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

THE SCOPE FOR DECREASING THE POLLUTION LOAD IN LEATHER PROCESSING

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I. INTRODUCTION

Processing hides and skins to convert them into leathers has long been an important industrial activity. The potential environmental impact of the processing has been regarded as an inevitable consequence of such activity.

Various technical methods for solving problems of the negative impact of hide processing on the environment 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 with conventional ones. Their characteristic consists mainly of decreasing the effluent pollution load, not using harmful chemicals and producing solid wastes which are utilizable as byproducts. To the second group belong wastewater treatment and environment-friendly solid waste handling and processing (2,3). Methods of both groups should be employed to prevent a negative impact of leather production on the environment.

This study is primarily focused on the pollution load discharged in effluents and the possibilities for its decrease. The aim is that tanners in selected South-East Asian countries, in addition to knowing how to produce and sell high quality leather, must also be familiar with techniques to decrease the pollution load discharged in effluents from individual processing operations and thus with preventing the unfavourable environmental impact of the leather production.

The possible decrease will be calculated for the case of a well managed tannery processing bovine hides into chrome tanned leathers. A pollution load reduction achieved by the introduction of advanced technologies based on low waste processing methods and demonstrated in the industrial scale will be taken into account. Industrially unproven and only experimental methods are not considered.

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

A. Soaking

Salt preserved hides are commonly used in conventional processing. The amount of soaking effluent discharged varies from 7 m^3/t up to 9 m^3/t raw hide, i.e. calculated on the basis of wet salted weight. For soaking dry hides, up to 20 m^3 water/t dried hide is required. The effluent pollution is formed mainly by salt, hide surface impurities, dirt and globular protein substances dissolved in water and salt solution. Typical pollution load of soaking effluents is presented in Table 1.

Table I
Pollution load of soaking effluents
Conventional processing

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

The main aim is to reduce the chloride load because salt is not eliminated in the course of physical, chemical and biological treatment of waste water. Several industrially proven methods have been recommended for reducing the chloride load:

- Shaking off the salt in special drums (1)

The load amount is decreased by approximately 8 %, i.e. 78 -104 kg Cl^-/t raw hide.

The removed salt is too dirty for direct use in the pickle liquors. Systems have been developed for salt recovery by heating to 400 °C but they are not being used in any tannery as yet.

- Preserving hides with a decreased amount of the salt combined with an admixture of some environmentally acceptable antiseptics (boric compounds, acetic acid, sodium sulphite, etc.) or commercial bactericides chemically based mainly on ethyldithiocarbamate and isothiazolin (1, 4). The load amount can be reduced by approximately one half, i.e. 43 - 57 kg Cl^-/t raw hide. However, the preservation efficiency would decrease.

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

The chloride content in soaking effluents would be theoretically eliminated; in practice a small amount of salt is often added when soaking non-salted hides 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 practice the organic load (COD, BOD) is influenced in the processing of unsalted hides (Table 2).

Table 2
Pollution load of soaking effluents of differently preserved hides

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

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

An advanced technology that could be applied at this stage is fleshing after washing the hides in the abattoir or after presoaking in the tannery (1, 6). It yields a lower quantity of fleshings at neutral pH, fleshings that are not contaminated with chemicals and create better conditions for protein and fat removal. Further fleshing before liming saves chemicals and can improve leather quality.

B. Liming

The processing of soaked hides in a bath containing sodium sulphide/hydrosulphide and lime is a basis of conventional unhairing and liming methods. The amount of liming effluents inclusive of washing waters discharged fluctuates in the range 9 - 15 m^3/t raw hide. Sulphides, lime, decomposition products of hair keratin, globular proteins and other non-collagen protein substances, saponified fraction of native fat etc. constitute the loading of liming effluents that are the most polluted wastewater streams. A standard pollution load of liming effluents is presented in Table 3:

Table 3
Pollution load of liming effluents inclusive of washing waters
Conventional processing

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

The implementation of advanced unhairing and liming methods is mainly aimed at reducing the pollution load of suspended solids, sulphides, COD, BOD and nitrogenous materials. A range of methods, industrially proven, has been taken into consideration for reducing the pollution load:

a) Recycling spent floats (1, 6)

Several recycling methods have been used in practice after being adapted to production conditions. A system of recycling individual spent floats from unhairing (without hair saving) and liming has been successfully tested. The unhairing spent float has been recycled for the second soak and the liming spent float for lime liquor in successive steps. A consequent decrease of the pollution load has been evaluated after 10 cycles of liming float and 20 cycles of unhairing float:

S^{2-} 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)
This recycling system has also been tested on a BOD and COD decrease (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 the recycling of 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 unhairing and opening up processes are used in two steps. According to local conditions the recycling systems also enable a decrease of the high level of water consumption in liming operations.

b) Hair-save liming (1, 6, 7)

Hair-save liming methods may be based on a controlled immunization of hair cystine. Sulphides destroy only non-immunized hair follicles while hair is released into the bath. The process requires a vessel equipped with an external circulation and filtration system thus enabling the hair removal 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

A hair-save system based on immunization with lime, unhairing with sulphides in immunization bath, continuous hair filtration and reliming in a residue of the immunization bath after adding fresh water has been tested at two levels of sulphide consumption (Table 6).

Comparison of conventional and hair-save liming

Na_2S 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 obvious that hair-save liming achieves a significant decrease in pollution load as follows:

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

A sulphide offer of 1.3% on salted weight has been proven in practice as a sufficient and reliable consumption in view of the pelt quality.

The hair-save system described above was evaluated in industrial practice (7) (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 from 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)

The enzymatic treatment can be considered as a cleaner technology only if no sulphide 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, an addition of sulphide or hydrosulphide is necessary.

d) Lime splitting (1, 6)

Splitting limed hides can be also considered as a cleaner technology since it saves chromium. Standard offer will be 15 - 18 kg Cr_2O_3 /t raw hide as opposed to 21 - 24 kg Cr_2O_3/t raw hide by lime non-splitting. Lime splitting yields waste that can be easily utilized as a by-product.

C. Deliming and bating

Pelt processing in a bath containing salts of a strong acid and a weak alkali (mainly ammonium salts), and proteolytic enzymes is the basis of conventional deliming and bating methods. The amount of deliming and bating effluents inclusive of washing waters fluctuates in the range 7 - 11 m^3/t raw hide. Calcium salts, mainly sulphates, residues of sulphides, degradation products of proteins (those of collagen and hair), remains of proteolytic enzymes agents etc. form the pollution load of deliming and bating effluents. A standard pollution load of these effluents is given in Table 8.

Table 8
Pollution load of deliming and bating effluents inclusive of washing waters
Conventional processing 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
NH_3-N	2.6 - 3.9
TKN	3 - 5
Cl^-	2 - 4
SO_4^{2-}	10 - 26

The implementation of advanced deliming and bating methods is aimed at reducing the pollution load of NH_3-N and SO_4^{2-} (in the case of ammonium sulphate deliming).

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 of ammonia-free deliming split pelt on the NH_3-N pollution load.

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

No.	Technology	NH_3-N	
		mg/l	kg/t raw hide
1	C AF	2210 43	2.65 0.052
2	C AF	2170 85	2.60 0.10
3	C AF	2210 104	2.65 0.12
4	C AF	2528 28	3.03 0.034
5	C AF	2100 30	2.52 0.036
Average	C AF	2243 58	2.69 0.070

The above figures show that ammonia-free deliming and bating has led to the 97% decrease of the NH_3-N load in effluents discharged from this processing operation.

When the pelt thickness is higher than 3.0 mm, mainly in the case of unsplit pelt, it may be necessary to add a small amount of ammonia salt for better deliming and bating within the allowed time limit.

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

Carbon dioxide neutralizes the lime and solubilizes the calcium salts in an over-saturated bath. Regarding the pH stabilization in the range from 6.5 to 7.0, acidic swelling cannot occur. In practice, a small amount of ammonia salts, e.g. up to 0.4% of ammonium sulphate per pelt weight, might have to be added when pelt thickness is higher than 3 mm or of non-split pelt. Hydrogen peroxide can be used before CO_2 insertion in order to eliminate the creation of H_2S.

In practice the decreased pollution load of effluents from ammonia-free deliming and bating is characterized as follows:

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 implies pickling, tanning and basifying. The amount of chrome tanning effluents inclusive of washing waters and sammying water fluctuates in the range 3 - 5 m^3/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 inclusive of washing waters
Conventional processing

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

The implementation of advanced chrome tanning methods is aimed first of all at reducing the pollution load of chrome. A range of industrially proven methods has been taken into account for reducing the chrome content in effluents discharged.*

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

The method is characterized by the following features:

- The use of considerably shorter floats (20 - 30% referred to pelt weight)
- The use of a higher temperature (40 - 42°C or higher), a prolongation of the tanning time, a higher pH value (4.0 - 4.7).
- The use of special self-basifying and masked chrome tanning agents.

An effect of chrome discharge decrease and chrome utilization increase when introducing the tanning with high exhaustion and fixing is apparent from Table 11.

Table 11
Comparison of chrome discharge and utilization 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
Utilization %	70	95 - 98

* *As this study is focused on producers of chrome tanned leathers, chrome-free tanning is not presented in this case as a solution to limit chrome discharge in effluents.*

The example in Table 11 shows that chrome tanning with high exhaustion and fixing enables:

- a decrease in the necessary chrome offer 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,
- an increase in the chrome utilization in tanning operations from 70% to 98%.

Additionally, there is a decrease in sulphate load from 30 - 55 kg/t to 17 - 36 kg/t raw hide which can be regarded as relevant.

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

Direct recycling systems can be classified as closed and open. Closed systems are based mostly on reusing only spent tanning floats and sammying water for tanning in successive cycles. They are utilized 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, however; in practice it depends upon establishing an equilibrium in the composition of recycled floats. Several recycling techniques of open systems are employed industrially:

- Reuse of separated pickling and tanning floats in successive cycles.
- Reuse of tanning float in the next cycle of pickling.
- Reuse of the mixture of tanning float and sammying water partly in pretanning, partly in tanning in the next cycle. The pretanning float is discharged daily.
- Reuse of the spent tanning float in the next cycle of tanning and the sammying water for the pickling float that is daily discharged.

Recycling techniques are mostly used in conventional tanning. According to the extent of their introduction, an increase in chrome utilization 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 maximum and minimum values respectively.

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

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

These indirect systems are based in principle on the precipitation of chrome containing effluents with alkalies. 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.

Note that recovery/recycle techniques differ in the kinds of precipitating alkalies, temperature of the flocculation, settling and dewatering conditions used as well as in the way of handling and reusing the filter cake.

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

E. Post tanning

This leather processing stage usually implies neutralization, retanning, dyeing and fat-liquoring. Effluent coming from the conventional post tanning fluctuates in the range 7 - 13 m^3/t raw hide inclusive of washing waters. Chrome, salts, residues of dyestuffs, fatliquoring agents, syntans, vegetable tannins and other organic matters measured by COD are the main pollutants. Concerning the chrome pollution generated in post tanning operations, about 50 % of the chromium is leached during retanning, 20 % during dyeing and 30 % during fatliquoring (16).

Chrome in metal complex dyestuffs is a usual but not significant 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 inclusive of washing waters from post tanning operations
Conventional processing

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 fixation of waterproofing agents. The following industrially proven approaches have been taken into consideration for reducing the pollution load.

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

Chrome in leather tanned by a high exhaustion method is sufficiently bonded and is not leachable to a significant degree during washing operations in post tanning. As it is obvious from the example in Table 11, the 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 with a high exhaustion method (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 neutralization (6, 17)

Special acrylic polymers with retanning effects are available for chrome fixing in the neutralization operation. 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 neutralization

Operation	Chrome	
	mg/l	kg/t raw hide
Neutralization, 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)

It has been shown in practice, even when the chrome utilization in tanning and post tanning is higher than 95%, 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. To reduce the chrome in sludge to 300 - 800 ppm (a range that is acceptable for landfilling and composting in some European countries), it is essential first of all to collect washing waters from post tanning operations and to precipitate with alkalies together with tanning effluents. In that case it is possible to decrease the total chrome load below 0.15 kg/t raw hide. Thus an estimate of decreasing the chrome content in sludge to 300 - 800 ppm is realistic.

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

To minimize 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 collected and not discharged in effluent. Well separated dust and fibres enable a decrease of the chrome load in effluent by 0.1 kg/t raw hide and contribute 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 due to 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.
- The addition of amphoteric polymers improves the exhaustion of dyes and fatliquoring agents in 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 used in retanning. Ammonia serves as a penetrator for dyestuffs. The amino-resins can be substituted with other filling agents. Ammonia as a penetrator is superfluous when using acrylic polymers in neutralization and retanning. In this way the NH_3-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 characterized by new and more efficient effects in the leather wet aftertreatment. When implementing new prefinishing technologies, it is necessary to avoid the utilization of:

- organic chemicals and preparations with extra high COD and BOD values,
- organic chemicals and preparations with a limited biodegradability, e.g. 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.

A number of these chemicals have been blacklisted by authorities in some countries.

F. Finishing

The finishing pollution load discharged in effluents is not significant from the point of view of an influence on the total pollution load from tannery effluents. The pollution load can be summarized as follows:

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

With regard to the composition of the pollution load, residues of polymer finishing dispersions and pigments are the main water pollutants which get into effluents from the water separator of spraying machines (1, 18).

Minimizing of the finishing pollution load is a matter of:

- proper control of spraying machine operation and their water separators,
- installation of new machines and equipment enabling a higher utilization of finishing chemicals and agents (roller coating machines, low-pressure spraying pistols, curtain coating machines),
- use of water based finishes,
- avoiding pigments containing environmentally risky heavy metals or other restricted products.

Water consumption represents an amount of 1 - 3 m^3/t raw hide. Water used for scrubbing the exhaust air should be recycled.

G. Summary of pollution load and possibilities for its decrease

Typical pollution values related to a conventional tannery process have been presented in the recommendation of I.U.L.T.C.S. Environmental Commission (IUE) (20). Pollution loads discharged in effluents from individual processing operations when utilizing conventional or advanced technologies are summarized 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

Methods industrially proven for decreasing the pollution loads have been discussed in preceding paragraphs. All the methods are individually practised but combinations are not used in any actual tannery. However, there are several tanneries in Scandinavia, which come near to discharging pollution loads similar to those presented in Table 14.

Mean values of pollution loads discharged from individual operations when applying conventional (C) and/or advanced (A) technology are compared for a better illustration in Figures 1-9.

Figure 1
Comparison of mean values of the suspended solids load

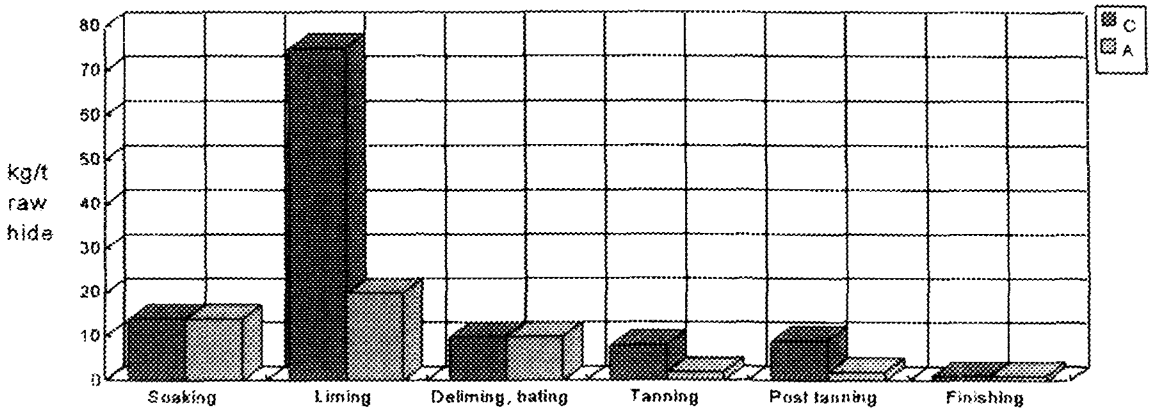


Figure 2
Comparison of mean values of the COD load

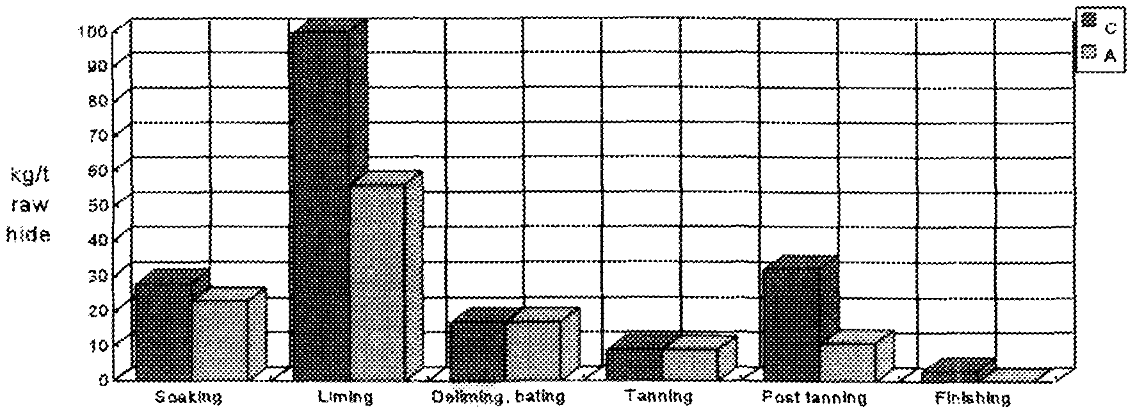


Figure 3
Comparison of mean values of the BOD load

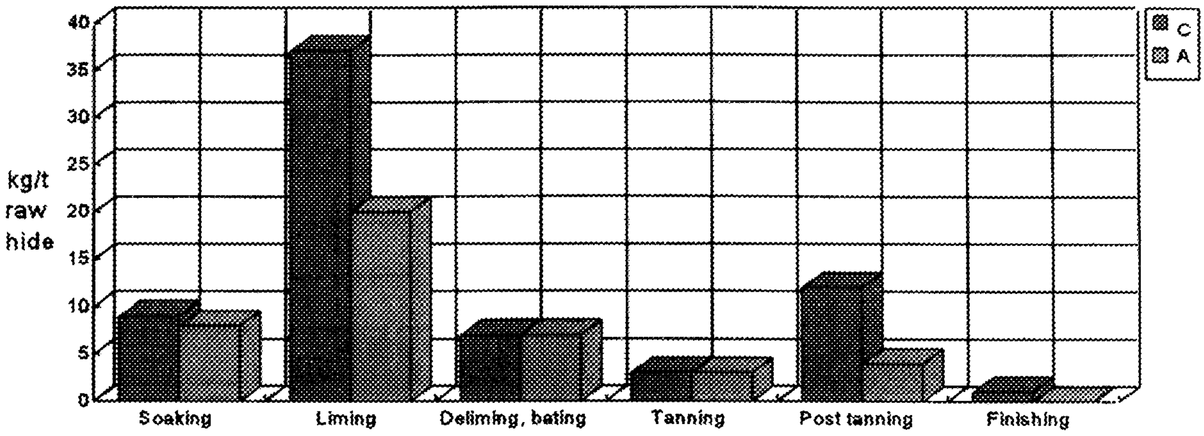


Figure 4
Comparison of mean values of the chrome load

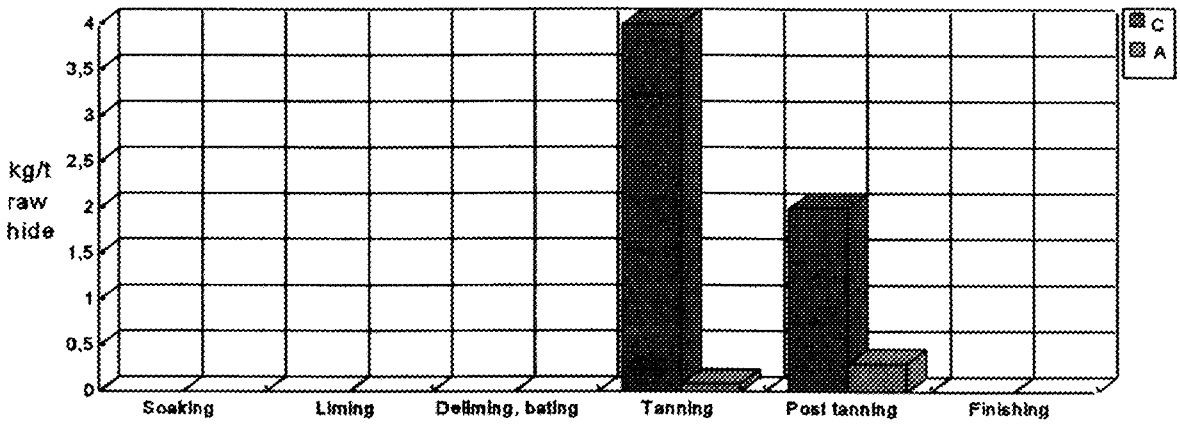


Figure 5
Comparison of mean values of the sulphide load

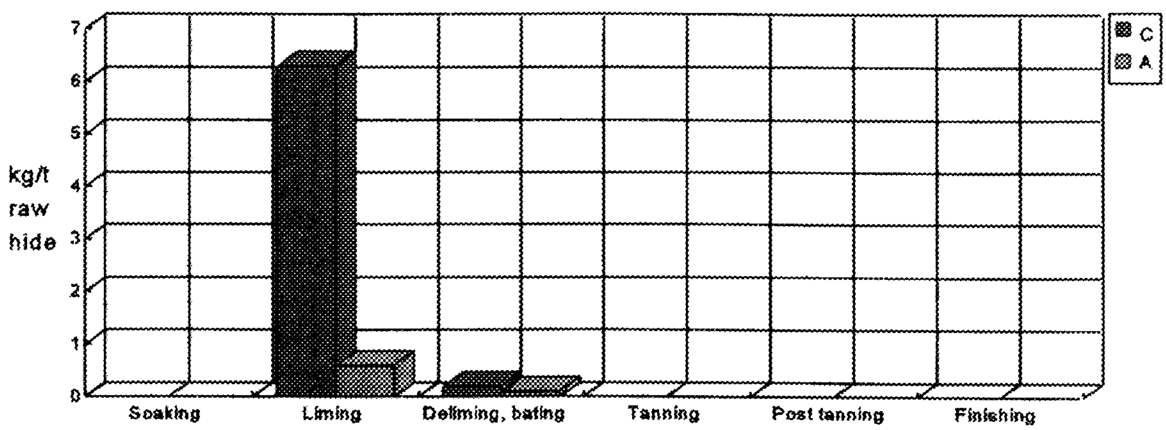


Figure 6
Comparison of mean values of the ammonium load

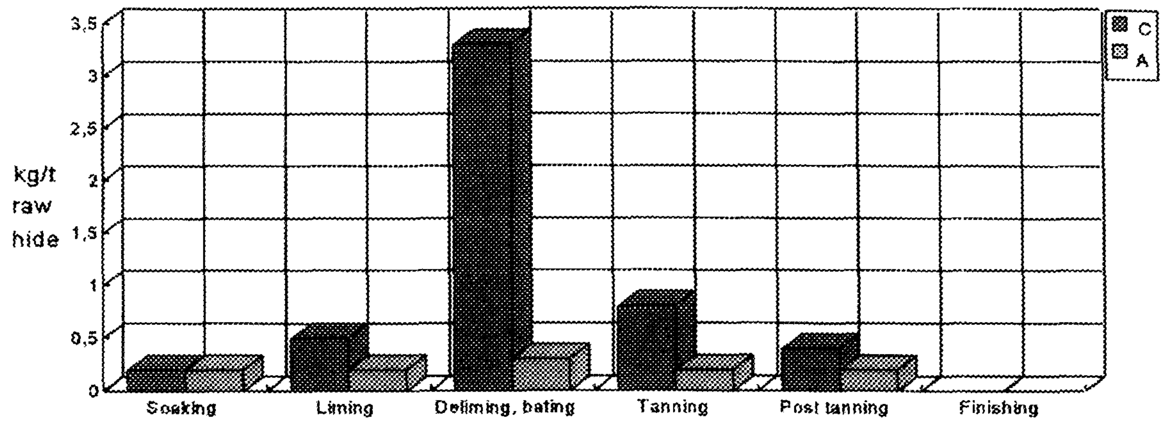


Figure 7
Comparison of mean values of the TKN load

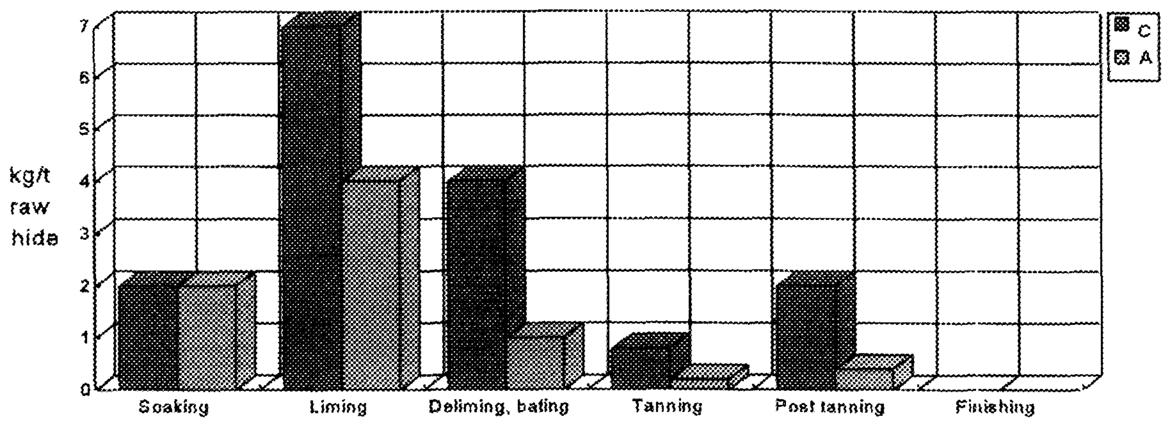


Figure 8
Comparison of mean values of the chloride load

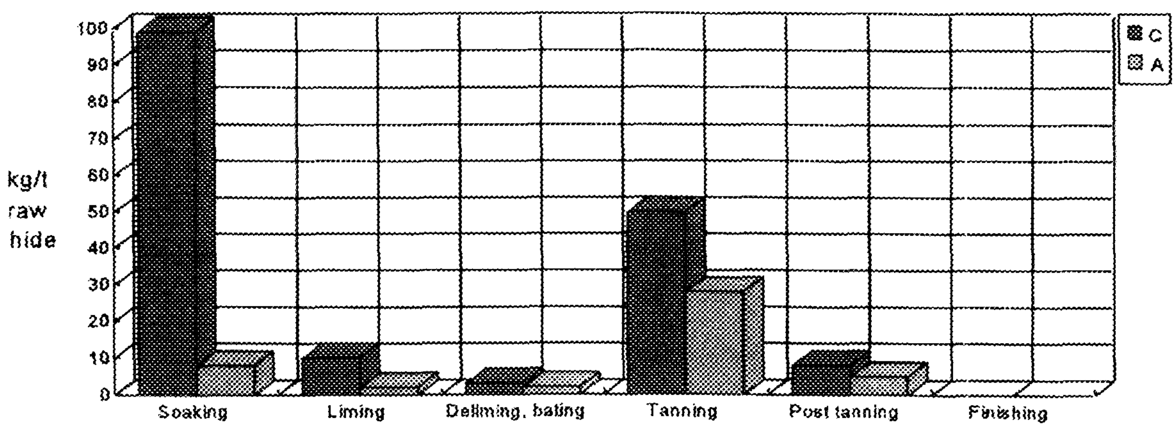
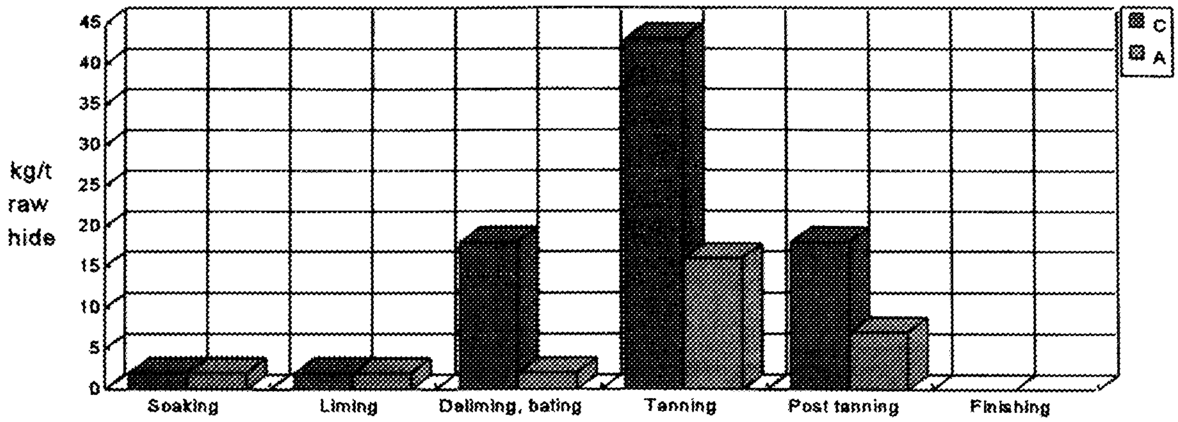


Figure 9
Comparison of mean values of the sulphate load



From the point of view of a share of the total load discharged, the significance of partial pollution loads when utilizing conventional or advanced technologies is further demonstrated in Figures 10-18.

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

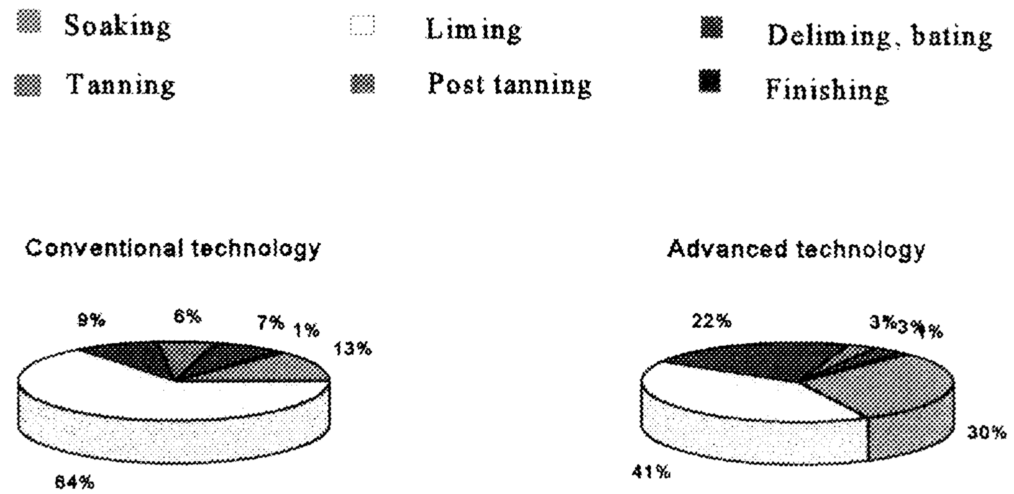


Figure 11
Share of the COD load discharged from individual operations (%)

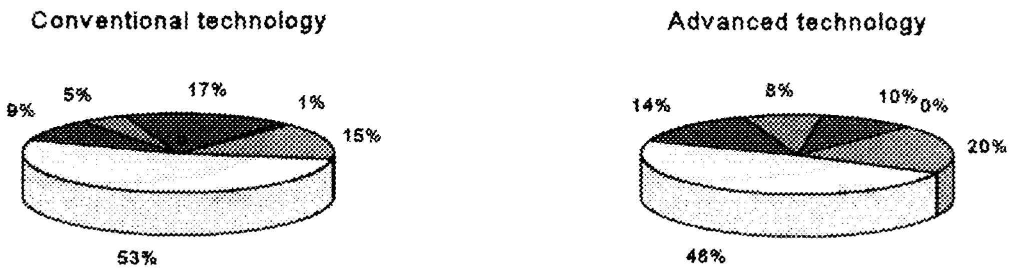


Figure 12
Share of the BOD load discharged from individual operations (%)

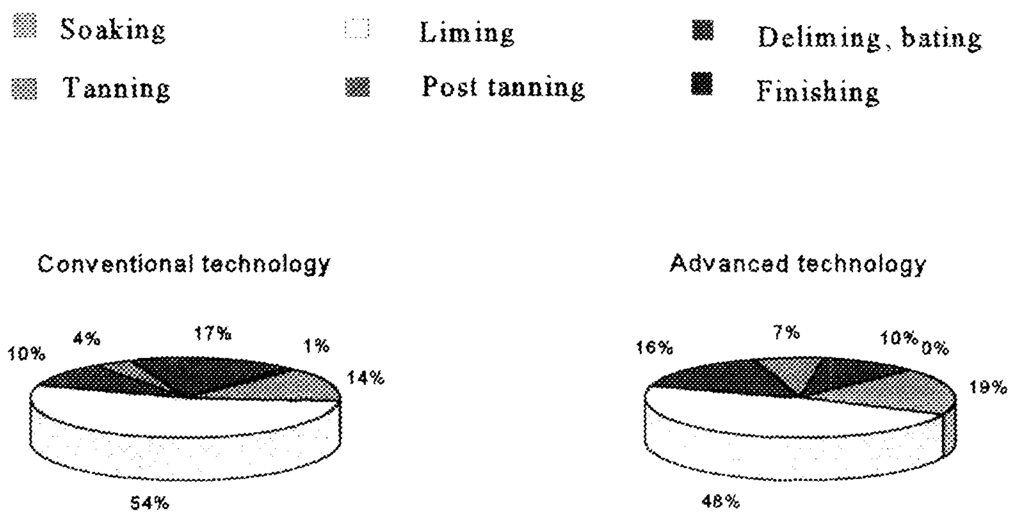


Figure 13
Share of the chrome load discharged from individual operations (%)

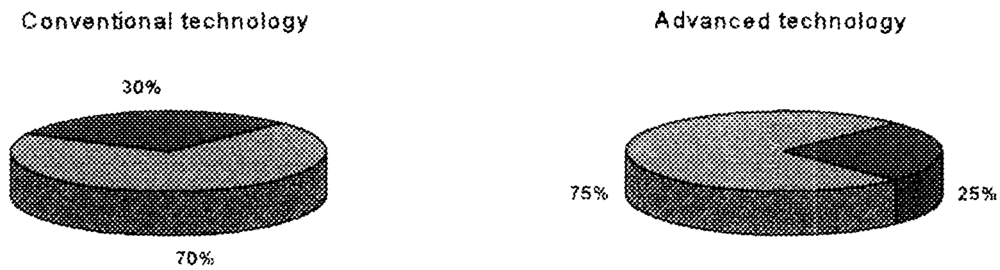


Figure 14
Share of the sulphide load discharged from individual operations (%)

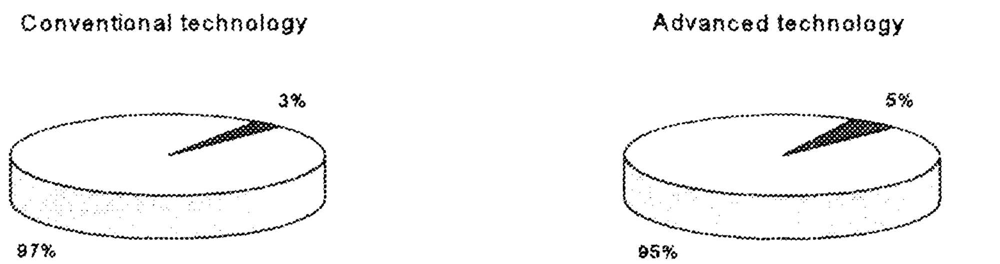


Figure 15
Share of the ammonium N load discharged from individual operations (%)

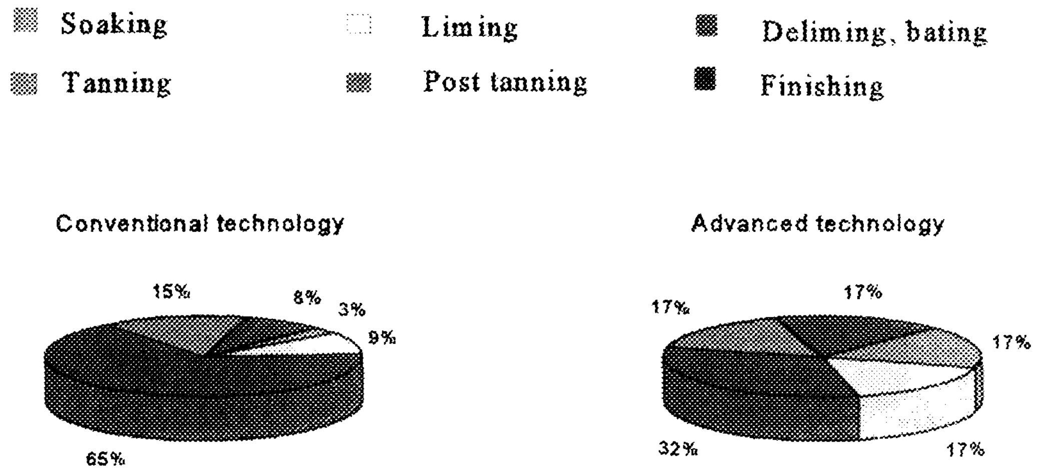


Figure 16
Share of the TKN load discharged from individual operations (%)

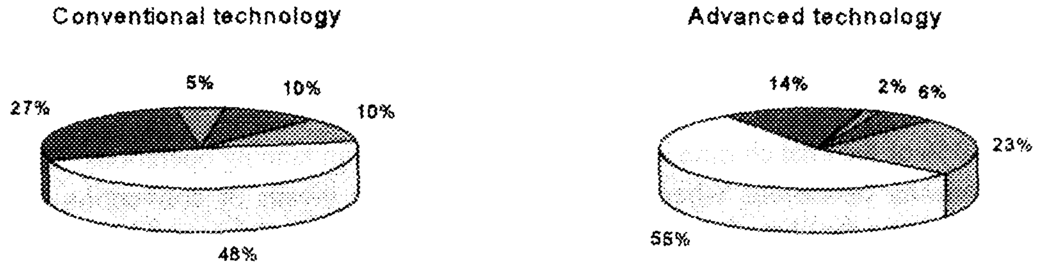


Figure 17
Share of the chloride load discharged from individual operations (%)

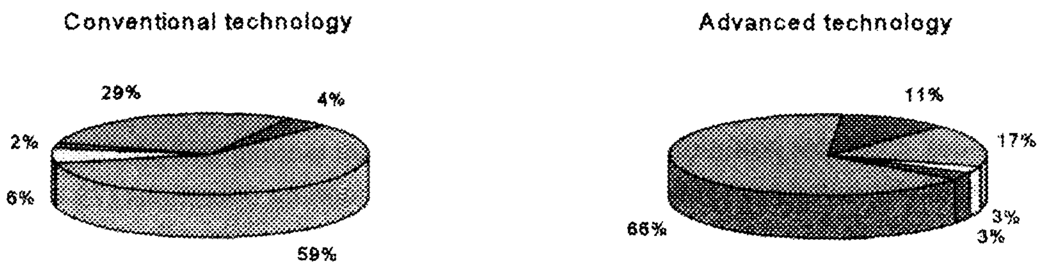
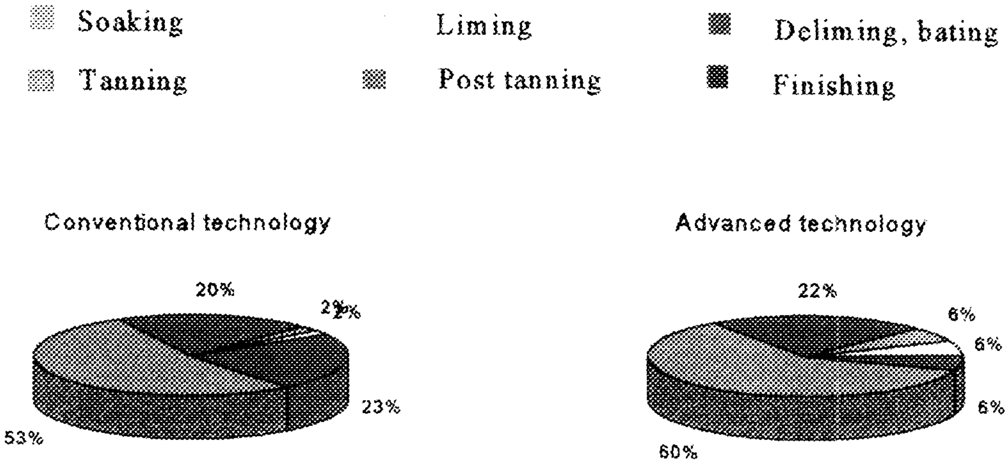


Figure 18
Share of the sulphate load discharged from individual operations (%)

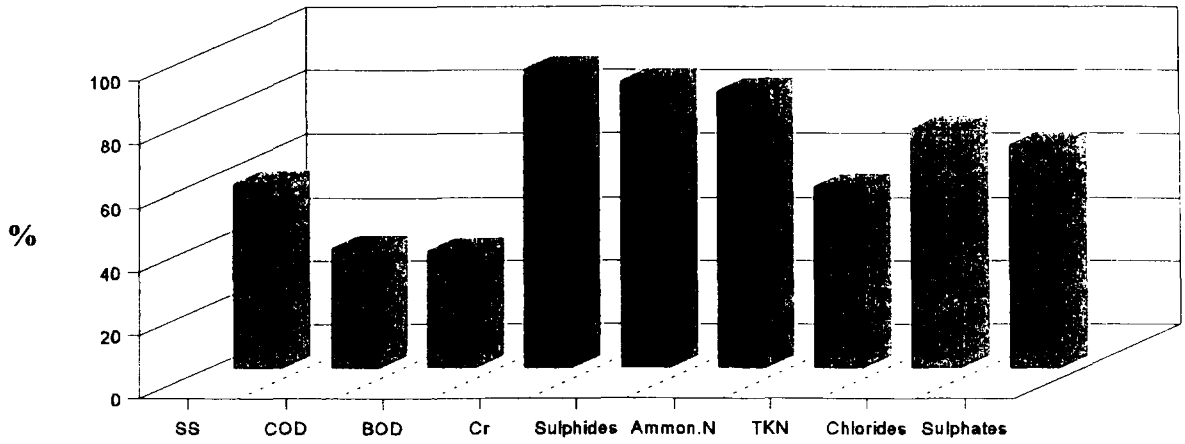


Several remarks can be made about Figures 10 - 18:

- Liming operations are the main source of suspended solids (41 - 64%) in effluents. Beamhouse operations (inclusive of deliming 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. Reducing the chrome load by means of advanced technology, residual chrome amount comes mainly from post tanning (75%).
- From the point of view of the sulphides load, practically the only source is in liming operations (95 - 97%). Residues of sulphides 3 - 5% are discharged in deliming and bating effluents.
- The highest portion of NH_3-N pollution (65%) comes from conventional deliming and bating. When performing ammonia-free deliming and bating, the share of the NH_3-N discharge is reduced to 32%.
- Concerning the TKN load, the most important portion (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 sources of chlorides (59%, and 29% respectively) discharged in effluents under standard conditions. When processing unsalted hides, chlorides pollution originates primarily from tanning and post tanning (77%).
- Sulphates come primarily from tanning and post tanning operations (73 - 82%). When performing ammonia-free deliming and bating in the place of ammonium sulphate deliming, the sulphate load in deliming and bating is changed (23%, and 6% respectively).

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

Figure 19
Comparison of decrease of the pollution loads discharged in effluent after introducing advanced technologies



The following decrease in pollution loads in the mixed effluent stream is to be expected after advanced technologies have been implemented:

- Suspended solids by 58%
- COD " 38%
- BOD " 37%
- Chrome " 94%
- Sulphides " 90%
- NH_3-N " 87%
- TKN " 57%
- Chlorides " 75%
- Sulphates " 70%

The pollution load decrease is connected with reducing the effluent volume discharged. The effluent volumes correspond to a level of water consumption in individual operations. This level depends on the type of vessels employed in wet operations, the technical equipment of vessels, the number of washing operations, the way of washing (continuous, batch) etc. The implementation of advanced technologies goes hand in hand with reducing water consumption.

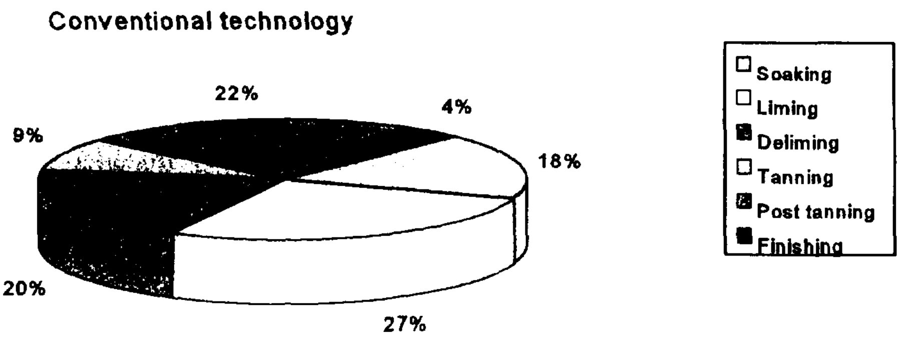
The water consumption in individual processing operations, i.e. the amount of effluents discharged, is summarized in Table 15.

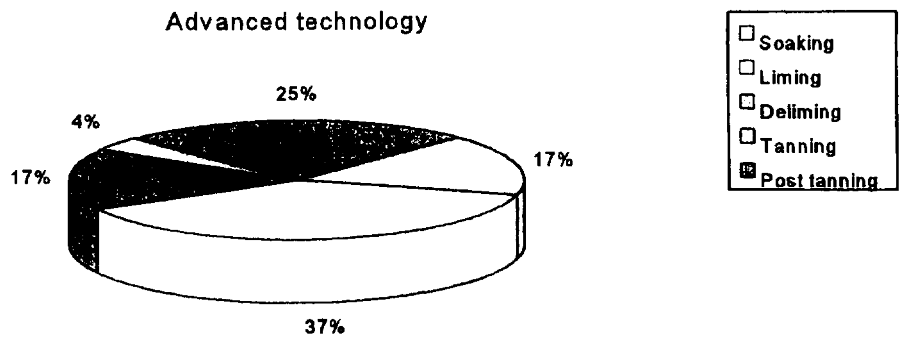
Table 15
Water consumption in individual processing operations
C - conventional technology
A - advanced technology

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

Additional to water needed for individual processing operations, a certain amount of water is used in pasting/vacuum driers, for cleaning, sanitary purposes etc. This water amounts to minimum 2-3 m^3/t raw hide in case of very good housekeeping. The share of the water consumption in individual processing operations on the total water consumption is apparent from the Figure 20.

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





Several remarks can be added to Table 15 and Figure 20:

It is clear that 62-70% of the total water discharge comes from the beamhouse operations, i.e. soaking, liming and unhairing, deliming and bating.

When operating the tannery at a water consumption of 56 m^3/t raw hide and more, the operation has to be uneconomical and consequently not environmentally friendly. When consuming less than 30 m^3/t raw hide, the tannery operation can be considered relatively well managed with good housekeeping.

Operating the tannery at a very low water consumption of around 12 m^3/t raw hide, presupposes the implementation of best available advanced technologies with excellent chemicals management and ideal housekeeping.

The main ways of decreasing the water consumption can be summarized 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 installations for pretreatment are necessary. The overall water consumption can be reduced by 30 - 50%.
- Reusing: There is an opportunity of replacing up to 60% of the beamhouse and tanning process floats by treated effluent.

At the present time, single methods of decreasing water consumption are practised in individual operations but no tannery operates within the total consumption of 12 m^3/t raw hide. However, there are several tanneries in Western Europe which come near to achieving this very low consumption.

H. Cost comparisons

The extent of a pollution load decrease depends on pollutant concentrations allowed to be discharged in effluent. The tanner has to proceed to the implementation of cleaner technologies and additional necessary measures leading to better utilization of chemicals so that corresponding regulations can be met. The tanner is interested in reasonable cost-effective technologies and 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 are compiled on the basis of British experience (21) in Table 16.

Table 16
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 - with ice - with biocide ice	 3.7 3.3 34.2

As far as chilling is concerned, one has to bear in mind that hides can be kept in refrigerated storage space for a maximum of three weeks. Relatively high capital cost is needed to provide a chilling device. In the case of preservation with ice, the storage duration is only 2 - 3 days and depends on the ambient temperature. One has to take into account the capital cost of the ice machine too. After adding a suitable biocide, preservation with ice becomes more effective but running costs 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) are applied to a costs comparison of hair save and hair burn liming (see Table 17).

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

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

Surplus costs of hair-save liming can be offset by savings in payment for effluent treatment in a communal treatment plant. In a Scandinavian tannery a decrease of 20 % of the BOD was observed in mixed tannery wastewater after introducing hair-save liming in operation. A saving of 36.4 US $/t w/s hides was calculated for payment for the treatment of effluent. Surplus costs of hair-save liming were thereby fully offset. The tanner, who is interested in introducing hair-save liming, has to take into account some capital cost necessary for circulating liquors and filtering equipment.

Other data from a tannery in Kenya processing dried skins (23) are available (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 Hair-saving - chemicals	 79.3 97.2
Increase	17.9

Assuming 1000 dried skins = 500 kg and a water content of 64 % in fresh skins (green weight), one may recalculate chemical costs in the following way:

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

This calculation suggests that the level of chemical costs in hair-save liming of soaked skins will be similar to 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 has been continuously developed and updated. One feature of new technological modifications is a reduction of chemical costs. A new Czech and Danish modification can be exemplified (7, 24). In both cases, practically the same level of chemical costs has been quoted, namely 37 US $/t w/s hide, both for hair burning, and hair saving.

c) Deliming

Two basic methods are applied to reducing the typical NH_3 pollution load discharged in effluent from deliming, namely ammonia-free deliming with commercial products and carbon dioxide deliming.

A chemical costs balance can be done for the model of ammonia-free deliming with a commercial product. Chemical costs of the procedure with an auxiliary based on esters of carboxylic acids and used in practice at 1.5 % on pelt weight have been compared with those of the conventional deliming procedure (2 % ammonium sulphate + 0.3 % formic acid) as follows:

- Conventional deliming 6.0 US $/t pelt weight
- Advanced deliming 38.0 US $/t pelt weight.

The result is that ammonia-free deliming with commercial products may be more than six times as expensive.

Another chemical costs balance can be done for a model of carbon dioxide deliming. The procedure with 0.2 % hydrogen peroxide, 1.5 % carbon dioxide and 0.3 % amonium sulphate has been compared with the conventional deliming as described above. One can obtain these figures:

- Conventional deliming 6.0 US $/t pelt weight
- Carbon dioxide deliming 7.2 US $/t pelt weight

On a basis of Austrian/American experience (25), running costs of the carbon dioxide deliming compared with the ammonium sulphate deliming have been evaluated and shown in Table 19.

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

Cost item	Costs US $ per 7 tonnes	
	$(NH_4)_2\ SO_4$ deliming	CO_2 deliming
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

When relating chemical costs in Table 19 to 1 tonne of pelt weight, one can obtain:

- Conventional deliming 7.9 US $/t pelt weight
- Carbon dioxide deliming 6.6 US $/t pelt weight

It may be said that chemical costs of both deliming types are similar. The figures quoted above substantiate the significantly lower electric power costs connected with the aeration in a biological wastewater treatment plant owing to an appreciable decrease of ammonium salts in the effluent. It is objectively demonstrated in Table 19 that this cleaner deliming technology contributes to savings in running costs.

Prices prevailing in the European market have been used in all the cases of costs comparison. In addition, one should emphasize a need of some capital costs for carbon dioxide deliming. Equipment needed includes a storage tank with a vaporiser, piping to deliming vessels, devices to regulate the CO_2 flow and control the pressure. Note that gas suppliers lease storage tanks with a vaporiser and include it in a price of the gas. This is the reason why prices of CO_2 may differ in the market.

d) Chrome tanning

Three fundamental methods are applied to reducing the chrome pollution load discharged in effluent; high exhaustion/high fixing chrome tanning; chrome recovery/reuse after precipitation and redissolving the chrome oxide hydrate; direct chrome liquor recycling.

An example of chemical costs ratio between two modifications of a high exhaustion chrome tanning 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% Cr_2O_3)

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 costs of chemicals will be increased by 20 - 36 %, if the chrome load discharged in effluent has to be reduced significantly in order to meet respective legislative requirements. On the other hand, about 30 % of the chrome offer will be saved, e.g. from 2.0 % to 1.4 % Cr_2O_3.

As regards the chrome recovery/reuse method, the technique used affects capital and running costs. Note that, as a rule, a press filter is not necessary for dewatering the chrome oxide precipitated with MgO. To take into account a daily chrome recovery capacity of 12 - 15 m^3 spent float, capital costs should be expected as follows:

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

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

Table 21
Annual operating costs of a chrome recovery plant.
Basic indications: processing capacity 3,000 t/year, recovery capacity 9 m^3/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 obvious from Table 21 that chemicals (MgO, sulphuric acid) contribute significantly (60 %) to operating costs. Chemical costs are evidently higher when spent floats are precipitated with MgO. The price of MgO is about 1.0 US $/kg depending upon where it is produced, while the price of sodium alkalies fluctuate in the range 0.3 - 0.8 US $/kg.

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

Considering a reasonable payback time of 3 years, the chrome recovery plant based on MgO precipitation without mechanical dewatering would be profitable at a capacity of 2.5 m^3/day (27). The higher the recovery plant capacity, the better should be the profitability. In general, however, cost effectiveness depends on the efficiency of collecting floats, efficiency of chemically treating the floats, and on capital and running costs.

The choice between chrome recovery/reuse and direct floats recycling depends on individual circumstances in the tannery concerned. With regard to any recycling technique the following features are common:

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

From the economical point of wiew, in general, there is no explicit recommendation as to the optimum method of the chrome reusing and saving.

e) Post tanning

Several commercial procedures involving high chrome fixing in neutralisation and high exhaustion of post tanning floats have been implemented in practice. Reduction of the chrome and COD/BOD pollution load discharged in effluent proves to be a matter of higher chemical costs. As an example, an advanced procedure based on chemicals of one reputable European supplier is compared to a conventional procedure with chemicals of the same supplier. 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 chemical costs will be higher by about 36 % in the case of special chrome fixing in the neutralization and high exhaustion of retanning/ fatliquoring/dyeing floats.

f) Finishing

The emission of volatile organic compounds (VOCs) is the main environmental implication of finishing. A minor problem is liquid/solid waste from spraying machines and water scrubbing of the exhaust air.

To control emissions to air in the work place and to ambient air, a level of mass emissions of VOCs related to the area of coated leather has been accepted in the EU. The mass emissions of VOCs should not exceed:

- 85 g/m^2 of coated leather for discharge of 10-25 kg VOCs/hour,
- 75 g/m^2 of coated leather for discharge over 25 kg VOCs/hour,
- 150 mg VOCs/m^3 of the air in all cases.

The most reliable way to estimate the solvent emission is to calculate the consumption. One has to bear in mind that the consumption comprises both the amount of solvents bought by the tannery, and contained in various finishing chemicals. Approximately 95 % of the amount of solvents consumed is found in the exhaust air from the finishing department. The remaining amount will evaporate from the leather later.

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 their application. At the point of application these products can contain up to 90 % of solvents.

Hence it follows that under standard operational conditions in spraying machine, it is practically impossible to reduce mass emissions of VOCs below the value of 85 g per m^2 of coated leather.

Water borne emulsions contain a lacquer phase with the solvent as an oil-in-water emulsion. These emulsions contain up to 35 % solvents and are diluted with water prior to the application. Water borne lacquer emulsions are used both as top and intermediate coats. Due to a decreased content of solvents they facilitate a reduction of VOCs below the value of 85 per m^2 of coated leather.

Aqueous finishing systems based predominantly on acrylic and linear aliphatic polyurethane products contain, as a rule, only 5 - 8 % solvents. The application of these finishing systems is of primary importance in meeting limits on VOCs as regards emissions to the air in work places. They are normally applied in base coats, but complete water-based finishing systems are offered by chemical suppliers for base and top coats as well. The main task in practice is to ensure the high fastness of leather finishes.

Finishing chemical costs of three top coat procedures are compared. The procedures have been offered for standard finishing of upper leather by one chemical supplier reputable in the leather world and proven in practice. They differ by applying solvents and/or water in top coat solutions. A base coat and intermediate coat are the same in all three procedures and based on products thinned by water. 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 $/m²
Procedure S	
- total	0.55
- after subtracting solvents	0.34
Procedure E	0.37
Procedure W	0.51

The results in Table 23 substantiate above all that solvents in the top coat lacquer (procedure S) are rather expensive and significantly affect the level of chemical costs. From this point of view chemical costs of the water-based top coat appear relatively favourable. Nowadays, VOCs mass emissions can be reduced to the permissible level by applying a water based finishing system.

Apart from changing over to low-solvent or solvent-free finishing processes, solvent emissions can be reduced by the implementation of improved methods of the finish application. The installation of high volume low pressure spray guns in the spray cabinet ensures that the overspray will be significantly decreased from around 40 % to 25 - 30 %. Substantial savings of finishing products and solvents are achieved by the application of a forward or reverse roller coating machine. The wastage is only 5 - 15 % against 40 % by conventional spraying. Savings in energy are a further advantage. However, roller coating is normally used in combination with a spraying technique.

Savings of finishing products and solvents are of primary importance in the economy of a tannery. Values of the organic solvents consumption and consequently evaporation in case of the spraying and roller coating application have been used according to (6). One can take into account two representative solvents used in leather finishing, i.e. butylacetate and isopropanol. Approximate prices of these solvents are as follows:

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

Costs of solvents related to 1 tonne of raw hides, consumed in leather finishing and afterwards evaporated are given in Table 24.

Table 24
Costs of solvents consumed in leather finishing

Finishing products system	Solvents consumed			
	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 results in Table 24 substantiate the importance of decreasing solvent consumption to lower operational costs by changing to low-solvent/solvent-free finishing systems and applying improved methods of the finish application.

III. CONCLUSIONS

It is known that conventional leather processing produces a high level of effluent loading. There are technologies available and industrially proven for decreasing the pollution load. This allows more efficient use of the sewage system and makes wastewater treatment more economic. The pollution load decrease is made possible by introducing advanced low waste technologies. These possibilities can be summarized as follows:

1. Soaking

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

2. Liming

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

Suspended solids are discharged in the amount 53 - 97 kg/t raw hide. A reduction to 14 - 26 kg/t is attainable. Organic pollution measured by COD/BOD is discharged in the amount 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. The discharge of sulphide amounts to 3.9 - 8.7 kg/t raw hide and can be decreased to 3 - 4 kg/t. The pollution measured by TKN is discharged in the amount 6 - 8 kg/t raw hide and can be decreased to 3 - 4 kg/t.

3. Deliming and bating

The main pollutants discharged in effluents are NH_3-N and sulphates in the case of ammonium sulphate deliming. NH_3-N is produced in the amount 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 NH_3-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 recycle/reuse and recovery recycling techniques, screening of spent floats and washing waters.

The amount of chrome pollution fluctuating in a range of 2 - 5 kg/t raw hide can be decreased to 0.05 - 0.1 kg/t. The chlorides pollution is discharged in the amount 40 - 60 kg/t raw hide. A decrease to 20 - 35 kg/t can be attainable. Sulphates pollution is discharged in the amount 30 - 55 kg/t raw hide. The pollution load can be decreased to 10 - 22 kg/t. The suspended solids pollution is discharged in the amount 5 - 10 kg/t raw hide. SS load is formed by 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 effluents. The following advanced methods have been industrially proven and implemented: chrome tanning with high exhaustion and fixing, chrome fixing in neutralization, precipitation of spent floats containing chrome, high exhaustion retanning, dyeing and fatliquoring and replacing the nitrogen compounds. By introducing these advanced methods the pollution load can be decreased 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

To minimize the finishing pollution load discharged in effluents is a matter of the proper control of spraying machine operation and their water separators, the installation of new spraying and coating machines providing a higher utilization of finishing chemicals and the use of 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, namely SS by 58%, COD 38%, BOD 37%, sulphides 90%, NH_3-N 87%, TKN 57%, chlorides 75% and sulphates 67%. Even though the pollution load of chrome can be decreased by 94% by introducing advanced technologies, the minimum residual load 0.15 kg/t raw hide can still cause difficulties in landfilling and composting of sludge from wastewater treatment under legislation in force in some West European countries. The amount of effluents produced can be decreased from 34 - 56 m^3/t raw hide to 12 m^3/t.

The extent of a pollution load decrease depends on the concentrations of pollutants allowed to be discharged in effluent. The tanner has to proceed to the implementation of cleaner technologies and additional inevitable measures leading to better utilization of chemicals so that corresponding regulations can be met.

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