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THE LEATHER INDUSTRY

1. INTRODUCTION

Leather making, even in highly Developed Countries, is today still much of an industrial art, with tannery managers and technologists employing their personal process. Similarly plant and equipment vary from tannery to tannery, as will capacity of production unit and end-product. Thus, although some basic similarities exist, these can be no universal definitives or even basic tannery process.

World production of hides and skins all over the world(FAO 1989):

World Production	Total (t wet salted - t w/s)	%
Hide (cow)	4926600.00	72.28
Sheepskin	934000.00	13.70
Goatskin	355000.00	5.21
Pigskin	600000.00	8.80
Total	6815600.00	100.00

The variety of leather that can be produced is reflected in the variety and complexity of processes required. However, the vast majority of hides and skins are chrome tanned in rotating process vessels. Processing is by batch and the size of batches is governed by the capacity of processing vessels.

A large amount of chemicals are used during the tanning processes. The main chemicals will be: Lime, Sodium Bisulphite, Sodium Sulphide, Ammonium Sulphate, Sodium Chloride, Calcium Formate, Sulphuric Acid, Sodium Carbonate, Bating Agent, Bactericides, Veg. Tans and Chrome Salts

The major sources of waste from tanneries can be divided into two groups

- a) Those constituents of the raw hide or skin which are necessarily removed during the tanning process. Including the hair or wool, various collagenous and non-collagenous proteins removed, natural fats, trimmings, splits, shavings, buffing dust and chemicals which may have been employed during the curing process.
- b) Surplus and residual chemicals from the tanning process.

2. PROCESS DESCRIPTION

2.1 Process Stages

- Salted or dried stock: preservation of hides and skins.

Beamhouse

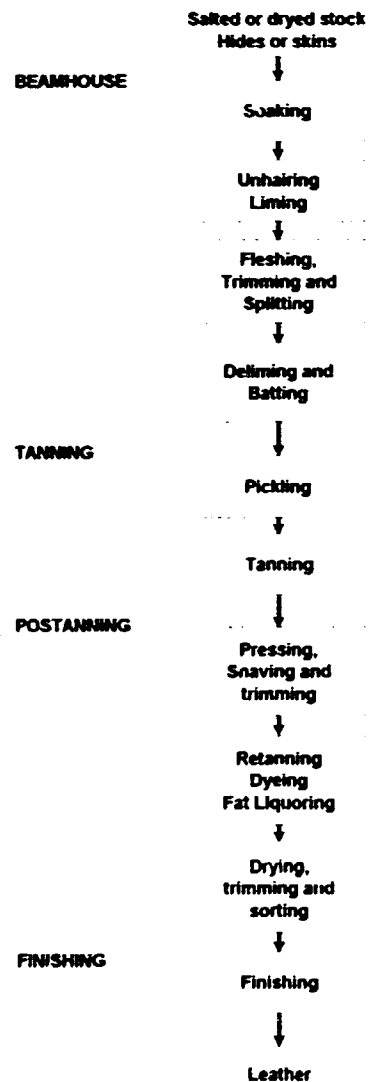
- Soaking: remove blood, dung, curing salt and water-soluble and saline-soluble proteins.
- Unhairing: complete dissolving of all hair.
- Fleshing: mechanical removal of extraneous tissue from the flesh side of the hides.
- Delimiting: remove hair remnants and degraded proteins and produce a more supple and elastic leather (Batting).

Tanning

- Pickling: give the required acidity to the skins to prevent the subsequent precipitation of chromium salts on the skins fibers.
- Tanning. The tanning process stabilizes the proteins (collagen) network of the hides or skins.

Post-Tanning

- Samming or pressing to remove moisture. Splitting and trimming: the thick hides will be split by a splitting machine.
- Retanning, fat-liquoring and dyeing. This is a combined process in which the semi-finished leathers will get a final tanning. Fat-liquoring: softening of the tanned hide.
- Drying, trimming and sorting
- Finishing. Surface coating, buffing, seasoning, plating, embossing, spraying and final sorting and measuring are the final stages of the hides and is known as the finishing stage.



2.2 Process Diagrams

Inputs			Process	Wastes		
Raw materials	Water	energy		Liquid	Solid	Gas
Skins hides, 1.000 kg NaCl, 300-500 kg (2)	-	n.a.	- Salted or dried stock -	-	NaCl, 50-100 kg (2)	-
NaOH, 1.6-16 kg Wetting ag. 4-16 kg Bactericide, small q.	3.000 - 10.000 kg	n.a.	- Soaking -	dirty, saline liquors 3.000 - 10.000 kg (3)	-	-
Lime, 20-100kg Sulphide, 10-40 kg	2.000 - 4.000 kg	n.a.	- Unhairing & Liming -	alkaline waste waters 3.000 kg (4)	-	Hydrogen sulphide
-	(5)	n.a.	- Fleshing, trimming & splitting -	(5)	Fleshings and trimings	-
Acids, 10 - 25 kg Hairing ag., 0.5-7 kg	500 - 1.000 kg	n.a.	- Deliming & Batting -	Alkaline waste waters 1.000 kg (6)	-	Ammonia

(1) w-s: wet-salted hides

(2) If the hides are wet-salted, a large amount of common salt is used. If a mechanical shake is carried out before soaking, solid NaCl can be obtained as a waste.

(3) This waste water can represent up to 51% of Cl⁻ in the global effluent.

(4) This waste water can represent up to 51% of BOD (30 kg) and COD (85 kg) in the global effluent, also it is the main source of sulphide (6 kg) and Kjendhal N(6 kg).

(5) During the fleshing process, large amounts of water are used.

(6) The deliming process represents up to 75% of the global ammonium N in the waste waters(4.1 kg).

Process	BOD	COD	TS	SS	N _k	N _{am}	Cl	S ²⁻
Soaking	10.0	40.0	170.0	15.0	1.5	-	82.0	-
Unhairing	30.0	85.0	125.0	60.0	6.0	0.3	12.0	6.0
Deliming	3.0	6.0	45.0	3.0	5.0	4.1	8.0	-

Table 2: Leather Industry - Tanning Processes						
Basis 1000 kg pelt hides (1)						
Inputs			Process	Wastes		
Raw materials	Water	Energy		Liquid	Solid	Gas
NaCl, 50 - 100 kg Acids, 6 - 15 kg Fungicides, 0.1 kg (2)	400 - 700 kg	n.a.	Pickling	Brine and acidic waters 300 - 500 kg (3)	-	-
Chrome Tanning Chrome salts (22-25% Cr ₂ O ₃), 80 - 20 kg Masking ag., 1 - 5 kg Basifying ag., 10 kg Fungicide, 1 kg (2)	800 - 900 kg	n.a.	Chrome tanning	Acidic wastewater containing Cr ^{VI} 1,000 kg.	-	-
Vegetable tanning Acids, 20 - 50 kg Tanning extract, 150-400 kg	1,000 - 2,000 kg (4)	n.a.	Vegetable tanning	Containing tanning extracts 1,000-2,000 kg	-	-
Others Syntans, 10 - 250 kg	1,000 - 2,000 kg (5)	n.a.	Other	1,000 - 2,000 kg	-	-

- (1) Pelt hides: after delimiting, the hides are weighted and this weight is the basis for the tanning processes.
- (2) Some tanneries only process the hides to the pickle or tanning (if carried out with chromium is called *blue stage*). Fungicide is added to preserve hides during store or transport.
- (3) The tanning process is carried out in the same bath as the pickling process. Up to 80% of bath is discharged
- (4) Carried out in pits with a countercurrent bath of vegetable tanning agents.
- (5) Alternative tanning agents like zirconium salts, cod oils, formaldehyde and others can be used.

Waste water compounds for the Tanning Process (kg/t w-s)									
(Chromium tanning)									
pH	TS	Tash	SS	BOD	COD	N _t	N _{am}	Cr	Cr ^{VI}
3.0	175.0	160.0	5.0	3.0	14.0	1.0	0.5	56.0	5.0

Table 3: Leather Industry - Post-tanning Processes						
Basis 1000 kg tanned hides (1)						
Inputs			Process	Wastes		
Raw materials	Water	Energy		Liquid	Solid	Gas
-	-	n.a.	- Pressing & Shaving	Press liquors	Shavings containing Cr	-
Tanning ag., 20 - 30kg Dyes & acids, 10-60kg Veg. oils, 30-100 kg	1.000 - 6.000 kg	n.a.	- Retanning, dyeing & fatliquoring	Acidic waste waters 1.000 - 6.000 kg (2)	-	-
-	-	n.a.	- Drying, trimming & sorting	-	Trimmings containing Cr	-
Surface coatings Organic solvents	-	n.a.	- Finishing	-	-	Solvent vapours (VOC's)
Leather Product						

(1) Tanned hides: after tanning, the hides are weighted and this weight is the basis for the post-tanning processes.

(2) Containing Cr if the retanning process has been carried out with chromium salts.

Waste water compounds for the Post-tanning Process (kg/t w-s)									
pH	TS	Tash	SS	BOD	COD	N_L	N_{am}	Cl	Cr³⁺
2.0	65.0	30.0	7.0	14.0	30.0	0.8	0.6	5.0	1.0

3. WATER CONSUMPTION

From the traditional process, it is not easy discerned what volume of water is used. This is due to the leather industries age-old system of calculating process volumes (floats) as a percentage of the weight of the goods.

Normally such floats are calculated on weighs at two strategic process points:

Limed and fleshed	Lime Pelt weight
Tanned, split and shaved	Shaved weight

This basis of calculation, overcomes the problem of the irregular size, shape and cure conditions of this natural heterogenous raw material. However, differing cure conditions affect the weight basis of processes before the Limed Pelt weighing.

Calculation of process water use proves difficult as some traditional processes refer to water washes running (this usually inefficiently controlled process, timed for 15-20 minutes, may use from 200 - 500% water, but is dependent on the flow rate of the water and the time employed).

The typical process would normally consume some 26 liters water per kg lime pelt weight or 30 liters per kg wet salted hides.

However, tanneries have historically been somewhat lavish with water use. Thus, nominal process usage of water in most tanneries are exceeded by at least 50%. A nominal consumption of 30 litres/kg-ws could represent an use of more than 45 litres/kg w-s hide.

4. WASTES

Bifurcating tannery wastes into two categories is usual: Solid Wastes and effluents. However, this is possibly an oversimplification; each individual tannery technology may determine whether a particular waste is separated initially as a solid, or discharged with the effluent where it will be accounted part of total solids (e.g., fleshings, shavings, buffing dust appear in varying volumes in liquid discharge or effluent).

4.1 Waste Waters or Effluents

The typical pollutants found in tanneries effluents employing traditional technologies are as follows:

	Beamhouse			Tanning	Post-tanning	Total	
	Soaking	Unhairing	Delimiting Bating			kg/t w-s	mg/l (1)
TS	170.00	125.00	45.00	175.00	65.00	580.00	12888.9
Total ash	150.00	75.00	35.00	160.00	30.00	450.00	10000.0
SS	15.00	60.00	3.00	5.00	7.00	90.00	2000.0
BGD ₅	10.00	30.00	3.00	3.00	14.00	60.00	1333.3
COD	40.00	85.00	6.00	14.00	30.00	175.00	3888.9
Kjel. N	1.50	6.00	5.00	1.00	0.80	14.30	317.8
NH ₄	-	0.30	4.10	0.50	0.60	5.50	122.2
S ²⁻	-	6.00	-	-	-	6.00	133.3
Cr	-	-	-	5.00	1.00	6.00	133.3
Cl	82.00	12.00	8.00	56.00	5.00	163.00	3622.2

(1) Assuming a water consumption of 45 l/kg w-s hide

4.2 Solid Wastes

From the ecological viewpoint the most significant solid waste characteristics may be:

The untanned collagenous wastes and fats (raw and soaked trimmings, often mixed with fleshings) which could lead to odours. However, provided they are not heavily contaminated with process chemicals, they are certainly a most suitable material for agricultural fertilizer.

The sulphide bearing wastes (trimmings and fleshings) from the hide in limed condition and beamhouse residues and sludges. They may give a rise in malodours hydrogen sulphide fumes, however, the concentration in this form is unlikely to be hazardous.

The chrome bearing wastes (shavings, buffing dust and sludge from equalized effluents). Sludges from effluent treatment may contain up to 3.5% chromium, leather fragments (buffing dust, shavings, scrap splits etc.) may content 2.0 - 5.0% Cr₂O₃. Most of the chrome within tanned leather fragments is chemically bound to the skin protein and not easily displaced.

Table 5: Leather Industry - Solid wastes (kg/t w-s hides) Basis 1000 kg w-s hides		
Untanned solids	Raw trimmings	120
	Fleshings	70 - 230
Tanned solids	Splittings	115
	Trimmings, shavings	110
Finished solids	Buffing dust	2
	Trimmings	32

4.3 Air Pollutants

The air pollutants are not the more important wastes in the leather industry, only some volatile organic chlorated (VOC) compounds emissions due to spray pigments (apply by hand or auto spray machine during the finishing process) and possible emissions of sulphydric acid (coming from the unhairing process) are of concern.

5. ALTERNATIVE TECHNOLOGIES

5.1 Raw hides and skins curing

5.1.1 Salted or dried stock

A possible total elimination of salt is already considered realistic. Ensuring the required quality of hides preservation is therefore necessary.

5.1.1.1 Supply fresh from slaughter houses direct to tanneries.

Conditions: Hides preserved by cooling to the temperature of 2 to 5°C or by hide chilling.

Preservation: Only for several days

Problems: Not to be considerate in hot climates countries

5.1.1.2 Radiation preservation, not yet been introduced industrially. Consist of irradiating fresh hides with a beam of electrons or with gamma-rays.

Preservation: For several weeks

5.1.1.3 Mechanically shaking the salt from hides before soaking in suitable equipment.

Profit: Up to 10% of salt from hide weight is removed.

Reuse: Preparation of pickling floats.

Preservation again, before thermal treatment at 340°C.

5.1.1.4 Other processes like recover from salt liquor that comes out of hides during the storing. It is based on flotation of organic polluting matters and subsequent vacuum evaporation of salt liquor.

Problems: More complicated and expensive.

5.1.1.5 Inorganic matters. Use SO_2 as active biocidal component.

-Gaseous SO_2

Preservation: 30 days depending upon SO_2 acting time

Problems: not suitable for the viewpoint of working environment.

-In drums with a bath containing Na_2SO_3 and acetic acid per hide weight.

Conditions: after preserving, storing the hides in a closed container is necessary.

Preservation: 1 month at 30°C or up to 2 months at 5°C .

-Use of acid metaspulphite together with aluminium sulphate.

Preservation: up to 4 months.

5.1.1.6 Organic matters. Only for short-term preservation. They are not highly effective but ecologically unsound chlorinated aromatic compounds. A mixture of acetic or propionic acid and methylurone derivative can be used.

5.1.1.7 Combined methods. Combined use of salt and special organic and inorganic compounds. In the future, commercial biocides are promising methods of preservation.

5.2 Beamhouse processes

5.2.1 Soaking

Alternative technologies reducing water consumption can be applied (See: **5.6 Water Reduction**)

5.2.2 Unhairing and Liming

A traditional unhairing and liming process account for more than 50% of the BOD and COD load in typical tannery effluents. Also, this is the main source of the ammonium and sulphide present in the wastewater effluent.

The common feature of almost unhairing and liming alternative methods is that hair is only loosened and not decomposed. The hair is then subsequently mechanically removed so that it does not come into waste waters (hair-saving methods).

The new technologies to avoid this large pollutant load are focussed into:

5.2.2.1 Reduced amounts and volume of lime/sulphide

These processes are hair saving methods carried out in pits or paddles using a lower dose

of sulphide. The main feature of them is to separate the unhairing and the liming processes into two steps.

Separate unhairing and liming processes. The unhairing process is carried out with a lower float (about 100 to 200% of water is used) and the sulphide concentration in the liming bath should not be exceeding 3.5 gr/l. The loosened hair is removed from the pelt and released into the bath due to mechanical action because of friction. It is then separated on screen equipment (if it is necessary, the hides can be unhaird by machine). After this, the pelts are limed with a lime bath.

Liming with hair immunization. The hides are processed in a bath with lime content between 1.0 and 1.5 % of hide weight and an auxiliary agent (based on thioglycolate). After 30 to 120 minutes, the immunization is interrupted by adding hydrosulphide or sulphide and the hair is released into the bath. The process requires a drum equipped with an external circulation and filtration system thus enabling removal of the hair from the bath. After unhairing, the pelt is limed. The pelt is then fleshed and split and returned into the filtrated unhairing bath with an addition of lime and possibly NaOH for a final liming.

Sirolime unhairing process. It is a multi bath system. The hides are processed in a short float with NaHS (about 1% hide weight). In 2 hours, a major amount of hair is loosened. The bath is drained, hides are washed and processed in a new short float with 1% of sodium chlorate and thus the remainder of the sulphide on the hair is oxidized. Hair loosening is finished after adding lime. If it is necessary, the pelt can be unhaird by machine and relimed in lime liquor. The hair from the unhairing bath is filtered.

Others. The *Darmstadt continuous process* uses a solution of sulphide with NaOH on the soaked hides by spraying. It uses a minimum dose of 3% sulphide per hide weight. After 10 to 20 minutes the hides are mechanically unhaird, fleshed and split. The hide structure is loosened in an enzymatic bath or in a solution of Na_2O_2 . It seems that has not yet been a successful industrial application of this method for a longer period.

A different concept is removal of the hide from cattle hides in the slaughter house itself by *thermal processing of freshly flayed hides* with water at 58°C. The hides need not then be unhaird with sulphide and the hide structure is loosened in the lime liquor.

5.2.2.2 Recycling of classical lime/sulphide liquors

The possibility of direct recycling of lime/sulphide liquors has been widely examined. These process lead to reduction of total sulphide consumptions and also reduction of the total amount of organic pollution in tannery effluents caused by unhairing and liming processes.

New recycling process based on separate unhairing and liming has been developed. The unhairing liquor is filtrated and after refilling with chemicals and water is reused. The hides are then washed very thoroughly. The washing bath is captured and used for soaking. The pelt is then limed in a lime liquor with an addition of NaOH for control of degree of swelling. The liming liquor is also captured and refilled with chemicals and water for the next cycle. The efficiency of this recycling method depends on the number of recycles and on the level of hair saving. For example, 20 days recycling and only partial

hair saving, sulphide contents in the waste water from liming is reduced by 80%, lime content by 93%, COD by 17% and BOD by 15% in comparison with the conventional method.

If recycling is made in a tannery, having facility to process such used lime liquors would still be necessary. Although recycling if theory may be continued indefinitely, occasionally discharging the liquor may be necessary, during a holiday shutdown, or if the liquor has been contaminated. Thus, a back up system of catalytic oxidation or similar should be available.

5.2.2.3 Substitution of traditional sulphide unhairing

Most of the major chemical supply houses have been engaged in the search for an economic, technically acceptable replacement for lime/sulphide unhairing and liming.

Unhairing with thiol-based compounds. Commercial preparations with thioglycolate as the active component are offered by commercial preparations for this purpose. A maximum 5% of these agents on hide weight are used. However, adding 0.5% of sulphide for perfect unhairing is common. After unhairing the pelt must be limed.

Amines-based compounds. For example the dimethyl amine is an effective agent, but its use is not recommended due to harmfulness of its gaseous products of decomposition.

5.2.2.4 Enzymatic processes

Proteolytic enzymes are used for unhairing. The dissolution of hair does not occur, only its loosening to such an extent that it can be removed by machine. The enzymatic unhairing system is usually time consuming (one or two days). A sulphide-lime processing is necessary for loosening the structure and swelling. The loosened hair can be removed by machine and the liquor can be recycled.

5.2.3 *Deliming and bating. Degreasing*

Some common characteristics of alternative methods are that ammonium salts are replaced by agents that not contain ammonium salts. Application of these methods then leads to reduction of ammonium nitrogen in tannery effluents.

5.2.3.1 Deliming without ammonium salts

Lactic acid. The lactic acid has a buffer effect at pH between 4.0 and 6.0. Because of that, dosing this acid by parts to avoid an acidic swelling of the pelt is necessary. The final pH from deliming is very low and from this fact hydrogen sulphide from rest of sulphide contained in the pelt can arise.

Hydrochloric acid. It can be used for deliming in a system with sodium hydrocarbonate. 1% hydrocarbonate per pelt weight is added in a bath with 100% water; after 10 minutes, diluted hydrochloric acid is added successively in three charges of a total amount of 1%. The bath is stabilized by adjusting the pH value from 7.0 to 8.0. After 40 minutes of

deliming it is possible to add the bating agent.

Magnesium sulphate. It is possible to delime pelts relatively well with a combination of 4% magnesium sulphate and sulphuric acid per pelt weight.

Commercial agents. These are based on esters of carboxylic acids which are split in alkali medium. They are added in quantities between 1 and 3% per pelt weight depending upon the thickness.

Carbon dioxide. In an over saturated bath, carbon dioxide neutralizes and solubilizes the calcium hydrocarbonate. The final pH is stabilized from 6.5 to 7.0 so that acidic swelling cannot occur.

5.2.3.2 Bating without ammonium salts

Ammonium free bating agents, which have an active agent based in the proteolytic enzymes of the pancreas, are offered by several producers. They are dosed in 0.01 to 0.25% per pelt weight.

5.3 Tanning processes

The tanning processes can be divided into three principal groups, according to the tanning agents used: Chrome tanning, Vegetable tanning and combined tanning.

5.3.1 Chrome tanning

The waste bath from tanning is the main source of chromium in a dissolved form discharged into tannery effluents. Approximately 80% come from this bath and the summing process (60 and 20% respectively).

5.3.1.1 High chrome exhaustion techniques

To achieve increased exhaustion of chromium, the following main modifications are followed:

Modifications on the pickling bath. The use of non swelling organic acids enables a substantial reduction of the salt in the pickling bath. At a temperature of 28 to 30°C, good pickling is achieved so that using only 1.6% chrome oxide is possible and reduces the chrome oxide in the waste water between 2.0 and 3.5 g/l using a bath of 100%

Higher temperature. A 40 to 42°C temperature and a prolongation of the tanning time contribute to a higher exhaustion of chrome. Tanning at a higher pH value (4.0 to 4.7) for which special self-basifying and masked chromium tanning agents are used has the same effect.

Use of short floats. Tanning in the residual volume of the bath of 20 to 30% that remains after draining the deliming and bating bath (so called dry tanning) can reach also high

exhaustion values for chromium tanning. The use of this method has an increased friction between leathers and the internal surface of the drum.

Special auxiliary tanning agents and chemicals. An exhaustion from 80 to 98% of chromium and a residual concentration of chrome oxide between 0.2 and 2.0 g/l (using 100% bath) can be achieved by using agents or auxiliary preparations developed by well know suppliers of specialty chemicals for the leather industry

Work directed towards higher levels of chrome fixation has concerned the incorporation of dicarboxylic acids and their salts into chrome tannage. Such materials had traditionally been introduced into pickle and chrome tanning processes as masking agents.

Arguing in favor of the high chrome fixation operations versus the efficiency of recycling system is that bleeding out of unfixed chrome from hides in later processes is reduced, as well as the more economic usage of chromium.

5.3.1.2 Recycling of used floats

Traditionally pickling and chrome tannage were carried out in separate floats. Today however, in most tanneries, short non equilibrium pickles to which chrome tan is later added, appear most usual.

Separation of the waste baths containing chromium from others baths are the prerequisites for any effective recycling system. The postanning waste baths cannot be used for recycling because they contain fat-liquoring agents, dyestuffs and various retanning and refilling organic matters.

General considerations about recycling systems

- One major problem of simple recycling systems is the low efficiency and erratic drainage of most drums in use. Such volume cannot be full recycled and the recycling system may only be partial.
- Employing recycling systems there will be a significant alteration in concentration of neutral salts.
- The mending of pickle/chrome liquors is possibly best accomplished in a holding pit so that at the contact of pelt/liquor a normal safe salt concentration is available to avoid swelling. If it is wished to prepare the liquor in the drum, normal precautions must be taken to first add the salt.
- Recycling also requires some regular control and monitoring; initially most liquors require analysis. Once the system has stabilized, control may be generally by way of simple test, with only occasional need for full analysis. The pH and specific gravity will give guidance as to the acidity and salt content.
- One further advantage of recycling spend liquors to the pickle process is that salinity in the effluent is greatly reduced. The principle of employing a liquor containing chromium as the pickle float is that the acid and salt from such liquor

penetrate the hide faster than the large chrome complexes, thus the pelt should be neither swollen nor ever-reactive when the chrome contacts the pelt.

Pickling float recycle for pickling. Pickling bath is accumulated and after mending fresh chemicals and water can be used for the next cycle. The chemical addition to restore the liquor to original strength may easily be calculated.

Such simple pickle regeneration although not affecting major toxic materials in effluents can, by reducing the salinity of tannery effluent, prove environmentally acceptable, especially in such areas where salinity has negative environmental effect. On the other side, the advantages of saving of chemical are self-evident.

Tanning float recycle for tanning. The waste tanning bath is accumulated separately as well, filtered through a suitable screen filter, its composition is modified and it is used in the next cycle. Chromium savings depends upon a level of exhausting of tanning bath and the number of cycles. In practice is usually from 15 to 40%.

Arnoldi and Covington outlined a typical basic recycle trial. In each tannery the basic parameters must be determined by measurement and analysis. This recycling system would affect an 24% reduction of new chrome offers and 57% reduction of chrome discharged

Tanning float recycle for pickling. Arnoldi and Covington found 70% tan float recycle to pickling possible with 25% saving of chrome offer and a 70% reduction of chrome discharged.

Pretanning. Pretanning is done between pickling and tanning when pelt is pretanned with a part of the accumulated waste baths from tanning including water from sammying and draining for 2 to 3 hours. The pretanned bath is discharged and then the pelt is tanned with a use of the residual part of the accumulated tanning waste baths after refilling their composition.

5.3.1.3 Recovery of chromium. Precipitation

The systems of liquor recycling will require an alteration of the technology applied in the tannery with several engineering works. An alternative approach requiring less technology is to continue with the normal tannage and collect the maximum volume of chrome liquors (float, drains, sammying extractions and possibly any preneutralization wash). These isolated chrome liquors are treated with and alkali to precipitate the chromium in the hydroxide form. From this form there are two possible means to use the chromium hydroxide:

- The hydroxide sludge may be passed to a filter press, the cake so formed may be redissolved with sulphuric acid and reused.
- The liquor may be left undisturbed overnight, virtually chrome free supernatant may then be draw off and discharged to the effluent stream and the remaining settled hydroxide sludge may be redissolved with acid in situ and subsequently reused.

The addition of sulphuric acid then must be with cooling due to the high heat of hydration and neutralization with sulphuric acid. After dissolving the liquor is diluted and stored for

a next use in the recycling tanning process.

If a high chrome fixation or exhaustion chrome tanner has carried out, the chromium in the effluents obtained can still yield over 200 mg/l chrome due to suspended fibers containing chrome. The system of precipitation and settlement of used chrome liquors would eradicate such chrome from the major chrome bearing liquors.

5.3.2 *Vegetable tanning*

This method of tanning is mainly applied in the production of sole leathers, some lining, fancy, binding and technical leathers. A mixture of several types of vegetable tanning agents or a combination with syntans is mostly used.

The main purpose of them is to increase the unsatisfactory exhaustion of tanning matters typical for conventional methods.

5.3.2.1 C-RPF process

Non-delimed pelt is firstly conditioned with acidically reacting special auxiliary agents. Pretanning and tanning is carried out in a short float with suitable syntans and relatively high exhaustion of tanning matters (about 75%). Only very small bath volumes are discharged.

5.3.2.2 LIRITAN process

Consists in a pit pretannage with polyphosphate and sulphuric acid followed by a pit pretannage for two days with a weak concentration of tanning agents (2 days more), three days in a counter current system with vegetable tanning agents at 35°C and finally in a drum at 45°C with a 45% of tanning agent. This process uses 12 days and can arise and exhaustion level of 95% of tanning agent applied.

5.3.3 *Combined tanning*

Their main purpose is to replace chromium salts at tanning and to reduce their consumption for the following reasons:

- To limit or avoid the discharge of chromium salts
- To limit or avoid production of solid wastes containing chromium salts (shavings, trimmings, ...).

Characteristic of alternative methods:

- The first phase of tanning is carried out without chromium. After this, the semi-product is shaved and processed by splitting giving chrome free solid wastes.
- The second phase of tanning is carried out using chromium salts, aluminium salts or vegetable/synthetic tanning agents.

5.3.3.1 Combined tanning with aluminium salts

The leathers tanned with aluminium salts have a low shrinkage temperature (70-75°C). These processes are also called white tanning. Used for some glove leathers. The waste baths from aluminium tanning are not toxic, however, the question of harmlessness of aluminium for water organisms has not yet been confirmed.

Aluminium-chromium tanning. Aluminium salt in an amount of 1 to 4% is used for pretanning. After shaving, the leathers are tanned with chromium salts tanning agents. More boil-resistant leathers are obtained.

Combination of aluminium and synthetic/vegetable tanning. The combination of aluminium salts with sulphated extract of mimosa is another way of increasing the stability of semi-processed leathers. Usually 10 to 15% per pelt weight of mimosa extract is used, added in two steps. After shaving the leathers are tanned with aluminium sulphate (10%). The shrinking temperature of such tanned leathers varies from 90 to 95°C.

Aluminium-aldehyde tanning. This method is only combined with other methods. The leathers tanned with aldehyde can be classified as white leathers, they are loose and of rather poor general properties. After the pretanning process the leathers are shaved and tanned with chromium salts.

5.3.3.2 Combined tanning with zircon salts

With zircon tanning it is possible to prepare pure white leathers with very good light-fastness properties. However, zircon tanning alone is very seldom used. It is necessary to use NaCl in pickling so that acidic swelling should not occur. Zircon salt commercial tanning is carried out in a 50% bath per pelt weight with 3 to 5% of zircon dioxide. Basifying must be very slow and can be used sodium hydrocarbonate or magnesium oxide.

It is recommended to use zircon and aldehyde processes combined for a production of white leathers.

5.3.3.2 Combined tanning with titanium salts

Interest in tanning properties of titanium salts has increased only due to their ecological harmless. Tanning takes a long time (12 to 36 hours) according to the thickness of the pelt.

There are several titanium process developed in Russian, India and USA.

5.3.3.3 Other tanning methods

With iron salts. Compounds of trivalent iron have tanning properties. Iron tanning has not been developed into practice due to:

- Ferric salts undergo a strong hydrolysis.
- During basification they act as a catalyst for oxidation of proteins. Decomposition of leathers may occur.
- Tanned leathers are of brown colour limiting dyeing possibilities.

With fats. Fats which contain unsaturated fatty acids, such as fish oils, also have tanning properties (chamois leathers). The delimed and bated pelt is treated with fish oil in a drum (30% fish oil per weight pelt). It is notable for its yellow shade, softness, stretchiness and waterproofness. Paraffinic sulphochlorides are also used for the same purpose.

5.4 Post-tanning processes

5.4.1 Retanning, Dyeing and Fat-liquoring

The most important pollutant in this stage is the organic matter. Tanners normally process for high exhaustion of retanning agents, dyes and fat liquors.

Exhaustion of retanning agents is mainly a question of time, quantity and pH and therefore the right combinations will lead to satisfactory results as long as the products are not toxic.

The process of dyeing and fat-liquoring involves acidification of float in order to fix these materials, but the lowering of the pH below 4 has the effect of releasing chromium into solution. This problem underlines the necessity of achieving very good fixation of the chromium compounds during the tanning process. The addition of amphoteric polymers can greatly improve the exhaustion of dyes and fat liquoring agents. Although this represents additional organic substance entering the system, significant reductions in COD can be achieved.

5.4.2 Finishing

Cleaner technologies will be the use of water based solvents in order to prevent the emission of VOC's. Between 30 and 50% of finish can be lost. Using a roll coating machine, losses may be as low as 5%. Exhaustion from spray machines and drying tunnels can be improved by efficient scrubbing to clear the air emission.

5.6 Water reduction

With variations in water consumption varying from 20 l/kg to more than 100 l/kg for technologies apparently similar in other respects, there is in many situations scope for conservation and considerable savings in this area. The major systems of water-saving technologies may be:

5.6.1 Increased volume control of processing and housekeeping waters

In a majority of tanneries only some 50% of water consumed is related to actual process requirement. The balance of water consumed appears to be due to extensive running water

washes, overflowing vessels, continually running pipes and over-frequent washing of floors and drums.

Reduction of overuse in this area, while cost-effective, would necessitate a serious worker training programme, coupled with installation of water flow meters or less sophisticated spring controlled valves, and a written code of practice for operators.

Considerable savings may be obtained with the introduction and control of simple housekeeping rules and equipment.

5.6.2 Batch versus running water washes

One of the major tannery wastages of water is the system of running water rinsing, whereby goods are run in a drum with a lattice door with water valve fully open, for 15-20 minutes. Control of such process is minimal, neither the flow rate of water or the time, being monitored. Some research centres showed that 50% of total water could often be saved by instituting batch washes as the following example:

1 st wash	250% water	20 minutes
	Drain	
2 nd wash	250% water	20 minutes
	Drain	

Such batch washing should also yield a greater uniformity of product.

5.6.3 Low float techniques in existent equipment.

The utilization of short floats, i.e. 40-80%, in traditional drums in place of traditional 100-250% floats, as well as yielding savings in water consumption and more rapid processing can effect appreciable volume of chemical input savings, due to higher effective concentration and increased mechanical action.

Joint acceptance of both batch washing and low floats have been reported to save upwards of 70% of water utilized in tannery activity. However, it must be noted that low floats may impose increased levels of wear and tear on drum bodies and drive.

5.6.4 Low float techniques using updated equipment (mixers).

The installation of hide processors (concrete mixers and Y partition units) is reported to yield water savings of 50% in addition to chemical savings. Such advantage is most unlikely to justify import of these units at high capital cost, when wooden drums may be constructed locally.

5.6.5 Recycling: direct reuse of water to less critical processes.

The installation of a recycling network, merely to save some 25-50% of water usage, is unlikely to prove economic, except in ultra-arid areas where water is both limited and expensive. But when

simple water recycling is coupled with recycling of specific individual floats (unhair or chrome) with savings in chemical offers the economies improve greatly, and must be seriously considered.

A large number of proposal have been published showing that it is technically feasible to recycle many relatively clean rinse and wash waters to other processes where the low concentration of chemicals in such waste will have positive advantage (or al least minimal negative effect).

5.6.5.1 Modified Bailey Process

Such system proposes that:

- Wash after bate and neutralization and subsequent clean wash float are recycled to the soak process.
- Part of the second lime wash is recycled to form the basis for a new lime liquor.

The Modified Bailey Process could reduce nominal water consumption from 17.1 l/kg down to 12.6 litres/kg, this is a reduction of some 26%.

The major requirement, in addition to collection sumps is the incorporation of a bifurcated drain whereby flow from any given drum could be directed either to the recycling networks or normal effluent sewer.

5.6.5.2 Slabbert Recycling System

The Slabbert Recycling system incorporates:

- Recycling of used lime and post lime washes for soaking
- Recycling of pickle/chrome tan and some washes.

A reported advantage of this system is that the residual alkalinity, from the used lime float, acts as an accelerator for the soaking operations .

5.6.5.3 Komanowskt and Senske Recycling System

This is a countercurrent system and incorporates:

- Simple reuse, without treatment for some liquors.
- Chemical adjustment for other liquors (ammonia removal).
- Certain physical treatment for a particular effluent (centrifuge).

The Komanowsky and Senske system would drastically reduce the volume of effluent, as the complete pretanning process would only utilize one float. With regard to developing Countries, it may be that such process would need unduly high levels of supervision, and certainly such a system would need to be practically proven at commrcial level, elsewhere, for some years before such a radical proposal could be implemented.

5.6.5.4 Vulliermet Recycling System

This system, separates the unhairing and liming processes and then recycles both simply (without treatment) and with treatment (protein separation). Technically Vulliermet's system has much to offer reducing volume of the effluent and lessening its total organic load, but, as with the Komanowsky and Senske system, will need proving at commercial

level before it may be recommended for developing countries.

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