

**IUE DOCUMENT ON
RECENT DEVELOPMENTS IN CLEANER
PRODUCTION AND
ENVIRONMENT PROTECTION IN
WORLD LEATHER SECTOR**



**INTERNATIONAL UNION OF ENVIRONMENT
(IUE) COMMISSION of
International Union of Leather Technologists and
Chemists Societies (IULTCS)**



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IUE DOCUMENTS ON RECENT DEVELOPMENTS IN CLEANER PRODUCTION AND ENVIRONMENT PROTECTION IN WORLD LEATHER SECTOR

BACKGROUND

The International Union of Environment (IUE) Commission of IULTCS has got 40 technical representatives from 26 member countries and invitees from United Nations Industrial Organization (UNIDO), European Union and other relevant organizations. The Chairman of the IUE Commission is Dr. S. Rajamani from India and Secretary is Mr. Thierry PONCET from CTC Lyon, France. The IUE Commission meets every year in one of the member countries. The meeting for the year 2008 was held during October 2008 at Rio de Janeiro along with XVII Latin-American Congress of Leather Technicians and Chemists. The meeting for the year 2009 has been scheduled during 11 to 14 October 2009 at Beijing along with XXX IULTCS Congress. The Chairman interacts regularly with IUE members and IULTCS as an executive committee member. The current list of IUE members with their addresses is attached.

The IUE Commission has developed technical guidelines and documents on viable cleaner production and environmental protection aspects based on the waste generation from different processes, environmental regulations in member countries and experience in field practices. The IUE Commission report contains eleven documents covering all salient aspects. The IUE documents have been translated in Spanish, Turkish, Portuguese and other regional languages. IUE Commission activities and Environmental updates in World Leather Sector are disseminated through IULTCS Website, presentation in National, Regional and International congresses and publication leather journals.

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IUE -1: RECOMMENDATIONS ON CLEANER TECHNOLOGIES FOR LEATHER PRODUCTION

2008 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 lorries, 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, benzalkonium chloride, sodium fluoride and boric acid. 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 countercurrent 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, it is 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 CO₂ 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 CO₂ 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 CO₂ 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 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.

On 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 alcohols are recommended instead of the more widely used ethoxylated alkylphenols, because they are more easily degraded and the use of the latter are to be restricted in the EU. 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 alkylphenol 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 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 $>70^{\circ}\text{C}$. 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 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 crosslinker, 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 benzidine and other 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 crosslinkers 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, are 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, chrome, dyes, lubricants, etc.

Updated by
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IUE – 2: RECOMMENDATIONS FOR TANNERY SOLID BY PRODUCT MANAGEMENT

2008 Updated Document

Aim of the document:

The International Union Environment Commission (IUE) 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 reuse of untanned solid waste is restricted or carefully controlled for human and animal food. The general recommendations collected by the Commission have to be adapted to local conditions and under the supervision of an expert.

General remark:

Please note that any untanned hide by-product (e.g. fleshings, trimmings, splits) from BSE (Bovine Spongiform Encephalopathy) regulated animals must be totally destroyed.

EU regulations for animals by-products do not allow hides and skins from BSE-infected animals in a tannery. It should be clearly noted that from the liming stage the skins are no longer considered an animal by-product by the regulations.

1. DUSTED SALT

The dusted salts may be reused for pickling after dissolution in water and clarification or filtration. Alternatively, the recovered salts could be used for a number of applications including foundry casting (in the mould), hypochlorite production and de-icing of roads. Dusted salt can be reused for curing but a preliminary heat treatment is required to reduce bacterial impact and to limit the presence of organic matter in recovered salt.

2. GREEN FLESHINGS

Green fleshings can be used in rendering plants for the recovery of grease and meat meal. These products must be clean, and contain minimal quantities of minerals.

More importantly, green fleshings are a valuable source of high quality tallow, a basic commodity with added value. In contrast to limed fleshings, green fleshings need little pH adjustment prior to enzyme processing. They produce much higher yield and the quality is good, because the fleshings are not previously subjected to prolonged alkaline treatment.

3. TRIMMINGS

The green and limed trimmings can be used with limed splits for tallow or gelatine production (see below).

4. LIMED FLESHINGS

4.1 Methane production

Untanned wastes mixed with farming, domestic and fish wastes can be used for methane production; full-scale plants are in operation in Denmark and Sweden.

Waste fleshings mixed with tannery sludge are digested to produce methane by grinding to 10 mm and warming to allow microbiological activity, with increased fat or grease content resulting in increased methane production. The volume of gas evolved (comprising 75% methane) is estimated to be 615 litres per kg of organic material introduced into the digester, after 25 to 30 days at 35°C. The residual solid phase is suitable for composting according to chromium content and can be applied directly to agricultural land as a soil improver. This technique is especially suited to warmer countries, where the necessary heat input is minimal. The input mix material for this system must have at least 70% of organic matter content to operate successfully. An industrial scale plant is in operation in India.

In Denmark, ferrous metal salts are added directly to the reaction vessel of the bio-gas reactor to avoid the generation of noxious and corrosive gases.

4.2 Grease and protein recovery

Hydrolysis leading to the recovery of animal grease and proteins can be achieved in two ways; either by a liquid hydrolysis (acid or alkali catalysed), or by enzymatic digestion at 35°C. Following hydrolysis or digestion, the emulsion must be heated to at least 50°C to separate the fat, protein and water components into separate phases. The protein phase contains 5 to 10% protein.

Limed fleshings must be acidified before enzyme treatment. They produce a low yield of tallow, because it considerably hydrolysed by the liming process; in addition the quality is low because of the high content of free fatty acid from that hydrolytic reaction.

Gaseous by-products of the process are hydrogen sulphide, mercaptans and odour, and it is therefore essential to exhaust these via a water wash or a scrubber system containing sodium hydroxide and sodium hypochlorite. However, in some places, the exhaust gases are passed into the air intakes of the boilers used for energy production, thereby eliminating the need for a scrubber. In some cases, a ferrous metal scrubber may be needed prior to the boiler to capture sulphides.

In respect of the capital and running costs, it is estimated that for economic viability, 10 tonnes of material must be processed per day.

A second process technology involves treatment with hydrogen peroxide and sulphuric acid at 35-40°C. For this, the fleshings must first be chopped to a particle size of 50-200 mm. The process produces two phases that can be separated by mechanical de-

watering; grease separates from the liquid phase, the yield being 10 to 12.5% of the original fleshings mass. A protein phase (20-25% dry solids) is also obtained and this can be used either as animal foodstuff after drying, or as fertiliser. Again, a minimum quantity of 10 tonnes per day needs to be processed for economic viability.

4.3 Composting

A mixture of waste fleshings and an appropriate bulking agent (also carbon source), with aeration, leads to compost production

5. RECOVERED HAIR

There are a number of reported promising uses for the recovered hair from hair-save processes. These include: felt production, slow degrading plant containers, keratin hydrolysate, cosmetics and pharmaceutical products (i.e. shampoo, amino acids, etc.)

5.1 Composting

Hair recovered through a hair-save process can be incorporated into existing composting processes, as it is a valuable source of nitrogen and organic carbon.

5.2 Fertiliser

Hair can be directly used as slow release source of organic nitrogen and carbon for fertilising purposes

5.3 Recovered hair from pigskins

Hair from pigskins is a valuable material that is used for brushes and other consumer products.

6. LIMED SPLITS

6.1 Gelatine production

Gelatine production by a specialised, purpose built process facility represents a major utilisation opportunity for lime splits, not suitable for tanning. The process involves lime hydrolysis; soluble gelatine is extracted in a series of hot water batches of increasing temperature at controlled pH. Different stages of purification, demineralisation, concentration and sterilisation are then required prior to final drying. The gelatine product is used by the food, photographic and pharmaceutical industries. Lower quality gelatine or glue can be produced by acid hydrolysis and hot water extraction.

6.2 Sausage casings

Specialised manufacturers use limed splits to produce high quality sausage casings. The casing manufacturer will impose restrictions on the process chemicals used in the beamhouse.

6.3 Pet chews

Delimed hide splits can be dried in moulds of various shapes, to produce dog chews.

6.4 Composting

Limed splits, high in nitrogen, low in carbon, will compost readily.

7. GREASE FROM DEGREASING PROCESS

Grease from the degreasing process can be used as a component of low grade fatliquors through a sulphitation process.

8. WHITE SPLITTINGS

As for lime splits, the wet white process produces splits that can be partially denatured to produce gelatine or collagen additives. However their use in human food production is restricted.

9. WHITE SHAVINGS

Wet white chemistry options can create environmentally friendly tanned waste; aldehyde tanned, syntan tanned, marginally vegetable tanned materials have little associated hazard. These shavings are particularly suitable for use as fertiliser or as a source for collagen hydrolysate. Aluminium containing shavings can be applied to non-acidic agricultural land, according to local regulations.

10. BLUE SPLITS AND SHAVINGS

10.1 Leather board manufacture

Companies are producing leatherboard from bovine chrome and vegetable shavings and splittings in several countries, although only shavings satisfying strict quality requirements are accepted for processing. The leather fibres are mixed with latex, and after coagulation, the mixture is de-watered, pressed and dried. The final product is obtained either as separated sheets or as a continuous material.

10.2 Chemical hydrolysis

One industrial gelatine manufacturing process blends the shavings with magnesium oxide and subsequently extracts 50% of the gelatine content with boiling water. A chromium containing slurry ('scutch') is generated as a waste.

Protein extraction can be improved with magnesium oxide assisted by enzymes. Liquid proteins can be used for industrial applications. The chrome cake can be recovered for chrome liquor production. Other alkaline agents, such as lime and sodium hydroxide are used industrially.

Acid hydrolysis utilises concentrated sulphuric acid with steam injection. The hydrolysate is neutralised with phosphates and supplemented with organic additives to produce a fertiliser.

The hydrolysate can also be used for different industrial applications, such as in retanning operations in tanneries, as a coagulating agent in the rubber industry, as complementary products for surfactants and as plasticiser in concrete production.

10.3 Thermal treatment

Various laboratory and industrial trials have demonstrated that chromium containing leather waste may be thermally treated to produce an ash containing approximately 50% chrome oxide, which is similar in nature to the mineral ore feedstock, sodium chromite, used by the chromium chemicals manufacturing industry. Sodium chromite, converted into chromate, is the precursor of most chromium chemicals, including chrome tanning agents.

10.4 Enzymatic treatment

Enzymatic digestion of shavings results in a high quality and valuable hydrolysate or gelatable protein and a protein contaminated chromium sludge. The hydrolysate can be used in retanning agents, as foam stabilisers, in the chipwood industry and gypsum industry. The chromium sludge can be reused in a dichromate reduction plant for the production of chromium sulphate. Full-scale factories processing shavings have been in operation in the Czech Republic and USA.

10.5 Brick making

Mixing of limited amounts of chrome shaving into clay for brick making is carried out in South America.

11. VEGETABLE TANNED WASTE

Vegetable tanned shavings and trimmings may be used in leatherboard or fertiliser production via a roasting or a wet fermentation process.

12. WASTE WATER SLUDGE

Wherever possible, the chromium from spent tanning liquors should be recovered and reused or used in other industry (e.g. steel). Alternatively, high exhaustion chrome tanning systems should be used. Either method will minimise the mass of chromium discharged.

The organic content of a soaking sludge can be reduced by 65 % in a UASB (upflow anaerobic sludge blanket) process.

Usual incineration of sludge (with or without leather waste), although technically feasible, will have limited application due to the economy of scale, and due to associated environmental problems (air pollution and possibility of chromium oxidation).

There is no risk-based justification for banning the application of chromium containing wastes to agricultural land. However, the chromium content of sludge applied to land must be limited in order to comply with existing regulations and requirements.

Mixing the sludge with clay and bricketting, solidification with fly ash and cement would minimise leaching of chromium.

13. BY-PRODUCTS YET TO BE UTILISED

- Buffing dust
- Crust and finished leather waste
- Finishing resins
- Chrome precipitated from post-tanning operations

Viable uses for all the above wastes need to be established.

14. ALL SOLID WASTE

One option for dealing with all solid waste is incineration, combustion of the organic content of feed material, with controlled availability of oxygen. However, this technology has a bad reputation for producing odour and the possibility of producing dangerous fly ash makes it less environmentally acceptable.

An alternative approach is gasification. Here, the organic content is converted to combustible gas by heat and the gas is in turn burned to maintain the process. The products are heat and stabilised, inert solid. The technology is relatively new, but been established as environmentally sound and has been successfully applied.

While these options are viable, the costs and environmental compliance implications may limit their application.

IUE Commission

October 2008

IUE – 3: DOCUMENT ON TOTAL DISSOLVED SOLIDS IN TANNERY EFFLUENT

2008 Updated Document

At present most raw hides and skins are preserved through a salting process, using between 30 to 50% of common salt on the weight of raw hide/skin.

Total dissolved solids (TDS or neutral electrolyte) has become a major problem in many countries. For example, some have set up regulations to limit the concentration of salts in effluents after waste water treatment; such as South Africa (1350 mg/l of TDS), Italy (1200 mg/l of chloride, 1000 mg/l of sulfate), India (2100 mg/l of TDS, 1000 mg/l of chloride, 1000 mg/l of sulfate). These limits apply for effluent from all industries, not just the leather industry.

In many cases these limits are difficult to achieve:

- TDS concentration is not reduced by conventional waste water treatments.
- Natural drying as a preservation method is limited to warm countries, where salting and energy are more expensive.
- Fresh processing of hides and skins needs a source of raw material that is constant in quality and quantity.
- Chilling hides or skins is feasible in many countries.
- Other preservative chemicals are suitable for short term preservation, but are not yet adapted for the long term.
- Some sodium chloride is necessary for pickling procedures before tanning.
- During leather production, various inorganic chemicals are added (for example, deliming may be conducted with ammonium chloride, chrome tanning salt typically contains 50% sodium sulfate, dyes may be diluted with electrolyte). These chemicals are routinely used and their replacement may not be simple.

Consideration must be given not only to the TDS concentration in the mixed effluent, but also to reducing the total TDS per kg of hides/skins processed.

Trimming and, where possible, preflashing are recommended to reduce the amount of salt added for preservation

Beside alternative preservation methods, there are a few established technologies to reduce TDS :

- Mechanical or manual removal of salt from hides and skins before soaking
- Organic acids compounds or CO₂ deliming instead of ammonium salts.
- Direct recycling of the pickling float.
- Direct recycling of tanning floats.
- Recycling of supernatant from chrome recovery.
- Use of liquid dyes and syntans, etc.
- Use of short float with reduced load of chemicals

TDS up to 20,000 mg/l and chlorides up to 10,000 mg/l do not substantially decrease the efficiency of biological treatment of tannery effluents.

High levels of TDS and sodium chloride are typically present in tannery effluent. The TDS concentration can reach 7,000 mg/l and in some cases more than 15,000 mg/l. The less water is used for leather production, the higher the TDS concentration.

Waste water treatment eliminates most of the suspended solids, large quantities of dissolved organic chemicals and ammoniacal nitrogen, but it has hardly any effect on TDS.

Current technologies under investigation to separate TDS in treated effluent are :

- Evaporation. This is used in some countries, achieved mostly by natural evaporation in lagoons, so the water cannot be reused. It requires a large area, taking into account typical average evaporation rates of not more than 5 mm per day in sunny conditions. This rate can be improved with technologies such as spraying. Multiple stages or vacuum flash evaporation cannot be considered economic.
- Reverse osmosis (RO). This technology is now being applied for tannery effluents to reduce TDS and recover quality water for re-use. It is a high-tech solution with relatively high investment and running costs. However it provides the possibility of recovering 70-80% of the initial float and TDS is reduced from the range of 8000 – 15000 mg/l to less than 500 mg/l. Proper tertiary treatment is necessary to achieve good results in RO treatment. The disposal of the remaining 20-30% of the initial float, containing high concentration of TDS (25-50 g/l), must be taken into account.

In either case, the TDS content is not actually treated or disposed of; it is merely separated from the rest of the effluent. The current disposal of waste neutral electrolyte remains a significant challenge for the global leather industry, particularly for those tanneries located in land-locked areas. The only sustainable solution is to eliminate it from preservation and processing as much as possible.

IUE Commission

October 2008

IUE - 4: ASSESSMENT FOR CHROMIUM CONTAINING WASTE FROM THE LEATHER INDUSTRY

2008 Updated document

Chromium (III) is the most widely used tanning agent in the leather industry; chromium(VI), the carcinogenic form, is not used in the tanning process. Chromium may be considered as a source of pollution due to the large volume of exhausted residual tanning floats and solid waste produced.

Cleaner technologies used to reduce chromium in wastewater, such as high exhaustion process, direct or indirect chromium recycling, cannot eliminate chromium from effluent completely, because there is typically significant discharge from post tanning. In addition, some chromium remains in sludge derived from tanning.

Total replacement of chromium has been attempted using combinations of metallic cations, for example titanium(IV), aluminium(III) and zirconium(IV), but the results obtained could not match chromium, in physical properties and character, but most importantly in hydrothermal stability. This makes such tannages unsatisfactory for most types of leather. Other options that have been proposed are: hydrolysable vegetable tannins, alone or in combination with a metal salt (semi metal tanning), condensed vegetable tannins, alone or in combination with an aldehydic crosslinker, synthetic organic tanning agents, alone or in combination with an aldehydic crosslinker. These traditional or new tannages can be used for some leathers, but none is suitable for all leather, like chrome.

Although apparently more ecologically acceptable, because they are derived from a natural, renewable resource, vegetable tanning cannot be considered more environmentally friendly than chrome tanning, due to the high pollution load and low treatability in conventional systems. Also vegetable tanned leather has different physical properties and limited modern applications. Vegetable tanned leather is less easily biodegraded than chrome leather. In both cases, the leather resists microbial attack, which is part of the definition of tanning. However, if the leather is damaged, chemically or thermally, it becomes vulnerable to enzymatic breakdown. In the case of chrome leather, it can be degraded with ease, because the tanning agent is completely bound to the collagen by the action of tanning. In the case of vegetable tanned leather, the tannins are weakly bound to collagen and are unaffected by chemical or thermal damage. Therefore, the tannins remain active, capable of interacting with attacking enzymes and deactivating their action: this makes vegetable tanned leather much more resistant to biological degradation.

Although chromium is an essential trace element for human health (glucose tolerance factor) (Iyengar 1989; Anderson 1989), there is no doubt that Cr(VI) compounds are both acutely and chronically toxic (Rinehart, 1989).

Cr(III) is less toxic than many other elements (Hg, Cd, Pb, Ni, Zn) to mammalian and aquatic organism, probably due to the low solubility of this element in its trivalent form

at pH>4 (Moore and Ramamoorthy, 1984). Similarly, Cr(III) compounds also have a very low mobility in soils and are thus relatively unavailable to plants (Adriano, 1986).

Compared to Cr(VI), the toxicity of Cr(III) (chromium sulphate) is insignificant. Some toxicity levels of chromium sulphate in neutral medium (that is to say chromium salts used in the tannery) are shown in the following table (Carré and all., 1983).

	Cr(III) (mg/l)	Cr(VI) (mg/l)
Algae (<i>Scenedesmus subspicatus</i>) CIG 50, 5 days	> solubility	0.42
Bacteria (<i>Enterobacter aerogenes</i>) CIG 50, 8±1 hours	> solubility	6.4
Bacteria (<i>Pseudomonas fluorescens</i>) IC 99.9 %, 4 hours	> solubility	250
Urban activated sludge IC 50, 3±1 hours	75 *	5.3
Daphnia (<i>Daphnia magna Strauss</i>) IC 50, 24 hours	7.5 - 9	0.4
Fish (<i>Brachydanio rerio</i>) IC 50, 24 hours	> solubility	95

* For CrCl₃ (Semsari and Gaid, 1993)

Note:

CIG - Concentration level Inhibiting Growth

IC - Inhibitory Concentration

The reducing characteristics of tannery sludge stabilise Cr(III) with respect to Cr(VI), due to the presence of organic matter and sulphide (Adriano,1986; Losi and Frankenberger, 1993). Field investigations concerning Cr migration in soils treated with tannery sludge (Dreiss, 1986) have demonstrated low Cr(III) mobility.

Conventional incineration of sludge (with or without leather waste), although technically feasible, has limited application due to associated environmental problems (air pollution and possibility of chromium oxidation). Incineration at elevated pH (9-10), in the presence of an excess of oxygen, can lead to conversion of Cr(III) to Cr(VI). However, newer methods allow thermal treatment of materials containing Cr(III), including sludge, without forming Cr(VI).

In 1994, the US EPA case in the United States Court of Appeal for the District of Columbia failed, because they could not prove that trivalent chrome in sludge is damaging to the environment. It is believed by the IUE Commission that for an integrated tannery, operating from raw hide to wet blue, the lowest practical chromium level is 5000 mg Cr(III) per kg dry solids in the mixed tannery sludge, which is achievable using the best available practices and cleanest technologies. In 2003, the Indian government decided to follow the IUE guideline on certain aspects. It is suggested that particular attention should be given to the application loading of chromium on the land and not the concentration of chromium in the sludge. In 2000, the European Commission decided not to add chromium-containing waste to the hazardous waste list (Decision 2000/573, July 23rd).

In some countries the concentration of Cr (III) per kg dry solids in sludge is limited for application to edible crops (ranging from 5000 to 100 mg Cr(III) per kg dry solids).

To obtain a level lower than 1000 mg Cr (III) per kg dry solids, it is necessary to process separately chromium containing effluents such as residual tanning floats and post-tanning floats.

The Commission will follow any new results in the field of utilisation of chromium containing sludge and will update this document accordingly.

IUE Commission

October 2008

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IUE - 5 :TYPICAL PERFORMANCE FOR TANNERY WASTE WATER TREATMENT

2007 Updated document

Parameters	COD (chemical oxygen demand)		BOD ₅ (biological oxygen demand)		Suspended Solids		Chromium		Sulfide		N (Kjeldahl)		Conductivity	Colour	Sludge Production
	%	mg/l	%	mg/l	%	mg/l	%	mg/l	%	mg/l	%	mg/l	mS	% Pt-Co unit	kg DS/ton rawhide
PRETREATMENT															
Grease removal (dissolved air flotation)	20-40														
Sulfide oxidation (liming and rinsing liquors)	10								10						
Chromium precipitation							2-10								
PRIMARY TREATMENT															
Mixing + Sedimentation	25-35		25-35		50-70		20-30				25-35				80
Mixing + Chemical treatment + Sedimentation	50-65		50-65		80-90		2-5		2-10		40-50				150-200
Mixing + Chemical treatment + Flotation	55-75		55-75		80-95		2-5		2-5		40-50				150-200
BIOLOGICAL TREATMENT															
Primary or chemical + Extended aeration	85-95	200-400	90-97	20-60	90-98	20-50	<1		<1	50	150				70-150 ⁽¹⁾
Primary or chemical + Extended aeration with nitrification. and denitrification	85-95	200-400	90-97	20-60	90-98	20-50	<1		<1	80-90	30-60				130-150 ⁽¹⁾
Primary or chemical + Aerated facultative lagoons	80-90	300-500	85-95	60-100	85-90	80-120	<1		<1	50	80				100-140
Anaerobic treatment (lagoon or UASB) ⁽²⁾	65-75	500-700	60-70	150-200	50-80	100-200	<2	0		20-30					60-100
Membrane biological reactor (MBR)	80-95	160-500	97-100	5 - 50	100	0	<0.5	99	<0.5						(3)
MBR + Reverse osmosis (RO)													< 0.7 ⁽⁴⁾		
Constructed wetlands (after primary treat.)	70-80	300-400	85-95	60-100										85-90	

⁽¹⁾ Without chemical treatment

⁽²⁾ Mixed with 75 % domestic sewage, UASB = upflow anaerobic sludge blanket

⁽³⁾ Approximately 7 % of the metabolised COD is incorporated into surplus sludge production, compared to 30 - 50% in a conventional activated sludge system

⁽⁴⁾ At 50% permeate recovery rate

The above data represents typical values for tannery waste water treatment efficiency for conventional process liquors for production of finished leather from raw material.

Salinity is not removed through primary and biological treatment. TDS can be increased by chemical treatment.

IUE- 6: POLLUTION VALUES FROM TANNERY PROCESSES UNDER CONDITIONS OF GOOD PRACTICE

Updated 2008

Values per tonne of rawhide	Water (m ³ /t)	COD (kg/t)	BOD ₅ (kg/t)	S.S. (kg/t)	Cr ³⁺ (kg/t)	S ²⁻ (kg/t)	TKN (kg/t)	Cl ⁻ (kg/t)	SO ₄ ²⁻ (kg/t)	Grease (kg/t)	TDS (kg/t)
BOVINE SALTED RAW HIDE PROCESS											
Beamhouse (soaking to bating)	7-25	120-160	40-60	70-120		2-9	9-14	120-150	5-20	5-8	200-300
Tanning operations	1-3	10-20	3-7	5-10	2-5		0-1	20-60	30-50	1-2	60-120
Post tanning	4-8	15-40	5-15	10-20	1-2		1-2	5-10	10-40	3-8	40-100
Finishing	0-1	0-10	0-4	0-5							
TOTAL	12-37	145-230	48-86	85-155	3-7	2-9	10-17	145-220	45-110	9-18	300-520
PIG SKINS											
Beamhouse	23-49	120-272	46-98	62-110		3-7	11-17	57-197	4-15	30-67	120-300
Tanning operations	2-5	10-18	3-6	4-8	2-4		0-1	20-37	26-45	1	40-120
Dyeing operations	5-10	10-25	3-9	8-15	1-2		1-2	3-6	10-40	3	20-80
Finishing	2-5	0-5	0-2	0-2							
TOTAL	32-69	140-320	52-115	70-135	3-6	3-7	12-20	80-240	40-100	34-71	180-500
Values in litres or grammes per skin	Water (l/skin)	COD (g/skin)	BOD ₅ (g/skin)	S.S. (g/skin)	Cr ³⁺ (g/skin)	S ²⁻ (g/skin)	TKN (g/skin)	Cl ⁻ (g/skin)	SO ₄ ²⁻ (g/skin)	Grease (g/skin)	TDS (g/skin)
SHEEPSKINS (wet-salted)											
Beamhouse	65-150	250-600	100-260	150-300		6-20	15-30	150-400	5-40		
Degreasing - Tanning	30-100	50-300	20-100	15-30	8-12		4-10	40-200	30-50	40-150	
Post tanning	15-35	30-100	15-35	10-20	1-3		2-4	20-40	10-20		
Finishing	0-10	0-5	0-2	0-2							
TOTAL	110-265	330-1005	135-397	175-352	9-15	6-20	21-44	210-640	45-110	40-150	
WOOL-ON SHEEPSKINS											
Beamhouse	160 - 240	550 - 1100	150 - 1000	100	-	-	16	400			600
Tanning operations	40 - 70	150 - 300	45 - 250	15	15	-	2	460		40-150	650
Dyeing operations	75 - 100	80	25 - 50	80	5	-	3	50			270
Finishing	-	-	-	-	-	-	-	-			
TOTAL	275 - 410	780 - 1500	220 - 1300	195	20	-	21	910		40-150	1520
bovine hides = goat skins											

It is important to note that all values relate to processing under conditions of good practice, and the ranges reflects variations in raw materials and processes.

Taking into account the increasing importance of water conservation, it must be pointed out that this practice leads to higher pollution level in terms of concentration.

For this reason, the IUE commission requests that the regulating authorities limit discharges in terms of mass rather than concentration.

IUE- 7: CHARGEABLE EFFLUENT PARAMETERS IN VARIOUS COUNTRIES

2008 Updated document

Country \ Parameter	Volume	COD	BOD ₅	SS	TKN	Heavy metals	TDS or EC	Sodium	Phosphorus	AOX	Settleable solids	Toxicity	Oxidised sulphur	pH
Australia	✓	✓	✓	✓	✓	✓	✓	✓	✓				✓	
Brazil (no charges)														
China (river + sewer)³	✓	✓	✓	✓	✓									✓ ¹
Czech Republic (river)	✓	✓		✓	✓	✓	✓		✓	✓				
Denmark³	✓		✓		✓	✓								
France (river + sewer)	✓	✓	✓	✓	✓	✓			✓	✓		✓		
Germany	✓	✓	✓		✓	✓			✓	✓		✓		
Greece (no charges)														
India	✓						✓							
Italy (sewer, river¹)	✓	✓		✓	✓	✓	✓							
Netherlands	✓	✓			✓	✓								
New Zealand (river + sewer)	✓		✓	✓										
Poland (river + sewer)	✓	✓	✓	✓	✓	✓	✓		✓					
Slovenia	✓	✓			✓	✓			✓	✓		✓		
South Africa	✓	✓		✓	✓ ²	✓ ¹					✓			✓ ¹
Spain	✓	✓		✓	✓		✓		✓			✓		
Sweden³	✓		✓		✓	✓								
Switzerland	✓	✓		✓	✓	✓	✓		✓					
Tunisia (sewer)	✓ ¹													
Turkey	✓													
United Kingdom	✓	✓		✓										

1. Charged only when standards are not met.

2. Ammoniacal nitrogen

3. Charges varies according to the region within the country

NOTE: It should be clearly understood these do not represent the national standard specifications in a country.

IUE – 8: RECOMMENDATIONS FOR ODOUR CONTROL IN TANNERY

2008 Updated Document

Odours in tanneries have various origins. They mainly originate from the putrefaction of hides, skins, trimmings and fleshings, from the release of hydrogen sulphide and ammonia, and from the use of volatile organic compounds (VOCs). They can also occur in the wastewater treatment both in effluent processing and in sludge dewatering. Odours are no longer accepted by communities. This document gives some recommendations for the control of odours both inside and outside tanneries.

Air treatment

Tanneries should be well ventilated and the air from odorous areas should be exhausted and treated. Air treatment can be done biologically by blowing the odorous air through a moist bio-filter bed (compost, peat, humus) rich in micro-organisms. For effective elimination of the odour, retention time of about 20 seconds is recommended. These biofilters are now widely used and are very cost effective. Air can also be scrubbed using chemical treatments (acid, alkali and oxidant washing of the air), but running costs are higher. Areas requiring treatment include delimiting drums and areas where VOCs such as glutaraldehyde and solvents are used.

Putrefaction

Care should be taken in the preservation and storage of wet salted hides/skins, particularly in hot weather. Cooling equipment can be used to maintain storage temperatures below 30°C.

Putrefaction of untanned solid waste can be an important source of odour. Wet waste should only be kept in the factory for a very limited time and can be partially stabilised with lime or by cooling.

Hydrogen sulphide

The very toxic gas hydrogen sulphide (H₂S) has the odour of rotten eggs and is released when sulphide-containing liquors or hides are acidified. This occurs in delimiting and when alkaline effluent liquors mix with acidic streams. Concentrations of 200 ppm H₂S for 1 min can cause loss of consciousness, 500 ppm causes a deep coma with convulsions and exposure for 1 min at 900 ppm causes death. The limits for exposure are 10 ppm for 8 hours or 15 ppm for 15 min. The odour threshold for H₂S is 0.08-2 ppm. H₂S is especially dangerous because at levels over 200 ppm the odour is no longer detectable by the human nose. Portable detection devices are therefore essential.

Delimiting should be done in a closed vessel to reduce release of both H₂S and ammonia. The addition of small quantities of oxidising compounds (such as hydrogen peroxide or sodium bisulphite) can reduce H₂S release during delimiting.

Effluent from unhairing and liming processes contains high concentrations of sulphide. These liquors should be oxidised, usually using manganese sulphate as a catalyst, before being mixed with acid effluent or being discharged to the general mixing tank

which generally has a pH of 8.5 - 9. Alkaline and acid floats should be kept separately in the tannery.

Wastewater treatment and sludges

Effluent is an important source of odour. H₂S release occurs at different steps and care should be taken to limit its formation by maintaining the pH over 10 in the equalising tank and in the sulphide oxidation tank. H₂S is also generated when sulphate containing liquors and sludges become anaerobic. Anaerobic conditions in tannery waste are odorous and dangerous. Low levels of manganese sulphate can help to avoid odours in treated effluent as it facilitates the oxidation of any sulphides present.

Tannery sludge storage in a thickener, or at a dry solid content below 30%, causes noxious odours. Sludges can be stabilised with lime to minimise odour problems. It is recommended that sludges are in the thickener for the minimum time and are quickly de-watered by centrifugation or filter press and dried. Biofilters can also be used to treat the air in areas where sludge is thickened and de-watered.

Volatile organic compounds

The VOCs in tanneries include solvents used in finishing, dry-cleaning and degreasing, cross-linking agents, polymeric finishing agents and volatile tanning agents.

The finishing step is one of the main sources of VOCs, for example, butyl acetate, ethyl acetate, acetone, methyl isobutylketone and methyl ethylketone. They should be restricted to a minimum.

Most VOCs used in tanneries have a strong smell and many of them, including aqueous-based products such as formaldehyde, glutaraldehyde, etc. are toxic when present in the air at low concentrations (there is a safety limit of 0.6 mg/m³ for formaldehyde). All areas where VOCs may be present should be well ventilated and the air should be exhausted and treated appropriately.

Solvent degreasing is a source of odour. Care should be taken to control odours during float recovery, solvent distillation or skins storage.

Cleaning solvents can be used in various steps of the process, mainly for maintenance purpose.

Storage of leather with finishes containing organic solvents can lead to occupational safety and health problems if ventilation is not adequate.

Updated by
IUE Commission
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IUE – 9: RECOMMENDATIONS FOR SEWERS ADAPTED FOR TANNERY EFFLUENTS

2008 Updated document

Common effluent treatment plants (CETP) are often used for collective treatment of tannery waste water. To reach the plant, sewers are used, but sometimes their characteristics are not adapted to the special requirements of typical tannery effluent. The following recommendations are proposed to prevent any damage or accident that might happen when using inadequate or inappropriate equipment.

1. Hydrogen sulfide

Acidification of any sulfide containing liquors generates hydrogen sulfide. Therefore alkaline and acid floats should be kept separate in the tannery.

All sulfur compounds can generate hydrogen sulfide mainly under anaerobic conditions. Tanneries processing raw hides/skins mainly use sodium sulfide to remove hair or wool. Tannery effluent may contain sodium sulfide and therefore it is highly dangerous for anybody to enter a sewer without proper monitoring and without respiratory safety equipment. Even with careful sulfide oxidation in the tannery, there is a risk (see IUE Recommendations for Odour Control in Tanneries) of H₂S being developed in the sewer under acidic conditions and this gas has severe effects on unprotected humans, depending on concentration and exposure time. It is recommended that mechanical systems are used to clean sewers.

Sulfide and other sulfur compounds are also a danger for concrete sewers, because they can be oxidised to sulfate, which solubilises the calcium content of cement and concrete and thereby damages the fabric of the sewer. It is recommended that tanneries should use plastic sewers or plastic lined sewers. PVC, polyethylene or fibre reinforced plastic sewers are suitable for transporting tannery effluent.

2. Solids deposit

Tannery effluent typically contains a large amount of suspended solids (1 to 3 g/l) and when the flow circulation is too slow, deposits can occur, so clogging is likely. It is recommended that smooth materials should be used for the sewer and to maintain a minimum slope of 1 cm per metre in length. Manholes should be installed at each angle of the sewer and the distance between two manholes should not exceed 50 metres.

In order to reduce clogging in the sewer, it is recommended that solid waste should be separated from effluent streams, by using a screening unit with holes or spaces between bars not larger than 10 mm. Some mechanical screening equipment with finer mesh (2 mm or less) can be used to reduce the quantity of hairs and fibres sent to the effluent treatment plant. Appropriate pretreatment is required if effluents are transferred to a common effluent treatment plant.

3. Rain water

In order to prevent any increase in volume of tannery effluent, it is recommended that rainwater from the tannery's roof should be collected as carefully as possible, then sent in a separate sewer to surface water disposal. Alternatively, if the collected volume is great enough to be of value, it might be used in processing, e.g. soaking or even dyeing, since it will be soft water.

IUE Commission
Updated October 2008

IUE – 10: DOCUMENT ON RESTRICTED PRODUCTS IN LEATHER

2007 Draft document **DRAFT**

Introduction

Regulations to prevent the presence of some restricted products are set up in various countries. These regulations are not necessarily based on risk assessments but are precautionary measures. The presence of these chemicals in the leather results from their inclusion in commercial products used at various stages of the tannery's operations.

1. Pentachlorophenol

This preservative was widely applied before the nineties, for improving the biocidal activity on raw hides and skins. Due to the risk of transformation into dioxin, it is now completely forbidden to use PCP in leather manufacture in Europe. However it can be found in wood used for the storage of raw hide, leather or leathersgoods. It is also possible to find it in some speciality chemicals to prevent bacterial growth. PCP traces can remain in the leather, at amounts higher than the 5 mg/kg limit. Care should be taken to prevent any risk of controlled or uncontrolled addition of PCP into leather. Up to now, Germany is the only country with a regulation for PCP in leather, where it should not exceed 5 mg/kg.

2. Forbidden amines

Azo dyes or pigments used for leather dyeing and finishing can produce some aryl amines considered as carcinogenic or potentially carcinogenic under reductive conditions. The restricted amines are listed below in the table:

CAS No.*	European Union No.	name	Synonym	Classification CE 76/769	German No.
92-67-1	202-177-1	4-amino diphenyl and salts		carcinogenic cat. 1	1
92-87-5	202-199-1	4,4'-diamino diphenyl and salts	benzidine and salts	carcinogenic cat. 1	2
95-69-2	202-441-6	4-chloro 2-methyl aniline	4-chloro-o-toluidine	IARC 2A**	3
91-59-8	202-080-4	2-naphthylamine and salts		carcinogenic cat. 1	4
106-47-8	203-401-0	4-chloro aniline	p-chloroaniline	IARC 2B**	5
615-05-4	210-406-1	4-methoxy-1,3-phenyl diamine	2,4-diaminoanisole	IARC 2B**	6
101-77-9	202-974-4	4,4'-diamino diphenyl methane		carcinogenic cat. 2	7
91-94-1	202-109-0	3,3'-dichloro benzidine		carcinogenic cat. 2	8

CAS No.	European Union No.	Name	Synonym	Classification CE 76/769	German No.
119-90-4	204-355-4	3,3'-dimethoxy benzidine	o-dianisidine and salts	carcinogenic cat. 2	9
119-93-7	204-358-0	3,3'-dimethyl benzidine	4,4'-bi-o-toluidine	carcinogenic cat. 2	10
838-88-0	212-658-8	3,3'-dimethyl-4,4'-diamino diphenyl methane	4,4'-methylene di-o-toluidine	carcinogenic cat. 2	11
120-71-8	204-419-1	2-methoxy-5-methylaniline	p-cresidine	IARC 2B**	12
101-14-4	202-918-9	4,4'-methylene-bis-(2-chloroaniline)	2,2'-dichloro-4,4'-methylene dianiline	carcinogenic cat. 2	13
101-80-4	202-977-0	4,4'-diamino diphenyl ether	4,4'-oxydianiline		14
139-65-1	205-370-9	4,4'-diamino diphenyl sulfide	4,4'-thiodianiline	IARC 2B**	15
95-53-4	202-429-0	2-aminotoluene	o-toluidine	carcinogenic cat. 2	16
95-80-7	202-453-1	2,4-diaminotoluene	2,4-toluene diamine	carcinogenic cat. 2	17
137-17-7	205-282-0	2,4,5-trimethyl aniline			18
97-56-3	202-591-2	4-amino-2',3-dimethyl azobenzene	o-amino azotoluene	carcinogenic cat. 2	F
60-09-3	200-453-6	4-aminoazobenzene		carcinogenic cat. 2	F
90-04-0	201-963-1	o-anisidine	2-methoxyaniline	carcinogenic cat. 2	F
99-55-8	202-765-8	2-amino-4 nitrotoluene			
92-93-3		4-nitro biphenyl		carcinogenic cat. 2	

*CAS : Chemical Abstract Services

**IARC 2A : probably carcinogenic, 2B : possibly carcinogenic)

All the dyes and pigments used for leather production must not contain or must not produce during their use any of the restricted amines (below detection limit of 30 mg/kg for carcinogenic compounds).

This regulation is enforced in Germany and the Netherlands and a EU directive has been proposed.

3. Hexavalent chromium

Regulations limiting the Cr(VI) content in leather are in place in certain countries. The detection limit is currently 10 mg/kg (IUC 18). Some hexavalent chromium *is alleged to* occur under strong oxidative conditions, especially when vegetable and animal fats, containing unsaturated fatty acids, are used for fatliquoring.

The reducing effect of vegetable tanning agents, synthetic fatliquors and dyes can prevent the oxidation effect of trivalent chromium even under ageing conditions.

4. Formaldehyde

Formaldehyde can be used in the tanning, retanning and finishing of leather. It is classified as toxic and with possible carcinogenic effect (cat. 3 in 67/548/CEE modified in 98). In the European Union, restricting limits on the concentration of free

formaldehyde in leather may vary from 20 ppm for leather used for young children to 100 ppm when the leather is in contact with the skin, 150 ppm for shoe uppers and 400 ppm for leather without permanent contact with the skin. Formaldehyde vapour permissible in the workplace has also been restricted in many countries, up to a level of 0.6 mg/m³ or 0.5 ppm.

For the tanning process, formaldehyde alone can be used for tanning gloving leather, sportswear and white military leather. It can be used as a pretanning agent, followed by oil tanning with unsaturated animal oil (usually cod liver oil), for chamois leather. It can also be used to prevent wool loosening in the early stages of wool-on sheepskin processing, by tanning the protein at the base of the follicle, conferring resistance to microbial attack. Today it is quite possible to replace most of these uses with safer products.

In retanning operations, it is recommended to use formaldehyde free syntans or combination of syntans giving formaldehyde free leather.

New aldehydic crosslinking products can replace formaldehyde for the fixation of protein finish and give the same gloss for box calf leather.

5. Other restricted chemicals

This list here is not exhaustive. Discussions are pending to include other chemicals: such as trichloro phenol (TCP) and tributyl tin (TBT), both used as biocidal and antifungal agents .

IUE Commission

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IUE – 11: DOCUMENT FOR OCCUPATIONAL HEALTH AND SAFETY IN THE USE OF CHEMICALS IN TANNERIES

2008 Updated document

Although other factors to establish occupational safety and health recommendations could be taken into account, such as health hazards and safety risks or safety of machines and installations, we have deliberately limited this document to the chemical aspect of safety.

1. INTRODUCTION

More than 250 different chemicals are used in the production of leather. Workers in the tannery are exposed to these chemicals in various ways:

- Inhalation in form of airborne substances (gases, dust, vapours, mist, aerosols and fumes).
- Ingestion, when workers are eating, drinking or smoking in the work area or by transfer from contaminated hands.
- Skin absorption or contact, generally through the pores or cuts/wounds of unprotected hands, arms and body.

Though each chemical is not necessarily hazardous to human health, the inherent source of the hazard can be either the chemical itself, any emission generated during the use or handling of the chemical (e.g. vapours, fumes, effluent) or the containers used for storage and transport of these chemicals.

The impact of such exposure can cause temporary effects: such as dizziness, headache, irritation of eyes, skin or lungs, allergic reactions, poisoning of liver, kidney or nervous system or collapse due to lack of oxygen. Longer term illness can occur: such as occupational asthma, ulcers, bronchitis or genetic defects. In some rare cases, even death has occurred.

Beside the adverse effect on the human body, chemicals can be the source and the cause of fire, corrosion and damage to structures and electrical installations and may have a harmful effect on the surrounding environment when released in an uncontrolled manner.

The following recommendations must be taken into account for chemical handling in chemical stores, in the tannery, in the analytical laboratory and in effluent treatment plant.

2. SAFETY INFORMATION ON CHEMICALS

2.1 Information on chemical container labels

Source: ILO – Code of practice

1. Trade name of the chemical
2. Identity of the chemical
3. Name, address and telephone number of supplier
4. Hazard symbols
5. Nature of special risks associated with the use of chemical
6. Safety precautions
7. Identification of the batch
8. Statement that a material safety data sheet giving additional information is available with the tanner
9. Classification assigned under the system established by the competent authority

Chemicals should not be brought into the tannery if they are not properly labelled or marked.

Please note that labels for points 2.1.4 and 2.1.5 are different for transport and handling.

2.2 Information in material safety data sheets

Source: EU safety data sheet (EU Directive 93/112 EEC)

1. Chemical product and company identification
2. Information on ingredients/composition of the chemical
3. Possible hazards classification
4. First aid measures
5. Fire fighting measures
6. Measures in case of accidental release (eg spillage)
7. Guidelines on handling and storage
8. Information on how to control exposure and what personal protective equipment to use
9. Physico-chemical properties of the product
10. Security and reactive ness of the chemical
11. Toxicological information
12. Ecotoxicological information
13. Guidelines on disposal
14. Guidelines on transport
15. Guidelines on classification and labelling

16. Any additional information for the safety and health of the workers

Information from the MSDS should be used to create safe working procedures. These procedures should be available at the work place. The aim is to provide useful, understandable information to the workers, in order to create a safe working environment.

Do not use new chemicals until information on them, as outlined above, is obtained.

3. CONTROL OF CHEMICAL HAZARDS

Workers are exposed to chemical hazards during:

1. Loading, unloading and handling of chemical containers in the chemical store;
2. Transfer of chemicals from containers in the chemical store;
3. Mixing of chemical recipes in the chemical store or workplace;
4. Transfer of chemicals from chemical store to the workplace;
5. Handling of chemicals in the workplace;
6. Loading/unloading of raw material/pelt/leather into/from pits, paddles, drums, machines;
7. Removal of chemical waste and effluent from the workplace;
8. Disposal of chemicals or effluent;
9. Washing and disposing of chemical containers

As chemicals emit fumes, mist, vapours or dust during storage and handling, any worker may be exposed to these airborne pollutants in any part of the workplace. Chemicals in liquid and gaseous form also affect the immediate neighbourhood, when released into drains or removed from the workplace by exhaust blowers and chimneys.

It is necessary to avoid chemical exposure of workers, whether through inhalation, ingestion or skin contact.

For safe handling of chemicals, several preventive measures must be taken.

Eliminate, whenever possible, hazardous chemicals from the workplace, for example:

- Replace organic solvent based chemicals by water based chemicals in degreasing and finishing.

Limit the chances of exposure to hazardous chemicals:

- Dose or transfer chemicals in fully or partly closed systems.
- Always put lids and covers on chemical containers.
- Use extraction systems on dry shaving, buffing, dedusting, spraying machines and chemical weighing.
- Control discharge of floats from paddles and drums with a hose or gutter connected to the sewer.
- Use hand or motor pumps for transferring hazardous chemicals such as acids.

- Whenever possible, instead of spraying, use equipment such as roller coating, which produces less emission to air.
- Reduce the concentration of airborne pollutants using ventilation and natural airflow.
- Ensure good housekeeping practices, such as regular cleaning of work areas, floors, walls and machines, removal of waste and adherence to safe storing and handling practices.
- Reduce the number of workers in areas with hazardous chemicals and limit access to areas where hazardous chemicals are likely to be present (chemical store, effluent treatment plant).
- Reduce the exposure time, eg do all weighing at one time.

As a last resort, prevent exposure to hazardous chemicals by the use of protective equipment.

- Gloves, boots and aprons should be available for every worker in the wet end of the tannery.
- Respirator type masks with particulate filters and glasses should be used when handling powder and liquid chemicals.

4. SAFE CHEMICALS STORAGE

4.1 Adequate storage facility

1. Storage of chemicals should be separated from production areas, occupied buildings, other storage areas, workshop or areas with a potential source of ignition.
2. The floor should be flat (for ease of handling) and non permeable to prevent soil pollution.
3. Emergency drains should be available and connected to the effluent treatment plant.
4. It should have at least two emergency exits to allow easy escape for personnel.
5. Electrical installations and other equipment for flammable chemicals should be "explosion proof".
6. Natural and artificial ventilation should be provided at low and high level.
7. Access should be restricted to authorised, trained personnel.
8. Fire fighting equipment, e.g. powder ABC, should be kept ready in a suitable location, which can be easily and conveniently accessed in an emergency.
9. A washbasin, eye/face rinsing station and safety shower should be available in or near the chemical store.

4.2 Adequate storage organisation

1. Keep chemicals that will react separated, eg acids away from sodium sulfide and alkali away from ammonium salts: any accidental mixing results in generating dangerous gas - H₂S, NH₃.
2. Design and install pipes, valves, etc. in such a way that creates physical hindrances to incorrect addition or mixing of incompatible chemicals, eg from a tanker lorry into the wrong storage tank (acid into a sulfide solution).
3. Group and store different chemicals according to their compatibility. For easier stockkeeping, provide boards indicating name, maximum, minimum and current stock for each group.
4. For maintaining better storage discipline, allot the specific storage areas for each group and mark the designated areas with yellow floor marking.
5. Avoid storage of chemicals directly on the floor.
6. Racks and shelves can store small containers such as dyes and fatliquors samples.
7. Heavier chemical containers – particularly those containing liquid chemicals (eg acids) – should be stored on wooden or plastic pallets at the floor level.
8. Barrels containing liquid hazardous chemicals must be stored in catch pits or in a walled area.
9. Ensure sufficient width for movement of persons and materials (more than one metre for handling of chemicals, more than two metres for movement of pallet or fork lift trucks).
10. Whenever possible, solvents and other flammable or pyrophoric chemicals should be stored in a separate chemical room.

5. SAFE CHEMICALS HANDLING

As a general principle, the quantity of chemicals in or at the work place should be restricted to that required for daily or batch use.

5.1 Training of workers

Training and education play important roles in the control of chemical hazards. People who work with chemicals should be aware of:

1. The possible health risks caused by chemicals
2. Safe working procedures
3. Care and use of protective equipment
4. Emergency and first-aid measures

Moreover, workers should be trained to identify when control measures fail and to interpret the labels provided on chemical containers.

Training is essential for new workers, while experienced workers should participate in regular refresher courses.

5.2 Transfer of chemicals from chemical containers

1. Make sure that the smaller containers used to transfer chemicals from the chemical store to the workplace are clearly labelled and marked.
2. When transferring chemicals, take advantage of simple tools or arrangements such as hand piston pumps (eg for acids) or positioning of barrels on horizontal racks (eg for fatliquors).
3. Do not use the same spoon, spatula, measuring cups for taking out different chemicals, to avoid contamination of chemicals.
4. Avoid mixing and preparing chemical recipes in the work area. Ideally, designate a separate area in your tannery.
5. Carrying of chemicals manually and in open containers should be avoided, to prevent spillage, distribution of vapours and chemical accidents. Use closed containers, trolleys and pallet trucks.

5.3 Basic rules and principles in handling chemicals

1. Never mix chemicals randomly and indiscriminately.
2. Always add concentrated acid to water, never water to acid.
3. Avoid breathing chemical fumes, dust or vapours using local exhaust ventilation. As a last resort use appropriate respirators.
4. Avoid skin contact with chemicals. Use safety goggles and other personal protective equipment, as required by the applicable material safety data sheet.
5. Wash hands with soap or other proprietary cleaner after handling chemicals.
6. Wash off chemical spills on skin or eyes immediately with running water.
7. Any chemical spillage should be reported to the supervisor, then cleaned up safely and without delay.
8. For a large size tannery, all chemicals should be distributed from a gangway located over the beamhouse, tanning and post-tanning drums. The gangway should be equipped with adapted tanks connected to the drum axle.
9. For a small size tannery, install a fixed funnel connected to the drum axle. Install steps to the funnel, which are not higher than 20 cm each. The upper edge of the funnel should not be higher than the hip of the worker when standing on the platform.

6. DISPOSAL OF CHEMICAL WASTE AND PACKING MATERIALS

Empty chemical containers can pose a safety risk and a health hazard, when not disposed of properly.

1. Remove empty chemical containers from the store and work areas.
2. Rinse out recoverable barrels and if possible use the rinsing water in processing. If not reused, the rinsing water is to be discharged to the effluent treatment plant.

3. Safely store the containers in a separate area of your tannery.
4. Do not pour or mix different waste chemicals into the same waste container or barrel.
5. Returning empty containers back to the supplier for refill and reuse is an option to be promoted.
6. Do not permit waste containers to be used for storing drinking water or food products.
7. Waste chemicals should be collected and disposed of according to local regulations.

IUE Commission
October 2008

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