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INTRODUCTION OF CLEANER LEATHER PRODUCTION METHODS-PROSPECTS AND CONSTRAINTS*

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SUMMARY

In order to reduce the ecological impact of leather production, new technologies were studied and applied, mainly in industrialized countries. These clean technologies can be applied at various stages of leather manufacture.

Regarding chemicals used for effluent treatment, a more efficient use of existing chemicals and some new specialties which are biodegradable can be found in tanning operations.

Modern equipment can improve the situation by reducing effluents or decreasing the solid waste discharge. New technologies are increasingly used, which are based on recovery or recycling techniques. It is important to point out that controls, which are necessary to run these clean technologies, can also lead to an improvement of quality of leathers produced.

This document presents some practical aspects of cleaner methods used on an industrial scale in European and North American tanneries.

It is, however, difficult to establish the level of investment necessary to implement these cleaner production methods

Tanners from developing countries, even when facing financial constraints, also have the possibility to apply the same methods, adapted to their particular production facilities.

CONTENTS

Subject	**Chemical**		**Equipment**		**Technology**	
Curing						
Fresh hides and skins						*
Cooling			*		*	
Partial salt elimination				*		
Antiseptics		*				
Soaking						
Antiseptics		*				
Fleshing						*
Unhairing-liming						
Enzymatic treatment		*				
Hair saving methods		*		*		
Direct recycling			*		*	
Splitting of limed pelts				*		
Deliming						
Carbon dioxide	*		*			
Weak acids		*				
Tanning						
Pickling float recycling			*		*	
Solvent free degreasing	*		*			
Wet white production		*				*
Tanning float recycling			*		*	
Partial recycling			*		*	
Precipitation method		*		*		
Improvement in exhaustion		*				*
Other mineral tanning		*				
Three compartments drums				*		*
Vegetable tanning						
Dry drum						*
Close circuit in pits		*				*
Dyeing						
Environmentally acceptable chemicals	*					
Three compartments drums				*		*
Through feed machine	*		*			
Finishing						
Water based finishes		*				
Roller coating				*		

REDUCTION OF POLLUTION OBTAINED IN CLEANER PRODUCTION METHOD

SUBJECT	
Curing	
Fresh hides and skins	No salt pollution in soaking
Chilling	No salt pollution in soaking
Partial salt elimination	Lower salt pollution (20 %)
Antiseptics	Lower toxicity
Soaking	
Antiseptics	Lower toxicity
Fleshing	Upgrading waste and lower chemicals consumption
Unhairing-liming	
Enzymatic treatment	Lower toxicity and organic pollution
Hair saving methods	Lower nitrogen and organic pollution
Direct recycling	Lower chemicals and organic pollution
Splitting of limed pelts	Upgrading waste and lower chemicals
Deliming	
Carbon dioxide	Less nitrogen (-40 %)
Weak acids	Less nitrogen
Tanning	
Pickling float recycling	Lower salt pollution
Solvent free degreasing	Lower toxicity (75 %) and COD
Wet white production	Upgrading waste
Tanning float recycling	Chromium recovery (90 %)
Partial recycling	Partial chromium recovery (60 %)
Precipitation method	Total chromium recovery (99 %)
Improvement in exhaustion	Good chromium uptake (95 %)
Other mineral tanning	No chromium tanning
Three compartments drums	Improvement in chromium recovery
Vegetable tanning	
Dry drum	Good vegetable tanning uptake (95 %)
Close circuit in pits	No effluent process and lower COD
Dyeing	
Environmentally acceptable chemicals	No heavy metals and lower AOX
Three compartments drums	Better uptake of chemicals
Through feed machine	No dyes in effluents
Finishing	
Water based finishes	No VOC emissions
Roller coating	Better uptake of chemicals

1 - RAW HIDE AND SKIN PRESERVATION

The way to preserve raw hides and skins is of a great importance to obtain good quality leather at the final stage, but it is also significant regarding salt and organic pollution generated during the soaking stage when hides and skins are washed.

Several possibilities are available to partially or totally eliminate the salinity and collect organic pollution at an early stage. It is very difficult to remove the salinity of the effluents as the technologies applied use costly equipment. In several countries, salt pollution is strongly restricted in order to protect the drinking water.

1-1 Treatment of fresh or cooled hides and skins

This type of treatment exists in many countries throughout the world. It was applied at the origin in large South American tanneries where 75 % of the total hides processed are fresh hides coming from slaughterhouses. Time elapsing between slaughtering and further treatment (e.g. beamhouse processing) must not exceed a few hours, mainly when the temperature of air is high.

Beyond this period, it is necessary to cool the hides and skins. Cold air is interesting if hides are transported over a long distance. Using ice gives faster cooling and easier freight conditions. Storage below 4_C yields good preservation up to three weeks.

Of course, sorting is difficult before hide treatment and this can cause great difficulties due to the disparity of the characteristics of hides and skins obtained in slaughterhouses. Cooling with cold air needs to be applied on individual hides and skins hung on hooks, as hides can maintain in a pile. a high temperature for many hours, even when the pile is in a cold room.

Regarding this problem, it is preferable to store hides and skins in cases filled with ice, before reaching the beamhouse. Such a process is gaining ground in Switzerland, Germany and Austria where regulations limit the use of salt for preservation. During the preparation of the ice. it is now possible to add biocide that will continue to protect the hide, even if the ice defreezes.

1-2 Partial salt elimination

When processing salted hides, salt represents about 20 % of the raw material's weight. It is possible to recover partially the preserving salt by shaking the hides either manually or mechanically by using a perforated and inclined rotating drum. Only the undissolved fraction may be recovered and possibly upgraded.

The quantity of salt that may be recovered through this process, used in several tanneries in Italy, is around 30 %. The salt, heated over 400 _C to eliminate organic materials, can be reused for hide preservation.

1-3 Preservation with antiseptics

Various solutions have been proposed for preservation with antiseptics. They make use of either traditional chemicals (boric acid, sodium sulphite, acetic acid) or newly developed antiseptics (thio-cyanomethylthio-benzothiazole TCMTB, isothiazolone, chloroacetamide,..) commercially available from several firms.

The latter products ensure satisfactory protection, but for a limited time, and the cost of treatment is currently high. They are twice as expensive as traditional chemicals whilst providing the same efficiency. It is however possible to use these chemicals before drying hides and skins, replaced the usual arsenic salts, that have a high toxicity and can prevent the exportation of raw hides and skins.

2 - SOAKING

2-1 Use of chemicals

Nowadays, the first phase of the tanning process is frequently speeded up by using enzymatic products, that can be considered less toxic than sulfide. In other respects, the use of less harmful antiseptics will reduce the overall toxicity of the waste while preventing excessively rapid bacterial growth.

Most of these products are more expensive than PCP (up to 5 times more) and may not have the same long-lasting effect.

The new antiseptics are clearly less toxic than some products currently used such as phenyl mercury acetate, trichlorophenate, pentachlorophenol PCP. The banning of PCP in leather, shoes and leathergoods imported in Germany has accelerated the withdrawal of this product in Asian and South American countries.

2-2 Soaking equipment

Apart from less toxic antiseptics, a real clean technology proposed for the first stage of leather manufacture is to perform the fleshing of green hides instead of limed or tanned hides. This would result in lower waste production at a pH close to neutral, which can then be easily processed to recover fats and proteins. It has also been suggested that splitting should be including in this stage, but this does not contribute to an improvement in the material balance.

The use of pits or paddles for soaking operations results in a higher consumption of water, mainly for the washing phases which are much less efficient when using drums. Even for drums, it can be recommended to operate with sequential washings instead of continuous rinsing. Water savings can amount to 50 % of the consumption during beamhouse operations.

3 - UNHAIRING-LIMING

The unhairing-liming operation is undoubtedly the largest contributor to the net pollution for tanneries. Conventionally, mixing the hides with lime and sodium sulfide leads to residual floats containing 55 % of suspended solids, 55 % of COD, 70 % of BOD_5, 40 % of nitrogen and 76 % of the toxicity of tannery effluent.

The unhairing-liming process only consumes 40 to 45 % of the lime and 50 to 55 % of sodium sulfide or sodium hydrosulfide in the treatment float. Various low-waste technologies exist to reduce the impact of the liming process on the quality of tannery effluent.

3-1 Enzymatic treatment

Much research has been carried out and pilot programs established with regard to the partial or even total replacement of sodium sulfide in the unhairing-liming process.

Today, except for small skins that are processed through sweating, the use of enzymatic products is mainly a partial substitution of sodium sulfide. On-site tests have yielded widely varying results that could not justify full-scale industrial use. A keratin-selective enzyme that does not attack collagen has yet to be found; such a process could result in a 30 % to 50 % reduction in pollution for this phase of the tannery process.

3-2 Hair saving unhairing-liming methods

Hair brings about an important discharge load of COD and nitrogen, and recovery systems enabling elimination from the treatment float before dissolution have been proposed. A new product commercialized by the Austrian firm OCW would make it possible to preserve the hair during the liming phase. These process can lead to a COD reduction of 15 to 20 % for the mixed effluent, and a total nitrogen decrease of 25 to 30 %. It is an advantage to filter off the loosened hair as soon as possible and higher COD and nitrogen reduction can be obtained.

For a traditionally equipped drum with a capacity of 4 tons hides, a minimum investment of US$ 50,000 is required. In new unit, the extra cost required for such a straining system with re-circulation of the float to the drum may be more justifiable. Several large tanneries in France have been operating for many years with drums equipped in this manner, but so far, no economically valid use for the recovered hair has been found. Residual hair can be used, however, for fertilization and composting.

3-3 Direct recycling of liming floats

In this system, the aim is maximum recovery of the residual float. Solid waste, in excess of a certain gauge (currently 1 mm) is separated, and the chemical content of the float is restored to its initial composition before being reused in another unhairing-liming operation.

Several large bovine tanneries, for shoe upper leather, use this recycling technology. Its implementation requires need the solution of a variety of technical problems The enrichment of dissolved organic matter is not higher than 3 times the conventional concentration, owing to the clean water intake at each cycle, resulting from swelling of hides and rate of recovery of float in drums. The presence of enzymes in the soaking stage requires careful washing before unhairing. The lower scudding effect observed at the end of the liming phase may be compensated by modifications in the process.

This technology, used for over 12 years in tanneries, holds much interest, as, in practice, it can save 35 to 40 % of the involved sodium sulfide, and almost 45 to 50 % of the conventional lime consumption.

Fine screening of the residual float rids the circuit of a substantial amount of organic matter. On the whole, 30 to 40 % of the COD and 35 % of the nitrogen may be eliminated from the mixed effluents. for an investment of US$ 90,000, for an average tannery processing 10 tons of raw hides per day

The principal limiting factors are : the quantity of hides to be processed (only large bovine hides can be treated with this process) and the qualification of the technical staff responsible for the laboratory analyses which are indispensable for a quality control of recycling. The quality of the leather produced might be affected negatively with this process, unless unhairing and opening up processes are used in two phases.

Savings in chemicals generally lead to a 3 to 4 years investment return rate even if the pollution control value is not considered in the balance.

3-4 Splitting limed hides

For most uses, bovine leather has to be split, i.e. reduced to a constant thickness adapted to the article produced (less than 1 mm for garment leather, from 1 to 1.5 mm for upholstery, from 1.5 to 2.5 mm for shoe upper). This operation yields a split of unequal thickness of which a significant part will be considered as waste. Faced with difficulties of upgrading the chromium-tanned crust waste, many tanners perform the splitting operation immediately after fleshing of limed hides. This lowers the amount of chromium salts needed for the tanning and yields a waste that can be easily recovered for the production of good quality skin gelatin.

3-5 CO_2 deliming

The deliming phase using ammonium salts, brings about considerable nitrogen pollution, estimated to be as much as 40 % of total discharge. The use of carbon dioxide seems to provide quite a few advantages as far as pollution is concerned, but equally in respect to the easy handling of chemicals. In practice, the only difficulties are related to the required distribution equipment from CO_2 storage. This technology avoids the use of nitrogen salts.

From a technical point of view, the results obtained are very favourable for light pelts (thickness lower than 3 mm). The CO_2 is injected directly in the axe of the drum. The application rate is 1 to 1.5 % of the weight of pelts.
For thicker hides, diffusion remains rather slow and requires much greater CO_2 amounts, and it is necessary to increase float temperature (up to 35 _C) and/or process duration, and/or to add small amount of deliming auxiliaries. A large amount of H_2S appears at the beginning of the reaction requiring pre-treatment with hydrogen peroxide.

Since the pH of CO_2 deliming float is lower than that used in common procedure, special ammonium free bates should be used

Currently, more than 100 European and American firms are using this technology, and the advantages of a process should ensure its rapid development. The cost of chemicals is slightly higher than the conventional scheme. It runs between US$ 0.7 to 2.5 per kg. As investment examples, the equipment needed, for a tannery processing 6 tons of bovine raw hides per day in three tanning drums, is about 15000 $, and the investment for a tannery processing 25 tons per day is about 50000 $.

3-6 Weak acid deliming

It is useful to mention the use of weak acid in deliming operations (lactic acid, acetic acid,...), but their cost limits their application to specific cases. This cost is 50 to 100 % greater than the conventional scheme, although the application rate is not more than 0.5 to 1 % of the pelt weight.

4 - TANNING OPERATIONS

Chromium tanning salts are used today in 90 % of tanning processes. Only the trivalent form is used for tanning operations and this chemical cannot be replaced, except for special purpose, to give the same quality of leather. If its concentration in waste exceeds an acceptable level (about 1 g per kg dry solid), it strongly limits any possibility of upgrading, or disposing of the waste at an acceptable cost.

Therefore, today the primary objective is the best possible use of chromium, as this substance remains irreplaceable. The operations that precede the actual tanning have an influence on the chromium salt behaviour on the hide, and clean technologies exists for pickling operations.

4-1 Recycling of pickling floats

For the same reasons that lead to a lowering of the quantity of salts discharged during soaking, the pickling phase is now more strictly controlled. An earlier limitation of the float volume to 50-60 %, led to a reduction of the amount of sodium chloride used in this stage of the process.

Today recycling of pickling floats is common practice in many tanneries to reduce salt pollution. After collection, the used float is sieved and its acidity (mainly from formic and sulfuric acids) is controlled in the laboratory. After readjustment to initial pH value, the float is reused for the following cycle. In practice, salt savings are about 80 % and reduced acid consumption is estimated at 25 %, although more formic acid is saved than sulphuric acid.

For "wool-on" sheepskins, the recycling of pickling, using long floats over 150 %, is current practice which gives good results. It is generally associated with the recycling of chromium float.

4-2 Degreasing operations

Sheep and goat skin degreasing is still widely used to improve tanning conditions. For a long time, tanneries have been carrying out this operation using non-miscible solvent, such as white spirit or kerosene, by itself or mixed with monochlorobenzene.

The first improvement, in view of the large amounts required (10 to 20 % on the pickle weight), included different and much less toxic substitute products. For example, degreasing agents are used directly on the pickled skins, without any float in the drum. The application rate is 1 to 4 % of the weight of pickled skins. Two or three washing steps follows. The float volumes are 50 to 100 % of the pickled skins weight.

Etoxylated fatty alcohols should be recommended instead of the more widely used etoxylated alkylphenols, given that they are more easily degraded. Nevertheless the effluent obtained by this method should equally be treated, given that its COD level may amount as much as 200,000 ppm, due to the content of natural grease and surfactants (1g/l of natural grease is about 2,900 ppm COD, and 1 g/l etoxylated alkylphenol is about 2,300 ppm COD).

However, the slightly lower degreasing quality obtained caused some tanners to abandon this technology and return to traditional solutions, while introducing a recovery phase into the process.

Accordingly, the degreasing float and the three extraction pickling brines have to be collected in a vertical tank. Three phases are obtained :

- A salty aqueous phase, which is perfectly reusable for a new extraction. The sodium chloride solution reaches 90 % of its initial concentration. The required concentrations of water and sodium chloride are adjusted before recycling.

- - An organic phase rich in solvents and combined fat/solvent, which may be regenerated through steam-stripping.
- - An intermediate emulsifying phase, which can be controlled by using little emulsifier and bringing the temperature of that phase to 50 _C.

All in all, 50 to 70 % of the solvent may be recovered, and distillation residues may occasionally be upgraded. This upgrading may only take place if large volumes are involved. Residues such as tallow may be then upgraded.

To this day, more than 30 solvent recycling units have been set up and are in operation in firms seeking a higher standard of degreasing. Most of them are shared between several tanneries because of the high cost. As an example, a unit that recovers 50 liters of solvent per hour costs US$ 45,000.

On "wool-on" lamb skins, it is a common practice to undertake a dry solvent extraction when crusted, but a degreasing phase with sodium carbonate takes place during the beamhouse process.

4-3 Wet-white production

In order to limit the amount of chrome-containing wastes obtained after tanning (mainly splits and shavings), these operations needs to be carried out earlier in the tanning process.

The splitting of limed hides, in spite of its reduced precision, has several advantages. Shaving, which increases skin temperature up to 65-70 _C, appears possible only once pretanning has already taken place. The use of aluminum salts as well as titanium, aluminum, magnesium and zirconium combinations, on their own or combined with dialdehyde-based synthetic tanning agents, makes it possible to split and shave the leather of which tanning and character are perfectly reversible.

In spite of the obvious advantages of a such a technology (good valorization of pretanned waste, possibility of sorting before tanning, and improvement in surface yield), certain factors limit the diffusion of such a process. Current retanning and dyeing processes have to be somewhat adapted, as they react differently on an aluminum pretanned leather. Drying and splitting technologies must also be adapted. Several European countries also limit the aluminum salt concentration in industrial effluent (eg. : maximum threshold of 12 mg Al/l in Italy, and 5 mg/l in France).

Today, one French tannery has been using this process in full scale production for 6 years, and some others are using this technology for a part of their production. In several European countries, some tanneries are using a similar process on a large scale, even if a slight increase of manufacturing costs has been observed.

4-4 Direct recycling of chrome tanning floats

Direct recycling of tanning floats remains the easiest method to apply, recover and reuse chromium salts from tanning operations.

After collection and sufficiently fine screening, the floats are controlled and the chromium amounts used in the previous cycle replaced by new chromium salts.

Depending on the tanning technology in use, the degree of exhaustion reached for each cycle may vary. In a conventional bovine tanning process, it is estimated that the direct recycling technology can save about 20 % of the chromium used in the conventional process.

On the other hand, for the treatment of wooly sheep skins (especially double face), this direct recycling makes it possible to reuse almost 50 % of the chromium introduced in the process, since tanning floats do not reach high exhaustion rates.

This recycling method may be repeated several times on the same float. However, it is limited by the occurrence of quality problems with delicate hides, and by the need to control residual floats (acidity and chromium concentration), a measurement which takes around 30 minutes.

Many bovine and sheepskins tanneries have experimented with this technology and have used it for several years. Nevertheless, there is a tendency to replace it by other simpler methods which are less sensitive to tanning preparation conditions.

This technology is specially adapted to small firms and is widely used throughout Europe.

4-5 Two-stage recycling of tanning floats

This method uses a 2-float tanning process and aims at respecting the quality of some types of skin.

The actual tanning float, containing 3 to 6 g of chromium per liter, is recovered, screened and used in the pretanning phase for the following batch. After pretanning, the used float containing 1.5 to 3 g/l of residual chromium has to be treated with another method to avoid chromium discharges to the treatment plant.

Three calf skins tanneries in France currently use this process.

4-6 Recycling after precipitation

This is the oldest and most conventional method. It allows collection of the tanning float along with the rinses, that sometimes occur at the end of the tanning, and the effluents from various post-tanning stages (washing, dripping, sammying, etc.).

After collection, screening and storage, the floats are precipitated with different types of coagulants including sodium hydroxide, sodium carbonate, magnesium oxide, and even lime when recycling is not possible. A flocculation with polyelectrolytes may follow.

The re-use of sludge after simple settling and acidification has been experimented and practiced. However the normal process consists of settling the chromium sludge, and treating it on a filter-press or vacuum filter. In the first case, there is no interest in excessive dryness of the cake, as difficulties could emerge during the next phase when the sludge are re-dissolved using sulphuric acid.

Large plants have operated under this scheme for many years in Germany, in Italy, in South America and in France.

Only large plants treating significant amounts of chromium can justifiably use the technology of recycling after precipitation and dewatering of the sludge. As a result, tanners collect their tanning residual bath for a common treatment. However, some small scale tanneries are using magnesium oxide precipitation and direct redissolution of the settled sludge for reuse as a tanning liquor.

The keys to obtaining less than 10 mg Cr^{3+}/l at the clarifier's outlet and in the filtrate are the quality of the collecting system for the chromium baths and the ensuing precipitation process. The recovery is than 99 % or more for chromium concentration in the residual floats of 3 to 6 g/l.
However, additional treatment methods are required to obtain less than 1 mg chromium/l at the end of the tanning unit. Different solutions can be envisaged, but they are expensive : an additional coagulation phase using aluminum sulphate, or sand filtration. The cost of such a treatment may be estimated at US$ 200,000 to treat roughly 100 m^3 of effluents from tanning and sammying operations per day.

4-7 Tanning products that improve the exhaustion rate

For the past few years, tanning and basification products have been available on the market which enable a tanning cycle inducing only small chromium wastes.

Developed by the German company, BAYER, tanning salts that are highly masked, associated with other classical tanning salts, result in residual floats currently containing less than 1 g of chromium per liter and even less than 500 mg of chromium per liter in specific cases. To obtain these results, skins have to be treated in very short floats (from 20 to 40 % water) and a high temperature increase has to be obtained at the end of the tanning operation.

One other German company, HENKEL, specifies the advantages of aluminum silicate of sodium in chromium tanning : aluminum silicate hydrolyses thereby consuming acid. The reaction has a tanning effect on the limed hides. This acid consumption provides better float exhaustion during the subsequent phase of chromium tanning. This means that the amount of chromium oxide may be reduced by about one fourth. The tanning is performed with 1.5 % Cr_2O_3 and 1.5 % aluminum silicate of sodium instead of 2 % Cr_2O_3 (% per weight of limed hides). In this manner, the chrome concentration in residual floats is only about 1 g Cr_2O_3/l ; the aluminum concentration is about 0.6 g Al_2O_3/l.

At the present time, similar products are marketed by an Italian company STOPANI. Testing undertaken in a French tannery using this technology demonstrated the excellent tanning quality and the low discharges of the sammying and the neutralization operations. Less than 10 g of chromium per ton of tanned hides is discharged in the effluent, this represents a recovery rate of 99 % of the chrome.

Other firms such a Chromogenia (a Spanish company) have developed basification products which improve the fixation of the chrome salts at the end of the tanning process. Residual float may then sometimes contain less than 500 mg Cr/l.

To avoid the risks of wearing of the grain side due to short floats, specific chemicals are offered by UNION, HENKEL and STAHL companies.

Tanning with such products can only be performed on split hides : the molecules are too large to penetrated adequately in the hide close to the grain side. When hides are split, the hide's reduced thickness makes this operation easier.

Tanning with high exhaustion chromium salts requires extensive monitoring and is rather difficult to control. Care must be taken so that the chromium penetrates deeply in the hide before fixing or marks may appear on the grain side.

When splitting is performed after tanning, classical chrome tanning agents whose the molecules are smaller must be used.

4-8 Other mineral tanning

Concurrently to chromium waste reduction tests, a number of experiments have been conducted aimed at substituting other products.

One substitution method is proposed by an English company ICI. It consists of associating 3 metallic cations, aluminum, titanium and magnesium to provide good quality white tanning.

However, the resulting leather remains far from the classical chromium- tanned leather, meaning that, this technology cannot be used for a wide number of articles. This product, the SYNEKTAN T.A.L., new to the market, is unlikely to be developed.

Among other attempts to substitute chromium, aluminum glutaraldehyde mixed tanning has to be cited. It is produced by the Hungarians in order to improve resistance to aluminum leeching. In spite of its industrial use in Hungary for several years, this process needs to be improved in order to limit the glutaraldehyde toxicity.

Many attempts to associate aluminum and vegetal tanning should be cited.

The leather obtained is similar to chromium-tanned leather ; yet remains sufficiently different that this technology could not be extended on a larger scale.

4-9 Improvements in tanning equipment

The wooden drum has always been associated with chromium tanning : however, its performances have been improved through many modifications which, first of all, allowed for the collection of baths. Although float collecting spouts appeared 15 years ago, a more recent innovation consists of removing the float through the axis, then pumping it back in the drum. This makes it possible to control the float's pH, exhaustion and temperature.

Concurrently, new equipment, mainly stainless steel drums with 3 compartments have appeared on the market, helping the float control processes. In spite of their smaller size, they provide other advantages. in particular with regard to wool-on skins that are very difficult to process in classical wooden drums.

5 - CLEAN TECHNOLOGIES IN VEGETABLE TANNING

Although this technology is well known, nowadays vegetable tanning is applied in a much more efficient manner. Two processes are currently applied to make sole leather and equipment leather. These include tanning in dry drums and tanning in vats with close circuits.

5-1 Tanning in dry drums

In order to avoid important discharges from paddle-vats, tanning of the bovine leather in drums for sole production was used about 20 years ago. Interesting results were obtained by this operation requiring a low float volume, and performed after conditioning of the leather. Today, this process is used for the majority of the leather sole production in Europe, and the residual tanning floats are extremely low (less than 10 % of the treated hides weight).

5-2 Tanning in vats without discharges

To obtain efficient dry tanning, intense mechanical work has to be applied to the skins. Tanners who produce a good quality sole leather believe it is harmful for the compactness and impermeability of the leather.

The preparation of leather with polyphosphates at 30-35_C, with the permanent circulation of the vegetable tanning solution in the vats, provides a tannin/non tannin ratio compatible with good tanning quality. This technology is used by about 10 tanneries in Europe. They use imported tannins (mimosa, quebracho) and local tannins such as chestnut.

6 - DYEING OPERATIONS

6-1 Chemicals

This generic term includes re-tanning, dyeing and fatliquoring. Today, the clean technologies suitable for this production cycle are principally based on the products used, especially dyes and pigments : chromium VI, lead and cadmium salts can still be found in some types of older dyes and pigments. But a more careful examination of the manufacturing characteristics of the products supplied throughout the world, and national regulations based upon the european legislation should lead to the complete elimination of those chemicals from the market.

Some azo-dyes, containing carcinogenic amino-components like benzidine, have also to be banned from tannery.

For re-tanning based on chromium III, the same problems encountered with tanning arise. In some cases, the concentration of this element in the discharge is quite equivalent. Good practices should lead to an elimination of this kind of retan, or a selective recovery circuit, but not a recycling system in the process itself.

Fatliquoring oils used in the tannery are often composed with chlorinated alkan sulphonates and fatty acid methylester sulphonates that are now questionable because of the organic halogen quantities they can generate.

As a result of the regulations on absorbable organic halogens AOX, the chlorinated fatliquoring products will be replaced. Various substitutes are on the market to satisfy new laws in this field.

For example, SOPROPO have developed a product which must be added to the fatliquoring oils. The oils are then converted into micro emulsions producing a significant reduction of COD in fatliquoring waste water.

Combined products such a Lubritan WP from Rohm and Haas and Densodul BA from BASF allow simultaneous re-tanning, fatliquoring and waterproofing.

6-2 Dyeing equipment

The use of classic wood drums for dyeing is unsuitable. This is why stainless steel drums with three compartments like washing machines appeared 15 years ago.

Well-known manufacturers of such equipment are UNIMATIK in Italy, RIAT in France, and DOSE in Germany. The continuous mechanical action on the hides, the changing of the drum's rotation, the constant temperature and recycling of the bath from the bottom to the top, improve the efficiency of the chemicals' penetration into the hides.

This type of equipment has proven to be particularly interesting from environmental point of view, as they permit dye savings (heating the bath at the end of the process increases the exhaustion from 15 or 20 %).

In addition, they enable dyeing in a very short float and require lower quantities of water for rinsing.

The rate of water in the float is only 100 % of the wet blue weight whereas it is 400 % in classic drums. Thus, the discharge load is reduced by 50 % and the product exhaustion rate reaches 90 %.

Finally, controls are eased during the rather complicated process of dyeing.

A three-compartment drum costs about US$ 55,000; that is the twice the price of a classic drum for the same capacity, but the duration of the whole process can be shorten, compared to a classical drum.

However, an amount of dye, although small, is discharged in the effluent at the end of each operation and the load is important : COD = 20 000 mg/l, BOD_5 = 7 000 mg/l and suspended solids = 600 mg/l.

Ten years ago, the Swiss company STAUB developed a machine to dye leather. This "through-feed" dyeing machine functions the same way as those used for in textiles : the leather passed between two conveyors in a dyeing float for 5 to 20 seconds. The leather is then wrung between two pressure rollers and directly introduced in a drier. The moisture saving is reduced to 70-100 %.

However, the development of this type of equipment is hampered because the dyes available on the market were not designed for this dyeing technology.

Now, new products developed by CIBA-GEIGY, and machines manufactured by Unimatik have been combined to dye crust leather of all thicknesses.

These devices may be used on all sorts of hides (bovine, sheep, goat, pig). A 2 200 mm-width machine is able to treat 2 760 m^2 hides/day (without any dye discharge).

This process is still experimental but dyeing machines are currently used in about 30 tanneries.

7 - CLEAN TECHNOLOGIES IN FINISHING

The finishing phase, a source of pollution not to be neglected, especially with regards to air, uses the same principals as dyeing as far as clean technology is concerned. As a matter of fact, efforts have been focused on the products and equipments in use.

7-1 Finishing products

In spite of increasing needs for quality leather and leather resistant to wet rubbing and to flexing in extreme temperature conditions, the development of finishing in solvent phase seems to be stopped. Efforts shown by chemicals producers are taking shape with a whole series of finishing resins in an aqueous phase, mainly with acrylic or polyurethane bases (or containing low quantities of miscible solvents such a N methyl, 2 pyrolydone or butyrolacetone).

The proposed systems call for efficient reticulant products on epoxide or zirconium bases providing good resistance to wet rubbing. With a few exceptions, the aqueous finishing applications seem ever increasing. Exceptions involve, in particular, calf skins on which casein and formaldehyde fixation are used. It is important to know that proposed new european regulations will soon limit to 70 g the quantity of solvent used for one square meter of leather.

For the same reasons as for dyeing, pigments must not contain any environmentally risky heavy metal or other restricted product.

On the other hand, finishing on transfer paper was developed. It enables the upgrading of flexing resistance and thin leather of medium quality in good conditions. Nevertheless, this technology remains costly and transfer foil failures are still current. This type of finishing doesn't seem to be increasing in use.

7-2 Finishing equipment

Almost exclusively in practice 10 years ago, finishing pistols largely contributed to the tanneries' degradation of the environment. This equipment was used to automatically spray the finishing chemicals on the leather and could not guarantee chemical losses less than 25-30 %, as opposed to sophisticated programming equipment adapted to the geometry of leather treatment.

The present increase in the use of roller coating machine has contributed to reduce losses of finishing chemicals up to about 3 %

Initially this machine was very basic, but has become more sophisticated in time, and can now treat thinner and softer skins. However, it seems unlikely that this equipment will ever be used to finish skins less than 0.8 mm thick, or skins with a thickness variation up to 0.4 mm. Deposited resin quantities vary from 1 to 25 g per square-foot depending on the technology in operation (direct or reverse application) and engraved roller used.

In Europe, 40 % of finishing operations are now performed with roller coating machines in spite of this equipment's lower productivity.

Curtain coating systems are not so up to date, but they strongly limit the wastage of finishing chemicals. Their use is however restricted to low quality leather that needs a thick coating.

The development of fine, clean technologies in finishing should continue in two directions : products and equipment.

A new finishing concept based on an air diluted resin (foam appearance) has been developed by GEMATA-LAMBERTI. It is applied with roller coating machines. Drying speed and easy handling of the products should make this an important development.

8 - COMMENTS

Clean technologies mainly associate :

- harmless chemicals with better use.
- a decrease or prevention of waste materials.
- processes which reduce volume or waste product toxicity.

However, leather production will always yield proteins in solution that should be eliminated through the most adapted resources. In the same time, the necessary production of important quantities of solid waste should be orientated towards easily upgradable refuse categories, i.e. non-chemically stabilized. In order to eliminate them as soon as possible in the fabric cycle, acceptable economic resources have to be found for their upgrading.

Finally, a search for new, less toxic products which can be used 100 % has to be carried out.

However, it must be pointed out that although they permit good or high reduction of the load in the effluent, some clean technologies aiming at reducing the liquid discharge cannot be used in the process line because they do not produce a finished leather similar to leather issued from a conventional process.

Others technologies exist, but they are still experimental and are reserved to specific use of the leather or are still difficult to operate. They need to be confirmed before application in leather manufacture.

9 - BASIS FOR AN ECOLOGICAL BOVINE LEATHER

Many tanners are thinking that it would be opportune to commercialize "Ecological" leather but at the present time, there is no definition of "green" leather.

However, it might be possible to list the characteristics for "green" leather, in terms of :

- The chemicals used.
- Water effluent.
- Solid effluent.

These are applicable to bovine leather and could be adapted to goat and sheepskin leather :

- Salt free curing
- Use of safe biocides
- Recovery and valorization of hairs
- Specific treatment or recycling of sulfides
- Valorization of fleshings
- Lime or white splitting or valorization of blue splits
- White shaving or valorization of blue shavings
- Deliming without either ammonia or chloride salts
- Very low chrome discharge, with environmental friendly replacement chemicals (below 0.5 mg/l in the mixed effluent)
- Low leacheable chromium (below 100 mg/kg dry leather)
- Retanning without either chromium or chemicals containing free phenol
- Dyeing with dyes without either benzidine or heavy metals
- Fatliquoring without AOX producing chemicals
- Finishing using VOC free chemicals, pigment without heavy metals, and roll coating equipment
- Waste water treatment with primary and biological stage for tannery effluents alone or mixed with domestic sewage
- Valorization of waste sludges in agriculture
- Valorization of tanned wastes, if any.

10 - QUALITY AND THE TANNERY

At the same time that industry in general is being confronted by ever-increasing legislation designed to protect the environment, there is equally a growing awareness that companies need to make more systematic and determined efforts int the domain of quality.

The ISO 9000 series of standards relating to quality assurance, published in 1986, define the foundations upon which the "client-supplier" relationship should be based. In these standards the concept of quality is equated to **customer satisfaction**, which goes over and above the simple notion of product conformity to include the economic factor of price and the ability to respect delivery dates, which equates to industrial efficiency !

The clean technologies that we have described have a certain complementarity with the quest for quality or customer satisfaction, not only will they help the tannery to remain competitive by minimizing future costs of effluent treatment, but they will necessitate stricter process control, which is one of the key features of quality assurance.

The ISO 9000 standards are concerned with all the quality related activities of the company including :

- company organization - roles and responsibilities,
- contract revue(order processing),
- purchasing,
- process control,
- testing (raw materials and product)...

Quality assurance systems are documented which means that all the activities of the company, to assure client satisfaction, **can be proved**. This is the means to attain **company certification** by an independent assessment body, which in some industrial areas is becoming a necessity.

The value of quality assurance for the tannery in Europe has been recognized and in 1992, a European Sprint Programme ref. RA 375 was initiated, concerning tanneries from six of seven European Countries. The overall aim of the project is to determine the best model of a Q/A system for the tannery and to promote its use throughout Europe.

At the present time, three tanneries have certified Quality Assurance Systems in the U.K.

Tanneries from : GREECE, ITALY, DENMARK, GERMANY, SPAIN, FRANCE and U.K. are in the process of installing such systems, as part of the European "Sprint Programme", and it is highly likely, but un-confirmed, that suppliers to the tanning industry are equally engaged in such a project.

Successful implementation of Quality Assurance is highly dependant upon management commitment, to our knowledge the progress made to date in this field by French tanners, should ensure that at least one company will formulate a request for company certification in 1994.