IUE 1 - Recommendations on Cleaner Technologies for Leather Production

2018 updated document

Introduction

The raw material of the leather industry is based on turning the food industry's waste product, animal hides and skins, into a desirable and useful end product. This relieves the food industry of what would be a major problem of disposal of the waste hides and skins.

This renewable source of raw material is used for such items as shoes and upholstery, which might otherwise have to be manufactured from alternative non-renewable products such as synthetic materials and other petrochemical based products.

The condition of the raw stock received by the tanning industry has a direct effect on the resulting cleaner technologies that can be applied.

Good farming practices are encouraged so that hides and skins do not suffer from ectoparasite infestation or damage inflicted by barbed wire, horns or other outside influences. Such damage has to be masked by the tanners involving extra processes using additional material resources and often creating added waste disposal problems (e.g. buffing dust, shavings etc.)

The amount of dung attached to an animal hide or skin as a direct result of poor farming practices also uses more natural resources and creates additional loadings on the effluent and the solid wastes which becomes the responsibility of the tanner.

Damage to the hide or skins, such as poor flaying practice at the abattoir, may also create increased waste disposal problems for the tanner.

All these factors have to be taken into account when considering the application of cleaner or clean technologies.

Aim of the document

The International Union Environment (IUE) Commission is concerned to take into account the technologies currently applied by the most advanced tanneries and not just to consider the latest developments from research units.

The general recommendations collected by the Commission have to be adapted to local conditions and under the supervision of a leather specialist and taking into account the requirements of the production.

The Commission understands that cleaner technology can be defined as the environmentally and economically best practicable technology (BATNEEC, best available technology not entailing excessive cost). Clean technology may be defined in terms of minimum environmental impact, towards which the industry is striving.

1. Raw stock

1.1 Preservation of fresh or cooled hides and skins

Fresh or uncured rawstock is available to tanneries in many countries. Whenever possible, treatment of fresh hides and skins is the best solution to reduce salt pollution. The time elapsing between slaughter and further treatment (whether curing itself or the initiating of wet processing in the tannery) must not exceed a few hours. When an abattoir and a tannery are operationally linked, fresh rawstock may be used, but excess above the capacity of the tannery must be handled differently.

Beyond this short period, it is necessary to cool the hides and skins, either in ice or cold air. Cold air is necessary if hides are to be transported over long distance. Storage below 4°C can extend preservation for up to three weeks, under ideal conditions, although some dehydration is to be expected. This system of retaining rawstock quality is used in Europe, by transporting rawstock in refrigerated trucks, but it is recognised that this may not be feasible or economical in developing economies. Rawstock may be preserved in ice, but storage is more problematical than chilling, due to melting of the ice, run-off of water and the potential for bacterial growth on wetted pelt.

1.2 Drying

Shade drying of small skins is a low cost and environmentally acceptable process in some climates. Controlled air-drying using heat pump or other system is suitable for any climate.

1.3 Dry salting

Dry salting, combining salt curing and shade drying, can minimise the amount of salt used for preservation of skins and hides.

1.4 Use of antiseptics

The use of antiseptics with low environment impact and toxicity can help to increase storage time of fresh or chilled hides and skins. Suitable preservatives that are used around the world include: TCMTB, isothiazolones, potassium dimethyl dithiocarbamate, sodium chlorite, and benzalkonium chloride. Their use must be regularly reviewed, to reflect changing legislation, because they will be discharged in the effluent.

Some of these agents, that may have both bactericidal and fungicidal properties, are also appropriate for soaking, pickle and wet blue preservation.

1.5 Partial salt elimination

It is possible to eliminate up to 10% of the salt added to hides and skins for preservation, by using hand shaking, mechanical brushes or a suitable drum. The salt can be reused for pickle processes after dissolution and removal of solids, but it must not be used for curing purposes because it is too contaminated with bacteria, particularly halophilic or halotolerant bacteria, which can cause so called red heat.

This method of salt recovery gives a partial answer to the salt pollution problem. Neither brine curing nor salt curing can be considered as cleaner technologies, even if pre-fleshing green hides reduces this waste. It is recognised that salt curing is one of the greater contributors to the environmental impact of tannery operations. Even recovering some of it has limited benefits, because its reuse is extremely limited, its ecological disposal is difficult impossible and the cost of fresh salt is so low.

2. Beamhouse Processing

The new generation of drums and processors facilitate efficient draining and washing, and allow the routine use of low floats for processing, thereby resulting in significant savings in water consumption.

2.1 Soaking

The consumption of fresh water can be minimised by using a counter-current system of washing, to concentrate the salt (if present) and the other soluble materials, such as dirt and blood.

Utilisation of all antiseptics used for preservation should be under regular review.

Additional cleaner technology that can be applied at this stage is the fleshing of green hides after soaking. It yields a lower quantity of fleshings, with a neutral pH. Green fleshings are more valuable than limed fleshings with regard to tallow recovery, because the green fleshings are not subjected to the hydrolysing liming process. In this way, the amount of recovered tallow is greater and the content of undesirable free fatty acid is much lower, so the quality is better.

An associated problem with this approach is the presence of dung on hides, which causes the fleshing blade to cut into hide, thereby damaging the pelt in an economically unacceptable way. Removal of dried-on dung by methods other than soaking is difficult. However, dung removal is a pre-requisite to processing. The problems associated with dung contamination may be pre-empted by utilisation of hides and skins, where available, from animals that have been reared through a quality assurance or clean hide scheme. These schemes generally require animal husbandry practices that minimise dung contamination.

2.2 Classical unhairing-liming process

The enzymatic treatment of hides and skins can be considered as a cleaner technology only if the amount of sodium sulphide is reduced substantially. However it is not yet possible to replace totally sodium sulphide in processing skins and hides. There are other agents available that reduce the amount of sulphide in liming, e.g. organic sulphur compounds (mercaptoethanol, salts of thioglycolic acid, formamidinesulphinic acid) and amines based proprietary products.

However, it should be borne in mind that all hair dissolving processes will contribute to the COD/BOD of tannery effluents.

2.3 Hair saving unhairing-liming methods

For traditional skin production, painting and sweating may be considered cleaner technologies. Recovery of hair before dissolution, either when it is separated during the liming, or at the end of a hair saving process, can lead to a COD reduction of 15-20% for the mixed tannery effluent, and a total nitrogen decrease of 25-30%.

It is an advantage to filter off the loosened hair as soon as possible and higher COD and nitrogen reduction can be obtained. This process can be considered as a cleaner technology if the hair is utilised, even as a nitrogen source.

There are several established methods of hair saving, routinely used in industry. However, is it recognised that they do not provide a complete effect, since each incorporates a hair dissolving step, to deal with residual short hairs.

2.4 The direct recycling of liming float

Direct recycling can be applied when there is a good control level in the tannery. Resulting advantages are savings in sodium sulphide (up to 40%) and in lime (up to 50%). It can give a decrease of 30-40% of the COD and 35% of the nitrogen for the mixed effluent.

The quality of the leather produced can be affected negatively through this recycling process, unless the unhairing and opening up processes are used in two steps. This is because the suspended melanin and undissolved cuticle fragments from the dissolved hair (referred to as scud) are driven into the grain by mechanical action, making it dirty.

This cleaner technology is industrialised in several large bovine tanneries for shoe upper leather. The success depends on how the hair is removed and how well the recycled liquors are cleaned up before they are recycled.

2.5 Splitting limed hides

Faced with the difficulties of upgrading the chromium-tanned split waste, splitting in the lime can be considered as a cleaner technology, as it saves chromium and yields a by-product that can be used for food casings or for the production of gelatine.

2.6 CO_2 deliming

Up to 40% of a tannery's production of ammoniacal nitrogen comes from the use of ammonium salts during the deliming process. Carbon dioxide deliming can be considered as a cleaner technology giving good results on light bovine pelts (thickness less than 3 mm). For thicker hides, it is necessary to increase float temperature (up to 35°C) and/or process duration and/or to add small amounts of deliming auxiliaries. In order to effectively eliminate the creation of hydrogen sulphide as the pH of the deliming solution falls, 0.1% hydrogen peroxide can be used to scavenge residual sulphide. The grain enamel should be allowed to delime for perhaps 5 minutes, to guard against oxidation damage, then the peroxide can be added safely.

If the pH falls below 7, in the case of black or red hides they may appear dirty due to the retention of melanin in the depleted grain layer.

If the pH of CO_2 deliming float is lower compared to common procedure, special bates can be used. Also, bates with a lower content of ammonium are available.

2.7 Other ammonium-free deliming

Ammonium-free deliming agents, such as weak acids or esters, can totally or partially replace ammonium salts used for conventional deliming. However, in comparison with CO_2

deliming the resulting COD is often higher, due to the contribution from the reagent. Cost and slowness of reaction make them less viable.

3. Tanning Operations

Chromium (III) tanning salts are used today in 85% of tanning processes around the world. Only the trivalent form is used for tanning operations and this chemical cannot be replaced by another to give the same quality of leather.

An argument for continuing to use basic chromium (III) sulphate is the ease of managing its discharge into the environment and its low environmental impact. Chromium (VI), a recognised carcinogen, is not used in leather manufacturing processes.

3.1 Reduced salt use in pickling floats

When pickling and tanning steps are separated, the recycling of pickling floats can save up to 80% of normal salt used and 20 to 25% of the pickling acid. When they are conducted as one step, the neutral electrolyte can still be recycled in the spent liquor and reused for pickling. However, in the absence of analytical data, it must be assumed that much of the formate in the system will be bound to chromium, either on the leather or in solution.

For wool-on sheepskins, using long floats over 150%, recycling of pickling and tanning liquors is current and routine practice. It is also feasible to recycle bating floats.

Salt concentrations in pickling floats can also be reduced by using non-swelling acids, which, however, might affect the leather character.

3.2 Degreasing operations

Solvent degreasing is still in use. This practice can lead to a cleaner technology when the solvent is recovered, the extraction brines are recycled and the natural grease is recovered for commercial use. Discharge of solvents is unavoidable with solvent degreasing, but alternative technologies can be applied for high quality skin production.

For wool-on lambskins, it is a common practice to undertake dry solvent extraction when crusted.

The use of non-solvent methods implies the use of higher amounts of surfactants. Ethoxylated fatty alcohol surfactants are recommended, because they are more easily degraded. The use of the ethoxylated nonylphenol surfactants is now regulated and restricted in the EU, they should not be used. The COD from aqueous treatment may amount as much as 200,000 mg/l, due to the content of natural grease and surfactants (1g/l of natural grease is about 2,900mg/l COD, and 1g/l ethoxylated surfactant is about 2,300mg/l COD).

To ensure complete mobilisation, aqueous degreasing would, ideally, be carried out at a temperature above the melting point of the grease. However, the melting point of the grease is normally very close to the shrinkage temperature of the skin. For example, the melting point of sheepskin grease is approximately 42°C, whereas the shrinkage temperature of sheepskin pickled pelt is approximately 50°C. Therefore, the risk of heat damage to the pelt precludes the use of temperatures above the melting point of the grease.

The grease may also be contained within lipocytes, further limiting its dispersal.

The aqueous degreasing of pigskins may be assisted by the use of proteolytic enzymes to degrade the lipocyte and, thus, mobilise the grease. However, this may not be possible for sheepskins where the fibre structure is more susceptible to the proteolytic activity of the enzyme.

3.3 Wet-white pre-tanning

The rationale behind this notion is to pre-tan or pre-treat the hide, in order to be able to split and shave prior to chrome tanning, so that less tanned waste is created. The rationale is to confer resistance to the frictional heating of the pelt surface during shaving. Ideally, the pre-treatment should be reversible, so that chrome tanning is conducted on unchanged pelt.

This process can be considered as a cleaner technology if the chemicals used are neither toxic nor cause adverse environmental impact. Aluminium (III), titanium (IV) and zirconium (IV) have been suggested for this role: they are not listed as hazardous, although restricted in several countries, but their degree of reversibility depends on how they have been applied. Aldehydic tanning agents can be considered as leading to a cleaner process, according to local regulations, but their reactions are completely irreversible, so contribute to a different character in the leather. Syntans are an option, because their action is more reversible.

The alternative approach is to change the properties of the pelt, to make it less prone to distort when the surface is struck by the shaving blade. This can be achieved by reducing the ability of the fibre structure to slip over itself: this is best achieved with hydrated silica, used in the fabric industry for the same purpose. Silica interacts weakly with collagen, in a non-tanning manner, and the effect can be reversed: any discharged silica has negligible environmental impact.

3.4 Direct recycling of chromium tanning floats

When applied under strict control, this can markedly limit chromium from tanning in the effluent. Savings can be obtained from the process: a reduction of 20% of the chromium used in a conventional tannery process, up to 50% for wool-on sheepskins, and substantial reduction in the amount of salt used, since it too is recycled.

Excess chromium containing liquor that cannot be easily recycled may be precipitated and then recycled. Usually such re-use produces wet blue that is a little different in colour.

Acidifying the recycled liquor to pH 1 can revert the chrome species to those in fresh chrome liquor.

3.5 Recovery after precipitation

When large quantities of chromium bearing floats are recovered, recycling after precipitation is another solution for chromium recovery. Precipitants that might be used include sodium carbonate, sodium hydroxide, and magnesium oxide. The difference between them is the effect they have on the precipitate: the faster the basifying reaction, which is dependent on the alkalinity and the solubility, the more voluminous is the precipitate and the slower is the settling rate. Therefore, the greatest sludge density is obtained using magnesium oxide. The addition of polyelectrolyte can improve flocculation.

Sludge obtained after sedimentation and optional filtration is re-dissolved in sulphuric acid, to control the desired basicity in the product. In order to ensure complete solubilisation of the chrome sludge, the reaction should be conducted at >70°C. For conventional tanning, it is possible, with this process, to obtain a clarified effluent, with less than 10 mg/l of chromium expressed in Cr, which might be reused for the next pickling or tanning float. The clarified effluent can also be reused for first soaking float.

Using recovered chrome for tanning results in wet blue that is slightly paler than conventional production. Further the re-use of precipitated chromium will lead to an increase in the neutral salts in the effluent.

3.6 High exhaustion tanning process

In order to reduce chromium concentration in the waste float, high exhaustion chromium salts, adapted basification products and/or temperature increase can be used. In essence, all proprietary options are based on higher astringency, by employing higher pH in basification, but most importantly elevated temperature.

3.7 Chromium-free tanning

In most cases, chromium (III) tanning should be considered as the best available technology. Many alternative formulations have been proposed, but none can exhibit the versatility of chromium (III) for making a wide variety of leathers. Also, the high hydrothermal stability of chrome leather is a prerequisite for many modern applications of leather.

Vegetable tanning is the traditional alternative to chrome tanning: conducted by a dry drum process, or in closed circuit vats, it can minimise waste and must be included in these considerations. Due to the high pollution load and slow biodegradability, conventional vegetable tanning cannot be considered more environmentally friendly than chrome tanning. Vegetable tanning has limited applications, because of the low hydrothermal stability, the filling effect and the hydrophilicity of the resulting leathers. Recovery of vegetable tanning floats by ultrafiltration is used in several European tanneries and the recovered tannins may be used in the tanning process.

Tanning with organic tanning agents, using polymers or condensed plant polyphenols with an aldehydic cross-linker, can produce mineral-free leather, matching the high hydrothermal stability of chrome leather. However, they do not have the same characteristics as chromium tanned leather, because they are much more filled and hydrophilic.

Metal-free leathers are being successfully used to produce high quality speciality leathers, for example, automotive leathers with good thermal stability.

Semi-metal tanning can produce chrome-free leather, with equally high hydrothermal stability. It is a combination of a metal salt, preferably but not exclusively aluminium (III), and a plant polyphenol containing pyrogallol groups, often in the form of hydrolysable tannins.

A life-cycle analysis of each process needs to be taken into account.

4. Post-tanning Operations

When the use of chromium is required for retanning operations, the same consideration should be given as for chrome tanning. Absence of environmentally unsound dyestuffs, especially those containing banned aromatic amines, and of halogenated oils in fatliquors, form essential elements of cleaner processing. High level of exhaustion for syntans, dyes and fatliquors are also to be considered: in each case, the chemical principles and conditions for reaction with the leather must be optimised.

5. Finishing Operations

The use of water-based finishes is fundamental for a cleaner process, but the inherent need to use cross-linkers should be kept in mind. Chemicals used in finishing must not contain any environmentally undesirable heavy metals or other restricted products. Water based formulations (containing low quantities of solvent) are available for spray dyeing. Finishing products have to meet the current limits imposed by environmental and workers health regulations. The equipment used is extensive. Roller coating or curtain coating machines are more desirable from an environmental point of view, but they cannot be used for all types of leather. For other types, spraying units with economisers and high volume low pressure (HVLP) spray guns can reduce discharges to the environment.

6. Recycling

6.1 Introduction

Recycling typically means a second utilisation for the same purpose, reuse may mean utilisation for different purposes and recovery incorporates an isolation step. Recovered material can then be recycled or reused.

Recycling technologies have been used for long time in vegetable tanning processes, indeed the conventional counter-current method incorporates recycling as a fundamental element of the technology.

Simple recycling technologies need some control to prevent any deviation in the tannery process. A laboratory with basic analytical equipment is desirable.

6.2 Beamhouse process

To reduce the volume of saline effluents, particularly if this segregated float needs to be evaporated or specifically processed, it is possible to reuse soaking floats in a counter current method, analogous to vegetable tanning. Here, the pelts progress into cleaner float and the contaminated floats move towards the dirt soak. Only the dirt soak liquor, in which dirt and salt are accumulated, is discharged to waste and treatment. This decreases the amount of water to be evaporated, when salinity is restricted, and reduces the presence of biocides in effluent. However, it does not solve the problem of what to do with the dirt soak solution. Lagooning, where feasible, reduces the volume, but the salt remains.

The unhairing-liming float can also be reused for the next process. It must be taken into account that the recovery rate of the liming float should not exceed 75 % in order to limit the nitrogen concentration. Besides recycling materials (pumps, fine screening, storage tanks), it is sometimes necessary to warm the float before reuse and also to screen or skim it in order to eliminate undesirable floating solids and to remove hair and grease from the surface. Without any sedimentation, an industrial recycling process can save 35 to 40% of sodium sulfide and 40 to 45% of the lime (with classical process quantities of 2.5 %). Excessive quantities of lime should be avoided during the process; it is worth recalling in this regard that the theoretical requirement for bovine hide is about 1.2%.

6.3 Tanning process

Degreasing float

When sheepskins are solvent degreased, recycling of the residual solvent after distillation is currently operated. Furthermore, the extraction brine is also easy to reuse, to save sodium chloride.

Pickling float

Recycling of pickling float has been proven to be highly satisfactory in terms of salt savings and partly for acid savings. There is no great difficulty if density and acidity of the float can be regularly controlled.

Tanning float

The most common practice is to collect the residual tanning float, to filter it, to adjust its acidity, then to reuse it as a new tanning float before adding fresh chromium salt. The recovered volume may be more than required for subsequent tanning operations, but it is possible to reuse the liquor in post tanning.

Another possibility is to use the tanning float for a pre-tanning process. In this case, 60% of the residual chromium can be recovered.

When pickling and tanning are carried out in the same float, it is also possible to collect the residual tanning float, to filter and acidify it and reuse it as a pickling float.

6.4 Post-tanning process

It is much less feasible to recycle post-tanning floats, since the chemical condition required for the steps may be different and steps tend to be conducted sequentially in the same float. Therefore the problem of contamination is compounded, especially since these steps vary greatly, even in a single factory. Thus, recycling technology cannot be recommended.

7. Water Management

Leather production is a water intensive industry, therefore measurement and control of consumption are important and essential points of water management

In many countries water has become a scarce commodity and the costs for the consumption and discharge of water increase regularly. Water has to be managed properly and several options are available to minimise the overall consumption of water.

Reduction: The first step is reduction of water consumption, with strict measurement and control of consumption. Low float processing, batch-type washing instead of rinsing and combining processes (compact recipes) are practical examples of technologies to reduce water consumption by 30% or more. However, lower volume of water will result in higher pollutants concentration, but that will be partially offset by the greater efficiency of shorter float process steps. Limits to reducing float length must be borne in mind, since not all processes benefit from reduced float length.

Recycling: Certain specific processes are suitable for recycling of floats, although in most cases installations for treatment are necessary. Examples are; soaking, liming, unhairing, pickling and chrome tanning liquors, which can reduce the overall water consumption by 20 - 40%.

Re-use: Biologically treated effluent offers the opportunity of replacing a certain amount of the process floats, such as the beam house process floats, with treated water. Depending on the type and efficiency of the treatment process additional operations might be necessary, such as filtration and disinfection, to meet the required water quality standards.

Membrane systems provide the possibility of reusing treated effluents, provided that most of the residual organic matter is removed and disposal of the concentrate is achievable.

8. Reduction in chemical use

Processes should be optimised with regard to chemical use to minimise waste. Reduced floats allow reduction in chemical use (liming, deliming and pickling). However, due regard should be placed on the chemical and biochemical principles of processing, in order to avoid the unnecessary excessive chemical use, for example, lime, sulphide, salt, chromium, dyes, lubricants, etc.