyard

### 4.5.1 Soaking

Reported techniques to reduce emissions are:

- use of un-salted hides or skins (see Section 4.4.1.1).
- use of clean hides or skins (see Section 4.5.1.1)
- recovery of the used salt (see Section 4.5.1.2)
- substitution of specific substances: biocides, surfactants, hypochlorite (see Sections 4.2.1, 4.2.3 and 4.2.5)
- optimisation of water consumption and process control (see Section 4.3.2).

After those measures are taken, the emissions from soaking can be reduced to the levels shown in Table 4.5.

**Table 4.5: Reduced emissions from soaking**

Parameter per tonne raw hide	Unit	Salted hides (calculated on salted weight)	Fresh or chilled hides
Water volume	m <sup>3</sup> /t	4	2
Total solids	kg/t	130	45
Suspended solids	kg/t	10	10
BOD <sub>5</sub>	kg/t	10	12
COD	kg/t	23	23
Total Kjeldahl nitrogen	kg/t	1.5	2
Chloride (Cl)	kg/t	55	5
<i>Source: [16, Frendrup 1999].</i>			

The figures in Table 4.5 are exclusive of contributions from manure, etc, e.g. 12 kg total solids, 2 kg BOD<sub>5</sub>, 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.

#### 4.5.1.1 Use of clean hides and skins

##### Description

An arrangement whereby animals presented for slaughter have less manure adhering to the exterior of the hide or skin. Possibly through a formal 'clean hides scheme'.

##### Technical description

Several co-operation projects between tanneries and hide dealers took place between 1995 and 2000 with the objective of increasing the cleanliness of the hides delivered to the tannery and reducing the environmental impact.

##### Achieved environmental benefits

Apart from improving the quality standard of the leather there is less waste and a lower BOD of waste water.

##### Environmental performance and operational data

By surveying the existing initiatives in Denmark, Sweden, New-Zealand, Australia, the UK and the Netherlands, the following common success factors were found:

- 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 slaughterhouses and suppliers should be long-term and stable (e.g. monthly rather than weekly);
- hides and 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.

#### **Cross-media effects**

None known.

#### **Technical considerations relevant to applicability**

May not be feasible in all market conditions.

#### **Economics**

May involve paying a premium to suppliers, but avoids paying hide prices for manure.

#### **Driving force for implementation**

Elimination of manure damage. Reduction of waste water BOD. Facilitates green fleshing.

#### **Example plants**

Several plants worldwide.

#### **Reference literature**

[41, Various 1998].

### **4.5.1.2 Removal of salt**

#### **Description**

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

#### **Technical description**

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

The reuse 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 salt crystals can scratch or produce abrasion of the grain during drumming.

#### **Achieved environmental benefits**

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.

#### **Environmental performance and operational data**

To test the efficacy of the technique, the treated batch of hides/skins may be shaken again and the loss in weight must not exceed 1 %.

#### **Cross-media effects**

The main disadvantage is the disposal of the salt. Landfilling of solid salt is not an environmentally sound option (high solubility) and is consequently forbidden in some Member States.

### **Technical considerations relevant to applicability**

The technique is applicable to both new and existing plants. The technique requires the installation of equipment for salt removal, which is available commercially. A main barrier for the implementation of the technique may be the use of recovered salt. Centralised collection systems have been implemented in tannery clusters in Italy (Arzignano). The cost for the collection and disposal of the salt is included in the cost for waste water treatment.

### **Economics**

The cost of salt recovery is high in comparison with the cost of fresh salt. The technique requires an investment in equipment for de-salting. If sterilisation for reuse is incorporated the fuel costs can be high.

### **Driving force for implementation**

Environmental reasons drive the use of this technique, specifically a reduction of the salt input into the soaking process and a consequent reduction of salt in the tannery effluent.

### **Example plants**

Tanneries in the Arzignano area (Italy).

### **Reference literature**

[56, Pearson et al. 1999] [16, Frendrup 1999] [96, Tinti 2008].

## **4.5.2 Green fleshing**

### **Description**

The fleshing process is applied at an earlier stage of processing.

### **Technical description**

Green fleshing is carried out either before any processing, or immediately after soaking; as opposed to lime fleshing which is carried out after liming.

Fleshings can be sold to renderers, or the tannery may have a plant in which fleshings are processed to produce tallow. When deciding on whether to green flesh or lime flesh, it is important to take into consideration the specifications of the renderer or the capability of the on-site plant.

The basic machine for fleshing is the same for green fleshing and fleshing after liming. However, a demanuring cylinder has to be installed in order to remove manure from the hides prior to fleshing if green fleshing is carried out.

### **Achieved environmental benefits**

The fleshings are free from liming and unhairing agents. Fleshing at this stage allows a more rapid and uniform penetration of chemicals into the hide.

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 % [56, Pearson et al. 1999]. Consequently, the waste water volume in the unhairing and liming step is reduced.

### **Environmental performance and operational data**

The process is difficult and risks damaging the hides, because of the differences in thickness of raw hides due to uneven hair length or adhering 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 dung

removal is sometimes necessary as well. However, where there is a significant amount of dried dung on the hides, dedunging may not be feasible due to damage to the hides (dung ball damage). [16, Frendrup 1999].

Further fleshing after liming (double fleshing) is usually necessary, and if this additional operation is needed, green fleshing becomes an undesirable technique with significant drawbacks in terms of production because it requires an additional process step. The hides have to be taken out of the process vessel after soaking in order to be fleshed and then put back into the process vessel again for unhairing 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 (subject to control under the Animal By-product Regulation (EC) n. 1069/2009) [ 161, EU 2009 ].

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 that would be incurred 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 new and existing plants. A retrofit is certainly economically more feasible if process steps are changed, because new machines have to be installed for green fleshing.

#### **Cross-media effects**

If hide damage during green fleshing reduces the amount of useful leather produced per hide, the environmental benefits may be eliminated.

The amount of fleshings generated during green fleshing is significantly lower than in the case of lime fleshing as only 120 – 150 kg per tonne raw hide is produced. The fleshings have lower water content and are easier and cheaper to process in a rendering plant. Conversely, green fleshings are more prone to putrefaction than limed fleshings. Green fleshings are subject to use restrictions under the Animal By-products Regulation, unlike some limed fleshings.

Though the quality of the tallow recovered from green fleshing is higher than that from limed fleshings, its use or disposal may be more restricted if biocides have been applied. It is also subject to control under the Animal By-products Regulation.

#### **Technical considerations relevant to applicability**

The circumstances in which the technique can be applied successfully are restricted, as noted above. Its use has been phased out by tanneries in Germany which used it.

#### **Economics**

The investment cost for a new fleshing machine is approximately EUR 130000 [91, Suppliers 2008]. The cost will be approximately the same for a fleshing machine suitable for green fleshing and for lime fleshing. The cost of the de-dunging cylinder must also be included. With some raw materials, hide damage may prohibit the technique on economic grounds.

#### **Driving force for implementation**

The technique is usually introduced for environmental reasons.

#### **Reference plant:**

A number of tanneries use green fleshing.

#### **Reference literature:**

[56, Pearson et al. 1999] [16, Frendrup 1999] [91, Suppliers 2008].

### 4.5.3 Unhairing and liming

Techniques to reduce the emissions from these stages of processing are:

- hair-save techniques
- reducing the sulphide consumption
- recycling spent sulphide liquors
- removing sulphide from the effluent.

These techniques are discussed in Sections 4.5.3.1 to 4.5.3.3.

#### 4.5.3.1 Hair-save techniques

##### Description

Unhairing is carried out by dissolving the hair root rather than the whole hair. The remaining hair is filtered out of the effluent. The concentration of hair breakdown products in the effluent is reduced.

##### Technical description

Hair-save processing has been developed for, in particular, the processing of bovine hides. 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 recovered hair may become an additional waste stream, for which a use or disposal route must be found, 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.

The hair-save unhairing techniques use the difference in chemical behaviour between the proteins keratin and collagen. Collagen is the leather-making protein of the hide while keratin is the insoluble protein containing cysteine of which hairs and wools and the older (upper) layer is mainly composed of. Keratin is stabilised through disulphide bonds (-S-S-). The fully developed keratin in hair, nails and the upper part of the epidermal layer is highly resistant to chemical or biological attack, except from sulphide which breaks down the disulphide bonds. The resistance of keratin to chemical degradation can be substantially increased by immunisation: treatment with alkali but without sulphides. The alkali transforms the sulphur cross-links into different, highly resistant thioether bonds. Mature keratin is much more easily immunised than immature keratin. This increases the difference in degradability between hair and hair roots; thus simplifying the hair-save unhairing technique. Immunisation can be achieved by using sodium hydroxide, lime or calcium hydroxide and usually takes 1 – 1.5 hours. Most commercial systems for hair-save unhairing are based on immunisation.

Several commercial hair-save techniques are on the market. Although these techniques are not suitable for all types of raw hides and leather products, high quality leathers are being produced. 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.

A hair-save technology for sheepskins, called painting, consists of the application of a semi-fluid 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 several hours. The painting of sheepskins is not further discussed in this section.

It is an advantage to filter off the loosened hair as soon as possible, and higher COD and nitrogen reduction can be obtained. This process can be considered to be a cleaner technology if the hair is utilised, even as a nitrogen source. There are several established methods of hair saving, routinely used in tanneries. They do not provide a complete effect, since each incorporates a hair-dissolving step, to deal with residual short hairs [99, IUE 2006].

Modern hair-save unhairing techniques use special equipment for recirculating the float and separating the hair. Hair separation is preferably carried out at the same time as hair loosening, so as to minimise the degradation of the hair. Drums equipped with recirculation as well as temperature and pH regulation are commercially available. The float is pumped out of the drum box and fed back in again through a hollow axle. A recirculation and filtering system can be fitted on existing drums provided that the drum axles can be used for float circulation. Another solution is filtration, after collecting the drained float in a pump sump and collecting the filtered float in a tank, where it can be pumped back to the unhairing vessels. In this case, it is possible to use one filtering unit for several vessels.

#### Achieved environmental benefits

Environmental benefits which may be achieved by the use of the technique are:

- a reduction of organic loads in the waste water
- a lower volume of sludges for disposal or treatment; and
- a saving on waste water treatment chemicals.

Table 4.6 shows the emission reductions achieved using hair-save technology, whether or not in combination with recycling and filtering the float.

**Table 4.6: Reduction of emissions from hair-save unhairing compared to hair-destroying techniques**

Discharge from hair-save unhairing <sup>(1)</sup>		% reduction compared to hair-destroying unhairing	
Emission parameter	kg per tonne of raw hide	In unhairing liquor <sup>(1)</sup>	In total tannery waste water
<b>Total solids</b>	60	30	8
<b>Suspended solids</b>	15	70	43
<b>BOD<sub>5</sub></b>	20	50	28
<b>COD</b>	50	50	28
<b>Nitrogen (TKN)</b>	2.5	55	22
<b>Ammonium nitrogen</b>	0.2	25	2
<b>Sulphide (S<sup>2-</sup>)</b>	0.6 – 1.2	50 – 60 <sup>(2)</sup>	50 – 60 <sup>(2)</sup>
<sup>(1)</sup> Including waste water from washing			
<sup>(2)</sup> The percentage reduction of the discharge is greater than the corresponding reduction of the dosage.			
<i>Source: [86, Frendrup 2000].</i>			

The sulphide discharge indicated in the table corresponds to 15 – 30 mg/l in the total waste water (at a water consumption rate of 40 m<sup>3</sup> per tonne raw hide). The discharge in the waste liquor varies greatly depending upon processing conditions; actual results are better or poorer than those cited in the table [ 86, Frendrup 2000 ].

#### Environmental performance and operational data

The volume of sludges coming from the waste water treatment plant is reduced by 15 – 30 % (reported by the German reference tannery). [16, Frendrup 1999] reports a reduction of the amount of sludge dry matter to 100 – 110 kg per tonne raw hide.

The amount of hair recovered 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 [16, Frendrup 1999]. Although it is difficult to find an economic outlet, hair can be reused as filling material or as a fertiliser (low rate of releasing nitrogen). See Section 4.11.1.

The hair-saving techniques for bovine hides are well known but they demand precise operating conditions and control. An example plant 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 process is carried out in three steps followed by washing, as described in Table 4.7.

**Table 4.7: Hair-save unhairing**

Immunisation	100 – 150 % water Add 1 – 1.5 % of reducing agent (based on e.g. inorganic sulphur compounds) or 1.5 % lime 45 – 60 minutes
Unhairing	Add 1 % NaHS (60 %) After 1 – 2 hours, hair separation
Re-liming	Add water up to 180 – 200 % Add 2 % lime Run for 60 minutes Drain the drum
Washing	Add 100 – 200 % water

### Cross-media effects

Once recovered, hair presents the tanner with the problem of coping with a solid by-product. If there is no recovery option, a balance has to be struck between, on the one hand, the savings in the waste water, the disposal 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).

### Technical considerations relevant to applicability

Hair-save technology is most applicable where a disposal route (or a beneficial use) is available for the saved hair. Where saved hair disposal is problematic and an existing waste water treatment plant can handle the high organic load of hair decomposition products the applicability of the technique is reduced.

### Economics

The economic impact of single cost items may vary widely, in particular the cost of hair disposal (or income from its sale) and savings in the costs of waste water treatment and sludge disposal in the locality.

If there is a market for recovered hair, this adds to the economic viability of the technique. In practice there are few options for the reuse of the recovered bovine hair (see Section 4.11.1.). When enzymes are used in the hair-saving process, the hair is no longer suitable for the production of felt.

Sheep wool and goat hair are easier to sell [8, Higham 1994].

The technique requires capital investment for existing tanneries. The investment cost for a drum (wooden, size 4 × 4 metres) equipped with a system for recycling water and with a filter for hair removal is around EUR 100 000 – 130 000 [91, Suppliers 2008]. Besides this cost, there will be costs for the concrete foundations.

An existing drum can be rebuilt introducing channels and washing systems to recycle the float in order to separate the hair. The cost is around EUR 5 000 – 10 000 [91, Suppliers 2008].

### Driving force for implementation

The major driving forces for implementation of hair-save unhairing techniques have been environmental requirements, and a wish to reduce the costs of waste water treatment.

### Example plants

Elmo Sweden AB, Rino Mastrotto Group – Division Calbe (Italy), Lapuan Nahka (Finland).



**Reference literature**

[33, BLC 1995] [3, Andres 1995] [27, BASF 1997] [16, Frendrup 1999] [17, UNEP 1991] [8, Higham 1994] [86, Frendrup 2000] [88, Germann 1997].

**4.5.3.2 Reducing sulphide consumption (low-sulphide unhairing)****Description**

The amount of inorganic sulphide used in unhairing is reduced by substituting organic sulphur compounds or enzyme preparations for part of the requirement.

**Technical description**

A total substitution of the sulphides used as an unhairing agent is currently not possible in practice, but their use can be reduced considerably, [27, BASF 1997] [16, Frendrup 1999] [8, Higham 1994]. In ovine skins, the necessary upgrading of the wool as a by-product hinders the reduction in the sulphide consumption for the unhairing operation.

A number of organic sulphur compounds including thioglycollate, thiourea derivatives, in particular mercaptoethanol, are used in commercial unhairing systems. All types are strong reducing agents, acting in the same way as sulphides. The advantage of their use is that they considerably reduce the amount of sulphides consumed and discharged with the waste water.

Enzymes and amines can be added to facilitate the unhairing and reduce the consumption of sulphides [15, Spain 1997]. [17, UNEP 1991]. 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. The use of enzymes in this technique may lead to damage to the grain surface.

For ovine skins, the partial replacement in the painting process of sulphides by thiols, amines or enzymes is not possible.

**Achieved environmental benefits**

The consumption and discharge of sulphides to the waste water using commercial low-sulphide systems are reduced by 40 – 70 % [37, Italy 1998]

**Environmental performance and operational data**

The sulphide dosages vary between different unhairing methods, as shown in Table 4.8.

Table 4.8: Sulphide dosages in various commercial unhairing methods

Method	kg of sulphide per tonne of raw hide
<b>Hair-dissolving lime-sulphide unhairing</b>	kg/t
Hair-dissolving lime-sulphide unhairing, minimum dosage	2.5 – 4.0
Hair-dissolving lime-sulphide unhairing, normal dosage	3.7 – 7.5
Minimum dosage for sulphide unhairing	0.6 – 1.2
<b>Hair-save lime-sulphide unhairing</b>	
European tannery	3.7
Australian NaHS method	4.7
Canadian NaHS/amine method	10.9 (5.4 – 8.1)
European tannery	3.7
<b>Thio compounds</b>	
Mercaptoethanol	2.5 – 5.1
Mercapto acetic salts	5.0 (3.7 – 6.2)
Mercapto acetic salts (Argentina)	3.7 – 3.8
Mercapto acetic salts with recycling	3.0
Mercapto acetic acid and sodium hydroxide	2.4
Formamidine sulphinic acid bovine hides	2.0 – 3.0
Formamidine sulphinic acid calfskins	2.5 – 3.3
Mercapto acetic salts with reducing agent	3.0 – 3.7
<b>Enzyme-assisted unhairing</b>	2.5 – 4.0
<b>Polysaccharides</b>	4.9
<i>Source: [86, Frentrup 2000].</i>	

### Cross-media effects

No negative cross-media effects when using organic sulphur compounds have been reported. 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 use of a low-sulphide liming system will have a positive effect on workplace safety, since the risk of the formation of hydrogen sulphide will be reduced.

### Technical considerations relevant to applicability

The technique can be applied to both new and existing plants. Low sulphide systems can be used either in hair-saving liming processes or in hair-destroying processes. The additional use of enzymes is not applicable to tanneries producing leather with a visible grain (e.g. aniline leather).

### Economics

The organic thio-compounds are much more expensive than sulphides. For economic reasons, these thio-compounds are usually used in conjunction with inorganic sulphides.

### Driving force for implementation

The main driving force is to reduce the consumption of sulphides and the content of sulphide in the waste water.

Workplace safety considerations may also drive the introduction of this technique, since the risk of hydrogen sulphide formation is reduced. This factor should not be overstated since precautions against the release of free thiols are required when using the technique.

#### **Example plants**

A number of companies within the EU use low-sulphide systems.

#### **Reference literature**

[37, Italy 1998] [16, Frendrup 1999] [8, Higham 1994] [27, BASF 1997] [86, Frendrup 2000].

### **4.5.3.3 Prevention of H<sub>2</sub>S emissions from effluents**

#### **Description**

Effluent pH control and treatments to remove the sulphide content.

#### **Technical description**

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

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 hydrogen sulphide when acidic effluents are mixed with effluents containing sulphide.

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

Sulphide removal from effluent is discussed in Section 4.9.2.

#### **Driving force for implementation**

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

- to avoid toxic gas concentrations within the tannery;
- to prevent emissions of hydrogen sulphide as an air pollutant;
- to reduce odour nuisance, which can occur even in very low H<sub>2</sub>S concentrations.

#### **Example plants**

Many tanneries in Europe take steps to curtail the formation and release of hydrogen sulphide.

#### **Reference literature:**

[17, UNEP 1991] [56, Pearson et al. 1999] [72, Germany 2000] [90, Tanneries 2008].

#### 4.5.4 Lime splitting

##### **Description**

Carrying out the splitting operation at an earlier stage of processing, so as to produce an untanned by-product.

##### **Technical description**

Splitting is a mechanical operation, in which the hide is divided horizontally into an outer 'grain' and a flesh layer (sometimes even a middle layer). The splitting can be done either after liming (lime splitting) or after chromium tanning, in the wet blue condition.

In many cases, the splitting of limed hides is more environmentally friendly than splitting after tanning (blue splitting).

Faced with the difficulties of upgrading the chromium-tanned-split waste, splitting in the lime can be considered to be a cleaner technology, as it saves chromium and yields a by-product that can be used for food casings or for the production of gelatine [99, IUE 2006].

Lime splitting has several advantages compared to the splitting of either tanned or crust materials:

- the area yield is improved compared with blue splitting due to maximum relaxation of the grain surface;
- chemical consumption in subsequent wet processes is reduced;
- processing time is reduced, due to a reduction in the overall thickness of the leathers;
- there is flexibility to carry out different tannages on split and grain layers.

On the other hand, limed pelts are more difficult to handle than 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 requires more safety precautions 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.

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). Regulations may limit the use of green and limed splits, if they contain bactericides, enzymes, or chemicals other than sulphide and lime.

Splitting at more than one stage of production requires different splitting machines to be installed.

##### **Achieved environmental benefits**

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 metre of leather produced in the process between liming and shaving are directly proportional to the weight of the lime split waste [33, BLC 1995].

A reduction in tanned solid waste is achieved.

##### **Environmental performance and operational data**

Limed splitting facilitates CO<sub>2</sub> deliming because it reduces hide thickness (see Section 4.5.5.1).

**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 sent for disposal. 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.

**Technical considerations relevant to applicability**

The technique is applicable to both new and existing installations but may require the purchase or modification of a splitting machine. The machines used for lime splitting or tanned splitting are basically the same but there are differences in the hardness and roughness of the rollers. The same machine cannot be used for both types of splitting.

**Economics**

Lime splitting is less advantageous where tanned splits can be sold as a co-product. It is less applicable where a proportion of a tannery's output is sold unsplit (full substance hides).

The investment costs for a new lime splitting machine (3000 mm) is around EUR 140 000 [91, Suppliers 2008]. The splitting machine can be used for either lime splitting or splitting after tanning, but not for both operations at the same time.

**Driving force for implementation**

The main driving force is to reduce the amount of solid waste containing chromium.

**Example plants**

Generally introduced across Europe.

**Reference literature**

[56, Pearson et al. 1999] [16, Frentrup 1999] [8, Higham 1994] [91, Suppliers 2008].

**4.5.5 Deliming and bating****4.5.5.1 Substitution of ammonium compounds by CO<sub>2</sub>****Description**

The use of ammonium compounds in deliming is replaced partially or completely by the injection of carbon dioxide gas.

**Technical description**

Carbon dioxide deliming is generally regarded as a practicable technique that can considerably reduce the environmental impact of this operation. A partial or complete substitution of ammonium salts used as deliming agents is possible for bovine hides.

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<sub>2</sub> is introduced into the float depends on the type of vessel used. In suitable drums, CO<sub>2</sub> can be injected in gaseous form through the gudgeon, or preferably, if the drum is equipped with a recirculation device, the CO<sub>2</sub>

can be added there to ensure better mixing. In mixers, the CO<sub>2</sub> is introduced directly by a lance. In pit-type vessels, the CO<sub>2</sub> is mixed in by a sparger pipe [33, BLC 1995] [3, Andres 1995].

If sufficient delimiting cannot be achieved using CO<sub>2</sub> alone, reduced quantities of ammonium salts or ammonium-free delimiting agents, such as weak acids or esters can be used. However, in comparison to delimiting with CO<sub>2</sub> alone, the resulting COD is higher, due to the contribution from the reagent. Cost and slowness of reaction make them less viable [99, IUE 2006].

Releases of H<sub>2</sub>S can be prevented by the addition of hydrogen peroxide (0.1 – 0.2 %) or (cheaper) sodium hydrogen sulphite. However, sodium hydrogen sulphite releases sulphur dioxide. Hydrogen peroxide can be corrosive to wooden drums [16, Frendrup 1999]. A system for automatic stoichiometric dosage of hydrogen peroxide has been developed, said to prevent both H<sub>2</sub>S generation and surplus H<sub>2</sub>O<sub>2</sub> in the drum. Treatment of extracted air can abate odour problems.

If the pH falls below 7, black or red hides may appear dirty due to the retention of melanin in the depleted grain layer [99, IUE 2006]. If the pH of the CO<sub>2</sub> delimiting float is lower than that obtained using ammonium salts, special bates can be used. Also, bates with a lower content of ammonium are available [99, IUE 2006].

The advantages of applying gaseous carbon dioxide are that little process control is necessary and the gas is easily injected into process vessels. If CO<sub>2</sub> is used in the delimiting, 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 delimiting 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 delimiting 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.

Generally, the delimiting time has to be extended [15, Spain 1997], [16, Frendrup 1999]. For thick, unsplit hides, accelerating auxiliary agents are available, or a small amount of ammonium salts or organic acids can be added.

The quality of the final product may not be affected for most uses, but some tanners report stiffening of the leather. The amount of chemicals used will decrease. A disadvantage with conventional delimiting 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 delimiting also improves the degreasing action, which may result in less detergent being used in the process or the use of milder detergents.

### **Achieved environmental benefits**

CO<sub>2</sub> delimiting can reduce nitrogenous discharges. In comparison to conventional techniques, with ammoniacal nitrogen emissions of 4 – 5 kg per tonne of raw material, with carbon dioxide delimiting, ammoniacal nitrogen levels of 0.02 kg per tonne of raw material can be achieved. A 20 – 30 % decrease in total Kjeldahl nitrogen emissions and a 30 – 50 % reduction in BOD in the effluent from the tanning process are possible [48, Kustula and Weaver 1998]. The release of gaseous ammonia from the delimiting process can be reduced or eliminated.

### **Environmental performance and operational data**

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<sub>2</sub> delimiting requires the installation of a pressurised storage tank for CO<sub>2</sub>, 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.

Carbon dioxide delimiting is a well-established technique applied on an industrial scale. The quality of the product and the applicability of carbon dioxide delimiting depend on several factors. The thickness of the hide is important. Thin or split hides (less than 1.5 mm) are easily delimited with carbon dioxide and the use of ammonium sulphate can be completely eliminated. The time required is the same or even less than with the conventional delimiting processes (approximately 1 – 1.5 hours).

Unsplit hides require long delimiting times if carbon dioxide delimiting is used as the sole delimiting agent. Using carbon dioxide in combination with other delimiting agents does not increase the time needed for complete delimiting of thick hides, and the ammonium sulphate amount can be reduced by 75 %.

Typically carbon dioxide consumption is 0.75 – 1.5 % based on weight. With thick or unsplit hides, the consumption is greater and additional chemicals or extended process time is needed. The delimiting is faster at higher temperatures (32 – 35 °C), but the temperature should not be so high as to damage the hides [48, Kustula and Weaver 1998].

The approximate discharges of ammoniacal nitrogen found when using different delimiting techniques are shown in Table 4.9.

**Table 4.9: Discharge of ammoniacal nitrogen during delimiting**

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

#### **Cross-media effects**

If the final pH of delimiting is lower than the pH after ammonium delimiting, there is a risk of hydrogen sulphide being generated. The addition of sodium hydrogen sulphite or hydrogen peroxide at the beginning of the delimiting can prevent the emission of hydrogen sulphide gas.

Excess CO<sub>2</sub> is released to the atmosphere.

#### **Technical considerations relevant to applicability**

The technique can be applied to both new and existing plants, and is applicable to bovine and, to a lesser extent, to ovine material.

Problems arise when CO<sub>2</sub> delimiting is applied to ovine skins which have been dewooled using sulphides, since the amount of sulphide used is greater than that for bovine hides. The larger amount of hydrogen sulphide released during the application of CO<sub>2</sub> cannot be controlled by oxidising with hydrogen peroxide due to the large amount required and the cost.

The complete replacement of ammonium compounds by CO<sub>2</sub> delimiting cannot be applied to the processing of materials whose thickness is over 1.5 mm. Moreover, the partial or complete replacement of ammonium compounds by CO<sub>2</sub> delimiting is also limited to both new and existing vessels which allow the use of or can be modified to use the CO<sub>2</sub> delimiting technique.

### **Economics**

The economics of the process are affected by prolonged production times and the cost of CO<sub>2</sub> and alternative bates as compared with the cost of ammonium salts [16, Frendrup 1999]. Cost savings are possible, especially in the treatment of ammonium and COD in the effluent.

The cost of running the process may be slightly higher than for conventional deliming. A tannery processing 25 tonnes of raw hides per day would need to invest about EUR 100 000.

Finland reports 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 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.

### **Driving force for implementation**

The main driving force for the implementation of this technique is a need or wish to reduce the discharge of ammoniacal nitrogen in the effluent. In odour-sensitive locations, the adoption of the technique may be driven by a need to reduce the emission of ammonia.

### **Example plants**

Carbon dioxide deliming is used at several plants in Europe.

### **Reference literature**

[33, BLC 1995] [3, Andres 1995] [16, Frendrup 1999] [15, Spain 1997] [8, Higham 1994] [41, Various 1998] [48, Kustula and Weaver 1998] [90, Tanneries 2008] [99, IUE 2006].

## **4.5.5.2 Substitution of ammonium compounds by organic acids**

### **Description**

Ammonium salts used in deliming are partially or completely replaced by weak organic acids.

### **Technical description**

Magnesium lactate, organic acids such as lactic acid, formic acid and acetic acids, or esters of organic acids can be used to substitute ammonium compounds in the deliming process. The advantage of substituting ammonium salts is that ammonia levels in the waste water are reduced.

### **Achieved environmental benefits**

Environmental benefits which can be achieved using this technique are a reduction of nitrogen in the effluents and a reduction of gaseous ammonia releases during deliming.

### **Environmental performance and operational data**

The deliming products are usually based on various organic and inorganic acids, esters of carboxylic acids, non-swelling aromatic acids etc. A deliming auxiliary based on esters of carboxylic acids will normally be added at a concentration of 1.5 % on pelt weight. The chemical is added together with water (200 % on pelt weight) and the process time is approximately 1 – 1.5 hours.

### **Cross-media effects**

These agents increase the COD load [16, Frendrup 1999]. 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.

**Technical considerations relevant to applicability**

The technique can be applied to both new and existing plants. Positive effects on the quality of the pelts are observed.

**Economics**

Ammonia-free deliming with commercial products may be more than six times as expensive as deliming with ammonium salts.

**Driving force for implementation**

The main driving force is the reduction of nitrogen discharge in the waste water. The reduction can be a demand from environmental authorities or a prerequisite from waste water treatment plants receiving water from the tannery. In odour-sensitive locations the adoption of the technique may be driven by a need to reduce the emission of ammonia.

**Example plants**

Many plants in Europe use ammonium-free or reduced ammonium deliming.

**Reference literature:**

[27, BASF 1997] [16, Frentrup 1999] [84, Ludvik J. 2000].

## 4.6 Tanyard operations

### 4.6.1 Pickling

#### 4.6.1.1 Salt-free and reduced salt pickling

##### Description

Pickling using alternatives to salt (NaCl) in the float.

##### Technical description

Salt-free systems, based on non-swelling polymeric sulphonic acids are available. The possibility of a partial substitution of chloride by using, e.g. aromatic sulphonic acids has also been reported.

##### Achieved environmental benefits

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 [91, Suppliers 2008].

##### Cross-media effects

The environmental effects of (aromatic) sulphonic acids in the effluent, compared to salt, are not clear. COD is certainly increased.

##### Technical considerations relevant to applicability

The technique can be applied to both new and existing plants. Using non-swelling acids modifies leather characteristics of the hide or skin for chrome tanning and dyeing. Dyed leather colour is different to that of a leather produced using a normal pickle and the whole tanning process has to be modified.

##### Economics

A tannery often uses formic acid and sulphuric acid for the pickling operation. The costs for the commercial alternatives are comparable to the cost for formic acid or, in some cases, are even lower. However, the total cost will be slightly higher for using salt-free or salt-reduced pickling compared to conventional pickling.

##### Driving force for implementation

The main driving force is the need to reduce the discharge of salt to the waste water.

##### Example plants

The technique is implemented in several plants where restrictions to salt apply due to local conditions (e.g. Arzignano in Italy).

##### Reference literature

[27, BASF 1997] [29, Renner 1995] [16, Frentrup 1999] [91, Suppliers 2008].

### 4.6.2 Degreasing

Emission reduction techniques for the degreasing of sheepskins are:

- a. substitute NPEs-based surfactants by ethoxylated alcohol-based surfactants (see Section 4.2.1);
- b. substitute halogenated organic solvents by non-halogenated solvents that will not contribute to AOX emissions (see Section 4.2.2.1);
- c. closed-loop machines (dry cleaning machines) with adequate abatement for organic solvent emissions (see for comparison Section 3.9.4.2).

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.

#### **4.6.2.1 Optimising the use of organic solvents in the dry degreasing of sheepskins**

##### **Description**

Recovery of degreasing solvents by distillation in closed cycle machines.

##### **Technical description**

Various chlorinated solvents, such as chlorinated aromatic and aliphatic compounds, are applied for degreasing wool-on sheepskins. Toxicity, flammability, explosion prevention, and releases to air (VOC) and soil are the major points of concern, with the emphasis depending on the particular solvent or the mixture of solvents used.

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 reused. However, 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.

##### **Achieved environmental benefits**

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. 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.

##### **Cross-media effects**

Residues carrying organic solvent with fat and grease are produced. If no recycling or reuse 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 treatments.

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.

##### **Technical considerations relevant to applicability**

The technique can be applied to both new and existing plants.

##### **Driving force for implementation**

The main driving forces are environmental reasons.

##### **Reference literature**

[36, Friis 1998].

### 4.6.3 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. Improved techniques for chromium tanning are described in Sections 4.6.3.1, 4.6.3.2, 4.6.3.3 and 4.6.3.4. Chromium balances for various techniques are shown in Table 4.10.

Improved methods of vegetable tanning are described in Section 4.6.3.7 and tanning with other tanning agents in Sections 4.6.3.5 and 4.6.3.6. Table 4.11 shows emissions data from the tanning process using chromium. It should be noted that some chromium is also discharged from the wet post-tanning processes due to leaching.

**Table 4.10: Chromium balances when using various techniques**

Chromium balance per unit raw hide (kg/t)					
	Long float conventional	Short float, self basifying, good management	High- exhaustion	Recycling	Recovery by precipitation
<b>Consumption</b>	21.5	15.5	10	12.4 – 13.1	
<b>Leather and leather waste</b>	13	9.6	9.6		
<b>Waste water (including tanning, draining, sammying)</b>	7.5	5.2	0.1	2.8 – 3.5 (for total discharge)	0.5 (for total discharge)
<b>Waste water (wet after- treatments)</b>	1	0.7	0.3		
<i>Source: [16, Frendrup 1999].</i>					

#### 4.6.3.1 Increasing the efficiency of chromium tanning

##### Description

Optimising the physical parameters of the process to increase the proportion of the conventional chrome-tanning agent taken up by the hides or skins.

##### Technical description

The chromium 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 chromium complex can be bound. Splitting after liming facilitates chromium penetration and reduces chemical input (see Section 4.5.4).

The next step is to ensure high efficiency in the process. The conventional chromium tanning carried out in long floats is characterised by poor exhaustion; with 30 – 50 % of the chromium applied being lost with the waste water [16, Frendrup 1999]. It has also been reported that an average of 40 % of the chromium input may be discharged [56, Pearson et al. 1999].

The chromium exhaustion in conventional tanning systems can be improved by the following process changes.

- The chromium input must be optimised during conventional chrome tanning to reduce the possible waste (lowest chromium offer possible should be used).
- Processing parameters, e.g. pH and temperature, must be optimised to increase chromium uptake (end values of above 50 °C and pH 4 are advantageous, if compatible with good leather properties). Tanning cannot start at a temperature higher than 30 °C.

The float temperature can be increased only progressively, during the tanning step, from the room temperature to the final one.

- Short floats reduce the chromium input, combining a low chromium input with a high chromium concentration.
- Enough time must be allowed for penetration and reaction of the chromium with the substrate (a long process time).

#### **Achieved environmental benefits**

Without introducing any new chemicals or techniques, tanners can significantly improve the chromium uptake (compared to about 60 % in normal operation):

- 70 – 80 % chromium uptake can be achieved by altering the physical parameters (temperature rise from 20 °C to 50 °C, pH from 3.5 to 4.5) of the tanning operation;
- up to 90 % chromium uptake by altering both physical and chemical parameters (float levels, chrome offers).

A reduced chromium discharge from the tanning process will lead to a lower amount of chromium in the sludge generated during waste water treatment

#### **Environmental performance and operational data**

The operational data will depend on the type of leather being produced, see Table 4.11.

#### **Technical considerations relevant to applicability**

The technique can be applied when new installations are built or when new drums are installed.

Extensive adaptation is required to use existing drums for heated processing. A heating system and automatic process control equipment are required. Not all existing drums are suitable for such adaptations.

#### **Driving force for implementation**

The obvious advantages are a reduction in: the consumption of tanning agents; waste water; waste treatment and effluents.

#### **Example plants**

A number of plants exist in Europe where the efficiency of chrome tanning is optimised by process adjustments.

#### **References**

[33, BLC 1995] [16, Frendrup 1999] [56, Pearson et al. 1999] [90, Tanneries 2008].

**Table 4.11: Emissions in waste water per tonne of raw hide from the chromium-tanning process (including pickling)**

Units per tonne of hide or skin		Short float chromium tanning and good management	Salt-free pickling, high exhaustion chromium tanning
Water volume	m <sup>3</sup> /t	1	0.5
Total solids	kg/t	150	80
Suspended solids	kg/t	7	7
BOD <sub>5</sub>	kg/t	3	3
COD	kg/t	7	7
TKN	kg/t	1	0.5
Ammoniacal nitrogen	kg/t	0.5	0.1
Chromium (Cr)	kg/t	5.2	0.1
Chloride (Cl <sup>-</sup> )	kg/t	60	28
Sulphate (SO <sub>4</sub> <sup>2-</sup> )	kg/t	30	16
Grease and oil (may be higher when fatliquor is added to the float)	kg/t	1.5	1.5
<i>Source: [16, Frendrup 1999].</i>			

#### 4.6.3.2 High-exhaustion chromium tanning

##### Description

High-exhaustion tanning includes the use of specific chemical products able to increase the chromium uptake combined with an optimisation of the tanning process parameters.

##### Technical description

There are two types of high-exhaustion systems.

In the first type, certain reactive groups are incorporated into the chrome tanning complexes. Chromium is reacted with dicarboxylic acid to form complexes of a suitable size for cross-linking.

In the second type, the collagen reactivity may be increased by increasing the number of carboxyl groups on the amino acid side chain in the collagen structure of the hides, in order to provide more sites for cross-linking. There are special agents (aromatic dicarbon acids, e.g. of adipic or phthalic acid, aldehyde carbon acids, e.g. glyoxylic acid), which enhance the number of links available for the binding of chromium in the collagen structure.

The technique was previously considered BAT in the 2003 BREF for the Tanning of Hides and Skins, but evidence showed that the technique should no longer be considered as such. The first rationale is that treatment of the process water (precipitation of chromium) becomes more difficult due to the masking agents used. The overall environmental benefits when using the technique are therefore considered to be lower than the environmental benefits using chromium removal techniques. The second rationale is that practical experiences from tanneries have indicated that the use of the technique causes negative effects on the leather grain quality.

##### Achieved environmental benefits

The principal environmental benefit which can be achieved by the use of high-exhaustion chromium tanning is a reduction in the emission of chromium compounds in the waste water. A comparison of those emissions with those from optimised conventional chromium tanning is shown in Table 4.11.

The concentration of chromium in effluent treatment sludge is also reduced.

Sodium sulphates or chlorides often dilute commercially available chromium tanning 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 chromium hydroxide difficult. Chromium cannot be precipitated completely, if aromatic dicarboxylic acids (e.g. phthalic acid) are used.

#### **Environmental performance and operational data**

Several commercial systems exist and the formulations differ, although the principle is the same. Table 4.10 shows the chromium balance for different chrome-tanning systems.

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 exhaustion depends on the process chosen and can reach 80 – 98 % (including good fixation) [8, Higham 1994]. A reduction of the chromium content in the waste water of 50 – 80 % has also been reported [37, Italy 1998].

It should be noted that even if an exhaustion of the tanning liquors is reported as up to 90 %, unfixed chromium may still be released in the subsequent wet after-treatment steps. Good fixation is therefore essential.

In conventional tanning 2 – 5 kg/t raw bovine hides (8 – 12 kg/t dry goatskins and sheepskins) of chromium salts are released via the spent liquors. With high-exhaustion chrome tanning, this quantity can be reduced to 0.3 – 0.6 kg/t raw bovine hide.

Leaching of chromium 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).

#### **Cross-media effects**

Masking agents used in high-exhaustion chrome tanning make the precipitation and the reuse of chromium hydroxide difficult. Chromium cannot be precipitated completely, if aromatic dicarboxylic acids (e.g. phthalic acid) are used.

#### **Technical considerations relevant to applicability**

The technique can be applied to both new and existing 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. The use of high-exhaustion tanning will alter the properties of the final product, so most leather products cannot be made using this technique.

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.

#### **Economics**

Savings in chromium may offset higher unit costs of the tanning chemicals involved compared to a conventional tanning process with an efficiency of 70 %.

#### **Driving force for implementation**

The main driving forces are environmental reasons such as the need to reduce the chromium discharge from the tanning process.

#### **Example plants**

Several plants in Europe were using high-exhaustion tanning systems, e.g. in the Netherlands, however the technique is no longer in use in Europe.

### Reference literature

[35, UBA 1997] [8, Higham 1994] [17, UNEP 1991] [42, Various 1995] [56, Pearson et al. 1999] [16, Frendrup 1999] [84, Ludvik J. 2000] [90, Tanneries 2008] [136, Ludvik, J (2) 2000], [137, Ludvik, J (3) 2000].

### 4.6.3.3 Recycling and reuse of chromium solutions

#### Description

Exhausted tanning floats are reused at either the pickling or tanning steps.

#### Technical description

There are two options for the recycling of exhausted tanning liquors.

##### 1. Recycle the tanning liquors to the pickling process

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 a brine solution, and then the pickle/chrome liquor is added. After the standard pickling time, the fresh chromium input is added.

##### 2. Recycling the tanning liquors to the 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 chromium powder is added to the drained pickled pelts (which carry about 20 % residual float) and then the recycled liquor is added.

In both cases some changes to the tanning process might be necessary, such as reducing the amount of masking agents and salts added. For both options a holding tank and a screening of the solutions are required. Recycling up to 10 times before discharge is possible. Chromium liquor builds up volume (instead of discharging to the environment).

Process control and monitoring are necessary for calculating and adjusting float strength (salt content, pH, etc.) and for checking impurities.

#### Achieved environmental benefits

The efficiency of the recycling is dependent on the efficiency of the tanning process itself.

##### 1. Recycling the tanning liquors to the pickling process

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 chromium input [33, BLC 1995] [6, Frendrup 1999].

Salt carried over in the spent tanning liquor allows for a reduction of 40 % in the salt added to the brine solution.

Chromium discharge in the effluent can be reduced by 50 % (reduction of 40 – 50 % from 5.9 to 2.8 – 3.5 kg Cr per tonne of raw hide in the waste water [16, Frendrup 1999].

##### 2. Recycling the tanning liquors to the tanning process

The fresh chromium input can be reduced by 25 % for bovine hides and up to 50 % for sheepskins. Chromium discharge in the effluents can be reduced by 60 %.

#### Environmental performance and operational data

No operational information provided.



**Cross-media effects**

No information provided.

**Technical considerations relevant to applicability**

No chromium-free pretanning option is possible. When there is a common chromium recycling unit that works well and takes up all the chromium liquors produced, recycling of the liquors may not be viable.

Quality losses may occur. The colour of the wet blue may change and subsequently may have an impact on the dyeing operations and the quality of the final product. 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. In addition, there seems to be a preference to increase the exhaustion of the chrome-tanning process, rather than to recycle the exhausted liquor due to quality reasons.

Recycling the tanning liquors to the pickling process can be applied to processes where pickling and tanning are carried out in the same float [33, BLC 1995]. Where the exhaustion of the chrome tanning is in excess of 80 %, direct recycling of the exhausted chromium liquor may not be economically feasible.

The technique can be applied to both new and existing plants. One limitation for the recycling and reuse of chromium solutions is that the volume that can be recycled is quite low since only main tanning floats can be recycled. However, chromium will also be discharged through washing baths and liquid expressed during the samming of the leather. This is one of the reasons why installations that previously used recycling of chromium solutions moved to chromium recovery through precipitation and subsequent reuse of re-dissolved chromium.

**Economics**

Running and capital costs are low, although the introduction of the technique requires at least a holding tank and a screen. Economic feasibility will depend on the exhaustion rate of the chrome tannage and the quantity of the chromium liquors generated. In general, the lower the exhaustion rate and the higher the volume of the floats, the higher the economic feasibility is. Furthermore, the final quality of the product will have a high impact on the sustainability of the technique.

**Driving force for implementation**

The main driving force is the wish to reduce the chemical consumption and the discharge of chromium into the effluent. However, the use of the techniques has not been widespread in Europe due to quality reasons and the limited environmental effect compared to chromium recovery through precipitation and separation.

**Example plants**

This option has been implemented in some tanneries in Australia and North America. This technique was used in Germany for the production of lower quality leather, but is no longer used.

**Reference literature**

[16, Frendrup 1999] [84, Ludvik J. 2000] [90, Tanneries 2008].

#### 4.6.3.4 Chromium recovery through precipitation and separation

##### Description

Separation of chromium salts from the aqueous effluent stream by precipitation, with dewatering of the precipitate. Re-solution of the precipitated chromium using sulphuric acid, for use as a partial substitute for fresh chromium salts; or use of the chromium sludge as a raw material by another industry.

##### Technical description

The technique is used for the treatment of effluents from the chromium-tanning process including washing floats and liquid from samming. It is based on the recovery of chromium from the effluents and its recycling into the production process.

From the chemical point of view, chromium(III) 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 chromium 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 or centrifuge 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, using fossil flour to absorb fats and other chemicals present in the spent chromium tanning liquors, more filter presses, more chemicals, more time, and higher costs are involved.

Chromium(III) can be recovered from the exhaust liquors (tanning liquors, samming water) from the conventional chrome-tanning process; chromium from high-exhaustion chromium salts is not recycled due to the low concentration. The liquors containing chromium 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  $\text{Cr}_2\text{O}_3$  as precipitate about 1.9 kg  $\text{H}_2\text{SO}_4$  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 chromium, but the stronger the alkali, the faster the rate of coagulation. One of the precipitation options given below 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 dewatering 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  $\text{Cr}_2\text{O}_3$  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 the pH to rise beyond 10, so that any sludge re-dissolving 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.

**Achieved environmental benefits**

Efficiencies of 95 – 98 %, 99 % and 99.9 % of chromium precipitation are reported. In the Netherlands, reported values, measured as total chromium in a daily composite sample, after sedimentation or flotation of the separate chromium-containing effluent before mixing, are 1 – 2 mg Cr/l. The same levels are achieved in some German tanneries. A tannery in Sweden normally achieves chromium concentrations of <1 mg/l in the separated effluent containing chromium after precipitation. The discharge to the treatment plant after this internal measure is about 0.4 kg chromium per tonne raw hide. Most of the chromium in the discharge to the waste water comes from the post-tanning operations (retanning, dyeing and fatliquoring) and these effluents are not passed through the chromium recovery unit.

Data from tanneries in the UK show chromium contents of 3000 – 6000 mg/l in the chromium liquors after tanning. Chromium precipitation can remove around 99.9 % of this chromium, which results in a concentration of chromium in the separated effluent of 3 – 5 mg/l and a concentration in the total effluent following mixing with beamhouse effluent of less than 1 mg/l.

The recovered chromium sulphate solution can be recycled into the tanning process by replacing up to 35 % of the 'fresh' added chrome tanning salt.

As the overall chromium utilisation ratio increases, the amount of chromium discharged to the waste water is reduced. This results in a reduction of chromium in sewage sludge and chromium discharged to the environment. No additional waste volume is built up.

In Table 4.10 the technique is compared to other methods of processing.

**Environmental performance and operational data**

Italy and Portugal each have one common chromium recycling unit. The plant in Italy was designed to receive 400 – 500 m<sup>3</sup> exhausted floats per day from about 250 operators. From this input the recovery plant produces 2000 kg Cr<sub>2</sub>O<sub>3</sub> per day, which is reused 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 reused 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.

One tannery uses the following recycling process. The effluent containing chromium 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<sub>2</sub>O<sub>3</sub>/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.

**Cross-media effects**

Chromium recovery requires the use of alkali, acids and auxiliaries. Consequently, the quantity of neutral salts discharged to the effluents is increased.

**Technical considerations relevant to applicability**

Chromium 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. Chromium recovered in this way resembles more closely the quality of fresh chromium, and therefore this system of chromium precipitation tends to be favoured over direct chromium recycling.

If the achieved quality of the final product is negatively affected by the use of recovered chromium, the chromium can be used for tanning of split, where there is a market for tanned splits.

The technique can be applied to both new and existing plants. It is independent of any local conditions and can be introduced in any tannery using chromium as a tanning agent. In practice, it has been applied in larger tanneries or in common effluent treatment plants. It is not appropriate for treating effluents from high-exhaustion chromium tanning.

Leathers produced using recycled chromium can be used for automotive upholstery, but are not necessarily suitable for other applications.

### **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 chromium liquors generated. In general, the lower the exhaustion rate during tanning and the higher the volume of the floats, the higher the economic feasibility.

The introduction of chromium recovery through precipitation and separation requires a substantial investment. Data from 2004 indicate that the investment cost for a chromium treatment plant for the treatment of 100 m<sup>3</sup> water containing chromium will be approximately EUR 350 000 – 450 000.

### **Driving force for implementation**

The main driving forces are to reduce the chromium discharge from the tanning process and to reduce chromium consumption, and in one case regional legislation.

### **Example plants**

Several central chromium 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. Some individual tanneries have also been able to implement chromium recovery on site, e.g. in Germany (e.g. Bader and Gmelich), Italy and Sweden (Elmo Sweden AB).

### **Reference literature**

[39, Greece 1998] [37, Italy 1998] [16, Frentrup 1999] [17, UNEP 1991] [33, BLC 1995], [29, Renner 1995] [7, Zimpel 1997] [91, Suppliers 2008].

#### **4.6.3.5 Pretanning with non-chrome tanning agents**

##### **Description**

Pretanning changes the physical and chemical characteristics of the leather and can be used as a mechanism to improve chromium uptake or reduce the input of chromium.

##### **Technical description**

The pretanning agents are aluminium salts, sometimes aluminium combined with polyacrylates, glutaraldehyde derivatives, syntans, titanium salts, or colloidal silica. The minimum dosage is 1.25 % aluminium oxide or 1.0 – 1.5 % glutaraldehyde or 0.75 % titanium oxide [16, Frentrup 1999].

Certain pretanning recipes can be combined with non-chromium tanning agents to produce chromium-free leather. It is believed that if a pretannage is applied and the physical parameters for chrome tanning are well controlled (temperature up to 60 °C, basify up to pH 4.2), the chromium input can be reduced from 8 to 5 % on the basis of limed weight.

Some pretanning agents can raise the shrinkage temperature of the collagen significantly. Pickling and pretanning can be combined, although pickling is not always necessary. Depending on the selection of tanning agents, pretanning can be performed without noticeably changing the characteristics of the leather, in order to be flexible in the choice of further processing. Pretanning can be followed by different tanning processes, such as chrome tanning, vegetable tanning or resin tanning.

#### **Achieved environmental benefits**

Pretanning with non-chromium agents can be used to improve the chromium uptake and reduce the chromium input, although the environmental impact of the pretanning agents must be carefully assessed. For example, aluminium carries higher environmental risks than chromium, because of its higher solubility.

Exhaustion in subsequent chrome tanning is enhanced from 93 % to 97 %. In one case, the subsequent chromium dosage was reduced from 15 kg Cr per tonne of raw hide in conventional tanning to 6.5 kg Cr per tonne of raw hide [16, Frendrup 1999]. However, the price of this improvement is the need to input pretanning 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, particulate matter) after this pretanning step are chromium-free, which in some cases is advantageous for reuse, recycling and disposal of the waste.

The shavings and trimmings, as they are basically organic materials, have proved to have excellent value as fertiliser, equal to that of chromium-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.

Fungicides have to be used in pretanning with glutaraldehyde, in doses higher than those required for chromium tanning.

#### **Technical considerations relevant to applicability**

Chromium-free pretanning may not be applicable if the chrome-tanning effect needs to be maintained in the final product, or when the pretanning effect results in an unacceptable colouration of the leather. The colour of the final wet blue can be greener, depending on the type of pretannage used. Problems arise because product specifications often require certain colours. The dyeing procedures then have to be adapted to the different shades of the material. 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 new and existing plants. Subsequent chemical and mechanical processes require modification.

Pretanned leather can be split and shaved, thus avoiding chromium shaving and further reducing the chromium input needed per square metre of leather produced. Furthermore, pretanning has been reported to improve the quality of the leather, particularly with regard to grain tightness.

### **Economics**

The wet white technique requires an extra process and consequently longer processing time and extra chemical costs.

### **Driving force for implementation**

The main driving force for implementation of the technique is to reduce the waste containing chromium.

### **Example plants**

Some plants in Europe use the technique.

### **Reference literature**

[33, BLC 1995] [3, Andres 1995] [27, BASF 1997] [16, Frendrup 1999].

## **4.6.3.6 Pretanning using aldehydes, producing chromium-free leather**

### **Description**

Pretanning with aldehydes, followed by more intensive retanning.

### **Technical description**

The development of wet white pretanning systems was undertaken to address environmental matters, in particular the reduction of chromium in effluent and solid waste. These systems have become more and more used for the production of chromium-free leather for specific applications. The largest user of chromium-free leather is the car industry which requires high performance leather. There are several processes possible for manufacturing wet white pretanned stock. Some aldehydes can be used as tanning agents and are widely used as pretanning agents for the production of chromium-free leather. Formaldehyde is no longer used in Europe for reasons of workplace safety. Glutaraldehyde, or more usually, glutaraldehyde derivatives, are widely used for pretanning. Pretanning with aldehydes can be seen as a stabilisation of the leather and has to be supplemented by additional tanning.

### **Achieved environmental benefits**

Reduction of the chromium emissions to the effluents (no chromium discharge) and less solid waste containing chromium. Glutaraldehyde is a widely used chemical. Extensive measures have been taken to monitor any negative effect in the urban sewage treatment plant, and no negative effects have been noticed. Oxazolidine may be used but detailed data about the environmental impact of this substance are not available yet.

### **Environmental performance and operational data**

The operational data will depend on the type of leather produced.

### **Cross-media effects**

Higher amounts of retanning agents and filling agents are required compared to chrome tanning. The skins and hides are only pretanned and a subsequent tanning is needed by, e.g. syntans or vegetable tanning agents.

Fungicides have to be used in pretanning with glutaraldehyde, in doses higher than those required for chromium tanning.

### **Technical considerations relevant to applicability**

The technique is applicable to both new and existing installations. It should be noted that a chromium-free wet white gives leather with different physical and dyeing properties. Aldehydes are often used in combination with vegetable tannins or syntans.

**Economics**

The cost of pretanning with glutaraldehyde compared to the chrome-tanning process is about 20 % higher. However, the possibilities for a disposal of waste tanned with chromium may become more difficult and expensive in the future.

**Driving force for implementation**

The main driver for the use of this technique is consumer demand. Particular properties, like low dry-shrinking of the leather are important for car upholstery. In the past, the main driver was to reduce the content of chromium in the waste water and solid waste.

**Example plants**

Several tanneries in Europe use the technique. In particular, installations producing leather for the car industry.

**Reference literature**

[ 85, Hauber and Knödler 2008 ].

**4.6.3.7 Pretanning followed by vegetable tanning with high uptake of tanning agents****Description**

Use of pretanning agents to aid tannin penetration and of short floats in drum tanning.

**Technical description**

Systems with a high degree of tanning exhaustion (~ 95 %) are available commercially. These systems have in common a pretanning step with e.g. polyphosphates and/or syntans. Syntans are synthetic tannins and, generally, these are prepared as salts of polyphenolic sulphonic acids, from different simple phenols or from natural phenolic compounds (as lignosulphonates) by sulphonation and condensation. The addition of syntans will make the vegetable tannins penetrate the hides quicker and hence reduce the tanning time.

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.

The leather is pickled and pretanned 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.

**Achieved environmental benefits**

Reduction in the COD and BOD of the effluent compared to vegetable tanning with a lower rate of uptake of vegetable tannins.

**Environmental performance and operational data**

Some rough operational data of the volumes and pollutant loadings of waste water per tonne of hide or skin are shown in Table 4.12.

**Table 4.12: Rough data of waste water volume and pollutant loadings per tonne of raw hide or skin from vegetable tanning including pickling, washing, and bleaching**

Quantity per tonne of hide or skin	Counter current pit	Drum	Salt-free pickling
Water volume, m <sup>3</sup>	3 – 4	3 – 4	
Total solids, kg	110 – 200	65 – 100	
Suspended solids, kg	10 – 15	10 – 15	
BOD <sub>5</sub> , kg	40 – 75	25 – 35	
COD, kg	120 – 220	70 – 110	
Chloride (Cl), kg	50		4
<i>Source: [16, Frendrup 1999].</i>			

### Cross-media effects

The extracts used in vegetable tanning contain from 60 % to 72 % of the actual tanning agents and 28 to 40 % of other compounds, for example sugar, salts, gums, insolubles, most of which are released to the waste water. Therefore, the overall uptake of tanning agents from the process will be in the order of 50 – 70 % of the tanning extract used.

### Technical considerations relevant to applicability

The technique with high exhaustion of vegetable tanning agents can be applied by both new and existing installations. It can be applied in pits or in drums or in a combination of the two (one possibility is to start the processes in pits but carry out the final tanning in a drum).

Vegetable tanning in a drum produces a type of leather with very different properties (softer and more flexible, less full) than the leather produced in a pit. Drum tanning lasts in general two or more days, while pit tanning may take one month or more.

### Economics

The chemicals are more expensive, but this is balanced by the saving in processing time. Since around 60 % of the market price of leather consists of the costs for the raw material, it is financially advantageous to reduce process time.

### Driving force for implementation

The main drivers for the process are to increase the uptake of vegetable tannins into the leather and thereby reduce the discharge of, in particular, COD and to reduce the process time for vegetable tanning.

### Example plants

Vegetable tanning using pretanning in order to increase the penetration and uptake is used by a number of tanneries in Europe.

### Reference literature

[3, Andres 1995] [6, Europa 1992] [8, Higham 1994] [16, Frendrup 1999] [56, Pearson et al. 1999] [127, Slaats 1995].



## 4.7 Post-tanning operations

Techniques to reduce the environmental impact of all post-tanning processes (described in Section 3.9.5) are available. These are discussed in Sections 4.7.1, 4.7.2, 4.7.3, 4.7.4, 4.7.5, 4.7.6 and 4.7.7.

### 4.7.1 Process changes to reduce metal discharges

#### Description

Use of high-exhaustion tanning, or ageing of chrome-tanned leather to reduce leaching of the chromium during post-tanning. Filtration of loose chrome-tanned leather fibres.

#### Technical description

Using a conventional technique, the amount of chromium in the waste water, deriving from the post-tanning operations, is approximately 1 kg per tonne raw hide arising as shown in Table 4.13.

**Table 4.13: Sources for chromium discharge during post-tanning operations**

Source of chromium discharge	kg chromium per tonne of raw hide
Leaching	0.6
In fine leather fibres	0.4
In metal complex dyes	0.03
<i>Source: [16, Frendrup 1999].</i>	

A reduction of the leaching of chromium during the post-tanning processes can be obtained either using high-exhaustion chrome-tanning systems or allowing the necessary time for the tanned leather to 'age' prior to the post-tanning processes.

A very important factor for obtaining a high degree of fixation of dyes and fatliquors is to end the operations at a relatively low pH (the pH could be brought down to approximately 3.5). However, lowering the pH below 4 is, at the same time, an important factor causing chromium to leach out from the leather.

Another source for chromium discharge from post-tanning operations is fine fibres from the shaving operation adhering to the leather surface and ending up in washing and neutralisation floats. The chrome leather fibres may be eliminated by screening, e.g. with a wedge wire screen. The screening may take place at the site or as a first treatment step when floats containing chromium from the post-tanning operations are treated.

In metal complex dyestuffs for leather, the coordinating metal atom is iron, chromium, copper or cobalt. The metal complex dyes form a stable bond with the leather and the metal is an integrated part of the dye molecule. The maximum contribution of chromium from this source if the leather is dyed properly is 0.3 % chromium in the leather and 0.03 – 0.05 kg chromium per tonne raw hide in the waste water. The slight increase in the metal content can be avoided if acid dyes without metals are used (provided that the same final properties, in particular with respect to light fastness, can be obtained).

#### Achieved environmental benefits

The quantity of metals (in particular chromium) in the waste water will be reduced

#### Environmental performance and operational data

Operational data will depend on the product that will be produced.

### **Cross-media effects**

A balance for the final pH of the dyeing has to be reached, since acidification of the leather at the end of the dyeing process in order to increase the dye fixation may give rise to increased leaching of chromium from the leather.

The screening of small fine fibres from the first washing during post-tanning will give rise to a solid waste.

### **Driving force for implementation**

The main driving force, in general, is to reduce the chromium discharge from the tannery. The main driving force for avoiding metals in metal complex dyes is to produce leather without metals.

### **Example plants**

A number of tanneries in Europe have implemented the technique.

### **Reference literature**

[16, Frentrup 1999] [90, Tanneries 2008].

## **4.7.2 Optimised retanning**

### **Description**

Optimisation of process parameters to ensure the maximum uptake of retanning chemicals.

### **Technical description**

Retanning 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.

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.

### **Achieved environmental benefits**

Reduced discharge of retanning agents to the waste water.

### **Environmental performance and operational data**

Operational data will depend on the properties of the final product.

### **Cross-media effects**

No cross-media effect identified.

### **Technical considerations relevant to applicability**

The technique is applicable to both new and existing installations

### **Driving force for implementation**

The main driving force is the reduction of discharge of retanning agents to the waste water.

### **Example plants**

A large number of tanneries in Europe are using the technique.

### **Reference literature**

[91, Suppliers 2008].

### 4.7.3 Optimised dyeing

#### Description

Optimisation of process parameters to ensure the maximum uptake of dyes.

#### Technical description

It is very desirable that the exhaustion of dyes is as high as possible and that the dyes are firmly bound to the leather. Dyeing auxiliaries such as amphoteric polymers may be applied in order to enhance the build-up of dye intensity. Furthermore, the degree of fixation of dyes is increased by processing at higher temperatures (60 °C) and a short float (100 %). Finally, a very important factor for obtaining a high degree of fixation of dyes is to end the operation at a relatively low pH value (pH is typically brought down to about 3.5).

#### Achieved environmental benefits

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 in some cases to the AOX. They colour the effluents or have to be assessed as single substances due to their high potential impact.

A high exhaustion of dyes prevents the waste water from being discoloured, indicating that the concentration of dyes in the waste water released from tanneries is below 10 ppm (as dye levels of 10 ppm or higher in waste water are visible to the eye).

#### Environmental performance and operational data

A normal addition of dyes to leather is in the range of 2 %, and uptakes up to 96 – 99 % can be achieved.

#### Cross-media effects

Lowering the pH below 4 is an important factor causing chromium to leach out from the leather.

#### Technical considerations relevant to applicability

The technique is applicable to both new and existing facilities but requires a high degree of control of the process parameters.

#### Economics

Dyes are generally more expensive than other chemical products in leather production and a high exhaustion (reduced wastage of dyes) will have a positive economic impact.

#### Driving force for implementation

The main drivers are aesthetic reasons (avoiding discoloured waste water) and economy (waste of expensive dyes).

#### Example plants

Many tanneries in the EU use high-exhaustion of dyes.

#### Reference literature

[91, Suppliers 2008] [113, Puentener 1998].

### 4.7.4 Optimised fatliquoring

#### Description

Optimisation of process parameters to ensure the maximum uptake of fatliquors.

#### Technical description

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. The addition of amphoteric polymers improves the exhaustion of fatliquors.

### **Achieved environmental benefits**

The COD in the waste water from the post-tanning operations may be reduced significantly. An exhaustion of fatliquor equivalent to 90 % of the original offer can be considered achievable [56, Pearson et al. 1999].

### **Environmental performance and operational data**

No operational data submitted.

### **Cross-media effects**

No cross-media effects identified.

### **Technical considerations relevant to applicability**

The technique is applicable to both new and existing installations.

### **Economics**

A study [84, Ludvik J. 2000] indicates that the chemical costs using a high-fixation and exhaustion system are 36 % higher than in conventional systems.

### **Driving force for implementation**

The main driving forces are environmental reasons.

### **Example plants**

The technique is used by a number of tanneries in Europe.

### **Reference literature**

[84, Ludvik J. 2000] [91, Suppliers 2008].

## **4.7.5 Substitution of nitrogenous compounds in post-tanning**

### **Description**

Substitution of amino resins and ammonia used as a dye 'penetrator'.

### **Technical description**

Nitrogen compounds are used at two stages of the post-tanning operations. Amino resins (urea-formaldehyde or melamine formaldehyde resins) are used in the retanning to give the leather fullness, and ammonia may be used as a 'penetrator' for dyes.

The amino resins can be substituted by other filling agents and ammonia can be substituted as a penetrator. Shoe leather tanneries have seldom used ammonia as dye penetrator, as the alkaline pH can cause the grain to loosen. Producers of chromium-tanned upholstery leather used to use ammonia, but with the discussions of hexavalent chromium in leather and the possibility of ammonia causing the formation of traces of hexavalent chromium in leather, many tanneries have now changed to other dye-penetrating agents.

Many tanneries in Europe are producing large amounts of chromium-free leathers for the automotive industry and there is no need to use ammonia to penetrate the dye. The chromium-free leather is so anionic that the anionic dyes penetrate without the use of any other chemical.

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 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.

#### **Achieved environmental benefits**

The contributions to the nitrogen load of the waste water is 0.2 kg organic bound nitrogen per tonne raw hide from the amino resins and approximately 1 kg ammonia nitrogen (0.6 – 1.6 kg) per tonne of raw hide from the dyes, respectively. These discharges of nitrogen can be avoided if the proposed techniques are used.

#### **Environmental performance and operational data**

Several commercial formulations exist and the operational data will depend on the chosen formulation.

#### **Cross-media effects**

No cross-media effects identified.

#### **Technical considerations relevant to applicability**

The techniques are available both for new and existing installations.

#### **Driving force for implementation**

One driving force for the substitution of ammonia as a penetrating agent is to avoid the possibility that traces of hexavalent chromium may be formed in the leather. Another driver for some tanneries is the need to reduce the nitrogen levels in their waste water.

#### **Example plants**

There are a number of tanneries in Europe using these techniques.

#### **Reference literature**

[84, Ludvik J. 2000] [91, Suppliers 2008].

### **4.7.6 Use of liquid and low dust dyes**

#### **Description**

Liquid dyes and de-dusted powdered dyes are used to achieve a reduction or the elimination of suspended particulate matter in the air exhausted from dye-handling areas.

#### **Technical description**

Liquid dyes and dyes generating low levels of particulate matter were developed to prevent health impacts by dust emissions on the workforce while handling the products. Practically all powder dyes have been de-dusted for many years. Dye suppliers normally test every batch and comply with dusting specifications using standard test methods. A small amount of an anti-dusting agent, such as paraffin oil (typically <1 %) is mixed in with the dye powder shortly before packing.

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 4.2.1).

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.

Powdered dyes are now usually produced in de-dusted form.

### **Achieved environmental benefits**

The main environmental benefit of the technique is a reduction or elimination of suspended particulate matter in the air exhausted from dye-handling areas.

### **Environmental performance and operational data**

The use of liquid dyes can cause the following problems:

- 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.

### **Cross-media effects**

The use of liquid dyes will increase the energy consumption for the transport of dyes, since high amounts of water will be included in the liquid dyes (transport of water).

### **Technical considerations relevant to applicability**

The techniques can be used by both new and existing installations.

### **Economics**

The use of liquid dyes is usually more expensive than using powder dyes, due to the manufacturing costs (i.e. solubilisation, addition of surfactants, and emulsifiers, etc.)

### **Driving force for implementation**

The original driving force for the implementation of these techniques is workplace safety. The use of automatic dye dosing is facilitated by using liquid dyes.

### **Reference literature**

[91, Suppliers 2008].

## **4.7.7 Drying**

The processes used to dry leather have considerable effects on the properties of the final material. The choice of drying method is therefore always governed by the type being manufactured.

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 in 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.

Improved drying techniques are described in details under Section 4.12.3.

## 4.8 Coating

Leather coating activities which consume more than 10 tonnes per year of **solvents** must comply with laws implementing the Solvent Emissions Directive (now replaced by Chapter V of Directive 2010/75/EU). A guidance document was produced on VOC substitution and reduction to comply with those requirements [116, AEAT Okopol 2009]. The emission limits which apply to the coating of leather are shown in Table 3.4.

While non-compliance with these limits, at a plant to which Chapter V applies, would indicate that BAT are not being applied, compliance with Chapter V does not confer an exemption from BAT considerations. Much lower solvent use rates can be achieved when producing certain types of leather.

For the purposes of Chapter V of Directive 2010/75/EU, solvents which are used in a coating process are assumed to be emitted unless they have been recovered.

### 4.8.1 Improved coating techniques

Continuous research and development in recent years has led to a drastic reduction in solvent emissions. This has been achieved by the introduction of new water-based coating materials, as well as more efficient methods of application such as improved spraying techniques and roller coating.

There are fundamental differences between curtain coating, roller coating, and spraying of leather. In particular, the types of leather production and coating materials for which each one is suitable are explained in the following sections.

#### 4.8.1.1 Casting/curtain coating

##### **Description**

The leather is fed through a curtain of liquid.

##### **Technical description**

The leather is fed through a curtain of liquid, which is deposited onto the leather surface. The technique is used for the application of heavy finish layers only.

##### **Achieved environmental benefits**

Reduced amounts of waste and solvent emissions to air are the main environmental benefits.

##### **Cross-media effects**

None known.

##### **Technical considerations relevant to applicability**

The technique can be applied to both new and existing 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. This technique may be used to apply finishes which have a high organic-solvent content.

##### **Economics**

The cost of the machine is around EUR 70 000 – 80 000 at year 2000 prices.

##### **Driving force for implementation**

No information submitted.



**Example plants**

Several plants in Europe.

**Reference literature**

[56, Pearson et al. 1999].

**4.8.1.2 Roller coating****Description**

The finish is applied by rollers.

**Technical 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 use it. More specialist models allowing for hot and cold applications of oils, waxes and microfoam products are also available on the market and are used in several tanneries in Europe.

The same conveyor/drying unit as for the spraying booth can be used.

**Achieved environmental benefits**

The more efficient application of coating materials leads to less waste and less solvent emission for the coating of a given area, to the benefit of the environment. The avoidance of the mist and solid particulate emissions associated with spraying is also beneficial.

**Environmental performance and operational data**

The operational data will entirely depend on the product that is being produced. Coating wastage rates of 3 – 5 % are reported [16, Frendrup 1999] as opposed to 40 % for conventional spraying.

**Cross-media effects**

No cross-media effects identified.

**Technical considerations relevant to applicability**

This technique is not as flexible as spraying and can be applied only for the production of leathers with a coated grain, not for aniline, aniline-type or semi-aniline leathers. The technique can be applied to both new and existing plants, but involves the purchase of new equipment.

**Economics**

The cost for a reversed roller coating machine (3000 mm) equipped with a feeder and three rolls is approximately EUR 175 000 [91, Suppliers 2008].

**Driving force for implementation**

The main driver is the need to reduce the discharge of solvents to the air.

**Example plants**

In Europe, finishing operations performed with roller coating machines are common.

### Reference literature

[16, Frentrup 1999] [56, Pearson et al. 1999] [91, Suppliers 2008].

### 4.8.1.3 Improved techniques for spray coating

#### Description

Spraying techniques with higher efficiency of coating transfer.

#### Technical description

##### High-volume low-pressure (HVLP) spray guns

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 technique 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 guns

The coating material itself is pressurised. It is then atomised at a spray nozzle without the use of air. Airless spraying is more suited for high application rates.

##### Computer-aided spraying

Computer aided spraying means that automated systems sense the area, either by a mechanical feeler, electric eye or ultrasonic system and control the opening of the guns so that they only spray when the leather is passing directly beneath them. The technique is widely available in more or less sophisticated versions. Care must be taken that the detection equipment is properly adjusted.

##### Achieved environmental benefits

HVLP and airless spraying improve spraying efficiency up to 75 %, compared to spraying efficiency as low as 30 % for conventional spraying operations [56, Pearson et al. 1999].

Computer-aided spraying can prevent 75 % of the finish being lost as overspray. The emissions of spray mists are reduced, and because coating efficiency is improved, solvent emissions are reduced too.

##### Environmental performance and operational data

HVLP or airless spraying may not be suitable for all coating materials. This situation is likely to change as low solvent coatings are improved.

##### Cross-media effects

No information submitted.

##### Technical considerations relevant to applicability

These techniques can be applied to both new and existing plants. Existing equipment can be retrofitted, but the costs and effort involved will depend on the type of systems already in place.

##### Economics

The cost of a new spraying machine was EUR 200 000 – 500 000 at year 2000 prices.

##### Driving force for implementation

The driving forces for the implementation of the techniques are a reduced wastage of coating materials and compliance with SED (now Chapter V) and other environmental requirements.

##### Example plants

Several plants in Europe have installed more efficient spraying machines.

**Reference literature**

[56, Pearson et al. 1999] [37, Italy 1998] [17, UNEP 1991] [16, Frendrup 1999], [3, Andres 1995].

**4.8.2 Water-based finishing****Description**

Use of finishing products which are dispersed in water rather than in solvent.

**Technical description**

In the finishing process, water-based systems are increasingly favoured because of environmental concerns about organic solvents and in order to comply with regulations [56, Pearson et al. 1999], [16, Frendrup 1999]. For applying the coating layers, different techniques can be used (see Section 4.8.1). Organic solvent-based processes in closed spray cabinets and closed drying systems, which offer an acceptable environmental performance, require cost-intensive abatement techniques (see Section 4.10).

In order to achieve equal characteristics with low organic solvent and water-based systems, cross-linking agents for the finishing polymers often have to be used. The toxicity of these agents is problematic, but commercial products offer the agents in a less toxic and less volatile form. Nevertheless, appropriate safety precautions are required when handling and applying these agents.

Organic solvents either are 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 reuse of the organic solvent.

The minimum requirement for organic solvent-based coatings is the recording of solvent consumption, to include not only the solvents bought as solvents, but also the solvents contained in the finishing chemicals. This is the only acceptable way to calculate the overall emissions of VOC, 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 [3, Andres 1995].

**Achieved environmental benefits**

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.

### **Environmental performance and operational data**

The suitability of water-based coatings is still dependent on the final product that is produced. The coatings are being improved, and the range of uses is being expanded.

### **Cross-media effects**

A cross-media effect is the higher energy consumption for drying water-based top-coats. There may also be an increase in the organic content of waste water from finishing.

### **Technical considerations relevant to applicability**

Base coats are generally water-based. If very high standards of top-coat resistance to wet-rubbing, wet-flexing and perspiration are required, then solvent-based systems cannot always be substituted by aqueous-based systems [16, Frendrup 1999].

### **Economics**

In general, solvent-based and water-based systems have similar costs.

### **Driving force for implementation**

The adoption of this technique was driven by a need to reduce of solvent emissions to the atmosphere, in compliance with the laws implementing Chapter V of the Industrial Emissions Directive (the former Solvent Emissions Directive).

### **Example plants**

Most tanneries in Europe have implemented water-based solvent finishing systems. Examples are Elmo Sweden AB (Sweden), Vogl (Austria), Rino Mastrotto Group (Italy), Gruppo Dani (Italy).

### **Reference literature**

[16, Frendrup 1999] [84, Ludvik J. 2000].

## 4.9 Waste water treatment

Waste water treatment consists of a selection of the following processes, applied either on site and/or off site:

- mechanical treatment
- physico-chemical treatment
- biological treatment
- biological nitrogen elimination.

The processes can be assembled in different combinations and implemented in two or three stages. Sedimentation is usually included in more than one stage.

Techniques of particular importance in the treatment of tannery effluents are as noted below:

- It is common to oxidise effluents containing sulphide before mixing with other effluents (in particular acidic effluents), because at a pH lower than 9.5, the formation of hydrogen sulphide gas can occur, (see Section 4.5.3.3). If sulphide-bearing effluents are to be mixed before full oxidation this should be done in an enclosed tank, with air extraction through a scrubber.
- Where chromium(III) precipitation is carried out it is common practice to segregate the effluent streams containing chromium from those that do not. The precipitated chromium can be recovered for recycling. Where segregation of flows is not possible, thorough mixing of effluents containing chromium 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, and holding capacity may need to be increased.
- The degree of on-site effluent treatment needed depends on the capacity available at an urban waste water or common effluent treatment plant. In some cases all effluent treatment may be conducted off site. Neither the volume nor the concentration of the effluent must exceed the treatment capacity of the off-site facilities.

In order to protect the receiving water, the conditions of the local environment may require achieving discharge concentrations below those associated with BAT.

Data from effluent treatment plants operated by tanneries are shown in Table 4.14 and an overview of the efficiency of the combination of waste water treatment measures is given in Table 4.15

Table 4.14: Reductions of selected parameters by effluent treatment plants operated by tanneries

Parameter			COD		BOD <sub>5</sub>		Total nitrogen		S <sup>2-</sup>		Cr <sup>3+</sup>		TSS		Water flow
			mg/l	%	mg/l	%	mg/l	%	mg/l	%	mg/l	%	mg/l	%	m <sup>3</sup> /d
Single tannery 1 (IT)	Influent	Reduction	9800	94.2	4133	99.7	320 <sup>(1)</sup>	92.8 <sup>(1)</sup>			6.6	96.8			1250
	Effluent		567		13		23 <sup>(1)</sup>				0.21				
Single tannery 4 (IT)	Influent	Reduction	5425	95.4			425 <sup>(1)</sup>	71.8 <sup>(1)</sup>		184					700
	Effluent		251		120 <sup>(1)</sup>										
Single tannery (DE) <sup>(2)</sup>	Influent	Reduction	~ 10 000	~ 96	~ 4000 – 6000 <sup>(3)</sup>	< 99.6	650 – 780	70 – 90	500 – 1000 <sup>(3)</sup> <sup>(5)</sup>	< 99.9	< 300 <sup>(6)</sup>	< 99.9 <sup>(6)</sup>			<sup>(7)</sup>
	Effluent		< 400		< 25 <sup>(3)</sup>		< 20 – 80 <sup>(4)</sup>				< 1 <sup>(3)</sup>				
Single tannery (DE) <sup>(8)</sup>	Influent	Reduction	3700 – 9970	~ 99			280 – 500	47 – 70			7 – 28 <sup>(10)</sup>	96.4 – 97.5 <sup>(10)</sup>			<sup>(11)</sup>
	Effluent		31 – 119		< 3 <sup>(9)</sup>		84 – 266				< 0.04 <sup>(9)</sup>				
Two tanneries (AT)	Influent	Reduction	5000 – 6000	94.5 – 99.1	2500 – 3000	99 – 99.8	250 – 500	60 – 85							
	Effluent		50 – 275		5 – 25		75 – 150								
Elmo tannery (SE)	Influent	Reduction	9000	95 – 96	4300	99.8 – 99.9	630	96.3 – 97.5			7	99 – 99.5			600
	Effluent		357 – 443		5.8 – 7.7		16 – 23				0.037 – 0.072				

<sup>(1)</sup> Data for total Kjeldahl nitrogen.

<sup>(2)</sup> Tannery carrying out chromium tanning processing bovine hides from raw hide to finished leather and raw hides to wet blue. Waste water treatment: two-stage biological treatment of total effluent after chromium recycling in the segregated effluent from the tanning process. (1st stage: biological treatment of chromium containing effluent, 2nd stage: biological treatment of effluent from the 1st stage together with the chromium-free alkaline effluent). The effluent values are met at every measurement at normal operating conditions unless otherwise indicated. Type of sampling: homogenised qualified random sample. Frequency of measurement: twice per week unless otherwise indicated.

<sup>(3)</sup> Frequency of measurement: once per week.

<sup>(4)</sup> 20 mg/l is achieved under optimised operating conditions. When the temperature drops below 12 °C the nitrifying bacteria are inhibited, therefore nitrification-denitrification activity cease almost completely.

<sup>(5)</sup> Concentration in the segregated alkaline sulphide-containing stream.

<sup>(6)</sup> Concentration of total chromium in the segregated chromium-containing stream (effluent from chromium recycling plant (1 – 3 mg/l) mixed with effluents from pretanning/finishing).

<sup>(7)</sup> Specific water consumption: 12 – 16 m<sup>3</sup>/t raw hide.

<sup>(8)</sup> Tannery carrying out chromium tanning processing bovine hides from raw hide to finished leather. Waste water treatment: biological treatment of total effluent, including chromium-containing effluents; denitrification not implemented on full scale; direct discharge. Values are minimum and maximum of monthly mean. Type of sampling: qualified random sample. Frequency of measurement of effluent values: at least 2 – 3 times per week unless otherwise indicated.

<sup>(9)</sup> These values are met at every measurement at normal operating conditions.

<sup>(10)</sup> Data for total chromium.

<sup>(11)</sup> Water consumption: 20 – 25 m<sup>3</sup>/t raw hides.

<sup>(12)</sup> Monthly averages.

Source: [ 90, Tanneries 2008 ] [ 156, Austria 2011 ] [ 157, Rydin 2011 ] [ 160, Germany 2012 ].

Table 4.15: Typical performance for tannery waste water treatment plants

Parameters <sup>(1)</sup>	COD		BOD <sub>5</sub>		Suspended Solids		Chromium		Sulphide		N (TKN)		Conductivity	Colour	Sludge production
	%	mg/l	%	mg/l	%	mg/l	%	mg/l	%	mg/l	%	mg/l	mS	% Pt-Co unit	kg DS/tonne raw hide
<b>Pretreatment</b>															
Grease removal (dissolved air flotation)	20 – 40														
Sulphide oxidation (liming and rinsing liquors)	10									10					
Chromium precipitation								2 – 10							
<b>Primary treatment</b>															
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
<b>Biological treatment</b>															
Primary or chemical + extended aeration	85 – 95	200 – 400	90 – 97	20 – 60	90 – 98	20 – 50		< 1		< 1	50	150			70 – 150 <sup>(2)</sup>
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 <sup>(2)</sup>
Primary or chemical + aerated facultative lagoons	80 – 90	300 – 500	85 – 95	60 – 100	85 – 90	80 – 120		< 1		< 1	50	80			100 – 140
Anaerobic treatment (lagoon or UASB) <sup>(3)</sup>	65 – 75	500 – 700	60 – 70	150 – 200	50 – 80	100 – 200		< 2	0		20 – 30				60 – 100
Membrane biological reactor (MBR)	80 – 95	160 – 500	97 – 100	5 – 50	100	0		< 0.5	99	< 0.5					<sup>(4)</sup>
MBR + reverse osmosis (RO)													< 0.7 <sup>(5)</sup>		
Constructed wetlands (after primary treatment)	70 – 80	300 – 400	85 – 95	60 – 100										85 – 90	

<sup>(1)</sup> The above data represents typical values for tannery waste water treatment efficiencies for conventional process liquors for the production of finished leather from raw material. Salinity is not removed through primary and biological treatment. TDS can be increased by chemical treatment.

<sup>(2)</sup> Without chemical treatment.

<sup>(3)</sup> Mixed with 75 % domestic sewage.

<sup>(4)</sup> Approximately 7 % of the metabolised COD is incorporated into surplus sludge production, compared to 30 – 50 % in a conventional activated sludge system.

<sup>(5)</sup> At 50 % permeate recovery rate.

Source:[100. IUE 2006].

### 4.9.1 Mechanical treatment

#### Description

Screening of gross solids, skimming of fats, oils, and greases and removal of solids by sedimentation.

#### Technical description

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. Mechanical treatment may also include **skimming** of fats, greases, and oils and gravity settling (**sedimentation**).

#### Achieved environmental benefits

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.

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.

#### Cross-media effects

A disposal route for the separated solid waste has to be found.

#### Technical considerations relevant to applicability

Mechanical treatment is applicable to both new and existing installations.

#### Driving force for implementation

The main driving force is to protect other treatment facilities against damage, clogging or fouling by solids.

#### Example plants

In principle, all waste water treatment plants in Europe use mechanical treatment at one or more stages of treatment.

#### Reference literature

[16, Frendrup 1999] [56, Pearson et al. 1999].

### 4.9.2 Physico-chemical treatment

#### Description

Sulphide oxidation, chromium precipitation, COD, and suspended solids removal by coagulation and flocculation.

#### Technical description

Physico-chemical treatment involves sulphide oxidation from beamhouse effluents, chromium precipitation, flow equalisation, physico-chemical treatment for COD removal and balancing. A typical scheme for physico-chemical treatment is given in Figure 4.3. Where chromium recovery is used, it is usual to treat chromium-bearing effluents separately from beamhouse effluents.



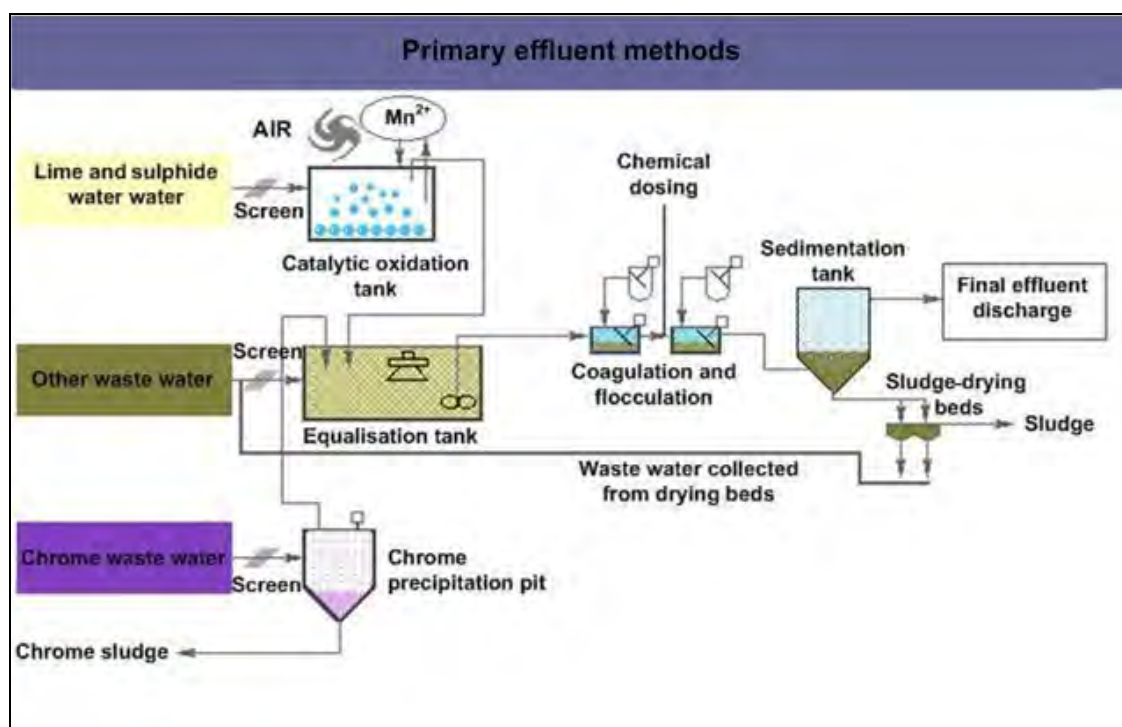


Figure 4.3: Typical scheme for physico-chemical treatment

### Sulphide removal

The prevention of gaseous hydrogen sulphide releases is described in Section 4.5.3.3. Sulphide removal from effluent can be achieved by catalytic oxidation (aeration in the presence of manganese salts) to thiosulphates and, in smaller quantities, into sulphates. 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 the presence of manganese salts or iron (II) salts to avoid odour production.

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. The most common system for tanneries is the use of catalytic oxidation using manganese sulphate as a catalyst.

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. 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 using auxiliary agents, or by 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 to sulphides (e.g. during storage in an homogenisation tank without sufficient mixing). For this reason, the treatment is not deemed suitable for lagoons. If catalytic oxidation of sulphides is carried out, there is a chance that compounds containing amines can be stripped from the effluent, resulting in odour

emissions. Biological oxidation of sulphides in effluent is also possible during biological treatment of the effluent.

If the effluent containing sulphide is mixed with effluents from vegetable tanning, sulphide oxidation is possible just using good aeration, alternatively, aluminium salts can be used because iron salts form black compounds with the vegetable tannins.

### **Precipitation of chromium**

Chromium(III) precipitation is a relatively simple technique and is more efficient if it is carried out in separated effluents after screening. The precipitation of chromium is achieved by increasing the pH to above 8 using an alkali such as calcium hydroxide, magnesium oxide, sodium carbonate, sodium hydroxide, and sodium aluminate. Chromium and other metals are precipitated as insoluble hydroxides. The pH value required for the precipitation depends upon the type of waste water containing chromium to be treated. Where chromium(III) precipitation is used it is common practice to segregate the effluent streams which contain chromium from those which do not and carry out chromium precipitation on segregated flows before effluent mixing. Where segregation of flows is not possible or where chromium recovery is not used, mixing in contained conditions can be used so that some or all of the alkalinity used to precipitate the chromium is provided by lime in the beamhouse effluent. Chromium recovery is discussed in Section 4.6.3.4.

The precipitation can be inhibited or reduced to an unsatisfactory level by the influence of residual organic matter, masking agents, other complexing agents, fats or dyestuffs in the waste water.

Suspended solids (leather fibres, etc.) must also be considered, as chromium 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 may be carried out after individual effluent flows have been pretreated, such as sulphide oxidation and chromium 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 be 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.

### **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 applied. If no chromium precipitation has been carried out at an earlier stage, chromium hydroxide will be formed at this stage and removed in the primary sludge. Ferrous sulphate also removes sulphides, but the disadvantages 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.

A 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 formed. These bubbles rise and 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.

#### **Achieved environmental benefits**

Achieved environmental benefits of the techniques are:

- a reduction of the concentration of substances in the waste water, particularly chromium and sulphides, and in chemical oxygen demand;
- preparation of the waste water for biological treatment.

#### **Environmental performance and operational data**

Operational data are extremely variable. Some environmental performance data are given in Table 4.14 and

Concentrations of sodium sulphide in separated effluents may be 0.6 to 8 g/l. In general, a well performing catalytic oxidation of a float containing sulphide will result in a sulphide concentration between 2 and 10 mg/l for separated effluents. Values as low as 0.5 mg/l may be achieved in the mixed effluent.

The German reference tannery, using manganese sulphate as a catalyst 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 [72, Germany 2000].

The catalytic oxidation of sulphide takes place in an aerated tank with the addition of manganese sulphate. The addition of manganese sulphate is normally around 100 – 200 g/m<sup>3</sup> of water. The residence time for the process is around one day.

#### **Cross-media effects**

Sulphide oxidation results in the formation of sulphate. The release of sulphate into the sewers may need to be limited because of the damage sulphates can cause to concrete sewers. The use of iron salts may turn the effluent black and increase the volume of primary sludge generated. Under anaerobic conditions, sulphates may revert to sulphides.

Sludge is produced, which is a waste for disposal. Additional process chemicals are consumed and water and energy use is increased.

#### **Technical considerations relevant to applicability**

All plants at which partial or complete effluent treatment are used can apply the techniques.

#### **Economics**

Capital and running costs are significant.

### **Driving force for implementation**

Reduction of the concentration of substances in the waste water to meet permit conditions and to reduce the load on the biological stages of treatment

### **Example plants**

All tannery effluent treatment uses some physico-chemical treatment.

### **Reference literature**

[16, Frendrup 1999] [140, EC 2003].

## **4.9.3 Biological treatment**

### **Description**

Aerobic biological waste water treatment using bio-aeration.

### **Technical description**

Effluent from tanneries after mechanical and (usually) physico-chemical treatment, is generally easily biodegradable in biological treatment plants. Tannery effluent may be treated with or without the addition of sewage from other sources. Small amounts of phosphate may need to be added to maintain the biological activity. Standard aerobic biological treatment plants are normally 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.

Sulphate-reducing bacteria flourish in anaerobic conditions. Precautions to prevent the release of hydrogen sulphide are necessary, either by exhaust gas treatment or by the removal of sulphur compounds prior to the anaerobic treatment.

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 combined with physico-chemical treatment can achieve a COD removal of up to 95 %. Biological treatment is now used without physico-chemical treatments in some effluent treatment plants, as a measure to reduce the total sludge output from the process.

Most biological treatment plants use the *activated sludge* (bio-aeration) method. This uses the metabolic activity of microorganisms 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.

Oxidation takes place in a continuously aerated tank. A retention time of 6 – 12 hours usually suffices. The energy consumption of a conventional activated sludge plant is about 1.08 – 1.8 MJ per kg of BOD<sub>5</sub> 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 3.6 MJ per kg of BOD<sub>5</sub> eliminated.

### **Achieved environmental benefits**

The technique can achieve a reduction of oxygen demand of the effluent, to a level where it can either be safely discharged to a water body or meet the specification of an organisation providing off-site treatment.

### **Environmental performance and operational data**

Operational data are extremely variable. Some environmental performance data are given in Table 4.14 and Table 4.15.

In some cases, the achieved environmental performance may be designed to meet permit conditions which have been specified in order to achieve compliance with environmental quality standards, and may go beyond what is BAT.

#### **Cross-media effects**

The main environmental issues of aerobic biological treatment arise from the introduction of oxygen into the system and its effects. Oxygen can be introduced by aeration which calls for a high energy input. Stripping of volatile substances from the waste water releases odours. Odorous air may need to be exhausted through a treatment system to clean it. Purified oxygen can also be used but brings its own costs. Containment of emissions to air from an oxidation ditch is impractical. Excess biological sludge forms a waste for disposal.

#### **Technical considerations relevant to applicability**

Biological waste water treatment is necessary before discharging waste water from tanneries to any natural water body. In some cases, waste water from tanneries is discharged to urban waste water treatment plants even after biological treatment.

#### **Economics**

Capital and operating costs are highly dependent on hydraulic and contaminant load. When effluent is sent for off-site treatment, the charges levied may vary with the concentration.

#### **Driving force for implementation**

Meeting discharge limits is usually the reason for the implementation of biological treatment.

#### **Example plants**

Elmo Sweden AB (Sweden), Bader (Germany), Hulshof (Netherlands), Acque del Chiampo, Arzignano (Italy), Cuoiodepur (Italy), Ecologica Naviglio (Italy).

#### **Reference literature**

[16, Frendrup 1999] [91, Suppliers 2008] [104, Rydin et al. 2006].

### **4.9.3.1 Biological nitrogen elimination**

#### **Description**

Nitrification of ammoniacal nitrogen, compounds to nitrates, followed by the reduction of nitrates to gaseous nitrogen.

#### **Technical description**

The ammonium compounds in the waste water originate mainly from the use of chemicals containing ammonium compounds in delimiting and dyeing and from proteins released in the beamhouse.

Nitrogen removal is a biological process performed in two main steps: nitrification and denitrification. A preliminary stage of the process is ammonification in which nitrogen in proteins is converted to ammoniacal nitrogen, and this technically precedes nitrification.

In the nitrification stage, the ammoniacal nitrogen is oxidised into nitrate. This process takes place under aerobic conditions, i.e. in the presence of free oxygen.

In the denitrification stage, the nitrate is biologically reduced to gaseous nitrogen, most of which escapes into the surrounding atmosphere. A further part of the nitrogen is bound in the biomass. Denitrification takes place under anoxic conditions, which means that free dissolved oxygen is not present in anoxic zones of the flocs.

Specially prepared cultures of *Candidatus Brocadia anammoxidans* or related species are used in some plants for biological nitrogen removal.

Denitrification must be managed in such a way as to avoid the re-formation of hydrogen sulphide. To prevent H<sub>2</sub>S emissions, a German tannery (see Example Plants below) combines the denitrification with the quasi-simultaneous biological oxidation of sulphides to sulphates.

#### Achieved environmental benefits

The reductions of the following environmental pressures are achieved:

- emissions of nitrogen compounds to aquatic environment, by closing the natural nitrogen circle;
- leakages of sulphur compounds to air and related odours emissions;
- consumption of chemicals.

#### Environmental performance and operational data

Illustrative figures for yearly values from a Swedish tannery are given in Table 4.16, showing that it is possible to achieve a reduction of the nitrogen discharge of more than 85 % from tannery waste water with an outlet concentration of around 16 – 23 mg/l of total nitrogen. For ammoniacal nitrogen, the reported monthly values for the period 2009 – 2011 are in general below 10 mg/l, with some exceptions during the summer months. The most recent data for the year 2011 show monthly values always below 10 mg/l.

**Table 4.16: Total nitrogen removal and ammoniacal nitrogen concentration in aqueous effluent**

Year	Total nitrogen (as N)			Ammoniacal nitrogen (as NH <sub>4</sub> -N)
	Incoming (mg/l)	Outgoing (mg/l)	Reduction (%)	Outgoing (mg/l)
2007	320	23	92.8	
2009	630	23	96.3	6.9
2010	630	16	97.5	5.2
2011				2.7
NB: Values are expressed as yearly averages, calculated from monthly values (flow proportional composite sample over the month).				
Source: [ 90, Tanneries 2008 ] [ 157, Rydin 2011 ] [ 158, Rydin 2012 ].				

In the Swedish example plant, the combination of aerobic and anoxic conditions (which is necessary for nitrogen removal) is created by switching off the aeration when denitrification is taking place.

The German tannery, starting from a concentration of 650 – 780 mg/l, in the last 12 years has achieved an average reduction of the total nitrogen of 90 %, with an operational range of 70 – 95 % (see Figure 4.4).

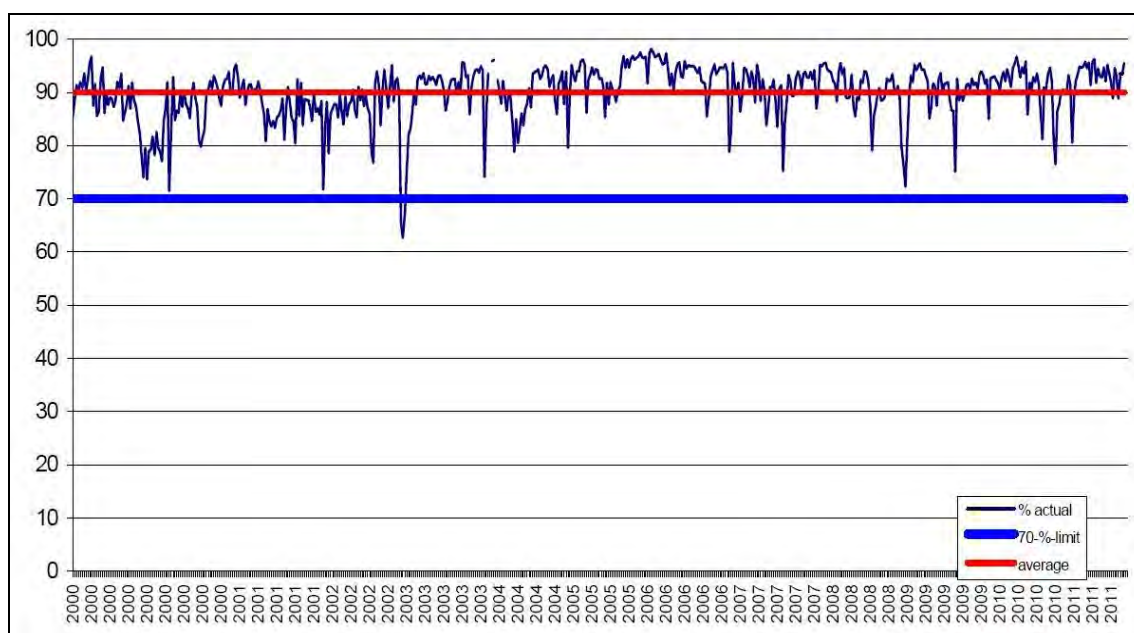


Figure 4.4: 12-year data series for nitrogen elimination rate in a German tannery

An ammoniacal nitrogen concentration of below 10 mg/l has been achieved most of the time, although during cold wintertime or after production stoppages, the results cannot be achieved. The combined biological oxidation of sulphides operated in this plant reduces the amount of alternative physico-chemical treatment, thereby reducing the use of chemicals and their associated cross-media effects described for sulphide removal under Section 4.9.2 [155, Bader 2011].

Nitrification/denitrification is vulnerable to toxic or inhibiting substances. In particular, fluctuations in the presence of significant chloride concentrations may be a problem for the technique. Other chemical nitrification inhibitors and higher concentrations of bactericides or fungicides can also inhibit the nitrification. A high degree of control and appropriate monitoring systems are necessary for a stable process.

Nitrification requires a long retention time, a low food-to-microorganism ratio, a high cell residence time (sludge age), and adequate buffering.

The optimal activity of the nitrifying bacteria employed in the first stage of the process occurs when the temperature within the treatment tank is above 20 °C. Activity ceases almost completely at temperatures below 12 °C. Nitrification and denitrification are therefore no longer possible below 12 °C. After warm-up periods, nitrification takes up to 20 days to reach stable process conditions.

#### Cross-media effects

The release of odours may occur unless specific precautions are taken to prevent it.

The use of electrical energy in the effluent treatment plant is increased by the addition of the nitrification step; however, the implementation of available energy-efficient techniques helps to control the increase. In addition, the denitrification step will decrease the energy consumption for aeration. In the German tannery, the specific overall energy consumption per unit of COD removed is maintained below 0.7 kWh/kg (or 2.5 MJ/kg), for all stages of the effluent treatment, including the nitrogen elimination. This is achieved by the use of inverter-driven electric motors and the application of regular, professionally skilled maintenance and operation.

### Technical considerations relevant to applicability

The technique can be introduced in connection with the building of new installations (waste water treatment plants). The technique may be difficult to implement into existing installations due to space requirements.

### Economics

The investment cost will be higher for a waste water treatment plant using the technique due to the larger sizes of treatment tanks needed in the waste water treatment plant.

For the Swedish example plant, the investment cost was around EUR 4.3 million (including EUR 914 000 received from the EU LIFE Financial Instrument) and the plant was dimensioned for a waste water flow of around 1250 m<sup>3</sup>/day. The running costs mainly consist of costs for personnel, chemicals, energy, maintenance, and sludge treatment. The costs for some parameters (personnel and energy) differ between EU countries and it may therefore be difficult to estimate the running cost at the European level. The total treatment cost for the dimensioned flow, including the investment cost (depreciation over 20 years, no interest rate) but excluding the cost for sludge handling, is around EUR 1.5 – 1.6 per m<sup>3</sup>, which is a competitive price for waste water treatment.

The German example plant reported investment costs at roughly EUR 220000 for its denitrification stage.

### Driving force for implementation

The driving force is the need to reduce the discharge of nitrogen compounds from tanneries to comply with permit conditions. This treatment is being gradually introduced in countries with strict nitrogen discharge limits.

### Example plants

- Elmo Sweden AB, Sweden
- Bader Leather, Germany.

### Reference literature

[104, Rydin and Svenson 2006] [ 155, Bader 2011 ] [ 158, Rydin 2012 ].

## 4.9.4 Post-purification treatments and sludge handling

### Description

Removal of suspended solids by sedimentation, sludge dewatering, secondary flotation.

### Technical description

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 (urban or off-site) waste water 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 to prevent too much turbulence and clogging. The segregation of solids might not be complete, resulting in the carryover 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 thicken further sludges.

**Achieved environmental benefits**

The main benefits for the environment from the use of the techniques are a reduction in suspended solids in the waste water and a reduced water content in the sludge (which increases the range of possibilities for its disposal).

**Cross-media effects**

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.

**Technical considerations relevant to applicability**

The technique can be applied in all plants producing sludges.

### **Economics**

The energy consumption is an important factor. Reduced transport costs for sludge disposal are an economic benefit.

### **Driving force for implementation**

The main driving forces for the use of the techniques are the production of a clearer effluent; a reduced water content in the sludge, and an increased range of possibilities for its disposal.

### **Example plants**

Many plants in Europe which carry out effluent treatment.

### **Reference literature**

[16, Frendrup 1999].

## 4.10 Air emissions abatement

### 4.10.1 Odour

#### Description

Techniques to control the emissions of odour to the air.

#### Technical description

Odours can arise from the decomposition of incorrectly cured or stored hides, accumulated wastes, beamhouse processes, and waste water treatment plants that are poorly controlled and maintained.

Odours are not necessarily harmful or toxic, but constitute a nuisance to affected neighbours, which in turn gives rise to complaints. Apart from a natural, distinct smell of raw hides, bacteria degrading the organic matter can cause 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 correct control of these operations. Wastes should be removed methodically before their decomposition causes problems.

Some toxic substances are also odorous, e.g. hydrogen sulphide, thiols, ammonia, amines, aldehydes, ketones, alcohols or organic acids. These releases may require abatement.

The releases from various process steps can be reduced by process-integrated measures discussed in Sections 4.4 and 4.5.3.3.

Treatment systems for exhaust air can be designed to remove toxic substances and odours, see Section 4.10.3.

### 4.10.2 Organic solvents

#### Description

Techniques to control the emission of organic solvents to the air.

#### Technical description

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 to optimise the application technique (see Sections 4.8.2 and 4.8.1).

Abatement techniques are important for the protection of the environment, but they shift the pollution 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 the recovery and reuse of organic solvents might only be feasible if a limited number of organic solvents are used.

There are various abatement techniques available to reduce VOC emissions:

- wet scrubbing
- adsorption
- bio-filter
- incineration.

Wet scrubbing is a standard technique for waste-gas treatment, but is most effective against dust and aerosols. Water-soluble solvents dissolve in the scrubbing water. The increased use of water-dispersed finishing materials, mainly based on glycols or alcohols, has meant that wet

scrubbing is now a more effective technique. Approximately 50 % of the solvent releases can now be removed by wet scrubbing [ 151, Rydin 2011 ].

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.

Bio-filters can be used. Besides removing odours they can be used to oxidise soluble 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 concentrations are high.

Incineration (catalytic or thermal) is a reliable, but expensive, method of abating organic solvent emissions and odours [8, Higham 1994].

### **Achieved environmental benefits**

Reduction of VOC emissions to the environment.

### **Cross-media effects**

Production of liquid or solid wastes, or incinerator exhaust gases.

### **Economics**

Incineration is unlikely to be economically viable on the small scale, and dealing with the low concentrations emitted from leather coating.

### **Driving force for implementation**

Legal restrictions now apply to some solvent emissions.

### **Reference literature**

[8, Higham 1994] [ 151, Rydin 2011 ] [ 153, Gerrard 1999 ] [ 162, DE 2010 ].

## **4.10.3 Ammonia, and hydrogen sulphide**

### **Description**

Abatement of ammonia and hydrogen sulphide by scrubbing and/or biofiltration.

### **Technical description**

After all primary measures for ammonia and hydrogen sulphide reduction have been used these substances are usually removed by extraction ventilation systems. Unless the attenuation available between the release point and receptors can reduce the concentration to a level below that at which odour nuisance is likely, exhaust air treatment will be required.

Lower concentrations of these substances can be abated by biofilters, but, at higher concentrations, they poison the microorganisms which carry out the treatment. At these concentrations, a wet scrubber may precede or replace the biofilter. Wet scrubbing of ammonia uses an acidic solution; and that of hydrogen sulphide uses an alkaline solution, such as hydrogen peroxide or a mixture of sodium hydroxide and sodium hypochlorite.

### **Achieved environmental benefits**

Reduction of odour nuisance.

**Cross-media effects**

Cross-media effects include:

- an increase in energy use by extraction systems
- the production of scrubber effluent.

**Driving force for implementation**

Odour abatement.

**Reference literature**

[ 153, Gerrard 1999 ].

**4.10.4 Dusts and other particulates****Description**

Techniques to control the emission of dusts and other particulate matter to the air.

**Technical description**

Airborne particulate matter can arise not only from mechanical operations such as milling, buffing and staking but also during handling of powdery process chemicals. Bating agents might use sawdust as a carrier. The parameters for assessing emissions of particulates are the concentration, the chemical content and the particle size.

Extraction of particle-laden air is undertaken for reasons of workplace safety. Filtration of the extracted air is necessary to protect the environment. With very efficient filtration, the air may be returned to the workplace.

For the most effective control of dust and to prevent fugitive emissions the considerations given below apply.

- Dust should be controlled at source, e.g. one tannery uses soluble packaging for dusty process chemicals.
- Operations and machines producing dust should be grouped in the same area to facilitate dust collection.
- Dust collection systems are designed and built for the material and the situation. 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 the desired suction pressure at the machine hood and smooth airflow. Due allowance should be made for the pressure drops of collection equipment.

Particulate matter collection techniques are presented in Table 4.17.

**Table 4.17: Techniques for particulate matter collection**

<b>Cyclones</b>	Cyclones allow highly efficient collection of the larger particles and have relatively low capital and running costs. They can also be used in combination with bag filters and wet scrubbers.
<b>Scrubbers</b>	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 soluble organic solvents and/or odours have to be removed at the same time.
<b>Bag filters</b>	Bag filters can provide an excellent solution, the choice of type and the area of filter fabric is critical to the efficiency. Bag filters must have automatic cleaning devices (e.g. reverse air jets) to remove the caked dust from the filter fabric. Moisture has to be avoided in order not to solidify the material on the filter matrix.

### Achieved environmental benefits

The reduction of particulate matter emissions to the air.

### Environmental performance and operational data

Dust emission levels of tanneries using wet scrubbers are shown in Table 4.26.

**Table 4.18:** Emission of particulate matter from finishing operations at tanneries using wet scrubbers

Tannery	Particulate matter (mg/Nm <sup>3</sup> )
1	1 – 6
2	4 – 12
3	3
4	0.7
5	0.4
6	1.6

### Cross-media effects

Collected material is a waste for disposal. The rate of energy use is increased.

### Technical considerations relevant to applicability

The technique is applicable to plants carrying out mechanical finishing.

### Economics

The investment cost for a properly designed system must be considered, as must the running costs related to the increased rate of energy use.

### Driving force for implementation

The driving force for the use of extraction is workplace safety. The driving force for particle arrestment is to prevent emissions to air.

### Example plants

Most plants carrying out mechanical finishing.

### References

[90, Tanneries 2008] [3, Andres 1995] [140, EC 2003].

## 4.11 Waste minimisation and management

Process-integrated techniques to reduce waste production inside installations are essential for an optimised waste treatment system. Waste treatment is still necessary for materials which cannot be reused.

Various solid or liquid waste fractions have to be considered. A large amount of waste consists of organic materials 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. Sometimes plants can be 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.

Since the implementation of the EU Directive on the landfill of waste (1999/31/EC), the landfill of untreated organic waste has become more difficult and in some Member States, effectively banned. One of the treatment methods for organic wastes which has become popular as a result is composting. Some tannery wastes are unsuitable for composting or require specific pretreatment.

### 4.11.1 Organic waste fractions and by-products

Organic materials are separated from the main product stream at various process stages. Some of these materials are by-products for which there are established uses, while others are wastes for which a disposal route must be found. This distinction is not a simple matter because users of particular by-products may not be available within an economic transport distance of a given tannery. Furthermore, the closure of secondary leather producers may preclude the processing of some by-products.

Some tannery by-products can be processed for human consumption in which case, food hygiene rules apply to their handling and storage (EU Regulation 853/2004).

Collagen can be obtained from, e.g. limed trimmings and splits. Collagen has various uses as meat and bakery product additives, in the manufacture of sausage casings, pharmaceuticals, cosmetics, and as additives to rubber products. Food grade gelatine can also be produced.

Materials or wastes separated before liming must be handled so as not to endanger animal health (EU Regulation 1069/2009). Rendering (in a plant licensed under those regulations) is often the only disposal route for such materials, but approval/licensing for the generation of biogas from raw fleshings may be available where suitable precautions are taken (see Section 4.12.4).

Waste and by-product streams not intended for food use and not needing treatment in a licensed plant may be subjected to rendering or other treatment:

- Technical gelatine and glue can be produced from untanned materials.
- Tallow recovery from limed trimmings, fleshings, and splits can be performed in rendering plants or on site. Limed trimmings, fleshings and splits may need pretreatment with acids before conversion. In some cases, tallow can be separated and recovered after a thermal pretreatment. Tallow may be used as a substitute fuel (see Section 4.12.5).
- Recovery of protein (protein hydrolysate), e.g. from splits, for conversion into fertiliser.
- Tanned wastes can be used in leather fibreboard production.

Further treatment options for organic waste and sludges from waste water treatment dependent on the composition are composting, recycling in agriculture, anaerobic digestion, and thermal treatment. Treatment to reduce the water content may be applied. Landfilling of tannery wastes is prohibited or severely restricted in some Member States.

Information on the use and disposal routes for specific types of by-products and wastes is summarised in Subsections 4.11.1.1, 4.11.1.2, 4.11.1.3, 4.11.1.4, 4.11.1.5, 4.11.1.6, and 4.11.1.7.

#### **4.11.1.1 Hair and wool use/disposal**

##### **Description**

Options for the use or disposal of hair and wool.

##### **Technical description**

Methods of hair saving, i.e. preventing the hair from being released via the waste water stream, are discussed in 'Hair-save techniques' (Section 4.5.3.1). If there are no options for reuse, the hair has to be disposed of. In some cases, the hair is not separated and is sent for disposal together with the waste water treatment sludges.

The hair residues from the unhairing step using hair-saving techniques 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 reuse of hair are summarised in Table 4.19. Hair can be used as a fertiliser because of the nitrogen content. Hair may also be landfilled after composting.

**Table 4.19: Options for dealing with hair**

	<b>Hair options</b>
<b>Uses as a by-product</b>	Filling material
<b>Reuse after preparation</b>	Protein hydrolysate
<b>Recycling as</b>	Fertiliser
<b>Other recovery</b>	Generation of biogas by anaerobic digestion

Sheep wool can be used by the textile industry, e.g. in carpet manufacture. Wool can also be composted together with other wastes (although the temperature of spontaneous ignition has to be taken into account).

##### **Achieved environmental benefits**

Some reductions of the environmental impact of disposal are achieved when hair or wool is used.

##### **Cross-media effects**

Sulphide odour production may cause problems at composting sites.

##### **Technical considerations relevant to applicability**

Utilisation of wool in the textile industry is only practical where the tannery is located near textile manufacturers.

External anaerobic digestion facilities may be reluctant to accept any wastes from a tannery.



**Economics**

Reuse or recycling may reduce disposal costs.

**Driving force for implementation**

The technique may be implemented either to achieve a reduction in disposal costs, or because of legal restrictions on landfill disposal, or both.

**4.11.1.2 Trimmings****Description**

Options for the reuse, recycling and disposal of trimmings.

An overview of options dealing with raw limed and tanned trimmings are given in Table 4.20.

**Table 4.20: Options for dealing with raw, limed, and tanned trimmings**

	Raw trimmings	Limed trimmings	Tanned trimmings
<b>Uses as a by-product</b>		Collagen production	Patchwork, small leather goods, etc.
<b>Reuse after preparation</b>		Production of technical gelatine, or tallow, or protein hydrolysate	Leather fibreboard production for non-finished trimmings. Protein hydrolysate
<b>Recycling as</b>	Hide glue	Hide glue	
<b>Other recovery</b>	Generation of biogas by anaerobic digestion	Generation of biogas by anaerobic digestion	Generation of biogas by anaerobic digestion

**4.11.1.3 Fleshings****Description**

Options for the reuse, recycling, and disposal of fleshings.

**Technical description**

Fleshings are produced either before (green fleshings) or after liming. The sulphide and lime content and the high pH from limed fleshings may reduce the acceptability of the residues in recycling facilities and make the technical processing more difficult.

Options for dealing with fleshings are listed in Table 4.21.

**Table 4.21: Options for dealing with fleshings**

Uses as a by-product	Type of by-product
<b>Reuse after preparation</b>	Protein hydrolysate, tallow
<b>Recycling as</b>	Hide glue
<b>Other recovery</b>	Generation of substitute fuel Generation of biogas by anaerobic digestion

Limed fleshings should not be subjected to anaerobic digestion without pretreatment to remove sulphides, unless the digestion plant is designed to cope with hydrogen sulphide production. Animal health controls restrict the disposal routes for green fleshings.

Energy can be recovered from fleshings (in a mixture with some other wastes) by the generation of biogas as a fuel (see Section 4.12.4) and the production of tallow as a fuel (see Section 4.12.5).

**Achieved environmental benefits**

A reduction of wastes sent for disposal and the production of energy or useful by-products.

**Cross-media effects**

Anaerobic digestion of limed fleshings has a potential to produce foul odours.

**Technical considerations relevant to applicability**

Availability of facilities or buyers in the vicinity of the tannery may affect availability.

Animal health controls restrict the disposal routes for green fleshings.

**Economics**

There may be a savings on disposal costs. There may be some return from the sale of by-products. Energy recovery may be economically beneficial.

Fees are charged for composting and rendering.

**Driving force for implementation**

The reduction of wastes sent for disposal is the principal reason for using the technique.

**Example plants**

Fangel, Denmark.

**4.11.1.4 Splits**

**Description**

Options for the reuse, recycling and disposal of splits.

**Technical description**

The **splitting** process can be performed in either the limed or the tanned condition (see Section 4.5.3.3). Depending on where the splitting takes place within the process line, further processing in different ways is feasible. Table 4.22 summarises the waste treatment options for untanned splits and for tanned splits together with shavings: composting and anaerobic treatment together with other waste fractions [10, Rydin and Frendrup 1993]. Depending on the quality, untanned splits can be used to produce hide glue, gelatine and sausage casings.

**Table 4.22: Options for dealing with untanned and tanned splits and trimmings**

	<b>Untanned splits</b>	<b>Tanned splits and trimmings</b>
<b>Uses as a by-product</b>	Processed further to leather production of sausage casings; Collagen production; Dog chews	Finished for use in patchwork, small leather goods, etc.; Collagen production
<b>Reuse after preparation</b>	Production of technical gelatine; Protein hydrolysate	Leather fibreboard production (from non-finished materials); Protein hydrolysate
<b>Recycling as</b>	Hide glue	
<b>Other recovery</b>	Generation of biogas by anaerobic digestion	

**Achieved environmental benefits**

Reduction of wastes sent for disposal.

**Technical considerations relevant to applicability**

Leather fibreboard production is carried out at only a few locations in Europe.

Parts of the tannery must comply with food safety legislation if limed materials are processed for edible collagen production.

Rendering plants and hide glue manufacturers may not be available in all cases.

**Economics**

Fees are charged for composting and rendering.

**Driving force for implementation**

The reduction of wastes sent for disposal is the principal reason for using the technique.

**4.11.1.5 Shavings****Description**

Options for the reuse, recycling and disposal of shavings.

**Technical description**

Shavings are produced in different sizes. Many of the recycling routes available for shavings are the same as for tanned splits [3, Andres 1995].

Chrome-tanned splits and shavings can be hydrolysed to produce chromium-containing sludge, fat and protein hydrolysate. Outlets have been found for the hydrolysate in various chemical and technical products [3, Andres 1995] [15, Spain 1997] [37, Italy 1998].

Certain tanned leather wastes are biodegradable, such as wet white shavings and vegetable-tanned shavings. This allows for a recycling route to produce soil improvers and fertilisers.

Energy is recovered from shavings in several Scandinavian tanneries.

**Achieved environmental benefits**

Reduction of wastes sent for disposal.

**Technical considerations relevant to applicability**

Leather fibreboard production is carried out at only a few locations in Europe.

Rendering plants and hide glue manufacturers may not be available in all cases.

**Economics**

Fees are charged for composting and rendering.

**Driving force for implementation**

The reduction of wastes sent for disposal is the principal reason for using the technique.

**Reference literature**

[3, Andres 1995] [15, Spain 1997] [37, Italy 1998].

#### 4.11.1.6 Dust from mechanical finishing

##### Description

Options for the disposal of dust from mechanical finishing.

##### Technical description

Leather dust from milling and buffing operations is a waste for which a disposal route must be found. In most cases, the fine fibres contain tanning and post-tanning agents.

#### 4.11.1.7 Fats, grease and oil

##### Description

Options for the disposal of fats, greases and oils

##### Technical description

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 on the commodity market. The grease emulsions may be cracked if aqueous degreasing has been applied, either in solvent emulsion or in solvent-free emulsion using surfactants. However, no market has 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 or reused, they give a good energy yield in a thermal treatment and anaerobic digestion. Options for dealing with fats, grease and oil are shown in Table 4.23.

**Table 4.23: Options for dealing with fats, grease, and oil**

<b>Uses as a by-product</b>	
<b>Reuse after preparation</b>	Commodity market (grease from solvent degreasing)
<b>Recycling as</b>	
<b>Other recovery</b>	Thermal treatment Generation of biogas by anaerobic digestion

##### Achieved environmental benefits

Some reduction of wastes sent for disposal is possible.

### 4.11.2 Disposal of effluent plant wastes

#### Description

Options for the disposal of effluent plant wastes.

#### Technical description

The principal measures to minimise the production of wastes in the effluent treatment plant are:

- reduction of the input of process agents in order to decrease the effluent concentration and consequently the generation of sludge;
- optimisation of the type and the amount of precipitation agents applied in the effluent treatment in order to reduce the amount of sludge;
- separation of specific fractions of residues and different waste water streams for efficient treatment and production of lower amounts of sludge;
- optimisation of the implementation of recovery and reuse measures aimed at reducing the amount of solid waste, of waste water that has to be treated, and of sludge;
- keeping the sludge amounts as low as possible by choice of waste water treatment methods.

Waste materials from effluent treatment consist of a small amount of coarse material and a large quantity of sludges of various kinds.

#### 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 options shown in Table 4.24.

**Table 4.24: Options for dealing with sludges from waste water treatment**

<b>Uses as a by-product</b>	
<b>Reuse after preparation</b>	Landscaping Agriculture Construction material for landfills
<b>Recycling as</b>	
<b>Other recovery</b>	Thermal treatment Generation of biogas by anaerobic digestion

#### Achieved environmental benefits

Some reduction of wastes sent for disposal is possible.

#### Technical considerations relevant to applicability

Available techniques in sludge disposal depend on the composition of the sludge and have to be assessed with reference to available facilities and national regulations and strategies.

External anaerobic digestion facilities may be reluctant to accept any wastes from a tannery.

#### Driving force for implementation

The legal restrictions on the landfilling of wastes provide the main impetus for using these techniques.

### 4.11.3 Disposal of other residues

#### Description

Options for the disposal of other residues.

#### Technical description

Other residues require further (off-site) treatment, apart from the options discussed above for recycling and reuse in the process units themselves. This includes the following wastes: salt, organic solvents, and chemicals used as process chemicals, auxiliaries, or cleansers, sludges from finishing, solids from air abatement (activated carbon, sludges from wet scrubbers), and packaging material.

#### Achieved environmental benefits

The appropriate disposal of non-reusable wastes is environmentally beneficial.

#### Cross-media effects

Disposal is still required.

#### Technical considerations relevant to applicability

Table 4.25 presents options for waste treatment and disposal for other waste fractions.

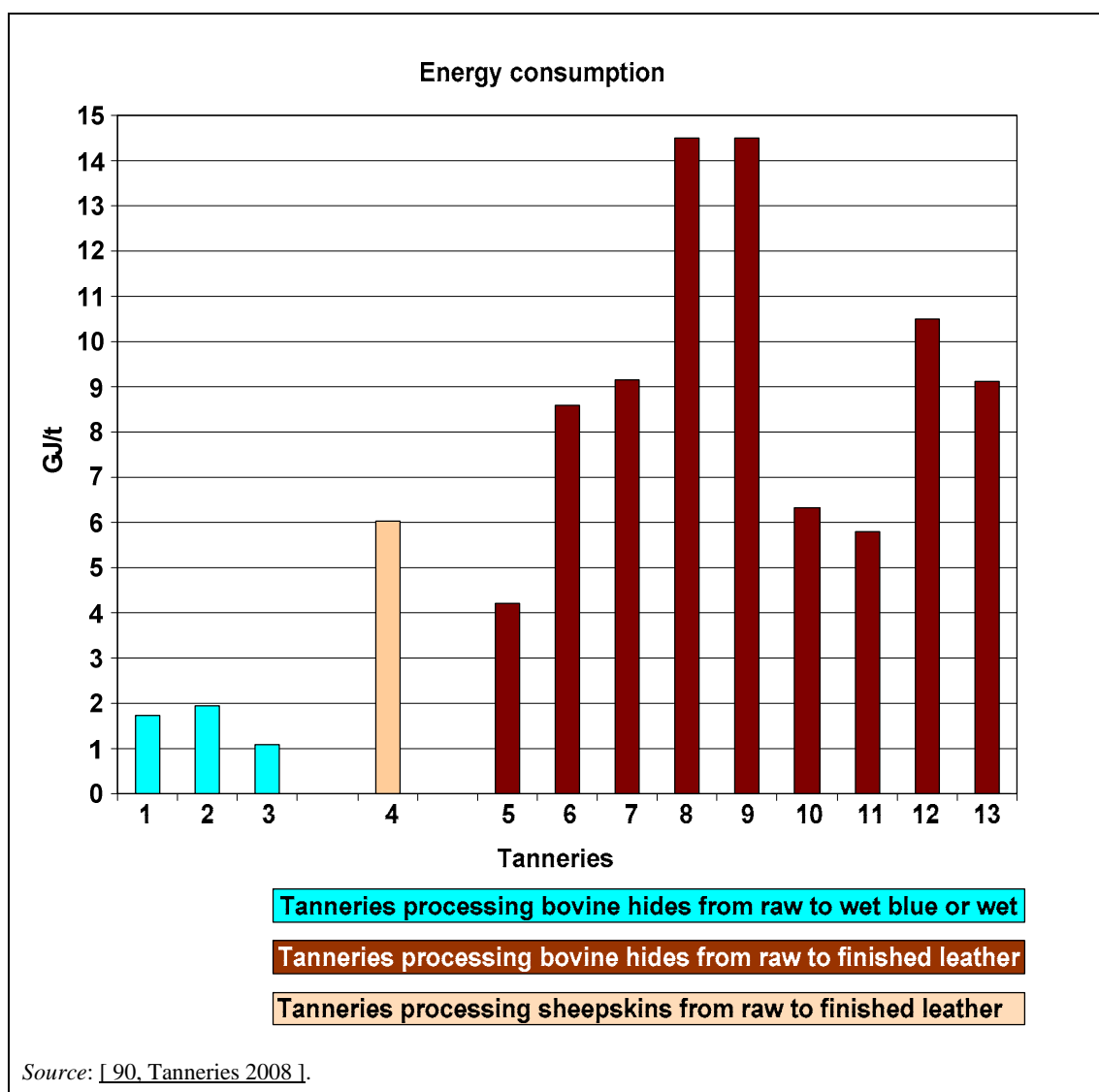
**Table 4.25: Waste treatment and disposal for other waste fractions**

Waste Material	Treatment and disposal options
<b>Chemicals</b>	Obsolete chemicals require specific treatment, according to their content .
<b>Finishing sludges</b>	The sludge generated in finishing requires specific treatment, according to the content.
<b>Sludges from wet-scrubbers</b>	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.
<b>Other residues from air abatement</b>	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.

## 4.12 Energy

The efficient generation distribution and use of energy is beneficial in environmental and economic terms. Some energy efficiency measures have applications in many industry sectors. These are covered by the horizontal reference document on Energy Efficiency [109, EC 2008]. This section deals with techniques specific to the leather making industry.

Figure 4.5 shows the use of all forms of energy in some energy efficient European tanneries in 2007 and 2008. The data have been calculated on the basis of tonnes of raw materials taken into the plants.



**Figure 4.5** Energy use in tanning

Additional aggregated information has also been reported from the following surveys .

- In German tanneries, the energy consumption for processing bovine hides from raw to finished leather is up to 12 GJ/t of raw material. About 37 % of the total energy (i.e. ~ 4.5 GJ) is used in the process steps from raw to wet blue or wet white [ 165, Germany 2012 ].
- In Austrian tanneries, the energy consumption for coated vegetable leather from raw hides in the automotive industry varies in the range 5.4 – 7.2 GJ/t, covering all the processes, including waste water treatment [ 166, Austria 2012 ].

### 4.12.1 Use of short floats

#### **Description**

The use of short floats to reduce energy use.

#### **Technical description**

The use of short floats is described in Section 4.3.2.

The use of short floats entails the starting and rotation of less balanced process vessels. There is an increase in the rate of use of electrical energy, but this is balanced by the shorter process times involved.

#### **Achieved environmental benefits**

Because it reduces process water heating the use of short floats can make an obvious difference to the energy use in a tannery.

#### **Technical considerations relevant to applicability**

See Section 4.3.2.

#### **Driving force for implementation**

This technique is used to achieve a reduction in the use of water and process chemicals, as well as energy.

#### **Example plants**

Short floats are now widely used in European plants.

#### **Reference literature**

[84, Ludvik J. 2000].

### 4.12.2 Energy recovery from process fluids

#### **Description**

Techniques to recover energy from process fluids.

#### **Technical description**

Energy savings can be achieved by heat pumps incorporating recovery systems. Waste heat can be used from and for other processes.

By means of heat exchangers, energy can be recovered from the waste process water, from condensate from vacuum dryers, from evaporated water from high frequency drying, or from exhaust air from drying.

The cooling water from the vacuum dryer, which is not polluted, can be used in the hot water supply.

#### **Achieved environmental benefits**

Reduced energy use may be achieved.

#### **Environmental performance and operational data**

Up to 75 % of waste heat from drying may be recovered.

About 10 – 20 % of the energy consumption of vacuum drying may be recovered for hot water supply needs.

See Section 4.12.3 for the heat pump technique in the drying process.



**Economics**

Recovery of thermal energy by the means of heat pumps is normally only economical at a price relation of:

$$\frac{\text{GJ (electric)}}{\text{GJ (thermal)}} < 2 - 2.5$$

**Example plants**

Tanneries in France have been reported to be implementing the heat pump technique.

**Reference literature**

[16, Frendrup 1999].

**4.12.3 Improved drying techniques****Description**

The improvement of drying techniques to reduce energy use.

**Technical description**

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.

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 reheating, drying installations should be run as continuously as possible. The heat capacity and heat transmission of new installations are as low as possible.

A system for the use of heat pumps in drying exists, developed in France (see Section 4.12.2). 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 the natural drying of the leather is the method with the lowest energy consumption but it is impractical for much of the year in many parts of Europe due to climatic conditions. These include low temperatures, high rainfall and the associated humidity, combined with unpredictable variations in all these factors.

For finish drying, infrared heating is an energy-saving method.

**Achieved environmental benefits**

Reduced energy use may be achieved.

**Environmental performance and operational data**

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.

The figures given in Table 4.26 are for the energy consumption of various drying methods, without and with the use of heat pumps.

**Table 4.26: Energy consumption of various drying methods**

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	

**Driving force for implementation**

The driving forces are to reduce energy costs and to meet energy use targets.

**Example plants**

Tanneries in France have been reported to be implementing the heat pump technique.

**Reference literature**

[56, Pearson et al. 1999] [105, Pfisterer 1986].

**4.12.4 Energy recovery from waste by digestion****Description**

Anaerobic digestion of organic waste fractions to produce a fuel gas.

**Technical description**

Anaerobic treatment of wastes is a well known technique which can be used to produce energy from waste and by-products from the leather industry. Green fleshings are suitable for biogas production, but are subject to appropriate animal health controls.

**Achieved environmental benefits**

A reduction of fossil fuel use, a reduction of CO<sub>2</sub> emissions and a reduction of the volumes of waste for disposal.

**Environmental performance and operational data**

It is possible to recover around 3 GJ per tonne of raw hide through digesting limed fleshings and waste water sludge.

**Cross-media effects**

The formation of hydrogen sulphide can occur during the process.

The final disposal routes for digestates from tannery wastes may be more restricted than those from anaerobic digestion of other wastes (see Section 3.5.3.3).

**Technical considerations relevant to applicability**

The technique is applicable to both new and existing installations. In practice, the technique will normally use waste material from several different sources (e.g. manure from agriculture).

**Economics**

The cost-benefit calculation depends on many parameters such as the amount of waste, cost of disposing of fleshings, gas or electricity price.

**Driving force for implementation**

Increasing energy prices and possible CO<sub>2</sub> emissions trading contribute to the case for energy recovery by biogas. Another driving force for the installation of a biogas plant is the increasing costs for the disposal of waste.

**Example plants**

Elmo Sweden AB.

**Reference literature**

[ 85, Hauber and Knödler 2008 ] [16, Frentrup 1999] [4, Andres 1997].

**4.12.5 Energy recovery from waste by combustion****Description**

Fat recovered from wastes is burnt as a fuel.

**Technical description**

Fleshings (and other fatty wastes) are minced to approximately 5 – 10 mm, heated to 75 – 85 °C and separated e.g. using tricanter into tallow (10 – 20 %), solids 'greaves' (35 – 55 %), and a water fraction (35 – 55 %). The tallow contains up to 99 % fat and can be used in an appropriate burner as a direct substitute for oil fuel; the calorific value is about 85 – 90 %. See also Sections 6.9.1 and 6.9.2.

**Achieved environmental benefits**

A reduction of fossil fuel use and a reduction of the volumes of waste for disposal can be achieved.

**Environmental performance and operational data**

The emissions from burning the substitute fuel generated from fleshings do not show significant differences regarding CO<sub>2</sub>, or CO compared to gas oil. Combustion of fat from the fleshings can cover 50 – 70 % of the total demand for thermal energy.

**Cross-media effects**

The technique also generates two different waste fractions which have to be disposed of. The water fraction represents an additional load on effluent treatment facilities, while the greaves have to be disposed of as waste.

### **Technical considerations relevant to applicability**

The method can be used on or off site. For on-site operation, the heat generated can be used in the tannery. Depending on the status of the material being burnt, compliance with waste incineration legislation will require a more complex plant.

### **Economics**

The cost-benefit analyses depend on local conditions. Important factors are the amount and the composition of the fleshings, the cost for disposal of the fleshings, the cost saved on the fuel which is replaced and the possibilities and costs for the disposal of the residue. The capital cost of the plant can be high, especially if compliance with waste incineration legislation is required.

### **Driving force for implementation**

The drivers are increasing energy prices and costs of disposal.

### **Example plants**

One tannery in Germany and several other tanneries in Europe run installations for the generation of substitute fuel on-site. An English sheepskin tannery gets 20 % of its thermal energy from the incineration of sheepskin fat.

### **Reference literature**

[ 85, Hauber and Knödler 2008 ].

## 4.13 Noise and vibration control

### Description

Techniques to control the emission of noise and vibration.

### Technical description

Good practice to control the emission of noise and vibration may use one or more of the techniques listed below.

- The prevention of noise generation at source. Preventative maintenance and replacement of old equipment can considerably reduce the noise levels generated
- Change of operating speeds so as to avoid creating resonances. Avoiding operation of several machines of the same type at the same speed.
- Placing as much distance as possible between the noise source and those likely to be affected by it.
- Use of resilient machine mountings and drives to prevent the transmission of vibration
- Using a building designed to contain the noise or a noise barrier.
- Silencing of exhaust outlets.

### Technical considerations relevant to applicability

In determining the degree of control required, it is usual to calculate or measure the sound pressure level close to the source and, knowing the desired end-point, calculate:

- the attenuation at the sensitive location already provided by the environment; and
- the additional attenuation required [117, EA 2002].

The desired end-point must be calculated taking into account the existing noise emissions from external sources. Noise which is particularly annoying because of its tonal character will need greater attenuation. The requirements of laws implementing the Environmental Noise Directive (Directive 2002/49/EC) will also need to be considered.

### Economics

Noise and vibration control measures can be costly to implement, especially in existing plants.

## 4.14 Monitoring

### Description

Monitoring techniques appropriate for the operation of a tannery.

### Technical considerations relevant to applicability

Monitoring of the environmental outputs and emissions from an industrial activity is essential to their effective control. These matters are covered by the Reference Document on the General Principles of Monitoring [110, EC 2003]. This section deals with techniques specific to the leather making industry.

**Water** – Standardised analysis and measurement methods exist for waste water effluent parameters such as COD, BOD, SS, TKN, ammonia, total chromium, 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.

**Particulate matter** emissions do not require frequent precise monitoring once the efficacy of the equipment has been proved. Indicative or secondary monitoring can be used to check for correct operation. For example, the functioning of filtration equipment can be monitored by measuring the pressure drop across the filter.

Where emissions of **hydrogen sulphide, ammonia or volatile organic compounds** are sufficient to need abatement equipment, correct operation of that equipment must be checked by indicative monitoring. Alternatively secondary indicators such as the pH or redox potential of the liquid at the outlet from a wet scrubber can be used for day to day monitoring.

The keeping of an **organic solvent** inventory is necessary to establish the total solvent emissions per m<sup>2</sup> of leather produced.

At sites where annoyance is likely to be caused, monitoring of hydrogen sulphide, ammonia and other **odorous substances** at the downwind boundary of the site may be required. Since H<sub>2</sub>S and NH<sub>3</sub> are detectable by humans in concentrations below the operational limits of portable measuring equipment, olfactory monitoring may be the only technique available. It is usual to deploy staff who do not work in the production areas for olfactory monitoring.

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. Monitoring requirements for the thermal treatment of wastes are specified in Chapter IV of the Directive.

**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 techniques, and is essential in good environmental management of emissions and in accident preparedness programmes (see Section 4.1).

**Energy** – The consumption of water, electricity, heat (steam and heating), and compressed air, should be recorded, as part of a programme to manage these resources. A total of all energy use at the installation should be calculated.

**Noise** – Where there are residences or other noise-sensitive locations near to the tannery, sound levels should be measured outside the tannery buildings on appropriate parts of the site. The measurement should include narrow band frequency analysis. When new equipment is installed, new measurements should be taken to detect any increase in the sound emissions or a change in their character.

**Economics**

Monitoring is expensive and adds to process costs.

## 4.15 Decommissioning

### Description

Techniques for the decommissioning of a tannery.

### Technical description

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 on the immediate surroundings, by remediation techniques, to leave the area in such a way that it can be reused (depending on the enforcement bodies' decisions 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, groundwater, air or soil.

Records must be kept during the operation of the tannery of the location on the site at which each process step is undertaken. Drainage routes and waste storage locations must be included. These records should be preserved systematically to allow the efficient planning of decommissioning. Additional records should be made each time activities or equipment are relocated, or when changes are made to process chemistry. See also Section 4.1.

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 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 prerequisites are to be considered for the final shutdown and what contamination might be caused.

The large quantities of raw materials and wastes handled by tanneries mean that the prevention of soil and groundwater contamination is a high priority with regards to spillage, storage, processing, and final decommissioning.

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,
- survey 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 of containers and process units of liquors, chemicals and residues; draining liquors from piping and retention units; and 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 reuse, 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 reusable 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 dusty materials 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 groundwater), and surface water can arise from:

- organic solvents
- oil
- chromium
- substances contained in waste.

Contamination from these sources might have been caused much earlier 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.

#### **Achieved environmental benefits**

Restoration of the site following the cessation of operations.

#### **Technical considerations relevant to applicability**

All closed sites.

#### **Economics**

A robust and properly documented decommissioning programme enhances the value of the land.

#### **Driving force for implementation**

Legislation of the Member State.



## 5 BAT CONCLUSIONS

### Scope

These BAT conclusions concern the following activities specified in Annex I to Directive 2010/75/EU, namely:

- 6.3 *'Tanning of hides and skins where the treatment capacity exceeds 12 tonnes of finished products per day'*;
- 6.11 *'Independently operated treatment of waste water not covered by Directive 91/271/EEC and discharged by an installation undertaking activities covered under 6.3 above'*.

Unless stated otherwise, the BAT conclusions presented can be applied to all installations subject to these BAT conclusions.

Other reference documents which are relevant for the activities covered by these BAT conclusions are the following:

Reference document	Subject
Energy Efficiency (ENE)	General energy efficiency
Economics and Cross-Media Effects (ECM)	Economics and cross-media effects of techniques
General Principles of Monitoring (MON)	Emissions and consumption monitoring
Emissions from storage (EFS)	Emissions from tanks, pipework and stored chemicals
Waste Incineration (WI)	Waste Incineration
Waste Treatments Industries (WT)	Waste Treatment

The techniques listed and described in these BAT conclusions are neither prescriptive nor exhaustive. Other techniques may be used that ensure at least an equivalent level of environmental protection.

## Definitions

For the purposes of these BAT conclusions, the following definitions apply:

<b>Beamhouse / Limeyard</b>	That portion of the tannery where the hides are soaked, limed, fleshed and unhaired; when necessary, prior to the tanning process.
<b>By-product</b>	Object or substance meeting the requirements of Article 5 of Directive 2008/98 EC or any succeeding directive.
<b>Existing plant</b>	A plant that is not a new plant.
<b>Existing processing vessel</b>	A processing vessel which is not a new processing vessel.
<b>New plant</b>	A plant first operated at the installation following the publication of these BAT conclusions or a complete replacement of a plant on the existing foundations of the installation following the publication of these BAT conclusions.
<b>New processing vessel</b>	A processing vessel first operated at the plant following the publication of these BAT conclusions or a complete rebuild of a processing vessel following the publication of these BAT conclusions.
<b>Tannery</b>	An installation that carries out the activity 'Tanning of hides and skins where the treatment capacity exceeds 12 tonnes of finished products per day' (Activity 6.3 of Annex I to Directive 2010/75/EU).
<b>Tanyard</b>	The part of the tannery where the processes of pickling and tanning are carried out.
<b>Urban waste water treatment plant</b>	A plant subject to Directive 91/271/EC.

## 5.1 General BAT conclusions for the tanning of hides and skins

### 5.1.1 Environmental management systems

1. In order to improve the overall environmental performance of a tannery, BAT is to implement and adhere to an environmental management system (EMS) that incorporates all of the following features:

- i. commitment of the management, including senior management;
- ii. definition of an environmental policy that includes the continuous improvement of the installation by the management;
- iii. planning and establishing the necessary procedures, objectives and targets, in conjunction with financial planning and investment;
- iv. implementation of procedures paying particular attention to:
  - (a) structure and responsibility;
  - (b) training, awareness and competence;
  - (c) communication;
  - (d) employee involvement;
  - (e) documentation;
  - (f) efficient process control;
  - (g) maintenance programmes;
  - (h) emergency preparedness and response;
  - (i) safeguarding compliance with environmental legislation;
- v. checking performance and taking corrective action, paying particular attention to:
  - (a) monitoring and measurement (see also the Reference Document on the General Principles of Monitoring);
  - (b) corrective and preventive action;
  - (c) maintenance of records;
  - (d) independent (where practicable) internal and external auditing in order to determine whether or not the EMS conforms to planned arrangements and has been properly implemented and maintained;
- vi. review of the EMS and its continuing suitability, adequacy and effectiveness by senior management;
- vii. following the development of cleaner technologies;
- viii. consideration for the environmental impacts from the eventual decommissioning of the installation at the stage of designing a new plant, and throughout its operating life;
- ix. application of sectoral benchmarking on a regular basis.

Specifically for the tanning of hides and skins, it is also important to consider the following potential features of the EMS:

- x. the maintenance of records of the locations on the site where particular process steps are carried out to facilitate decommissioning;
- xi. other items listed under BAT conclusion 2.

#### **Applicability**

The scope (e.g. level of details) and nature of the EMS (e.g. standardised or non-standardised) will generally be related to the nature, scale and complexity of the installation, and the range of environmental impacts it may have.

### 5.1.2 Good housekeeping

**2. In order to minimise the environmental impact of the production process, BAT is to apply the principles of good housekeeping by applying the following techniques in combination:**

- i. careful selection and control of substances and raw materials (e.g. quality of hides, quality of chemicals);
- ii. input–output analysis with a chemical inventory, including quantities and toxicological properties;
- iii. minimisation of the use of chemicals to the minimum level required by the quality specifications of the final product;
- iv. careful handling and storage of raw materials and finished products in order to reduce spills, accidents and water wastage;
- v. segregation of waste streams, where practicable, in order to allow for the recycling of certain waste streams;
- vi. monitoring of critical process parameters to ensure stability of the production process;
- vii. regular maintenance of the systems for the treatment of effluents;
- viii. review of options for the reuse of process/washing water;
- ix. review of waste disposal options.

## 5.2 Monitoring

3. BAT is to monitor emissions and other relevant process parameters, including those indicated below, with the given associated frequency and to monitor emissions according to EN standards. If EN standards are not available, BAT is to use ISO, national or other international standards that ensure the provision of data of an equivalent scientific quality.

	Parameter	Frequency	Applicability
a	Measurement of water consumption in the two process stages: up to tanning and post-tanning, and recording of production in the same period.	At least monthly.	Applicable to plants carrying out wet processing.
b	Recording of the quantities of process chemicals used in each process step and recording of production in the same period.	At least yearly.	Generally applicable.
c	Monitoring of the sulphide concentration and total chromium concentration in the final effluent after treatment for direct discharge to receiving water, by using flow proportional 24-hour composite samples.  Monitoring of the sulphide concentration and total chromium concentration after chromium precipitation for indirect discharge, by using flow proportional 24-hour composite samples	On a weekly or monthly basis.	The monitoring of chromium concentration is applicable to on-site or off-site plants which undertake chromium precipitation.  Where economically viable, the monitoring of sulphide concentration is applicable to plants carrying out some part of effluent treatment on site or off site for treating waste waters from tanneries.
d	Monitoring of chemical oxygen demand (COD), biochemical oxygen demand (BOD) and ammoniacal nitrogen after on-site or off-site effluent treatment for direct discharges to receiving water, by using flow-proportional 24-hour composite samples.  Monitoring of total suspended solids after effluent treatment after on-site or off-site effluent treatment for direct discharges to receiving water.	On a weekly or monthly basis.  More frequent measurements in case process changes are needed.	Applicable to plants carrying out some part of effluent treatment on site or off site for treating waste waters from tanneries.
e	Monitoring of halogenated organic compounds after on-site or off-site effluent treatment for direct discharges to receiving water.	On a regular basis.	Applicable to plants where halogenated organic compounds are used in the production process and are susceptible to being released into receiving water.
f	Measurement of pH or redox potential at the liquid outlet of wet scrubbers.	Continuously.	Applicable to plants using wet scrubbing to abate hydrogen sulphide or ammonia emissions to the air.

	<b>Parameter</b>	<b>Frequency</b>	<b>Applicability</b>
<b>g</b>	<b>The keeping of a solvent inventory on an annual basis, and recording of production in the same period.</b>	On an annual basis.	Applicable to plants carrying out finishing using solvents and using water-borne coatings or similar materials to limit the solvent input.
<b>h</b>	<b>Monitoring of volatile organic compound emissions at the outlet of abatement equipment, and recording of production.</b>	Continuously or periodically.	Applicable to plants carrying out finishing using solvents and employing abatement.
<b>i</b>	<b>Indicative monitoring of the pressure drop across bag filters.</b>	On a regular basis.	Applicable to plants using bag filters to abate particulate matter emissions, where there is a direct discharge to the atmosphere.
<b>j</b>	<b>Testing of the capture efficiency of wet scrubbing systems.</b>	Annually.	Applicable to plants using wet scrubbing to abate particulate matter emissions, where there is a direct discharge to the atmosphere.
<b>k</b>	<b>Recording of the quantities of process residues sent for recovery, reuse, recycling, and disposal.</b>	On a regular basis.	Generally applicable.
<b>l</b>	<b>Recording of all forms of energy use and of production in the same period.</b>	On a regular basis.	Generally applicable.



### 5.3 Minimising water consumption

4. In order to minimise water consumption, BAT is to use one or both of the techniques given below.

Technique		Description	Applicability
a	<b>The optimisation of water use in all wet process steps, including the use of batch washing instead of running water washes</b>	Optimisation of water use is achieved by determining the optimum quantity required for each process step and introducing the correct quantity using measuring equipment. Batch washing involves washing of hides and skins during processing by introducing the required quantity of clean water into the processing vessel and using the action of the vessel to achieve the required agitation, as opposed to running water washes which use the inflow and outflow of large quantities of water.	Applies to all plants carrying out wet processing.
b	<b>The use of short floats</b>	Short floats are reduced amounts of process water in proportion to the amount of hides or skins being processed as compared to traditional practices. There is a lower limit to this reduction because the water also functions as a lubricant and coolant for the hides or skins during processing. The rotation of process vessels containing a limited amount of water requires more robust geared drives because the mass being rotated is uneven.	This technique cannot be applied in the dyeing process step and for the processing of calfskins.  Applicability is also limited to: <ul style="list-style-type: none"> <li>• new processing vessels;</li> <li>• existing processing vessels that allow the use of, or can be modified to use, short floats.</li> </ul>

The review of options for the reuse of process/washing water is part of an Environmental Management System (see BAT 1) and of the principles of good housekeeping (see BAT 2).

#### The BAT-associated consumption levels for water

See Table 5.1 (for bovine hides) and Table 5.2 (for sheepskins)

**Table 5.1: BAT-associated consumption levels for water for the processing of bovine hides**

Process stages	Water consumption per tonne of raw hide <sup>(1)</sup> (m <sup>3</sup> /t)	
	Unsalted hides	Salted hides
Raw to wet blue/white	10 to 15	13 to 18
Post-tanning processes and finishing	6 to 10	6 to 10
Total	16 to 25	19 to 28

<sup>(1)</sup> Monthly average values. Processing of calfskins and vegetable tanning may require a higher water consumption.

Table 5.2: BAT-associated consumption levels for water for the processing of sheepskins

Process stages	Specific water consumption <sup>(1)</sup>
	litres per skin
Raw to pickle	65 to 80
Pickle to wet blue	30 to 55
Post-tanning processes and finishing	15 to 45
Total	110 to 180

<sup>(1)</sup> Monthly average values. Wool-on sheepskins may require a higher water consumption.















**Applicability**

Applies only to plants carrying out sulphide unhairing.

**5.6.2 Volatile organic compounds**

- 18. In order to reduce the airborne emissions of halogenated volatile organic compounds, BAT is to replace halogenated volatile organic compounds used in the process with substances that are not halogenated.**

**Description**

Replacement of halogenated solvents by non-halogenated solvents.

**Applicability**

Does not apply to the dry degreasing of sheepskins carried out in closed cycle machines.

- 19. In order to reduce airborne emissions of volatile organic compounds (VOC) from finishing, BAT is to use one or a combination of the techniques given below, priority being given to the first one.**

Technique		Description
a	The use of water-borne coatings in combination with an efficient application system	Limiting emissions of volatile organic compounds by the use of water-borne coatings, with each coat applied by one of the following: curtain coating or roller coating or improved spraying techniques.
b	The use of extraction ventilation and an abatement system	Treating the exhaust air by the use of an extraction system fitted with one or more of the following: wet scrubbing, adsorption, bio-filtration or incineration.

**BAT-associated solvent use levels and BAT-associated emission levels for VOC**

Both the solvent use rates associated with the use of water-borne coatings in combination with an efficient application system and the BAT-AEL range for specific VOC emissions where an extraction ventilation and abatement system is used as an alternative to the use of water-borne finishing materials are given in Table 5.5.

**Table 5.5 BAT-associated solvent use levels and BAT-AELs for VOC emissions**

Parameter	Type of production		BAT-associated environmental performance levels
			g/m <sup>2</sup> (annual average values per unit of finished leather)
Solvent use levels	Where water-borne coatings are used in combination with an efficient application system	Upholstery and automotive leather	10 – 25
		Footwear, garment, and leather goods leathers	40 – 85
		Coated leathers (coating thickness > 0.15 mm)	115 – 150
VOC emissions	Where an extraction ventilation and abatement system is used as an alternative to the use of water-borne finishing materials		9 – 23 <sup>(1)</sup>

<sup>(1)</sup> BAT-AEL range expressed as total carbon.







## 5.8 Energy

26. In order to reduce energy consumed in drying, BAT is to optimise the preparation for drying by samming or any other mechanical dewatering.

27. In order to reduce energy consumption for wet processes, BAT is to use short floats.

### Description

Reducing the energy used to heat water by reducing hot water use.

### Applicability

The technique cannot be applied in the dyeing process step and for the processing of calfskins.

Applicability is also limited to:

- new processing vessels;
- existing processing vessels that allow the use of, or can be modified to use, short floats.

### BAT-associated energy consumption rates

See Table 5.7.

**Table 5.6: Specific energy consumption associated with BAT**

Activity stages	Specific energy consumption per unit of raw material <sup>(1)</sup>
	GJ/t
Processing bovine hides from raw to wet blue or wet white	< 3
Processing bovine hides from raw to finished leather	< 14
Processing sheepskins from raw to finished leather	< 6

<sup>(1)</sup> The energy consumption values (expressed as an annual average not corrected to primary energy) cover the energy use in the production process including electricity and the total heating for indoor spaces, but excluding the energy use for waste water treatment.



## 6 EMERGING TECHNIQUES

In this chapter, promising new pollution prevention and control techniques are presented that are under development. Techniques considered to be 'emerging' are those currently being developed which might form the basis for BAT in the future, even if they have not yet been applied in full-scale operations.

Information will include, if available, a description of the technique, the potential efficiency, a preliminary cost estimate, data availability, an assessment of the status of development, and a reference.

Emerging techniques considered in this document are listed in Table 6.1.

**Table 6.1: Emerging techniques considered**

Process steps	Specific processes
Curing	Use of recovered salt
Degreasing	Solvent degreasing using dimethyl ether
Tanning	Extraction of vegetables tannins from grape pips
	Use of a cross linking agent derived from olive waste
Post-tanning	Continuous retanning and dyeing
	Use of fat recycled from sheepskin degreasing in fatliquors
Finishing	Organic solvent-free finishing
	Dry abatement of volatile compounds from tanneries
Membrane techniques	Application of membrane techniques in processes
	Use of membrane bioreactor (MBR) for enhanced biological effluent treatment
Waste water treatment	Use of biofilm waste water abatement technique
Use of enzymes	Use of enzymes in various process steps
Waste treatment	Gasification of leather waste
	Biodiesel production from tallow from the leather industry

































## 6.9 Waste treatment

### 6.9.1 Gasification of leather waste

#### Description

Gasification is a technique for the production of fuel gas from materials containing organic components. The basic principle of gasification is heating in a reduced oxygen atmosphere, releasing a mixture of gaseous breakdown products which can be used as a fuel.

Theoretically any organic material can be gasified. A pilot plant was used to demonstrate the applicability of the process to tannery wastes [126, Bowden W. 2003]. A tannery will soon be using a gasifier and thermal oxidiser to provide heating, replacing fossil fuel.

The feedstock is dried and fed to the gasifier. It is heated in a reducing (oxygen-starved) atmosphere to produce a combustible gas (fuel gas) made up primarily of carbon monoxide, hydrogen, methane and quantities of carbon dioxide, nitrogen and higher hydrocarbons. This gas is burnt in a thermal oxidiser and heat is recovered using a conventional boiler. The plant was constructed to comply with the requirements of Directive 2000/76/EEC on waste incineration (now Chapter IV of Directive 2010/75/EC).

#### Achieved environmental benefits

A disposal route is provided for organic wastes. Fossil fuel use is reduced.

#### Cross-media effects

A small amount of ash is produced in the gasifier, which is disposed of as a solid waste.

#### Operational data

Commissioning of a plant is taking place.

#### Applicability

The technique can be applied to all types of leather waste. The plant must be constructed at the tannery in order to obtain the benefit of the recovered heat. The costs of compliance with waste incineration legislation determine the minimum size of tannery which can use the technique.

#### Economics

High investment and the costs of compliance with waste incineration legislation are considerable. Reduced fuel costs.

#### Driving force for implementation

The main driving force for the tannery that has implemented the technique was the need for a long-term method for the disposal of its waste.

#### Status of development

A plant has been constructed and put into operation.

#### Reference literature

[126, Bowden W. 2003].

### 6.9.2 Biodiesel production from tallow

#### Description

Biodiesel is a substitute fuel, obtained from renewable biological sources like vegetable and animal oils and fats, with similar properties to diesel. It is produced from vegetable oils, tallow and used cooking oil, by trans-esterification.















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<b>Fogging</b>	the propensity of finished leather to release condensable volatile matter. The limitation of this property is an important specification for automotive leathers.
<b>Grain</b>	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.
<b>Greaves</b>	the solid residue which remains after rendering or fat extraction.
<b>Green fleshing</b>	fleshing done prior to liming and unhairing.
<b>Hard COD</b>	total residual COD, including the inert non-treatable fraction and that part beyond the capacity of a particular treatment.
<b>Hides</b>	the pelts of large animals, such as cattle or horses.
<b>Horse'</b>	wooden or plastic trestle on which hides or skins are piled up to age after tanning or fatliquoring.
<b>Inclined processor</b>	another name for a mixer.
<b>Leather</b>	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.
<b>Limed hide or skin</b>	hide or skin obtained after elimination of hair, epidermis and subcutaneous tissue. This is the name given to hides and skins after liming.
<b>Lime fleshing</b>	fleshing done after the liming and unhairing.
<b>Liming</b>	is the process which causes a controlled alkaline hydrolysis of the collagen in order to remove the hair or wool, epidermis and subcutaneous tissue and thus to give a certain flexibility to the leather.
<b>Mineral tanning</b>	the tanning process where the tanning agents are mineral salts such as those of chromium, (or occasionally aluminium, or zirconium).
<b>Mixer</b>	cylindrical processing vessel, open at one end, rotating about an inclined axis. Also known as an inclined processor. An example is shown in Figure 2.2.
<b>Neutralisation</b>	bringing the tanned hides to a pH suitable for the process of retanning, dyeing and fatliquoring.
<b>New (installation, plant or processing vessel)</b>	an installation, plant or processing vessel introduced onto the site of the installation following the publication of the bat conclusions.
<b>Ovine</b>	of or from sheep.

<b>Painting</b>	unhairing a 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.
<b>Particulate Matter (as an air pollutant)</b>	solid or liquid particles small enough to be suspended in air. Unless a size fraction is stated particulate matter includes all sizes of particles which can become suspended.
<b>Pickled pelt</b>	a skin after pickling and able to be sold at this stage.
<b>Pickling</b>	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.
<b>Pit</b>	an open tank (often set into the ground).
<b>Plating</b>	flattening leather by heat and pressure.
<b>Qualified random sample</b>	a composite sample of at least five random samples taken over a maximum period of two hours at intervals of no less than two minutes, and blended.
<b>Raw hide</b>	hide as received by the tannery; or the commodity consisting of such hides.
<b>Rawhide</b>	material consisting of hide (or skin) which been cleaned and dried, but not tanned. May be a tannery by-product.
<b>Retanning</b>	subjecting a skin or hide, which has been more or less completely tanned, to a second tanning process involving similar or, more usually, different tanning materials, to produce leather with specific properties.
<b>Rinsing / running water washes</b>	washing accomplished by the continuous inflow and outflow of water in a treatment apparatus. Now unusual because of the high water consumption.
<b>Salting</b>	curing using dry salt (NaCl) hides or skins are dried as a result.
<b>Samming or Sammying</b>	mechanical reduction of water content by squeezing between rollers. Produces an effluent containing substances used in the preceding step.
<b>Setting out</b>	mechanical finishing process to flatten the surface. Removes some water.
<b>Shavings</b>	leather particles obtained during thickness levelling on leather with the help of a cylinder equipped with cutting blades.
<b>Soaking</b>	first process in the manufacture of leather, to rehydrate and wash the hides or skins.
<b>Short float</b>	volume of float (relative to the weight of the skins, hides or leather) which is less than that used in conventional processing. There is a lower limit to this reduction because the water also functions as a lubricant and coolant for the hides or

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	skins during processing. The rotation of process vessels containing a limited amount of water requires more robust geared drives because the mass being rotated is uneven. When less water is present, the quantity of each process chemical discarded unreacted is reduced. There is also a reduction in the energy used to heat water, because heated water use is reduced.
<b>Skin</b>	the pelt of a small animal, such as calf, pig or sheep.
<b>Split</b>	the non-grain part of a split hide.
<b>Splitting</b>	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.
<b>Staking</b>	softening and stretching of leather.
<b>Tallow</b>	non-edible or 'technical' fat.
<b>Syntans or syn-tans</b>	synthetic tanning agents.
<b>Tanning (process step)</b>	stabilisation of collagen fibres by tanning agents so that the hide or skin is no longer susceptible to putrefaction or rotting. For clarity, the general meaning of tanning has been used only in defining the scope of the BREF.
<b>Tanyard</b>	the part of the tannery where the processes of pickling and tanning are carried out.
<b>Total Kjeldahl Nitrogen</b>	the sum of nitrogen present as organic nitrogen, ammonia and ammonium compounds measured using the Kjeldahl technique.
<b>Trimming</b>	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.
<b>Trimming</b>	the residues arising from the trimming the hides and skins.
<b>Upholstery leather</b>	leather manufactured for covering furniture, or seats of aircraft or vehicles.
<b>Urban waste water treatment plant</b>	a plant subject to Directive 91/271/EEC.
<b>Vegetable tanning</b>	the tanning process carried out with vegetable tanning agents, which are leached from wood, bark, leaves, roots etc.
<b>Wetting back</b>	re-hydration.
<b>Wet blue</b>	a hide or skin which has been limed and chromium-tanned, therefore blue in colour, and left moist. It may be stored or traded in this state.

**Wet white**

a hide or skin which has been limed and has been tanned with non-chromium agents and therefore remains off-white in colour, and moist. May be stored for a limited period or traded.





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