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**Regional Programme for Pollution Control in the Tanning Industry
in South-East Asia**

**THE SCOPE FOR DECREASING POLLUTION LOAD
IN LEATHER PROCESSING**

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I. INTRODUCTION

Processing hides and skins and converting them into leathers has long been an important industrial activity. The negative environmental impact of the processing has been regarded as an inevitable consequence of that activity.

The technical methods for reducing the negative environmental impact of hide processing fall into two broad groups. The first group involves the introduction of processing technologies usually termed low-waste or cleaner technologies (1) that can be regarded as advanced technologies in comparison to conventional methods. Mainly aimed at decreasing the effluent pollution load, they avoid the use of harmful chemicals and produce solid wastes which can be used as by-products. The second group encompasses the treatment of wastewater and the environment-friendly handling and processing of solid waste (2,3). The methods applied in both groups should be used to prevent leather production impacting negatively on the environment.

This study is primarily focused on the pollution load discharged in effluents and the scope for decreasing that load. In addition to knowing how to produce and sell high quality leather, tanners must also be familiar with techniques for decreasing the pollution load discharged in effluents from individual processing operations. The study aims at heightening tanners' awareness of those techniques. It calculates the decreases possible in a well-managed tannery processing bovine hides into chrome tanned leathers and describes how pollution load can be reduced by introducing advanced technologies based on low-waste processing methods that have been proven on an industrial scale will be taken into account. The study does not consider industrially unproven and purely experimental methods.

II. POLLUTION LOAD OF INDIVIDUAL PROCESSING OPERATIONS AND SCOPE FOR REDUCTION

A. Soaking

In conventional processing salt-preserved hides are commonly used. Calculated on the basis of wet salted weight, the amount of soaking effluent discharged varies from 7 m³/t up to 9 m³/t raw hide. When soaking dry hides, up to 20 m³ water/t dried hide is required. The most important pollutants in soaking effluents are: salt, hide surface impurities, dirt and globular protein substances dissolved in water and salt solution. The typical pollution load of soaking effluents is presented in Table 1.

Table 1 Pollution load of soaking effluents, *Conventional process*

Pollution	Load kg/t raw hide
Suspended solids, SS	11 - 17
Chemical oxygen demand, COD	22 - 33
Biochemical oxygen demand, BOD	7 - 11
NH ₃ -N	0.1 - 0.2
Total Kjeldahl nitrogen, TKN	1 - 2
Cl ⁻	85 - 113
SO ₄ ²⁻	1 - 2

Obviously, the primary aim here is to reduce the chloride load because salt is not eliminated when waste water undergoes physical, chemical and biological treatment. Several industrially proven for reducing chloride load methods have been recommended:

- Shaking the salt off in special drums (1)

The amount of pollution load is decreased by approximately 8 %, i.e. 78 -104 kg Cl⁻/t raw hide. The salt thus removed is often considered too dirty for direct use in the pickle liquors. Salt recovery systems have been developed involving heating to 400°C, none of which, however, is being used at the tannery level.

- Decreasing the amount of salt used to preserve hides by adding some environmentally acceptable antiseptics (such as acetic acid and sodium sulphite) or commercial chemical bactericides based mainly on ethyldithiocarbamate and isothiazolin (1, 4).

Whereas this method reduces the pollution load by approximately one half, i.e. 43 - 57 kg Cl⁻/t raw hide, it decreases preservation efficiency.

- Processing green hides, e.g. unsalted fresh hides (cooled, chilled) (1, 5, 6).

This method would theoretically eliminate the chloride content in soaking effluents; in practice, however, when soaking non-salted hides, a small amount of salt is often added in order to bring some hide components into the solution. In that case, the chloride load is found in a range of 5 - 10 kg Cl⁻/t raw hide. In fact, the organic load (COD, BOD) is influenced in the course of processing unsalted hides (see Table 2).

Table 2 **Pollution load of soaking effluents of differently preserved hides**

Pollution	Load kg/t raw hide	
	salted	unsalted
Total solids range	159 - 231	32 - 42
Average	195	38
COD range	20 - 23	12 - 19
Average	21	16
BOD range	7.7 - 8.1	6.3 - 10
Average	7.9	8.8

No significant differences in the organic pollution load have been registered when soaking salted/unsalted hides. The variances in the total solids load are associated with chloride elimination.

One advanced technology could be applied at this stage: fleshing after washing the hides in the abattoir or after presoaking in the tannery (1, 6). The process yields a lower quantity of fleshings at neutral pH, free from chemical contamination and better suited for protein and fat removal. Further fleshing before liming saves chemicals and can thus improve leather quality.

B. Unhairing/Liming

Processing soaked hides in a bath containing sodium sulphide/hydrosulphide and lime constitutes a basis for conventional unhairing and liming methods. The amount of liming effluents, including washing, fluctuates between 9 and 15 m³/t raw hide. Sulphides, lime, decomposed hair keratin, globular protein and other non-collagen protein, as well as saponified fractions of native fat constitute the load of liming effluents making them the most polluted wastewater streams. A typical pollution load in liming effluents is presented in Table 3.

Table 3 **Pollution load of liming effluents, including washing waters**
Conventional process

Pollution	Load kg/t raw hide
SS	53 - 97
COD	79 - 122
BOD	28 - 45
S ²⁻	3.9 - 8.7
NH ₃ -N	0.4 - 0.5
TKN	6 - 8
Cl ⁻	5 - 15
SO ₄ ²⁻	1 - 2

Advanced unhairing and liming methods are mainly aimed at reducing the pollution load of suspended solids, sulphides, COD, BOD and nitrogenous materials. A range of industrially proven methods for reducing the pollution load are presented below:

a) Recycling spent floats (1, 6)

Several recycling methods adapted to specific production conditions have been used in practice. The recycling of individual spent floats from unhairing (without hair saving) and liming has been successfully tested. The unhairing spent float is recycled for the second soak and the liming spent float is re-used in the lime liquor in successive steps. After 10 liming float cycles and 20 unhairing float cycles, the resultant decrease in the pollution load was evaluated:

S²⁻ : from 2.4 kg/t to 0.7 kg/t raw hide (70% decrease)
Ca (OH)₂ : from 4.1 kg/t to 0.28 kg/t raw hide (93% decrease)

The same recycling system has also been tested as a means of decreasing BOD and COD (see Table 4)

Table 4 **BOD and COD pollution load of selected liming effluents**
Comparison of systems with/without recycling

Operation	Recycling	Pollution load kg/t raw hide	
		COD	BOD
Second soak	without	3.8	1.6
	With	10.8	5.7
Unhairing	without	-	-
	With	9.4	3.2
Liming	without	33.0	12.0
	With	6.9	3.8
Total	without	36.8	13.6
	With	27.1	12.7

It is evident from Table 4 that recycling spent floats can contribute slightly to lowering the BOD and COD pollution load (7%, 26% respectively) in soaking. The leather quality, however, might be negatively affected by the recycling process, unless the unhairing and opening-up processes are completed in two discrete steps. Depending on local conditions, the recycling systems also permit a decrease in the high level of water consumption in liming operations.

b) Sulphide-lime based hair-save unhairing and liming (1, 6, 7)

Most hair-save liming methods are based on the controlled immunisation of hair cystine. Sulphides destroy only non-immunised hair follicles while the hair is released into a bath. The process requires a vessel equipped with an external circulation and filtration system so that the hair can be removed from the bath. After unhairing, the pelt is limed. The potential for decreasing pollution load when using hair-save liming is presented in Table 5.

Table 5 Selected pollution load of liming effluents
Comparison of conventional technology and hair-save liming

Pollution load kg/t raw hide	Technology		Decrease %
	conventional	hair-save	
SS	53 - 97	14 - 26	73
COD	79 - 122	46 - 77	40
S ²⁻	3.9 - 8.7	2.9 - 6.5	26

One hair-save system is based on immunisation with lime, unhairing with sulphides in an immunisation bath, continuous hair filtration and reliming in a residue of the immunisation bath after adding fresh water. It has been tested at two levels of sulphide dosage (see Table 6).

Table 6 Pollution load of liming effluents at two levels of sulphide dosage
Comparison of conventional and hair-save liming

Na ₂ S offer %	Technology	Pollution load kg/t raw hide					
		total solids			dissolved solids		
		TKN	BOD	COD	TKN	BOD	COD
1.7 - 2.0	conventional	5.3	20.0	78.8	3.9	16.9	56.2
	hair-saving	2.4	15.7	44.2	2.1	14.1	36.2
1.3	conventional	5.6	20.2	86.8	4.2	15.4	55.9
	hair-saving	2.6	15.5	43.1	2.2	13.2	33.4

From Table 6 it is evident that hair-save liming achieves a significant decrease in pollution load of the following order:

- Total solids: 55% TKN, 21% BOD, 44% COD
- Dissolved solids: 47% TKN, 17% BOD, 36% COD

Practice has shown that from the standpoint of pelt quality, a sulphide offer of 1.3% on salted weight is both sufficient and reliable. The hair-save system described above has been evaluated on industrial scale (7), see Table 7.

Table 7 Comparison of selected values of pollution load from industrial practice
Conventional and hair-save liming

Pollution load kg/t raw hide		Liming	
		conventional	hair-saving
Total solids	dry matter	74.6	53.3
	ash	37.8	35.5
	org. matter	36.8	17.8
	TKN	5.00	2.18
Dissolved solids	dry matter	56.0	47.6
	ash	31.2	34.2
	org. matter	24.8	13.4
	TKN	3.35	1.89

According to the values achieved during industrial application, the pollution load of hair-save liming effluents is lower than conventional liming.

- By 46 - 52% for organic matter dry solids
- By 43 - 56% for TKN

c) Enzymatic unhairing (1, 6, 8, 9)

Enzymatic treatment can only be considered a cleaner technology if no sulphide or a significantly lower amount thereof is added during the process. When compared to conventional processing, 30 - 50 % COD reduction can result in beamhouse effluent. In practice when processing cattle hides, sulphide or hydrosulphide has to be added.

d) Lime splitting (1, 6)

Splitting limed hides can be also considered a cleaner technology since it saves chromium and other chemicals. Standard offer is 15 - 18 kg Cr_2O_3 /t raw hide as opposed to 21 - 24 kg Cr_2O_3 /t raw hide for conventional wet-blue splitting. Lime splitting yields waste that can be easily utilised as a by-product.

C. Deliming and bating

Conventional deliming and bating methods are based on processing pelts in a bath containing salts derived from a strong acid and a weak alkali (mainly ammonium salts) together with proteolytic enzymes. The amount of deliming and bating effluents, including washing waters, fluctuates between 7 and 11 m^3 /t raw hide. Calcium salts (mainly sulphates), sulphide residues, degraded proteins (collagen and hair) and residual proteolytic enzymatic agents and the like constitute the main pollution load of deliming and bating effluents. A typical pollution load of these effluents is given in Table 8.

Table 8 **Pollution load of deliming and bating effluents inclusive of washing waters**
Conventional process with ammonium sulphate deliming

Pollution	Load kg/t raw hide
SS	8 - 12
COD	13 - 20
BOD	5 - 9
S^{2-}	0.1 - 0.3
$\text{NH}_3\text{-N}$	2.6 - 3.9
TKN	3 - 5
Cl^-	2 - 4
SO_4^{2-}	10 - 26

Advanced deliming and bating methods aim at reducing the pollution load of $\text{NH}_3\text{-N}$ and SO_4^{2-} .

a) Ammonia-free deliming and bating with commercial products (6, 10, 11)

These deliming products are usually based on various organic and inorganic acids, esters of carboxylic acids, non-swelling aromatic acids etc. Bating products are based on active components, i.e. proteolytic enzymes, without admixture of ammonium salts. Table 9 shows the effect on the $\text{NH}_3\text{-N}$ pollution load attributable to ammonia-free deliming and bating of split pelts.

Table 9 Ammonia concentration and load in delimiting and bating effluents
Comparison of ammonia-free delimiting and bating (AF) with conventional technology (C)

No.	Technology	NH ₃ -N	
		mg/l	kg/t raw hide
1	C	2210	2.65
	AF	43	0.052
2	C	2170	2.60
	AF	85	0.10
3	C	2210	2.65
	AF	104	0.12
4	C	2528	3.03
	AF	28	0.034
5	C	2100	2.52
	AF	30	0.036
Average	C	2243	2.69
	AF	58	0.070

The above figures show that ammonia-free delimiting and bating has led to a 97% decrease in the NH₃-N load in effluents discharged from this processing operation.

When the pelt thickness is greater than 3.0 mm (mainly the case with unsplit pelt), a small amount of ammonia salt may have to be added to ensure better delimiting and bating within the permissible time limit.

b) Carbon dioxide delimiting (1, 6, 12, 13)

Carbon dioxide neutralises the lime and solubilises the calcium salts in an over-saturated bath. When pH stabilisation ranges 6.5 to 7.0, acidic swelling cannot occur. In practice, however, a small amount of ammonia salts (up to 0.4% of ammonium sulphate per pelt weight) might have to be added when pelt thickness is greater than 3 mm or non-split pelt is being used. Hydrogen peroxide can be used prior to CO₂ being inserted so as to eliminate the build-up of H₂S.

In practice the decreased pollution load of effluents emanating from ammonia-free delimiting and bating is of the following order:

NH ₃ -N	0.2 - 0.4 kg/t raw hide
TKN	0.6 - 1.5 kg/t raw hide
SO ₄ ²⁻	1 - 2 kg/t raw hide

D. Chrome tanning

The basic scheme of conventional chrome tanning process involves pickling, tanning and basifying. The amount of chrome tanning effluents, including washing waters and sammying water, fluctuates in the range of 3 - 5 m³/t raw hide. Chrome, chlorides and sulphates are the main pollutants. A typical pollution load of these effluents is given in Table 10:

Table 10 **Pollution load of chrome tanning effluents, including washing waters**
Conventional process

Pollution	Load kg/t raw hide
SS	5 - 10
COD	7 - 11
BOD	2 - 4
Cr	2 - 5
NH ₃ -N	0.6 - 0.9
TKN	0.6 - 0.9
Cl ⁻	40 - 60
SO ₄ ²⁻	30 - 55

Advanced chrome tanning methods primarily aim at reducing the pollution load of chrome. A range of industrially proven methods for reducing the chrome content in effluents discharged were considered and are presented below.¹

a) High-exhaustion tanning process (1, 6, 14)

The method features the following characteristics:

- Use of considerably shorter floats (20 - 30% related to pelt weight)
- Use of higher temperatures (40 - 42°C or higher), prolongation of tanning time and higher pH value (4.0 - 4.7)
- Use of special self-basifying and masked chrome tanning agents.

High-exhaustion and chrome fixing bring about a decrease in chrome discharge and an increase in chrome utilisation. These effects are apparent in Table 11.

Table 11 **Comparison of chrome discharge and utilisation in conventional and advanced tanning with high-exhaustion and chrome fixing**

Chrome amount kg/t raw hide	Technology	
	conventional	high-exhaustion
Offer	15	10
Discharge:		
spent tanning float	3.2	0.03 - 0.05
draining and sammying water	0.6	0.02 - 0.05
post-tanning float	0.7	0.1 - 0.4
total	4.5	0.15 - 0.50
Utilisation %	70	95 - 98

The example in Table 11 shows that chrome tanning with high-exhaustion and fixing brings about:

- A decrease in the chrome offer required from 15 kg/t to 10 kg/t raw hide,
- A decrease in the chrome discharged from spent tanning floats, draining and sammying water from 3.8 kg/t to 0.05 - 0.1 kg/t raw hide,

¹ As this study is focused on producers of chrome-tanned leather, chrome-free tanning has not been presented in this case as a means of limiting chrome discharge in effluents.

- An increase in chrome utilisation in tanning operations from 70% to 98%.

Furthermore, the sulphate load drops from 30 - 55 kg/t to 17 - 36 kg/t raw hide, a relevant decrease.

b) Recycling/reuse techniques (1, 6, 14, 15)

Direct recycling systems can be classified as closed and open. Closed systems are mostly based on reusing only spent tanning floats and sammying water for tanning in successive cycles. They are utilised when working with short floats and powder chrome tanning agents. In open systems, the float volume increases during recycling. The number of cycles is not limited; in practice, however; this depends upon the establishment of an equilibrium in the composition of recycled floats. Several open-system recycling techniques are employed industrially:

- Reuse of separated pickling and tanning floats in successive cycles.
- Reuse of tanning float in the subsequent pickling cycle.
- Reuse of the mixture of tanning float and sammying water partly in pretanning, partly in tanning in the subsequent cycle. The pretanning float is discharged each day.
- Reuse of the spent tanning float in the subsequent tanning cycle and recycle of the sammying water for the pickling float that is discharged on a daily basis.

Recycling techniques are mostly used in conventional tanning. According to the extent of their use, an increase in chrome utilisation from 70% up to 95% and a decrease in chrome discharge from 2 - 5 kg/t to 0.1 - 0.25 kg/t raw hide should be regarded as maxima and minima, respectively.

Recycling systems also decrease the sulphate load in effluents and according to the extent of their use, a decrease from 30 - 55 kg/t to 10 - 22 kg/t raw hide can be attained.

c) Recovery/recycling techniques (1, 6, 14)

In principle, these indirect systems are based on the precipitation of chrome containing effluents with alkalis. After settling, thickening and dewatering of the chrome oxide suspension, the filter cake is dissolved in sulphuric acid. After modifying the basicity, the basic chromium sulphate solution can be reused for tanning.

It is to be noted that recovery/recycling techniques differ in terms of the precipitating alkalis, flocculation temperatures, settling and dewatering conditions used as well as the manner of handling and reusing the filter cake.

With a well-managed effluents collection and processing system, a decrease in the amount of chrome discharged in tanning effluents from 2-5 kg/t to 0.1 - 0.25 kg/t raw hide can be observed.

E. Post-tanning (wet finishing)

This leather processing stage usually implies neutralisation, retanning, dyeing and fatliquoring. Effluent from conventional post-tanning fluctuates in the range 7 - 13 m³/t raw hide, including washing waters. Chrome, salts, dyestuff residues, fatliquoring agents, syntans, vegetable tannins and other organic matter, typically measured by COD, are the main pollutants. As for the chrome pollution generated in post-tanning operations, about 50 % of the chromium emanates from retanning, while 20 % is leached during dyeing and 30 % during fatliquoring (16).

Chrome in metal complex dyestuffs is a usual, but insignificant source of chrome in post-tanning effluents. Under normal conditions, a load of 0.03 - 0.05 kg Cr/t raw hide has been observed (6). A typical pollution load of effluents from post-tanning operations is given in Table 12.

Table 12 **Pollution load of effluents including washing waters from post-tanning operations**

Conventional process

Pollution	Load kg/t raw hide
SS	6 - 11
COD	24 - 40
BOD	8 - 15
Cr	1 - 2
NH ₃ -N	0.3 - 0.5
TKN	1 - 2
Cl ⁻	5 - 10
SO ₄ ²⁻	10 - 25

The implementation of advanced post-tanning methods is aimed at reducing the pollution load of chrome, sulphates, COD, SS and nitrogenous compounds. The chrome discharge in post-tanning operations can be higher when some chrome is used for retanning or fixing waterproofing agents. The following industrially proven approaches for reducing pollution load were considered.

a) High-exhaustion chrome tanning (6, 14, 17)

Chrome in leather tanned by a high-exhaustion method is sufficiently bonded and to a significant degree unleachable during post-tanning washing operations. As can be seen from the example presented in Table 11, chrome discharge in post-tanning floats can be decreased from 0.7 kg/t to 0.1 - 0.4 kg/t raw hide.

A decreased chrome offer in tanning associated with high-exhaustion methods (Table 11) contributes to a lower amount of sulphates discharged in post-tanning floats, especially when the pelt has been tanned after ammonia-free deliming and bating.

b) Chrome fixing in neutralisation (6, 17)

Special acrylic polymers with retanning effects are available for chrome fixing during the neutralisation stage. An example of chrome concentrations in post-tanning effluents is given in Table 13.

Table 13 **Chrome discharge in effluents from post-tanning with chrome fixing in neutralisation**

Operation	Chrome	
	mg/l	kg/t raw hide
Neutralisation, retanning	11	0.06
I. washing	14	0.10
Dyeing, fatliquoring	11	0.06
II. washing	7	0.05
Total	-	0.27

c) Chrome precipitation (6, 14)

Even when the chrome utilisation in tanning and post-tanning exceeds 95%, about 0.2 - 0.5 kg Cr/t raw hide is discharged in effluents and produces more than 1000 ppm of chrome in sludge dry matter. In order to reduce the chrome in sludge to 300 - 800 ppm (a range that is acceptable for landfilling and composting in some countries), it is essential first to collect washing waters from post-tanning operations and to precipitate them with alkalis, together with tanning effluents. Under these conditions, the total chrome load can be reduced to less than 0.15 kg/t raw hide, thus making a decrease in the chrome content in sludge to 300 - 800 ppm a realistic proposition.

d) Buffing dust and leather fibre separation (6, 14)

In order to minimise the total discharge of chrome in effluents, buffing dust should be collected and not discharged in effluent. Spent floats and washing waters from tanning and post-tanning operations have to be screened; leather fibres must be collected and not discharged in effluent. Separating the dust and fibres in an effective manner results in a decrease in the chrome load in effluent by 0.1 kg/t raw hide and contributes to reducing the SS load to 1 - 2 kg/t raw hide in tanning and post-tanning operations.

e) High-exhaustion retanning, dyeing and fatliquoring (6, 17, 18, 19)

A high COD level is typical for post-tanning effluents on account of the insufficient exhaustion of chemicals in post-tanning operations. Exhaustion can be increased in a number of ways:

- High temperature (60°C), short float (max. 100 %), low pH at the end of post-tanning (pH 3.5), long processing time and as low a dosage of chemicals as possible.
- Addition of amphoteric polymers improves the exhaustion of dyes and fatliquoring agents to a significant extent. A COD discharge of 24 - 40 kg/t can be reduced to 10 - 12 kg/t raw hide.

f) Replacing nitrogenous compounds (6, 18)

Compounds based on urea-formaldehyde or melamine-formaldehyde resins are often used in retanning. Ammonia facilitates the penetration of dyestuffs. The amino-resins can be replaced by other filling agents. Ammonia is superfluous as a penetrator when using acrylic polymers in neutralisation and retanning. In this way the NH₃-N load of 0.3 - 0.5 kg/t raw hide and TKN load of 1 - 2 kg/t raw hide can be decreased to 0.1 - 0.2 kg/t raw hide and 0.2 - 0.5 kg/t raw hide, respectively.

g) Phasing out environmentally hazardous compounds (1, 17, 18)

Modern technologies are based on procedures with chemicals characterised by new and more efficient effects in leather wet after-treatment. When implementing new pre-finishing technologies, it is necessary to avoid the utilisation of:

- Organic chemicals and preparations with high COD and BOD values
- Organic chemicals and preparations with limited biodegradability, for example alkylphenyl-ethoxylates as emulsifiers
- Fatliquoring agents based on chlorinated paraffins
- Benzidine and other azo-dyes which may be reduced to carcinogenic amines.

- Dyes containing risky heavy metals such as lead, cadmium and chrome VI

In most countries, a number of these chemicals have been blacklisted by the authorities,

F. Finishing

The finishing pollution load discharged in effluents is not significant in terms of influence on the total pollution load from tannery effluents. The pollution load can be summarised as follows:

SS	0 - 2 kg/t raw hide
COD	0 - 5 kg/t raw hide
BOD	0 - 2 kg/t raw hide

As for the composition of the pollution load, residues of polymer finishing dispersions and pigments are the main water pollutants which enter effluents via the water separator in the spraying machines (1, 18).

Minimising the pollution load during finishing is a matter of:

- Properly checking the spraying machines and their water separators
- Installing machines and equipment that permit more effective use of finishing chemicals and agents (roller coating machines, high-volume low-pressure sprayguns, curtain coating machines)
- Using pure water-based finishes
- Avoiding pigments containing environmentally hazardous heavy metals or other restricted products

Water consumption runs to 1 - 3 m³/t raw hide. Water used to scrub the exhaust air should be recycled.

G. Summary review of pollution load factors and their possible decrease

Typical pollution values related to a conventional tannery process provided by the IULTCS Environmental Commission (IUE) (20) together with pollution loads discharged in effluents from individual processing operations when utilising conventional or advanced technologies are summarised in Table 14.

Table 14 **Summary of pollution loads discharged in effluents from individual processing operations**
C - Conventional technology
A - Advanced technology

Operation	Technology	Pollution load kg/t raw hide								
		SS	COD	BOD	Cr	S ²⁻	NH ₃ -N	TKN	Cl ⁻	SO ₄ ²⁻
Soaking	C	11 - 17	22 - 33	7 - 11	-	-	0.1 - 0.2	1 - 2	85 - 113	1 - 2
	A	11 - 17	20 - 25	7 - 9	-	-	0.1 - 0.2	1 - 2	5 - 10	1 - 2
Liming	C	53 - 97	79 - 122	28 - 45	-	3.9 - 8.7	0.4 - 0.5	6 - 8	5 - 15	1 - 2
	A	14 - 26	46 - 65	16 - 24	-	0.4 - 0.7	0.1 - 0.2	3 - 4	1 - 2	1 - 2
Deliming, bating	C	8 - 12	13 - 20	5 - 9	-	0.1 - 0.3	2.6 - 3.9	3 - 5	2 - 4	10 - 26
	A	8 - 12	13 - 20	5 - 9	-	0 - 0.1	0.2 - 0.4	0.6 - 1.5	1 - 2	1 - 2
Tanning	C	5 - 10	7 - 11	2 - 4	2 - 5	-	0.6 - 0.9	0.6 - 0.9	40 - 60	30 - 55
	A	1 - 2	7 - 11	2 - 4	0.05 - 0.1	-	0.1 - 0.2	0.1 - 0.2	20 - 35	10 - 22
Post- tanning	C	6 - 11	24 - 40	8 - 15	1 - 2	-	0.3 - 0.5	1 - 2	5 - 10	10 - 25
	A	1 - 2	10 - 12	3 - 5	0.1 - 0.4	-	0.1 - 0.2	0.2 - 0.5	3 - 6	4 - 9
Finishing	C	0 - 2	0 - 5	0 - 2	-	-	-	-	-	-
	A	0 - 2	0	0	-	-	-	-	-	-
Total	C	83 - 149	145 - 231	50 - 86	3 - 7	4 - 9	4 - 6	12 - 18	137 - 202	52 - 110
	A	35 - 61	96 - 133	33 - 51	0.15 - 0.5	0.4 - 0.8	0.6 - 1.2	5 - 8	30 - 55	17 - 37

In the preceding chapters, industrially proven methods for decreasing pollution loads have been discussed. All the methods are performed as individual operations, but it is quite improbable that there is a tannery implementing all of them. That notwithstanding, several tanneries in the world come close to discharging pollution loads similar to those presented in Table 14.

As a better illustration, mean values of pollution loads discharged during the various operations when applying conventional (C) and/or advanced (A) technologies are compared in Figures 1-9.

Figure 1 Comparison of mean values of the suspended solids load

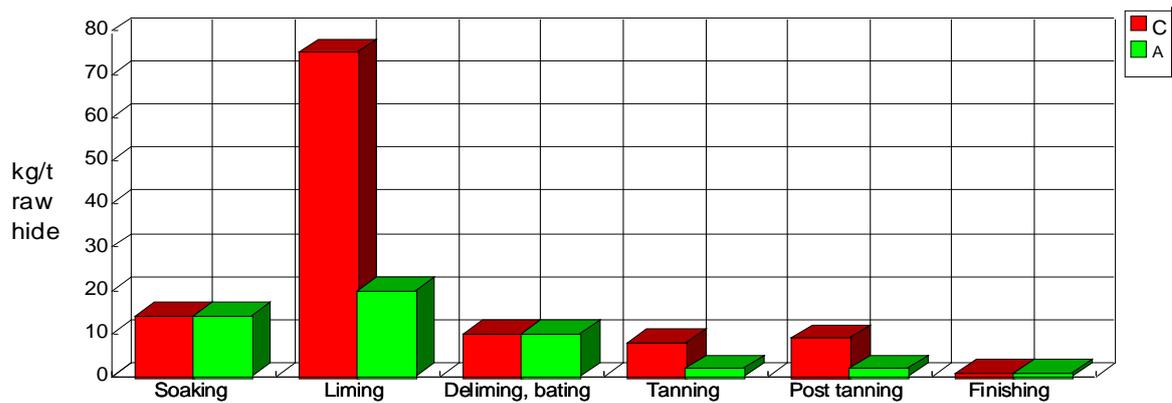


Figure 2 Comparison of mean values of the COD load

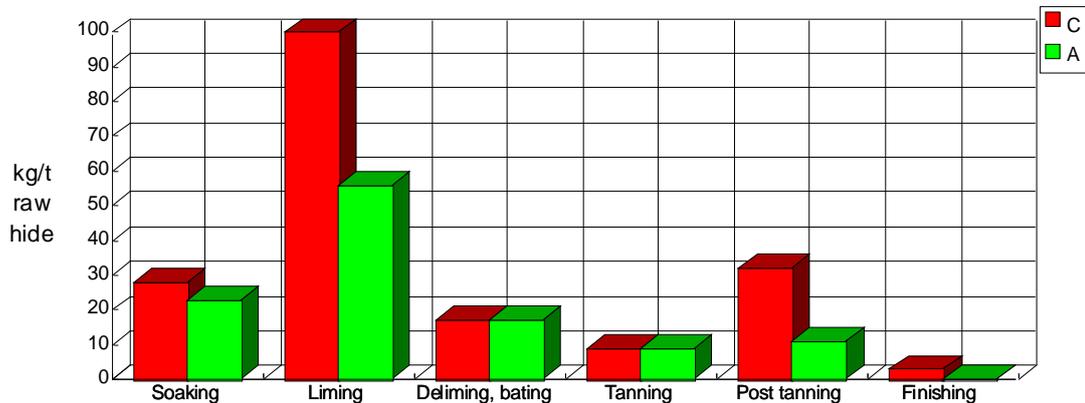


Figure 3 Comparison of mean values of the BOD load

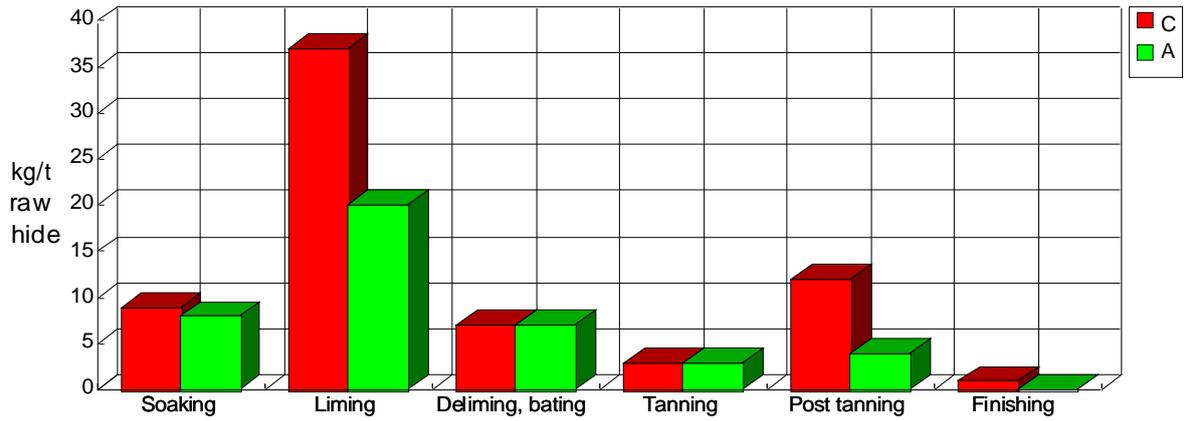


Figure 4 Comparison of mean values of the chrome load

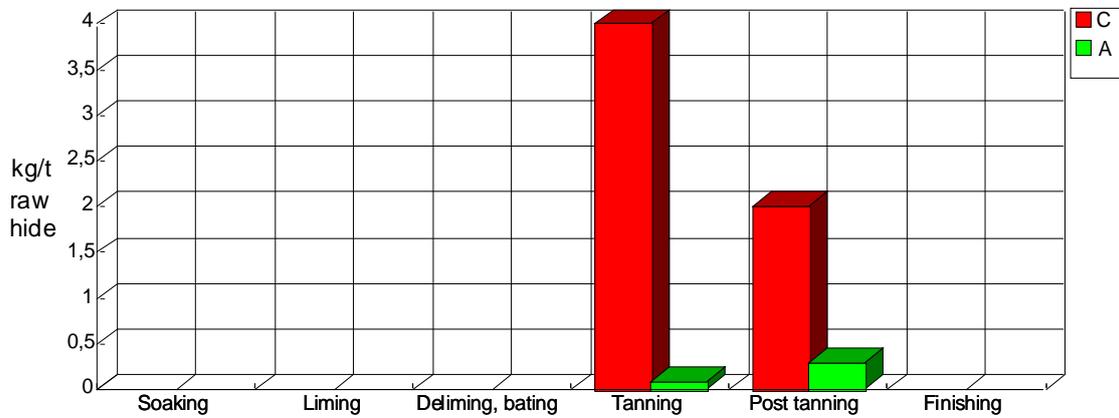


Figure 5 Comparison of mean values of the sulphide load

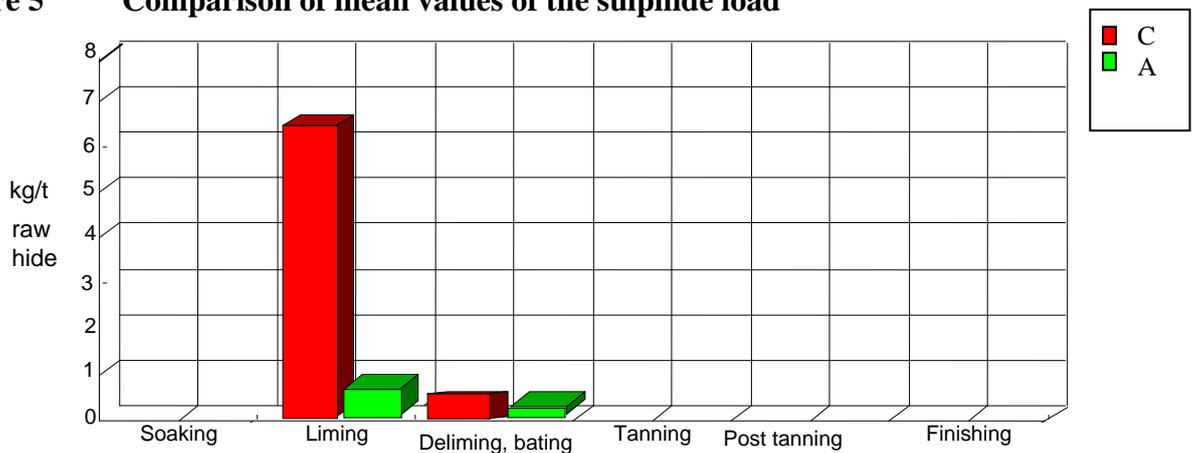


Figure 6 Comparison of mean values of the ammonium load

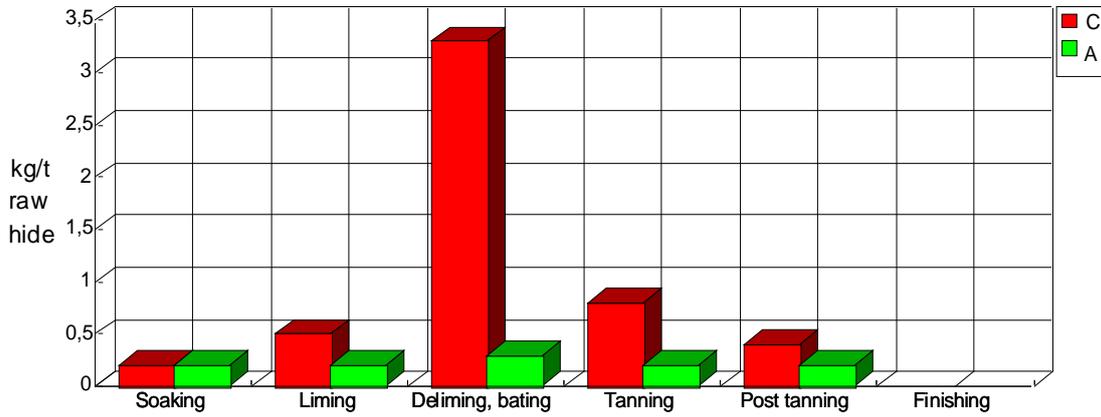


Figure 7 Comparison of mean values of the TKN load

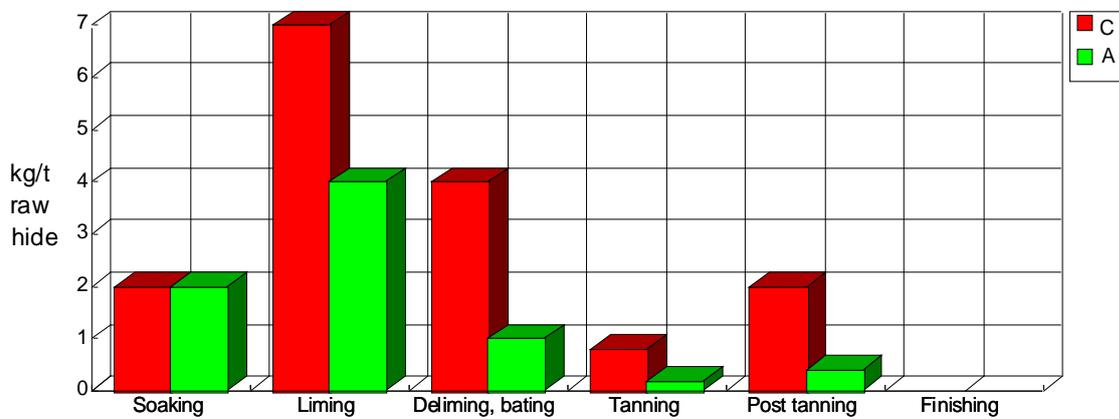


Figure 8 Comparison of mean values of the chloride load

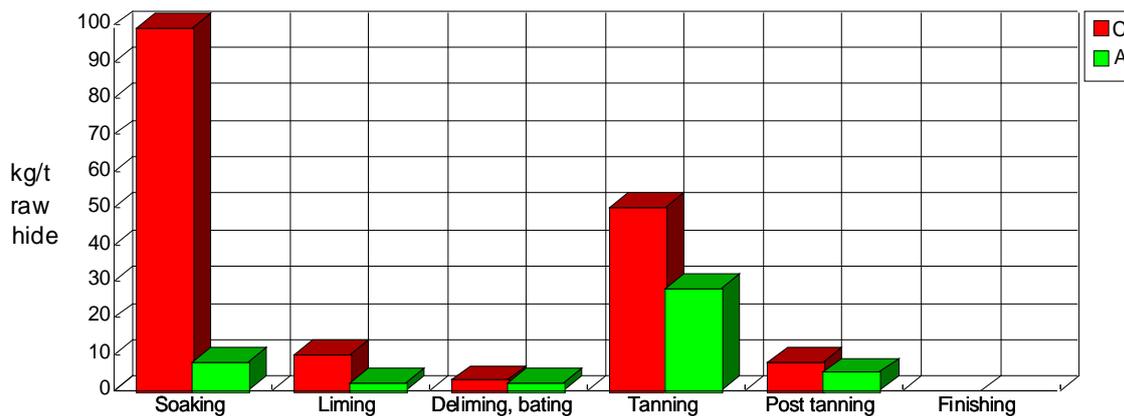
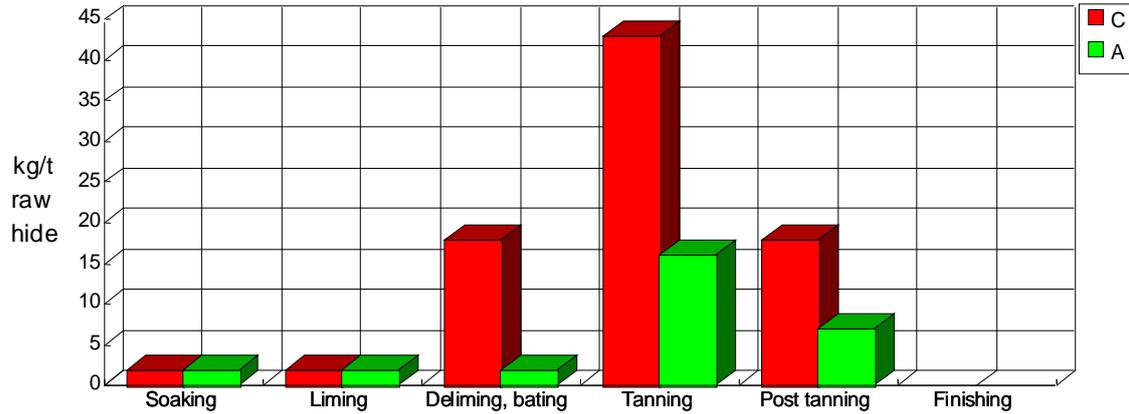
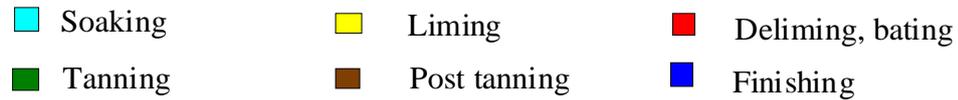


Figure 9 Comparison of mean values of the sulphate load

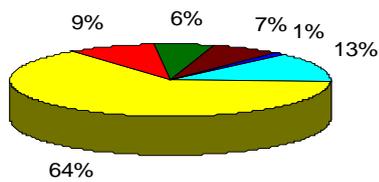


In terms of the shares of total load discharged, the significance of partial pollution loads when utilising conventional or advanced technologies is further demonstrated in Figures 10-18.

Figure 10 Share of the suspended solids load discharged from individual operations (%)



Conventional technology



Advanced technology

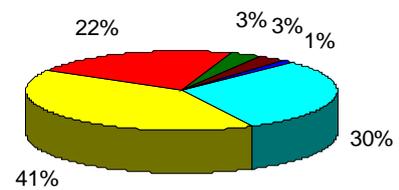
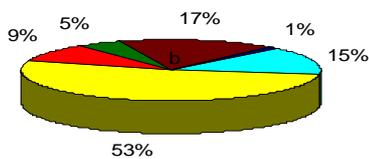


Figure 11 Share of the COD load discharged from individual operations (%)

Conventional technology



Advanced technology

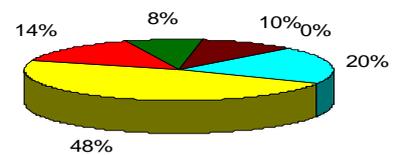


Figure 12 Share of the BOD load discharged from individual operations (%)

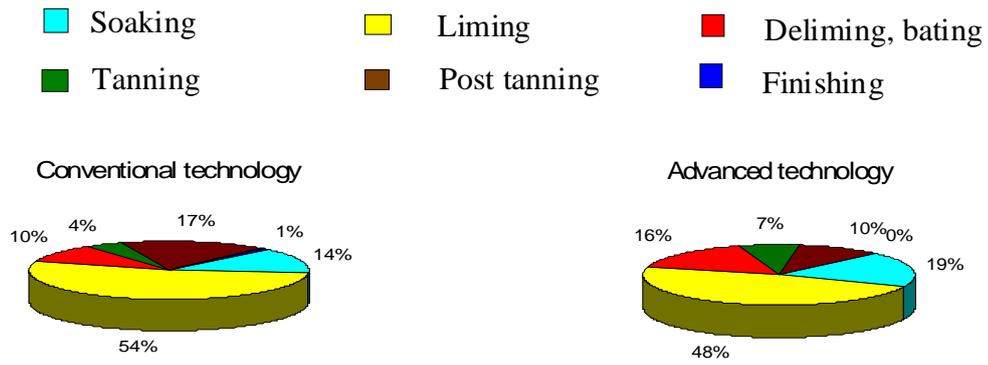


Figure 13 Share of the chrome load discharged from individual operations (%)

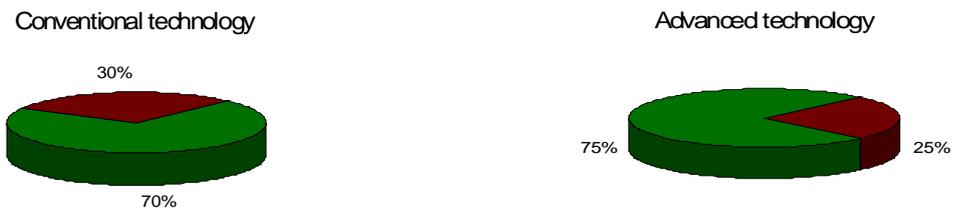


Figure 14 Share of the sulphide load discharged from individual operations (%)



Figure 15 Share of the ammonium N load discharged from individual operations (%)

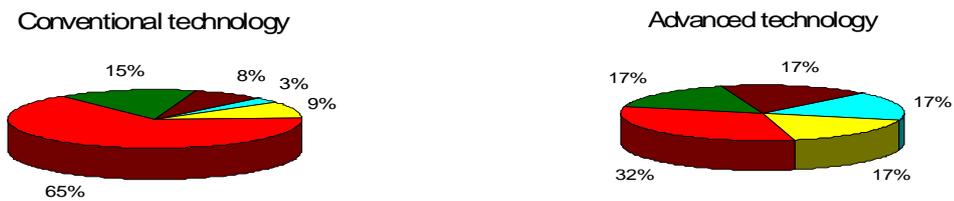


Figure 16 Share of the TKN load discharged from individual operations (%)



Figure 17 Share of the chloride load discharged from individual operations (%)

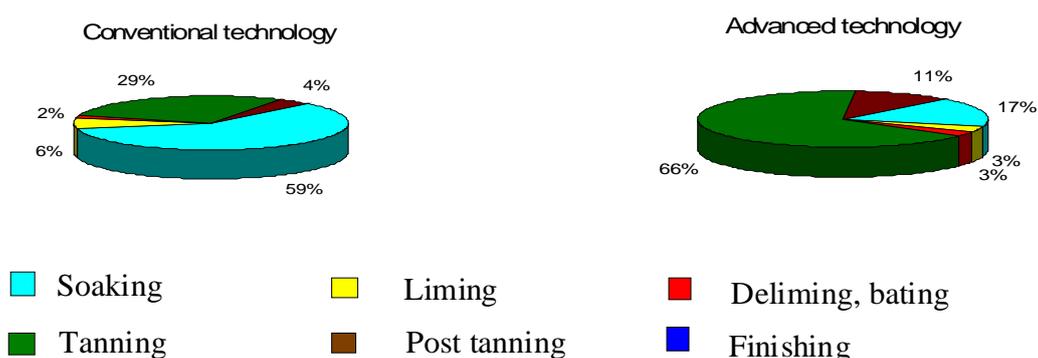
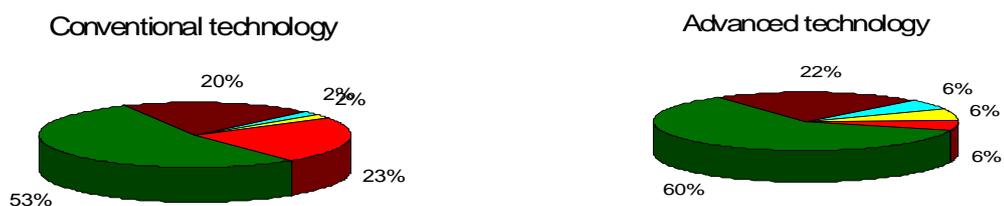


Figure 18 Share of the sulphate load discharged from individual operations (%)



With respect to Figures 10 – 18, it should be noted that:

- Liming operations are the main source of suspended solids (41 - 64%) in effluents. Beamhouse operations (including delimiting and bating) produce 86 - 93% of the total SS load in effluents.
- Liming operations are the main source of COD (48 - 53%) and BOD (48 - 54%) in effluents. Beamhouse operations produce 77 - 82% of the total COD and 77 - 83% of the total BOD load in effluents.
- 70 % of the total chrome load in effluents comes from tanning operations, 30% from post-tanning operations when processing leathers by means of conventional technology. After reducing the chrome load by means of advanced technology, the main amount of residual chrome comes from post-tanning (75%).
- Practically the sole source of the sulphides load is liming (95 - 97%). Sulphide residues of the order of 3 - 5% are discharged in delimiting and bating effluents.

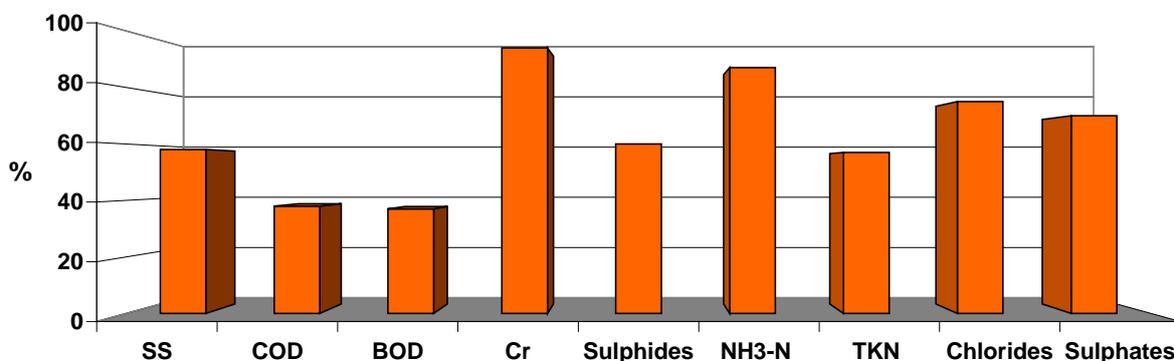
- The highest portion of NH₃-N pollution (65%) comes from conventional deliming and bating. Ammonia-free deliming and bating reduces the share of the NH₃-N discharge is reduced to 32%.
- As for the TKN load, the most significant amount (48 - 55%) is discharged from liming operations. Beamhouse operations produce 85 - 92% of the total TKN load in effluents.
- Soaking and tanning operations are the main source of chlorides (59%, and 29%, respectively) discharged in effluents under standard conditions. When processing unsalted hides, chloride pollution originates primarily from tanning and post-tanning (77%).
- Sulphates emanate primarily from tanning and post-tanning operations (73 - 82%). When performing ammonia-free deliming and bating (instead of ammonium sulphate deliming) reduces the sulphate load from deliming and bating from 23% to 6%.

On introducing advanced technologies, the following overall decreases in pollution loads in the mixed effluent stream are to be expected:

Suspended solids	by 58%
COD	by 38%
BOD	by 37%
Chrome	by 94%
Sulphides	by 60%
NH ₃ -N	by 87%
TKN	by 57%
Chlorides	by 75%
Sulphates	by 70%

The decrease in the individual pollution loads with regard to the values given in Table 14 when introducing advanced technologies is summarised in Figure 19.

Figure 19 Decrease in the pollution loads in effluent after introducing advanced technologies, %



Note: Catalytic oxidation of sulphide in beamhouse streams is actually on-site (pre)treatment rather than cleaner process; the same applies for chrome recovery without recycling/reuse.

Introducing advanced technologies goes hand in hand with reducing water consumption. The effluent volumes correspond to the level of water consumption in individual operations. The latter level depends on the type of vessels used in wet operations, the technical configuration of the vessels, the number of washing operations, the washing mode (continuous, batch) and

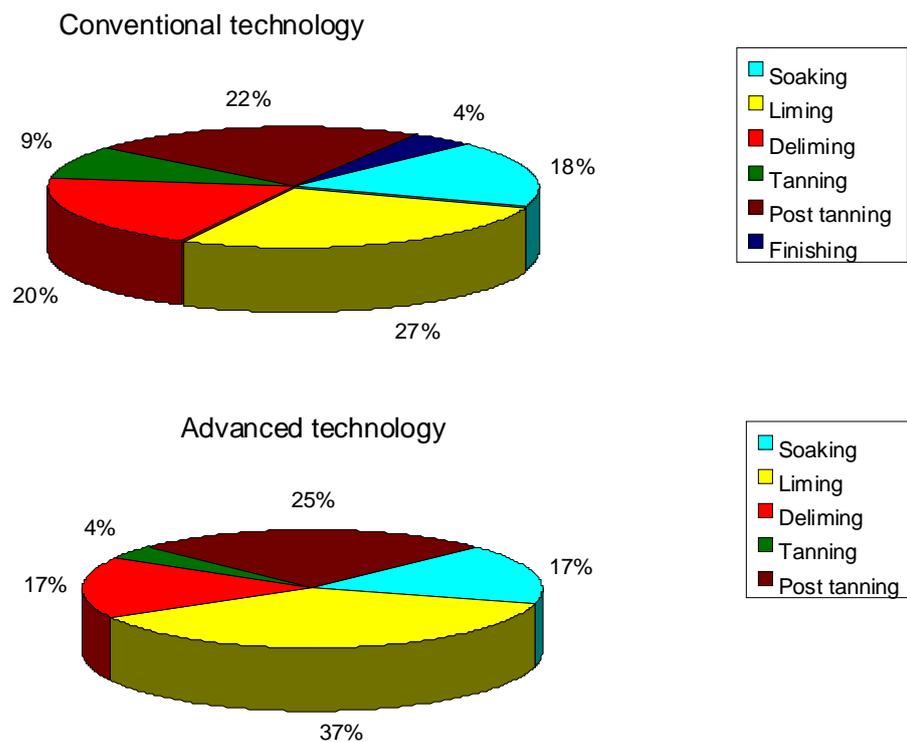
similar factors. Water consumption in individual processing operations, i.e. the amount of effluents discharged, is summarised in Table 15.

Table 15 Water consumption in individual processing operations
C - Conventional technology
A - Advanced technology

Operation	Discharge m ³ /t raw hide	
	C	A
Soaking	7 - 9	2.0
Liming	9 - 15	4.5
Deliming, bating	7 - 11	2.0
Tanning	3 - 5	0.5
Post-tanning	7 - 13	3.0
Finishing	1 - 3	0
Total	34 -56	12

In addition to the water required for individual processing operations, a certain amount of water is used in pasting/vacuum dryers, for cleaning, or sanitary and similar purposes. The minimum volume required is 2-3 m³/t raw hide under conditions of very good housekeeping. The share of individual processing operations in total consumption is shown in Figure 20.

Figure 20 Share of individual processing operations in total water consumption when applying conventional or advanced technology



With respect to Table 15 and Figure 20, it should be noted that:

62-70% of the total water discharge clearly comes from beamhouse operations, i.e. soaking, liming and unhairing, delimiting and bating.

Water consumption of 56 m³/t raw hide or more is uneconomical, and hence environmentally unfriendly. With less than 30 m³/t raw hide, the tannery operation can be considered relatively well managed, with good housekeeping.

Operating the tannery at a very low rate of water consumption, around 12 m³/t raw hide, presupposes the implementation of the best available advanced technologies coupled with excellent chemicals management and ideal housekeeping. However, the resultant effluent is highly concentrated and difficult to treat.

A decrease in water consumption is mainly achieved as follows (1):

- **Reducing:** Short float processing, batch-wise washing instead of rinsing and combining processes can reduce water consumption by 30% and more.
- **Recycling:** Soaking, liming, unhairing, pickling and chrome tanning liquors are examples of floats suitable for recycling, although in most cases pre-treatment equipment has to be installed. Overall water consumption can be reduced by 30 - 50%.
- **Reusing:** Up to 60% of the beamhouse and tanning process floats can be replaced by treated effluent.

At present, different methods of decreasing water consumption are practised in individual operations, but no tannery has succeeded in limiting total consumption to 12 m³/t raw hide. Several tanneries in Western Europe, however, come close to achieving this very low consumption.

H. Cost comparisons

The extent to which pollution loads are decreased is often linked to the pollutant concentrations/loads that tanneries are permitted to discharge in effluent. Invariably, tanners have to introduce clean technologies and other measures essential to the better utilisation of chemicals so that the corresponding regulations can be met. Tanners are interested in reasonable cost-effective technologies and other operational measures in leather processing, provided they do not lower the commercial value of the leather and its properties.

a) Soaking

Several industrially proven methods have been recommended for reducing the chloride load. All the methods are associated with short term preservation. Running costs of selected preservation methods, including conventional salting, shown in Table 16 have been compiled on the basis of British experience (21).

Table 16 Comparison of running costs of preservation methods
Application: 370 kg NaCl per 1 tonne green hide
370 kg ice per 1 tonne green hide
370 kg ice with 0,5% biocide per 1 tonne green hide

Method	Running costs US\$/t green hide
Conventional - salting	37.0
Advanced	
- chilling	3.7
- with ice	3.3
- with biocide ice	34.2

As for chilling, it must be borne in mind that hides can be kept in refrigerated storage space for a maximum of three weeks. Providing chilling facilities entails relatively high capital costs. When storing with ice, the maximum period of storage is only 2 - 3 days, depending on the ambient temperature. The investment costs associated with the acquisition of an ice-machine also have to be taken into account. If a suitable biocide is added, the effectiveness of ice-preservation method increases; the running costs, however, will be ten times higher.

b) Liming

Hair-save liming can be regarded as the most reliable way of decreasing the BOD, COD, TKN, SS and sulphide pollution load in effluent discharged from hide processing. Data obtained in one Scandinavian tannery processing bovine hides (22) have been used in a comparison of the costs associated with hair-save and hair-burn liming (see Table 17).

Table 17 Costs comparison of hair-save and hair-burn liming

Type of liming	Running costs US \$/t w/s hides
Hair burning - chemicals	42.0
Hair-saving - chemicals	66.4
- hair disposal	8.9
- total	75.3
Difference	33.3

The additional costs incurred in hair-save liming can be offset by savings in terms of effluent treatment costs. In a Scandinavian tannery, a decrease of 20 % of the BOD was observed in mixed tannery wastewater after introducing hair-save liming. Paying for the treatment of effluent in a communal plant incurred savings of US\$ 36.4 /t w/s hides, thus offsetting to the

full the additional costs of introducing hair-save liming. Tanners interested in introducing hair-save liming must take into account the capital costs required for circulating liquors and filtering equipment.

Other data from a tannery in Kenya processing dried skins (23) are available (see Table 18).

Table 18 Costs of chemicals in hair pulping and hair-save liming of skins

Type of liming	Costs US \$/1000 dried skins
Hair pulping - chemicals	79.3
Hair-saving - chemicals	97.2
Increase	17.9

Assuming 1000 dried skins = 500 kg and a water content in fresh skins of 64 % (green weight), the chemical costs may be recalculated as follows:

- Hair pulping US \$ 56.6/ t green weight
- Hair saving US \$ 69.4 /t green weight.

This calculation suggests that the order of chemical costs in hair-save liming of skins is similar to that of bovine hides. In each case hair-save liming is more expensive than conventional hair burning by about 23 - 58 %.

Hair-save liming of bovine hides is undergoing continuous development and modernisation. One feature of the latest technological modifications is a reduction in chemical costs, as demonstrated by a recent Czech and Danish modification (7, 24). In both cases, practically the same level of chemical costs has been quoted: 37 US \$/t w/s hide, for both hair-burning, and hair-saving processes.

c) Deliming

Two basic methods are applied to reduce the typical NH₃ pollution load discharged in effluent from deliming,: (a) deliming with ammonia-free commercial products and (b) carbon dioxide deliming.

Using a model, a chemical costs balance can be calculated for ammonia-free deliming based on a commercial product. The chemical costs of the procedure using an auxiliary based on esters of carboxylic acids in the amount of 1.5 % on pelt weight have been compared with those accruing in a conventional deliming procedure (2 % ammonium sulphate + 0.3 % formic acid). The outcome is as follows:

- Conventional deliming US \$ 6.0/t pelt weight
- Deliming with specialty chemicals US \$ 38.0/t pelt weight.

Ammonia-free deliming with commercial products may thus be more than six times as expensive. Using a model once more, a chemical costs balance can be calculated for carbon dioxide deliming. The procedure based on 0.2 % hydrogen peroxide, 1.5 % carbon

dioxide and 0.3 % ammonium sulphate is compared with the conventional delimiting procedure described above. The following figures can be obtained:

- Cost of conventional delimiting US \$6.0 /t pelt weight
- Cost of carbon dioxide delimiting US \$7.2 /t pelt weight

Based on Austrian and American experience (25), the running costs of carbon dioxide delimiting compared with those of ammonium sulphate delimiting have been evaluated. They are shown in Table 19.

Table 19 **Running costs of carbon dioxide and ammonium sulphate delimiting**
Conditions: Bull hides split to 4.5 mm, drum loading 7 tonnes

Cost item	Costs US \$ per 7 tonnes	
	(NH ₄) ₂ SO ₄ delimiting	CO ₂ delimiting
Chemicals	55.6	45.9
Water	5.3	3.5
Electric power for aeration	13.4	5.1
Sewer maintenance	6.6	4.4
Total	80.9	58.9

On relating the chemical costs in Table 19 to 1 tonne of pelt weight, it follows that:

- Cost of conventional delimiting US \$ 7.9/t pelt weight
- Cost of carbon dioxide delimiting US \$ 6.6/t pelt weight

It could be claimed that the chemical costs of both delimiting processes are similar. The figures quoted above substantiate the significantly lower electric power costs associated with aeration in a biological wastewater treatment plant owing to an appreciable decrease in the amount of ammonium salts in the effluent. They also show that this cleaner delimiting technology contributes to savings in running costs.

All the above cost comparisons have been based on prices prevailing in the European market. In addition, the capital cost requirements associated with carbon dioxide delimiting should not be overlooked. The equipment needed includes a storage tank with a vaporiser, piping to delimiting vessels, devices to regulate the flow of CO₂ and control the pressure. It is to be noted that gas suppliers lease storage tanks fitted with vaporisers and include the rental cost in the gas price. Prices for CO₂ may thus differ depending on the market.

d) Chrome tanning

In practice, three basic methods are used to reduce the chrome pollution load discharged in effluent: (i) high-exhaustion/high fixing chrome tanning; (ii) chrome recovery/reuse after precipitation and redissolving the chrome oxide hydrate; and (iii) direct chrome liquor recycling.

An example of the chemical costs ratio between two modifications of a high-exhaustion chrome tanning process and a conventional tanning is shown in Table 20.

Table 20 Chemicals costs of high-exhaustion tanning compared to conventional tanning (chrome offer 2.0% Cr₂O₃)

Modification A High-exhaustion procedure with self-basifying and organic masked chrome tannin

Modification B High-exhaustion/high fixing procedure with self-basifying/organic masked chrome tannin and glyoxylic acid in pickling

Operation	Chemicals costs USD/t pelt weight		
	Conventional tanning	High-exhaustion tanning	
		A	B
Pickling	14.2	11.1	46.7
Tanning	83.7	106.5	86.5
Total	97.9	117.6	133.2

It follows from Table 20 that the operational chemical costs will increase by 20 - 36 %, if the chrome load discharged in effluent has to be reduced significantly in order to meet specific legislative requirements. On the other hand, about 30 % of the chrome offer will be saved, once it is reduced from 2.0 % to 1.4 % Cr₂O₃.

As for the chrome recovery/reuse method, the technique used affects both capital and running costs. It is to be noted that, as a rule, a press filter is not needed to dewater the chrome oxide precipitated with MgO. For a daily chrome recovery capacity of 12 - 15 m³ of spent float, capital costs of the following order should be expected:

Chrome recovery with sodium alkali precipitation: US \$ 150,000 - 200,000
 Chrome recovery with magnesium oxide precipitation: US \$ 60,000 - 80,000

As regards the running costs, details of the annual operating costs of an Indian chrome recovery plant are available (26). Relevant data are summarised in Table 21.

Table 21 Annual operating costs of a chrome recovery plant.
Basic parameters: processing capacity 3,000 t/year, recovery capacity 9 m³/d of spent floats, precipitation with MgO, no mechanical dewatering.

Operating costs	US \$
Maintenance	1,500
Labour	1,000
Chemicals	9,000
Electricity	0,500
Miscellaneous	2,000
Total operating costs	14,000
Financial costs	7,800
Depreciation	5,200
Total annual costs	27,000

It is evident from Table 21 that chemicals (MgO, H₂SO₄) contribute significantly (60 %) to operating costs. Chemical costs are evidently higher when spent floats are precipitated with MgO. MgO costs about US \$ 1.0 /kg depending upon where it is produced, while sodium alkalis cost between US \$ 0.3 and 0.8/kg.

In addition, it follows from the data relating to the Indian chrome recovery plant that total annual costs associated with processed hides amount to US \$ 9 /t raw hides. In the majority of cases when mechanical dewatering of the chrome precipitate is applied, total annual costs related to 1 tonne of processed hides will be correspondingly higher.

Assuming a reasonable payback period of three years, a chrome recovery plant based on MgO precipitation without mechanical dewatering could be profitable at a capacity of 2.5 m³/day (27). The higher the recovery plant capacity, the better the profitability – or it should be. In general, however, cost-effectiveness depends on the efficiency of float collection and the chemical treatment of float, as well as on capital and running costs.

Choosing between chrome recovery/reuse and direct float recycling depends on the individual circumstances prevailing in the tannery. All recycling techniques have the following features in common:

- Lower capital costs
- No additional chemicals
- Lower running costs
- Excess float volume
- Lower efficiency of chrome reuse in practice

In general economic terms, in general, no explicit recommendation can be given as to the optimum method of reusing and saving chrome.

e) Post-tanning

Several commercial procedures involving high chrome fixing in neutralisation and high-exhaustion of post-tanning floats have been implemented. Reducing the chrome and COD/BOD pollution load discharged in effluent transpires to be a matter of higher chemical costs. By way of example, an advanced procedure based on chemicals offered by one reputable European supplier is compared to a conventional procedure with chemicals of the same supplier. The results are given in Table 22.

Table 22 Chemicals costs comparison of conventional and advanced post-tanning procedure with high chrome fixing/high floats exhaustion

Procedure	Chemical costs US \$/t shaved weight
Conventional	417
Advanced	569
Increase	152

Data in Table 22 demonstrate that the chemical costs associated with special chrome fixing in the neutralisation and high-exhaustion of retanning/ fatliquoring/dyeing floats are some 36% higher than in conventional procedures.

f) Finishing

The emission of volatile organic compounds (VOCs) is the main environmental issue associated with finishing. A minor problem arises in connection with liquid/solid waste emanating from spraying machines and the exhaust air scrubbers.

In order to control emissions into the air in the work place and to ambient air, mass emission levels for VOCs related to coated leather have been set by the EU. Mass emissions of VOCs should not exceed:

- 85 g/m² of coated leather for discharges of 10-25 kg VOCs/hour,
- 75 g/m² of coated leather for discharges of more than 25 kg VOCs/hour,
- 150 mg VOCs/m³ of air in all cases.

The most reliable means of estimating the solvent emission is to calculate it in terms of consumption. It should be borne in mind that the consumption comprises both the amount of solvents bought by the tannery and those contained in various finishing chemicals. Approximately 95% of the amount of solvents used is found in the exhaust air emanating from the finishing department. The amount remaining will evaporate from the leather at a later stage. Finishing systems fall into three groups:

- Solvent-based lacquers
- Water-borne lacquer emulsions
- Solvent-free, water-based systems

Solvent-based lacquers are used primarily as top lacquers and diluted with a solvent prior to application. At the point of application, these products can contain up to 90 % solvents. It thus follows that when using a spraying machine under standard operational conditions, it is practically impossible to reduce mass emissions of VOCs to a level below 85 g per m² of coated leather.

Water-borne emulsions contain a lacquer phase with the solvent acting as an oil-in-water emulsion. These emulsions contain up to 35 % solvents and are diluted with water prior to application. Water-borne lacquer emulsions are used as both top and intermediate coats. Owing to the lower solvent content, they help to reduce the emission of VOCs to a level below 85 g per m² of coated leather.

As a rule, aqueous finishing systems, for the most part based on acrylic and linear aliphatic polyurethane products, contain only 5 - 8 % solvents. The application of these finishing systems is essential to meeting the limits on the emission of VOCs into the air in work places. They are normally applied in base coats, but complete water-based finishing systems are offered by chemical suppliers for both base and top coats. However, the main constraint is the high degree of fastness required for some types of leather (automotive, upholstery).

The finishing chemical costs of three top coat procedures have been compared. The procedures are for standard finishing of upper leather as offered by reputable supplier of

chemicals, the difference being the application of solvents and/or water in top coat solutions. The base and intermediate coats are the same in all three procedures; they are based on diluted products. The results of the comparison are presented in Table 23.

Table 23 Chemicals costs of various top coats in standard finishing of upper leather
Coat amount 150 g/m²

Procedure S: Solvent-based lacquer
Procedure E: Water borne lacquer emulsion
Procedure W: Water-based top coat

Top coat	Chemicals US \$/m ²
Procedure S	
- total	0.55
- after subtracting solvents	0.34
Procedure E	0.37
Procedure W	0.51

The results in Table 23 demonstrate quite clearly that solvents used in the top coat lacquer (procedure S) are rather expensive and have a significant bearing on chemical costs. From this point of view, the chemical costs associated with the water-based top coat appear relatively favourable. Nowadays, for most types of leather mass emissions of VOCs can be reduced to the permissible level by applying a water-based finishing system.

Apart from switching over to low-solvent or solvent-free finishing processes, solvent emissions can be reduced by improving the methods for applying the finish. Installing high-volume, low-pressure sprayguns in the spray cabinet ensures that overspray will be reduced from around 40 % to 25 - 30 %. Substantial savings in terms of finishing products and solvents are achieved by using a forward or reverse roller coating machine. Wastage is only 5 - 15 % as against about 40 % with conventional spraying. Energy savings are an added benefit. However, roller coating is normally used in combination with spraying.

Savings in terms of finishing products and solvents are of primary importance tannery economics. The levels of organic solvent consumption and evaporation (in the case of the spraying and roller coating application) have been calculated according to (6). Two representative solvents used in leather finishing, butylacetate and isopropanol, have been taken into account. These solvents cost approximately:

Butylacetate US \$ 2.0/kg
Isopropanol US \$ 1.0/kg

The costs of solvents used in leather finishing and afterwards evaporated relative to 1 tonne of raw hides are given in Table 24.

Table 24 Costs of solvents used in leather finishing

Finishing products system	Solvents used			
	Spraying		Roller coating	
	kg/t raw hides	US \$/t raw hides	kg/t raw hides	US \$/t raw hides
Solvent-based	25	25-50	9	9-18
Water-based	5.4	5.4-10.8	3.2	3.2-6.4

The figures in Table 24 underscore the importance of decreasing solvent consumption and the need to lower operational costs by switching to low-solvent/solvent-free finishing systems and using improved methods for applying the finish.

III. CONCLUSIONS

Conventional leather processing produces a high effluent load. Industrially proven technologies for decreasing the pollution load are available. They permit the more efficient use of sewage systems and ensure more economic wastewater treatment. The decrease in pollution load is achieved by introducing advanced low-waste technologies which can be summarised as follows:

1. Soaking

The main pollutant discharged in soaking some effluents is chloride (85 - 113 kg/t raw hide). Shaking the salt off in special drums, can decrease the amount by 8%. Processing hides with lower amounts of the salt combined with an acceptable antiseptic can reduce the load by one half. Processing green hides helps to decrease the chloride load in soaking effluent to 5 - 10 kg/t raw hide.

2. Liming

The main pollutants discharged in liming effluents are SS, COD, BOD, sulphides and TKN. A pollution load decrease can be achieved by introducing spent float recycling and hair-save liming.

Suspended solids are normally discharged in the order 53 - 97 kg/t raw hide. Reduction to 14 - 26 kg/t is possible. Organic pollution measured in terms of COD/BOD is discharged in the order of 79 - 122 kg/t raw hide, and 28 - 45 kg/t raw hide, respectively. The pollution load can be decreased to 46 - 65 kg/t and 16 - 24 kg/t respectively. Sulphide discharge amounts to 3.9 - 8.7 kg/t raw hide; it can be decreased to 3 - 4 kg/t. When measured in terms of TKN, the pollution discharged is in the order of 6 - 8 kg/t raw hide; it can be decreased to 3 - 4 kg/t.

3. Deliming and bating

In ammonium sulphate deliming, the main pollutants discharged in effluents are $\text{NH}_3\text{-N}$ and sulphates. $\text{NH}_3\text{-N}$ is produced in the order of 2.6-3.9 kg/t raw hide, sulphates 10 - 26 kg/t raw hide. The pollution load can be decreased to 0.2 - 0.4 kg/t of $\text{NH}_3\text{-N}$ and 1 - 2 kg/t of sulphates by introducing ammonia-free deliming and bating methods.

4. Chrome tanning

Chrome, chloride, sulphate and suspended solids constitute the main pollutants discharged from pickling and tanning operations. The pollution load can be decreased by introducing chrome tanning methods with high-exhaustion and fixing, methods based on direct recycle/reuse and recovery recycling techniques, screening of spent floats and washing waters.

The amount of chrome pollution which ranges between 2 - 5 kg/t raw hide can be decreased to 0.05 - 0.1 kg/t. The chloride pollution discharged is in the order of 40 - 60 kg/t raw hide; decrease to 20 - 35 kg/t is possible. Sulphate pollution discharged is in the order of 30 - 55 kg/t raw hide; the pollution load can be decreased to 10 - 22 kg/t. The suspended solids (SS) pollution discharged is in the order of 5 - 10 kg/t raw hide. The SS load is made up of buffing dust and leather fibres which contribute to the high chrome load discharged in effluents. It is possible to reduce this load to 1 - 2 kg/t raw hide.

5. Post-tanning

Various organic materials (24 -40 kg COD/t raw hide), neutral salts as chlorides (5 - 10 kg/t raw hide) and sulphates (10 - 25 kg/t raw hide), chrome (1 - 2 kg/t raw hide) and suspended solids (6 - 11 kg/t raw hide) are the main pollutants discharged in post-tanning effluents. The following advanced methods have been industrially proven and implemented: chrome tanning with high-exhaustion and fixing, chrome fixing in neutralisation, precipitation of spent floats containing chrome, high-exhaustion retanning, dyeing and fatliquoring and replacing nitrogen compounds. By introducing these advanced methods, the pollution load can be reduced in the case of chrome to 0.1 - 0.4 kg/t, chlorides 3 - 6 kg/t, sulphates 4-9 kg/t, suspended solids 1 - 2 kg/t and COD 10 -12 kg/t raw hide.

6. Finishing

Minimising the pollution load discharged in finishing effluents is a matter of properly checking the operation of the spraying machines and water separators, installing new spraying and coating machines that ensure more effective utilisation of finishing chemicals, using water-based finishes, etc.

7. Total pollution load decrease

By introducing industrially proven low-waste advanced methods, the total pollution load discharged in effluents can be reduced in a well managed tannery in the following amounts: SS by 58%, COD by 38%, BOD by 37%, sulphides by 90%, NH₃-N by 87%, TKN by 57%, chlorides by 75% and sulphates by 67%. Even though the chrome pollution load can be decreased by 94% on introducing advanced technologies, the minimum residual load 0.15 kg/t raw hide can still cause difficulties when using landfills and composting sludge from wastewater treatment on account of the regulations currently in force in some countries. The amount of effluents produced can be decreased from 34 - 56 m³/t raw hide to 12 m³/t.

The degree to which pollution load needs to be decreased depends on the concentrations of pollutants that can be legally discharged in effluent. The tanner has to implement cleaner technologies and adopt other additional mandatory measures that ensure the more effective utilisation of chemicals so that ultimately the respective regulations are observed.

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