UNITED
NATIONS
INDUSTRIAL
DEVELOPMENT
ORGANIZATION

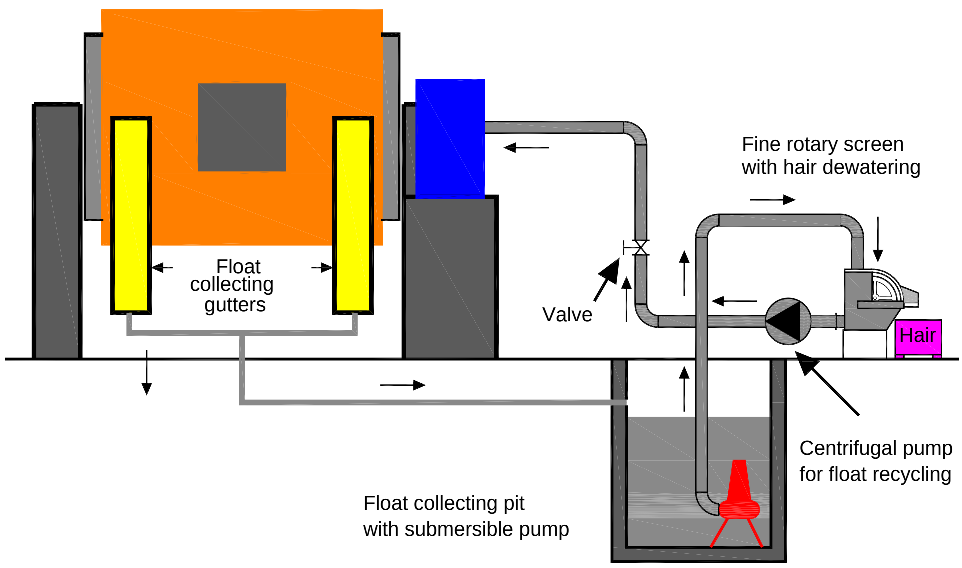
August 2012

Eighteenth Session of the LEATHER AND LEATHER PRODUCTS INDUSTRY PANEL
Shanghai, China, 01 – 05 September 2012

Cleaner leather technologies
Suitable for tanneries in developing countries

HAIR-SAVE LIMING PROCESS

Synopsis for the Visual Training Tools (VTT)



Prepared by
Jakov Buljan, consultant on leather industry

Project Manager
Ivan Kráľ, Industrial Development Officer

Preface

The primary task of all cleaner technologies is to reduce the amount and possibly change the nature of pollution emissions and thus reduce the pressure and costs of end-of-pipe treatment.

However, generally, absorption of new technologies in leather sector is traditionally slow, established methods last for long.

The main reason is that, despite considerable progress made during last few decades, leather manufacture is still a mixture of science and technology and craft, the nature of some processes not fully understood. Keen to preserve the most important aspect, the quality of leather produced, tanners are very reluctant to modify the existing process and possibly negatively influence the quality.

Quite often tanners' reluctance is due to the fact that some methods promoted are seen as rather academic and not proven at industrial scale; alternatively, technologies offered by suppliers of chemicals rely on a range of proprietary products and may lack the broader perspective.

Also, owing to inherent characteristics of the raw material and desired properties of the finished leather, cleaner tanning methods have their limitations; ultimately, a substantial percentage of all raw material and chemicals input has to end as waste.

There is no doubt that from the holistic, macro- and long-term perspective, environment-friendly tanning methods are more favourable and cheaper. However, for an individual tanner, as a rule, cleaner technology methods, due to cost of more sophisticated equipment and specialty chemicals are costlier; the main benefits are better conditions in the plant, better image with international buyers etc.

More specifically, it s expected that cleaner technologies result in:

- Lower water consumption – better preservation of rapidly diminishing water resources
- Lower TDS content/salinity – lower risk of affecting the usability of the receiving river water for irrigation and livestock watering;
- Proportionally higher volume of solid wastes suitable for processing into saleable by-products;
- Lower BOD, COD and Nitrogen content within acceptable range – protection of aquatic life, avoidance of eutrophication;
- Low level of chromium in CETP sludge – the scope for land application and/or composting;
- Lower hazardous and/or unpleasant air emissions
- Appropriate occupational health and safety (OSH) standards – better work conditions, less accidents

As the main sources of actual or perceived pollution, processes in the beamhouse (soaking, unhairing/liming and deliming) and tanyard (chrome tanning) are addressed first, dry finishing (coating) typically dealt with later on.

In late 90-ties, in addition to papers on treatment of wastes, UNIDO had also prepared a number of studies dealing with environmental issues, including cleaner technologies methods: *The scope for decreasing pollution load in leather processing, Mass balance in leather processing, Hair-save unhairing methods in leather processing, Chrome management in the tanyard, Chrome balance in leather processing* etc.

In conformity with recommendations of UNIDO Leather and Leather Products Industry Panel meeting in Addis Ababa in 2010, UNIDO has launched a series of (animated) Visual Training Tools (VTT) mostly tuned to needs of tanneries in developing countries.

In that context the earlier studies have been revisited and new papers, addressing specific issues/processes are prepared, to serve as both practical updated reference as well as the basis for synopsis for VTTs on cleaner leather technologies methods; also, while providing the main theoretical principles these papers are primarily practice oriented and are not intended to replace but rather to supplement the fully-fledged textbooks.

Acknowledgements

The information and views as well as tables drawings, photos etc. in this paper are primarily intended to serve as background material for UNIDO workshops in developing countries.

They are drawn from author's own experience, several UNIDO documents and reports as well as various manufacturers' promotional materials placed on web. Various information originating from IULTCS papers, EU BREF and C. Money are gratefully acknowledged.

Mr. M. Bosnić provided invaluable assistance by preparing most of the drawings and flow-charts.

Table of contents

Tables

Figures

Photos

---

[1] *Extract from the paper by Liu Wentao and Li Guoying XXXI IULTCS Congress, Valencia, 2011*

Photos 6. and 7. Examples of self-cleaning static wedge wire screens
Photo 8. Rotary screen Konica, external feed
Photo 9. Rotary screen Konica, close look of the filtering drum
Photo 10. Screw type screen with compactor and container
Photo 11. Rotating disc screen
Photo 12. Rotating disc screen in operation

Soaking and liming with hair-burn unhairing

The purpose of the soaking process is to bring the hides and skins to condition very similar to that shortly after flaying. It is important to have them fully rehydrated and to remove any manure, and dirt as well as the major part of any preservation substance used, usually common salt.

In addition to it, the major part of interfibrillary substances consisting of non-collagenous proteins (albumins, globulins and elastin) as well as glycosaminoglycans (di-/polysaccharides) are removed thus making the raw material better prepared for further processing.

The soaking process varies a lot to suit the type of raw material (cattle hides, sheep, goat skins) and the preservation method (fresh/chilled, brined, wet or dry salted, dried). Accordingly, it is carried out in low speed rotating drums (hides) or paddles (woolly and/or dried skins). In industrial type of leather processing soaking in pits has been virtually abandoned. Rewetting is normally supported by applications of appropriate surfactants and sometimes enzyme based auxiliaries.

Mainly for environmental reasons, soaking of hides should be followed by fleshing operation ("green fleshing") as there is a much wider scope for utilisation of native than limed fleshings; consumption of liming chemicals is also somewhat reduced.

The main aims of the liming process are:

- removal of hair (wool) and epidermis
- removal of any interfibrillary components remaining after soaking and "opening up" of the fibre structure, including an acceptable level of swelling
- partial saponification of the natural grease
- liberation of tanning active groups

The well-known stability/non-solubility of keratin, its resistance to chemical attacks is due to strong bisulphide cross linking (intermolecular or intramolecular) of cystine, the amino acid richly present in keratin's structure. Some strong reducing agents such as traditionally used sodium sulphide – Na_2S and sodium hydrosulphide – NaHS are able to break down the bisulphide bond[2]:

$$\mathrm{R{-}S{-}S{-}R} \longrightarrow 2\ \mathrm{R{-}SH}$$

Cystine **Cysteine**

In the conventional liming – hair burning process, the liming chemicals either destroy the hair and epidermis completely or loosen them to such an extent that they can be removed mechanically without any difficulty. At the same time, they bring about a certain amount of swelling (plumping) of the fibre structure and partial saponification and emulsification of the hide fat. The liming is usually carried out with hydrated lime – $Ca(OH)_2$ and sodium sulphide – Na_2S and/or sodium hydrosulphide – NaHS, which has a less pronounced plumping effect.

---

[2] *Strong oxidative agents such as $NaClO_2$ or Na_2O_2 are also able to break this bond but for various operational limitations, including OSH aspects, oxidative unhairing has not been accepted by the industry.*

The so called low sulphide liming based on organic sulphurous compounds liquors as well as enzymes supported liming and unhairing are also relevant.

Reliming with straight lime (straight reliming) is sometimes used for production of very soft leathers, when especially good opening of the fibre structure is required or the levelness of the dyeing has to meet some particularly high demands.

In addition to high water consumption, soaking and liming with hair-burning are the most polluting part of the entire process of leather manufacture in terms of nearly all key parameters (BOD, COD, Suspended Solids, TDS/salinity and nitrogen). Thus, it is quite understandable that they have been among primary targets of various pollution prevention attempts.
Since the soaking step and the resulting high TDS are mainly dependent on the preservation method, they will be addressed in a separate paper dealing with TDS/salinity of tannery effluents.

Principles of hair-save unhairing

Whether in the form of liming hides in pits or sweating skins, hair-save unhairing has been used since time immemorial. Hair-save lime-sulphide unhairing dates from the 1880´s and was widely practiced. Modern, rapid commercial methods, however, were only developed in the period 1980-1990, with the advent of the requisite equipment (mixers or drums fitted to recirculate the liquor and separate the loosened hair). The main reasons for use of hair-save in modern times are:

- significant decrease of organic pollution load
- significantly lower volume of sludge for reuse or disposal
- lower costs of effluent treatment (chemicals, energy)

The presently prevailing hair-save process utilises conventional chemicals normally used in the hair-burning system (lime and sulphide) but applying them in a somewhat different manner resulting in proven environmental benefits; enhanced leather properties are also likely whereas claims about improved area yields are not quite convincing.

The principle of the method is quite simple: the hair fibre is firstly partially immunized by an alkali (lime) to be subsequently removed by the action of sulphide and ultimately recovered by filtration.

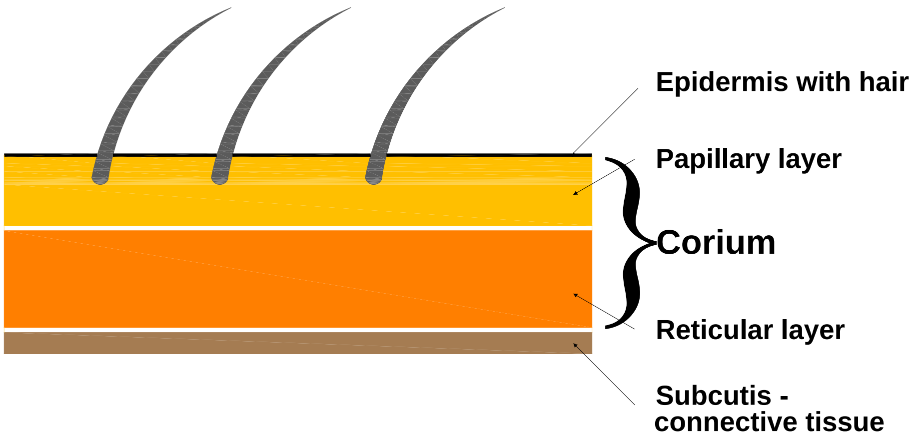


Figure 1. A schematic cross-section of bovine hide

This is possible because the fully developed keratin in hair, nails and the upper part of the epidermal layer is highly resistant to chemical or biological attack, except from sulphide which breaks down the disulphide bonds. The immature keratin found in hair roots, hair root sheaths, and the lower layer of the epidermis, however, is more easily degraded and dissolved.

The resistance of keratin to chemical degradation can be substantially increased by immunisation i.e. treatment with an alkali, but without sulphide. The alkali transforms the sulphur cross-links into different, highly resistant thioether bonds. Mature keratin is much more easily immunised than immature keratin. This increases the difference in degradability between hair and hair roots, thus simplifying the hair-save unhairing process.

The point at which the hair breaks is decisive to the success of the process; the lower the breakage down the hair shaft in the follicle, the better the process. Any hair debris remaining in the follicle is a problem, especially with black-haired hides.

Immunisation can be achieved by using sodium hydroxide, lime or calcium hydroxide; it usually takes 1-1.5 hours. Most commercial systems for hair-save unhairing are based on immunisation.

A careful balance between insufficient immunisation and over-immunisation must be maintained. In the event of over-immunisation, the hair cannot be loosened satisfactorily in the subsequent unhairing stage. Obviously, the amount and use of a reducing agent, the amount of alkali as well as the time and temperature of immunisation are critical for the success of the process.

The structure of the basement membrane (and consequently that of the corium-epidermis junction) is mainly based on protein-protein links, although protein-carbohydrate interaction and a few sulphur bridges also play a role. The basement membrane thus becomes a target for selective proteolytic enzymes, and an attack on the basement membrane is an essential feature in enzymatic and lyotropic unhairings

In all modern methods, a separate mechanical unhairing step is no longer included. The hair is loosened by intensive mechanical action during the chemical unhairing process. This mechanical action entails a risk of abrasion, and hence damage to the grain. Suitable measures must be taken in order to prevent this (for example, by adding slip agents).

After loosening, the hair must be separated from the liquor as soon as possible in order to minimise the pollution load since prolonged immersion may to some degree dissolve the hair substance and reduce the filterability of the hair.

An increase in temperature accelerates the unhairing process. The layers of relevance to hair-save unhairing are highly susceptible to changes in temperature, the upper limit being the temperature at which risk of damage to the hide substance is incurred. Temperatures up to 30^0C are considered safe, whereas at 35^0C the hide substance is drastically damaged, especially in the grain layer.

In tropical countries where fresh water temperatures may be higher than 30^0C, it may be necessary to use paddles instead of drums for unhairing and/or adding ice to reduce heat induced by friction.

For reasons not fully understood it seems that hair-save unhairing method works better on hides preserved by salting than on fresh hides; again, given the almost insurmountable environmental problems associated with salinity this aspect should not impede switching to processing fresh/chilled hides wherever possible.

Painting

Painting is a traditional hair-save method for calf, sheep, hair-sheep and goat skins; also, it is obligatory where the hair/wool is valuable. Although the chemicals used are the same as in lime-sulphide hair-save process, the application is quite different: skins are painted by hand or on a machine on the flesh side with a paste consisting of sodium sulphide, lime or china clay or organic thickeners and water. Typically, to the solution containing about 10 % sodium sulphide (9^0Bé) lime is added until about 15^0Bé; the final density of the paste of about 20 ^{0}Bé or more is achieved by adding kaolin (china clay).

A tanner bent over the *beam* using a special curved knife to remove flesh or hair roots and epidermis is the traditional symbol of the trade.

Figure 2. Old days: a tanner and his beam

After painting, the skins are stacked in a pile, hair side against hair side. The unhairing chemicals penetrate the skin from the flesh side and destroy the hair roots. It is then a simple task to scud off the hair that is not in contact with the unhairing chemicals. The hair is practically intact (and thus easier to sell), although some attack at the end of the hair root end may be discernible. Mechanical unhairing and re-liming are necessary; in larger tanneries both painting and mechanical unhairing are done by machines, partially compensating for disadvantages of the painting method: it is labour intensive, requires more space and usually takes more time.

Photo 1. A pile of painted sheep skins

The hair from goats and hair-sheep skins used to have some specific local applications. Being a very special case, processing and marketing of wool is not addressed here.

Hair-save lime-sulphide unhairing

The minimum sulphide dosage in hair-save lime-sulphide unhairing is approximately 0.25-0.5% sodium sulphide flake (60% Na_2S) or 0.6-1.2 kg S^{2-} per tonne salted raw hide .

The critical concentration of sulphide in the liquor, below which the hair remains unaffected and above which it is destroyed, depends on several variables: length of float, lime dosage, pH, temperature, process time, intensity of mechanical action and hair length. Approximate ranges are as follows:

% float	% sodium sulphide flake (60% Na_2S)	kg S^{2-}/tonne raw hide
50-100	0.5	1.25
200	1.0	2.5
300	1.5	3.7

Table 1. Approximate sulphide dosing ranges

In industrial practice, the minimum figures for hair-dissolving lime sulphide unhairing are approximately 200% float and 1.5% Na_2S flake, corresponding to 3.7 kg S^{2-} per tonne raw hide. Normally, a dosage ranging between 1.5 and 3% (equivalent to 3.7-7.4 kg S^{2-} per tonne raw hide) is used.

Thus, the basic recipe in summary is as follows[3]:

Immunisation: Max. 150% water 28°C

1.5 % lime

45 minutes (15 min. rotation)

Unhairing: + 1.5 % sodium sulphide flake (60% Na_2S)

After $1^{3/4}$- 2 hours filtration until clear

Reliming: + water up to 180-200%
2% lime

Run at low speed (2-3 rpm) approx. 14 hours

In order to obtain a perfectly clean pelt grain, a minimal amount of enzyme is added to the reliming liquor.

The advantage of the method is that o proprietary products are used and the chemical costs are comparatively low.

---

[3] Generally, it is taken that the concentration/purity of lime – $Ca(OH)_2$ is 100%, Na_2S 60-62 % and NaHS 95 %. Lime is added as suspension but very often directly from bags.

A range of different processes, based on the modified **Sirolime process** (a specific process developed by CSIRO, Australia) have been used successfully for green hides in Australia. One of them is given below:

Soak
130% water, 30^oC
0.2% NaHS
0.5% soda ash
0.61% triethanolamine
0.25% surfactant
pH 9-10.8, drum 2 hours, high speed (4-6 rpm)

Immunise (same float)
1.6% lime
Drum 45 min, high speed

Depilation
0.95% NaHS
Drum 30 min, high speed

Filtration
High speed, 3hours

Relime
0.25% NaHS
0.75% lime
Medium drum speed

Some lime liquor may be reused. Total lime 2.35% , total NaHS, 1.4%, no Na_2S.

Unhairing with organic sulphur compounds

Three types of organic sulphur compounds were used in proprietary products based unhairing systems:

- Mercaptoethanol
- Salts of mercaptoacetic acid (thioglycolic acid)
- Formamidinesulphinic acid

These compounds are strong reducing agents, acting in the same way as sulphides. The advantage of their use is that they considerably reduce the amount of sulphide consumed and discharged with the wastewater. On the other hand, these chemicals are much more expensive so they are mostly used in instances where effects other than environmental improvement are sought. For example, liming with these compounds yields a lower degree of swelling than using lime and sulphide only with possible positive effect on the area yield and the smoothness of the grain.

The use of mercapto products requires the application of occupational health standards and the same protective measures as the use of sulphides. Free mercaptanes in the air are actually more toxic than hydrogen sulphide, but for several reasons (such as higher oxidation rate during the process, lower tendency to generate free mercaptanes, and the latter's higher boiling point) the risk of mercaptane vapours being released into the atmosphere is considerably lower than is the case for hydrogen sulphide. Owing to their high oxidability, thio-compounds have to be thoroughly mixed on being added to the float. In any case, suppliers normally provide detailed guidelines for their use.

Enzymatic unhairing

Putrefaction of the hide swiftly leads to a loosening of the hair, owing to the enzymatic action of the putrefactive bacteria and the degradation of the hide itself. This phenomenon can be most frequently observed when storing insufficiently conserved hides in a hot climate.

As said earlier, the bacteria first attack the basement membrane and the basal cell layer of the epidermis, leading to a loosening of the hair; the attack, however, later extends to the hide substance itself.

Enzymatic processes is hard to control; commercial preparations containing proteolytic enzymes attack the collagen of the grain layer to a certain degree too, leading to looseness of grain and grain sueding. Moreover, enzymes alone cannot eliminate the ground and fine hair completely. Thus, it is unlikely that an unhairing process exclusively based on the use of enzymes will ever be practically possible. Also, enzyme preparations are expensive and in most cases the environmental benefits they offer are an insufficient to justify the cost.

Enzymes, however, are extensively used to support alkaline immunisation-sulphide unhairing to eliminate ground and fine hair and to obtain cleaner pelts.

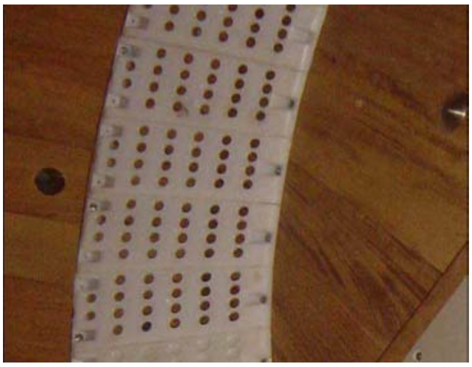
Finally, enzyme unhairing has been used on long-haired goatskins since the grain layer on goatskins is more resistant to enzymatic attack than that on skins or hides of other species.

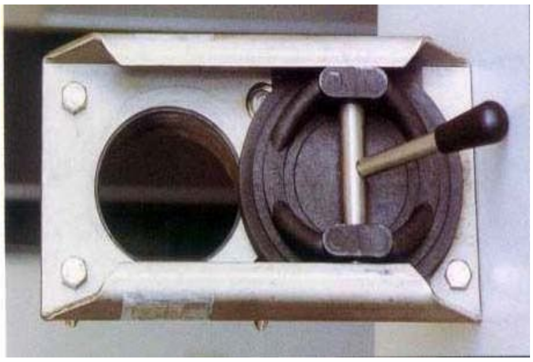
Hair separation and float recirculation equipment

Modern hair-save unhairing processes require equipment for recirculating the float and separating the hair.

Hair separation is preferably carried out at the same time as hair loosening so as to minimise degradation of the hair. Modern drums are equipped with recirculation as well as temperature and pH regulations are commercially available. The float is pumped out of the drum laboratory box and fed back in again through a hollow axle.

In older drums without recirculation laboratory box, a recirculation and filtering system can be fitted provided that the drum axles can be used for float circulation. For that purpose it is necessary to install perforated plastic or wooden elements inside the drum (on one or both sides, if the drum is big enough), drill holes of not less than 80 or 100 mm. diameter) on the external side and fix of a manual valve; again, depending on the drum size, semi-circular float collecting gutters are fitted on one or both sides of the drum (see pictures below).





Photos 2. and 3. Perforated plastic elements and manual valve for float recirculation

Photo 4. Semi-circular gutters with draining pipes

Photo 5. A battery of drums with semi-circular float collection gutters

As for mixers, the filtering unit is fitted into the existing recirculation system. Recirculation in a mixer may release greater quantities of gas than recirculation in a drum and that is why methods which entail the risk of generating toxic or malodorous gases should not be carried out in a mixer.

Each drum requires a filtering unit; alternatively, if one filtering unit is to serve several drums (at most two or three), unhairing should be carried out in the individual drums with a time lag of approximately two hours (the time needed for hair-loosening and recirculation).

Another frequently used solution is to drain the float into a sump with a pump, sent it to the filtering unit, separate the hair and then pump the screened float back to the drum. In this case, it is possible to use one filtering unit for several vessels. This set up is simple to install and it can also be used in tanneries using paddles.

It is important that the filtering capacity is sufficient to maintain the appropriate recirculation speed and complete filtering process within required time; the typical flow capacity of commercial recirculation-filtering systems is 600-1000 l/min. Various types of sieves can be used to separate the hair; the float may be pumped to the sieve through the vessel's existing circulation pump or via separate pumps. With suitable filtering equipment, up to 90% of the loosened hair can be recovered. Nowadays most of the screening systems on the market are combined with dewatering devices.

Static wedge wire screen

The filtered float flows through the screen plate whereas the hair slides down the screen plate and drops into a container. A suitable mesh gauge is 0.5-1.0 mm. Many tanneries use static wedge wire screens to separate leather or hide fibres from the waste water. Vibrating wedge wire screens are also available. Sometimes only the screen is in stainless steel whereas the frame is made of plastic material.

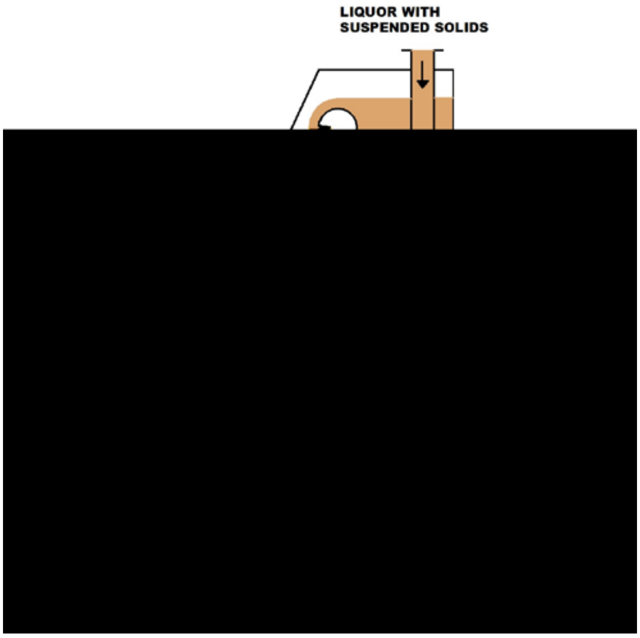


Figure 3. Operation principle of the self-cleaning static wedge wire screen

Some among many models suitable for hair filtering:

Photos 6. and 7. Examples of self-cleaning static wedge wire screens

Rotating drum sieve

Here the cylindrical wedge wire surface serves as a filter. The float is fed onto the outside cylindrical surface of the drum. The filtered float passes through the surface into the drum and the hair is scraped from the drum surface by means of a doctor blade. The centrifugal pump sends the screened float back to drum.

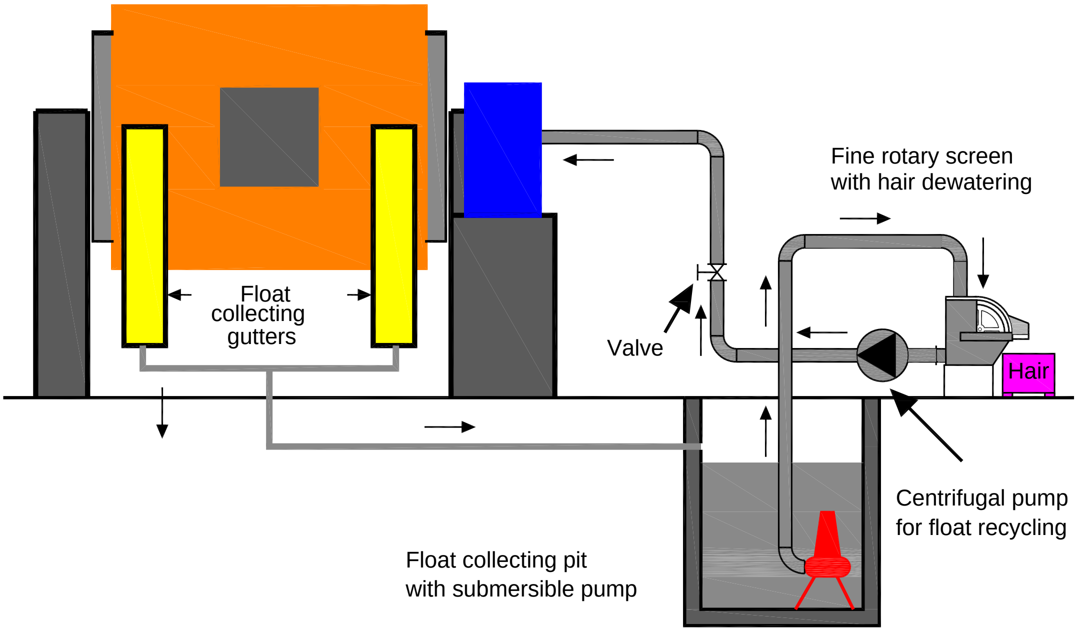


Figure 4. Hair-save system with rotary drum filter and collecting pit

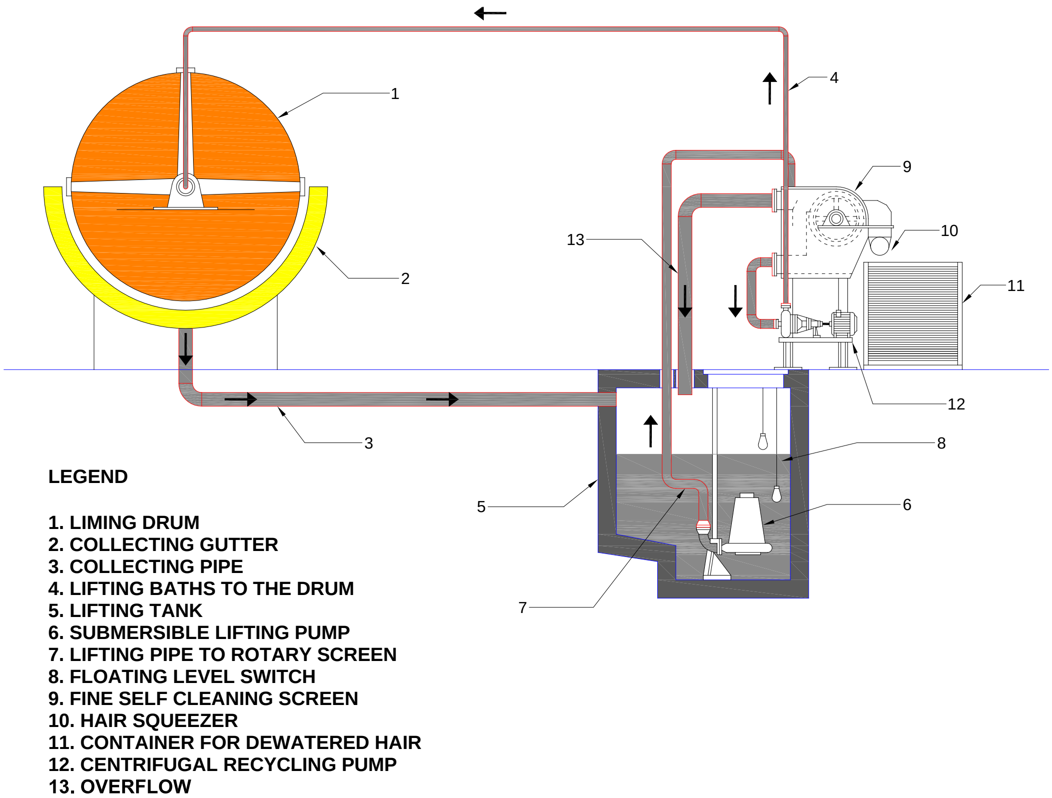


Figure 5. Hair-save set up, cross-section view

Alternatively, the float is fed into the drum, the filtered float flows through the cylindrical surface, and the hair is transported through the drum by gravity (an inclined drum) or, more effectively, by a screw conveyor, whereafter it is collected in a container at the end of the drum and subjected to some kind of dewatering.

Photo 8. Rotary screen Konica, external feed

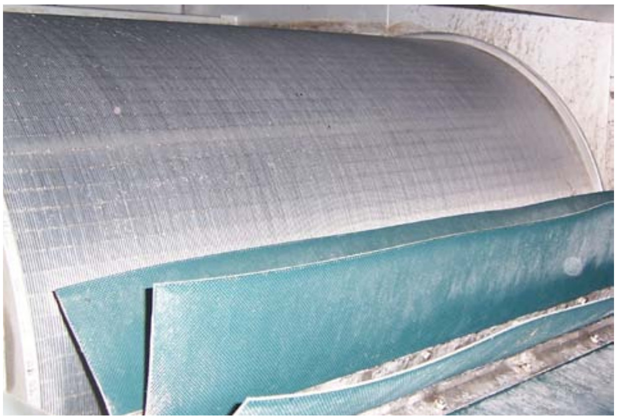
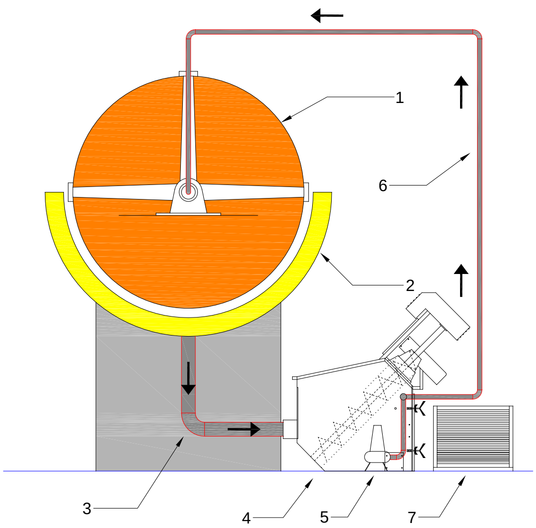


Photo 9. Rotary screen Konica, close look of the filtering drum

Screw type press with compactor

Here the hair separation takes place in the filtering pipe with a semicircular section of the perforated plate with a screw scraping the inner surface; the hair is dewatered in the rubber cone section.

If the drums are at 100 – 120 cm above ground level the press can be fed by gravity, otherwise the float has to be pumped.



LEGEND

1. LIMING DRUM
2. COLLECTING GUTTER
3. COLLECTING PIPE
4. FINE SELF CLEANING SCREW SCREEN
   WITH HAIR SQUEEZER
5. SUBMERSIBLE RECYCLING PUMP
6. SCREENED BATH TO THE DRUM
7. CONTAINER FOR DEWATERED HAIR

Figure 6. Screw type screen with hair dewatering, schematic cross-section view

Photo 10. Screw type screen with compactor and container

Rotating disc screen

It consists of two fine mesh conical discs on a rotating axle often positioned between two liming drums. The float is pumped between two discs, the filtered float flows sidewise whereas the hair is collected in front and taken away for dewatering.

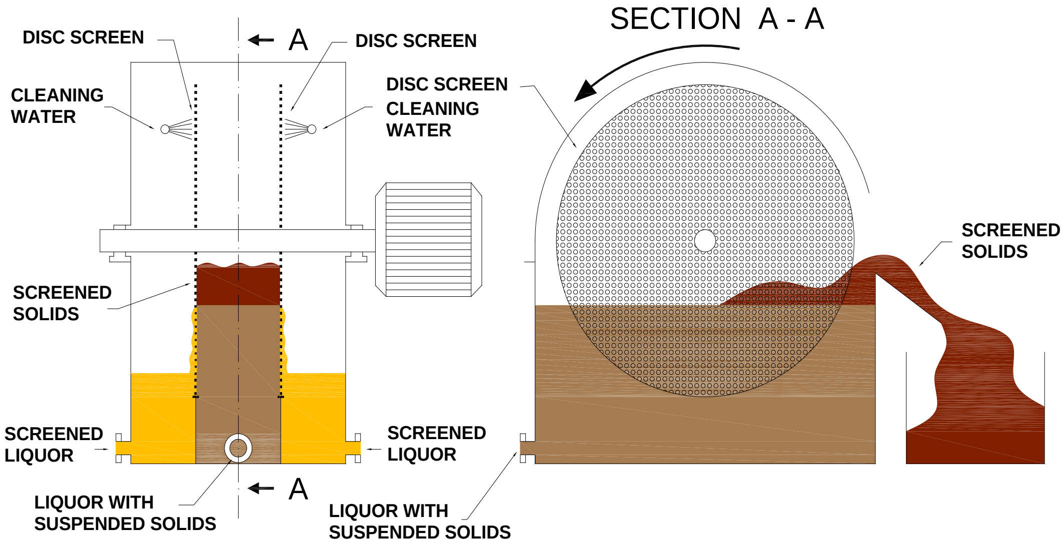


Figure 7. Operation principle of rotating disc screen

The screen operates at variable rotation speed that should be adjusted to the local operating conditions (inlet flow, amount of hair etc.). Proper cleaning of the filtration surface is essential for maintaining good efficiency.

Photo 11. Rotating disc screen

Photo 12. Rotating disc screen in operation

Dewatering separated hair is not always easy, but it is important for further handling.

Economic viability

The cost of introducing hair-save unhairing depend on the host factors such as tannery size, the scope of retrofitting existing drums vs. purchase of modern drums with recirculation systems, availability of chemicals etc.

At the same time, difficulties to cope with environmental challenges, in particular to meet specific pollutants discharge limits e.g. nitrogen may prevail over other considerations and induce the tannery to switch to hair-save. In any case, every cost-benefit analysis of hair-save unhairing has to consider the following aspects under specific local conditions:

- Chemicals
- Investment (including financing), maintenance and depreciation
- (Improved) leather quality
- Savings in environmental costs (raw water, waste water treatment, sludge disposal costs)
- Energy
- Labour
- Hair disposal options (income from sale or cost of disposal)

The claims about increased area yield do not appear sufficiently supported by reliable figures.

Generally it is believed that the costs of chemicals for hair-dissolving and lime-sulphide hair-save are of the same magnitude; if the latter is enzyme-assisted the cost is likely to be somewhat higher but worth the additional cost.

As a rule, the costs of using specialty, proprietary hair-save systems are higher, sometimes substantially.

Scope for hair utilisation or disposal

Nowadays environmental and possible cost benefits prevail over the problem of coping with yet another solid by-product.

The quantity of hair recovered in relation to the weight of raw hide varies considerably. Basically it depends on hair length and hide thickness and, in turn, these properties are linked to animal breed, gender, age, season etc. Typical ranges are given in the table below.

	% drained hair	**% hair dry matter**
Heavy bovine hides	10-15*	3-5*
Light bovine hides	15-20*	5-7*
Calf skin	20-40**	10-13**
Sheep or goat skin	60-90**	20-30**

* *Calculated on salted weight*
****Calculated on dry weight*

Table 2. The amount of hair in relation to hide/skin weight

The dry matter content of the drained hair is approximately 33% whereas at the end of the process it is 15-20%.

After dewatering to 35% dry matter, the hair does not give rise to any odour when deposited as waste.

To avoid rapid putrefaction of the proteinaceous matter in the float adhering to the hair and development of malodour the hair must be dewatered as swiftly as possible; normally, mechanical screens for hair filtering include hair dewatering as well. The sulphide content in fresh, wet hair is approximately 80-100 ppm. Sulphide, however, oxidises easily; within three to four hours, the sulphide content is less than 10 ppm and after a day the sulphide has totally disappeared. For some uses, including agriculture, the hair has to be washed primarily to remove the residual salt (sodium) very harmful for the soil. Full stabilization is achieved by simple drying.

The composition of such stabilised hair varies a lot, the following table to be taken as indicative.

Component	%
Moisture	3.5
Protein	73.1
Extractable grease	2.9
Ash	16.8
Chlorides	3.2
Calcium	3.4
Phosphorus	0.1

Table 3. A typical composition of stabilised hair from hair-save unhairing

Numerous proposals for bovine hair utilization, often speculative or founded on the strength of laboratory scale tests, have been advanced. A broad scope in that respect is shown in Annex 2.

However, in reality there are only two areas of wider applications for hair recovered from hair-saving processes:

- agricultural fertiliser & composting
- animal feedstuffs.

Currently, in both areas, by far prevail applications of partially or fully hydrolysed hair. Uses of non-hydrolysed bovine hair, mainly based on its fibrous properties (e.g. felting) are insignificant.

Several companies in different countries produce organic nitrogen fertiliser prepared from partially hydrolysed, pelleted hair.

As a source of slow-releasing organic nitrogen, hair is a valuable soil conditioner usually marketed as a special product primarily for orchards, market gardens, nurseries and private gardens; this coincides with use of wool textile waste before the advent of synthetic ammonia based fertilisers. Adding phosphorus may also increase the fertilising effect.

Composting, typically in windrows, is a process involving the accelerated aerobic degradation of organic waste materials by natural micro-organisms requiring a specific carbon-nitrogen ratio in the substrate, the optimum being approx. C:N = 25-35:1. In hair, this ratio is 3-4:1. This means that hair has to be mixed with other waste materials which act as suppliers of carbon (sawdust or wood chips, household and garden refuse, etc.) The optimum water content in the composting mixture is approximately 50%. Hair which has not been degraded is useful because it endows the compost with a long-term effect.

Hair protein can be used in the production of animal feedstuffs. Owing to a deficit of two essential amino acids, lysine and methionine, it cannot be used as the sole protein component in the feed. However, its metabolic energy content is high and it is useful as a feed supplement Owing to its high cysteine content, it is especially valuable as an ingredient in poultry feed, in all respects comparable to feather meal. The use of hair protein in feedstuff presupposes hydrolysis at high temperature and pressure, preferably carried out in a rendering plant.

Waste hair has been also in specific market niches such as in the production of biologically degradable flower pots or anti-weed soil covering. To a limited extent, hair has also been used in the production of foaming agents for fire-extinguishers. Furthermore, following laboratory and pilot scale attempts elsewhere, industrial production of retanning agent based on hydrolyzed hair has been launched in Foshan, China.

Despite immunisation, the hair recovered from modern unhairing processes is degraded somewhat through chemical and mechanical action in the drum, its fibre strength reduced, making it inferior to synthetic fibres for production of industrial felts.

Impact on pollution load

A wealth of information is available on the environmental load and impact of hair-save unhairing, much of which is provided by the suppliers of commercial systems. The following table presents a considered evaluation of what can be achieved in practice:

	Discharge from hair-save unhairing* ***kg/tonne raw hide***	**% reduction compared to hair-pulping**	
		In unhairing liquor*	**In total tannery waste water**
Total solids	60	30	8
Suspended solids	15	70	43
BOD_5	20	50	28
COD	50	50	28
Kjeldahl nitrogen	2.5	55	22
Ammonium nitrogen	0.2	25	2
Sulphide (S^{2-})	0.6-1.2	50-60**	50-60**

* *Including waste water from washing*

** *The percentage reduction of the discharge is greater than the corresponding reduction of the dosage*

Table 4. Pollution load: hair-save vs. hair pulping, decrease in %

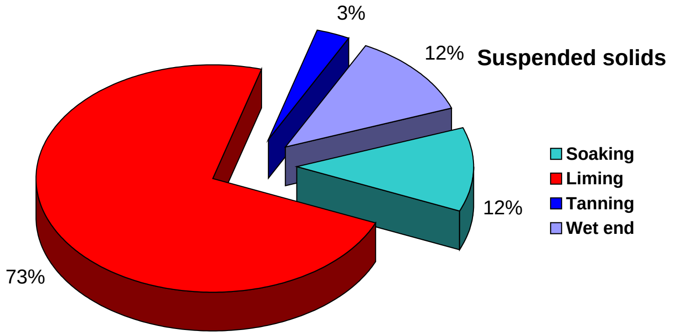
The sulphide discharge indicated in the table corresponds to 15-30 mg/l in the total waste water (at a water consumption rate of 40 m^3 per tonne raw hide). The discharge with the waste liquor varies greatly depending upon processing conditions; actual results are better or poorer than those cited in the table. Also, although Kjeldahl nitrogen load decrease is just over 20 % in some cases it is very relevant for achieving the prescribed discharge limit.

	Liming		**1^{st} Washing**		**2^{nd} Washing***	
	Hair pulping *mg/l*	**Hair saving *mg/l***	**Hair pulping *mg/l***	**Hair saving *mg/l***	**Hair pulping *mg/l***	**Hair saving *mg/l***
COD	58700	21700	18350	6600	8900	
TDS	63100	35700	29000	9000	14100	
SS	14600	8500	11000	2000	4600	
S^{2-}	2300	1350	870	280	410	

* *2^{nd} washing was not necessary for hair saving*

Table 5. A case study: Hair burning vs. hair-save, comparison of pollution load (concentrations)

The impact of hair-save on the amount suspended solids in effluent is quite enlightening:



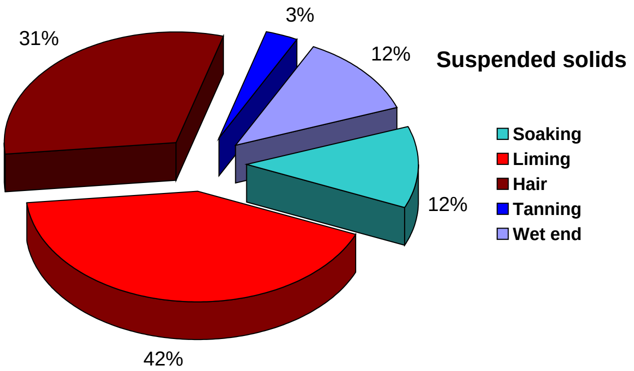


Figure 8. Hair-burning vs. hair-save liming: comparison of amounts of suspended solids (SS)

It is evident that introducing hair-save unhairing is only a partial solution to waste water problems; seen in relation to the total tannery discharge, sulphide and suspended solids are the quantities most reduced and, to a lesser extent, $BOD_{5,}$ COD, and, as shown earlier Kjeldahl nitrogen. Thus, despite reducing the sulphide discharge, subsequent treatment is still essential. Under these circumstances, each tannery must decide for itself whether hair-save unhairing is a worthwhile proposition. In any case, if substantial improvements in the waste water discharge are to be achieved, hair-save unhairing must be accompanied by the use of cleaner technologies in all other stages of the processing.

Conclusions

- Introducing hair-save unhairing is not necessarily an advantage for every tannery; each individual tannery must decide for itself whether it is worthwhile introducing the method as the optimum solution depends on specific local conditions.
- The starting point in any consideration should be a cost-benefit analysis encompassing:

  i) savings in overall effluent treatment costs, especially those related to treatment and disposal of sludge
  ii) possible additional costs of the method selected;
  iii) necessity to attain pollutants discharge standards, especially nitrogen and TDS limits
  iv) possible impact/improvements in leather quality
  v) favourable image/marketing effects ("eco-leather", eco-labelling);
  vi) economic implications of hair disposal

- In evaluating a method, occupational safety and health (OSH) aspect must also be taken into consideration.
- In the course of introducing hair-save unhairing, other processes in the tannery should, as far as possible, remain unchanged.
- Environmental authorities may set specific requirements. As far as possible, these should be known well in advance so as to have adequate time in which to implement the new method.
- Before any new technology is introduced, it is important to ascertain whether, in terms of environmental and occupational safety, it is equal to, better than or maybe inferior to, the technology it is going to replace. If needed, information on product toxicity must be obtained from the supplier.
- When evaluating a new technology, factors not directly related to the tannery (e.g. production of chemicals) should also be taken into consideration ('life cycle thinking').
- As with all cleaner technologies, hair-save unhairing presents only a partial solution to a tannery's environmental problems. A tannery that produces nothing but finished leather is utopian; cleaner technologies will never make end-of-pipe treatment unnecessary.
- Hair-save unhairing must be seen as a partial, but important element in the general optimisation of the production, including environmental aspects and better housekeeping.
- Combining hair-save unhairing with partial recycling of lime float and use of second, final washing float for the first (dirty) soak is possibly the optimum approach from both practical and environmental aspect.
- Sulphide elimination is rather easily achieved through an end-of-pipe treatment, usually by catalytic oxidation.
- Only some 22% of the total nitrogen content in waste water is eliminated by hair-save unhairing. If nitrogen is a key problem, the hair-save unhairing must be supplemented by deliming without ammonium salts (for example, using carbon dioxide).

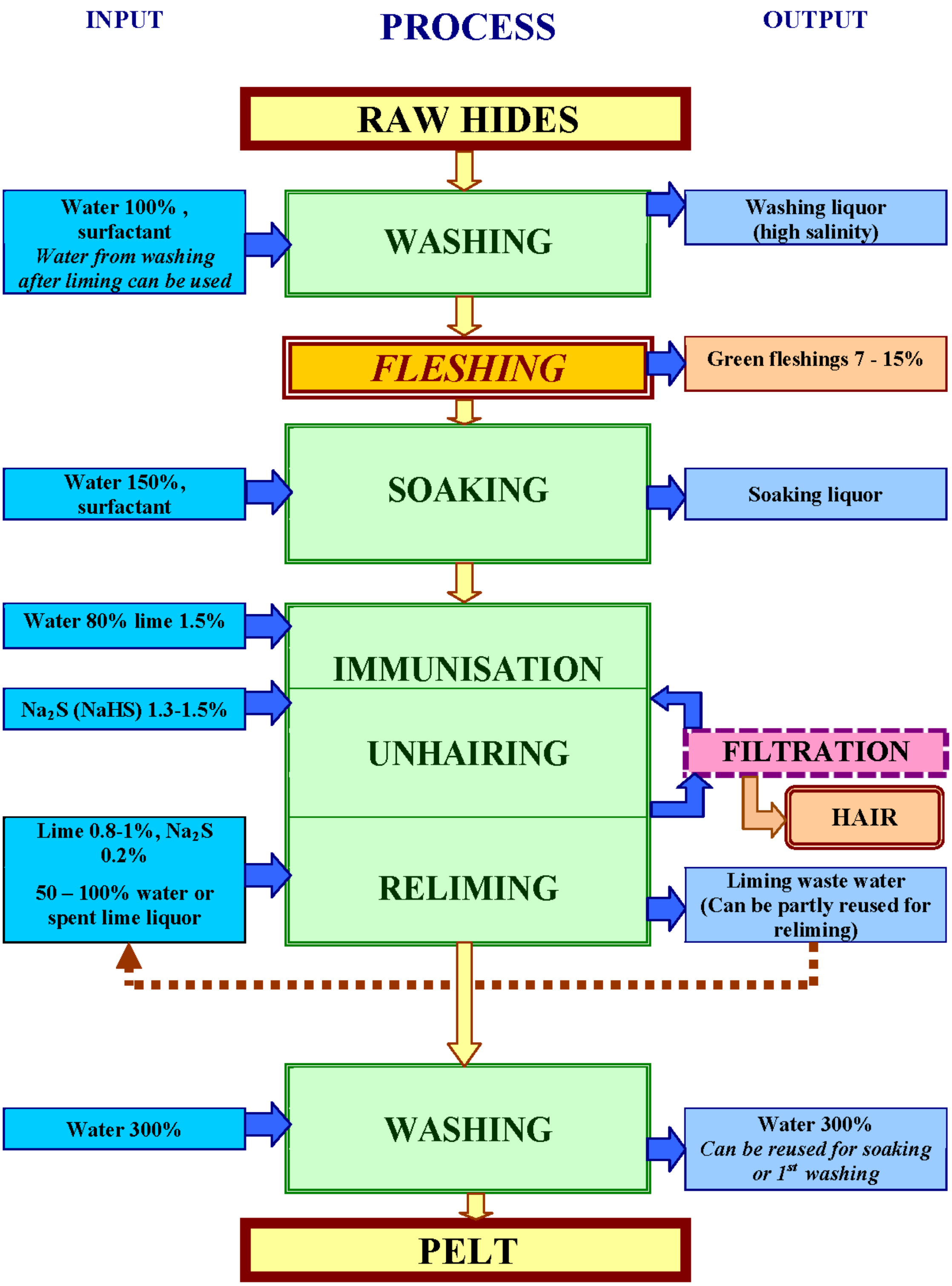
- Nearly all methods on the market claim to improve leather quality and increase area yields. These claims, however, cannot be taken at face value; they have to be verified in industrial trials over several months.
- Float collection and filtration after chemical unhairing is in practice the easiest method to implement using existing equipment. It thus entails relatively low investment costs. Cheap and simple screens can be selected, yet this approach is not optimal in terms of hair quality and reducing the waste water load.
- At present, the most realistic possibilities for utilising the hair recovered seem to be as a soil additive or animal feed. Slow degrading hair protein is especially beneficial in soils in dry regions prone to desertification, since it increases the humus content of the soil.

References

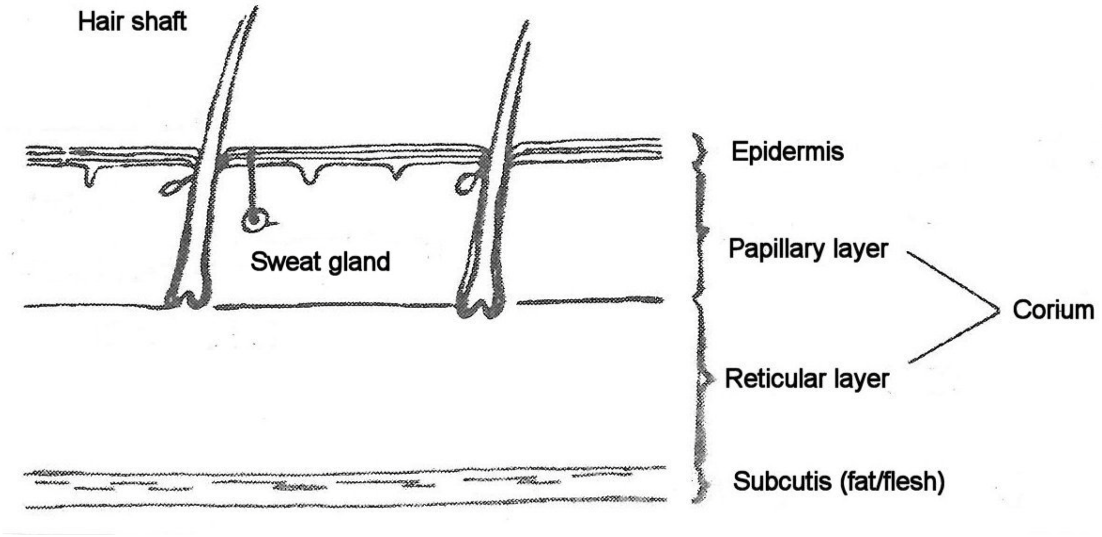
1. UNIDO Project US/RAS/92/120: Assistance in Pollution Control in the Tanning Industry in South-East Asia.
2. E Heidemann: Fundamentals of Leather Manufacturing. Darmstadt 1993.
3. E. Heidemann et al.: The mechanism of hair-save unhairing in drum according to the immunisation principle. Das Leder 39, 165 (1988).
4. C.A. Money: Unhairing and dewooling - requirements for quality and the environment. JSLTC 80, 175 (1996).
5. A. Zissel: Beamhouse work. In: H. Herfeld (ed): Bibliothek des Leders, Vol. 2, Frankfurt am Main 1988.
6. K. Bienkiewicz: Physical chemistry of leather making. Malabar, Florida 1983.
7. Z. Ko⊆enek et al: Hair saving liming in Ko⟩elu⟩ny Ltd., Otrokovice, Czech Republic. IULTCS XXIII. Congress, Friedrichshafen 15-20/5 1995.
8. Catherine Money, personal communication.
9. R.W. Cranston et al.: Development of a hair-recovery process for unhairing of hides. IULTCS XVIII Congress, Venezia 15-17/9 1983.
10. R.W. Cranston et al.: Practical considerations on the Sirolime process. JSLTC 70, 50 (1986).
11. R.W. Cranston et al.: Development of the Sirolime unhairing process. JALCA 81, 347 (1986).
12. T.G. Blair: The Blair Hair System. Lea. Mfr. 104, No. 12,18 (1986).
13. T.G. Blair: Environmentally friendly wet end liming procedures assisted by amine chemicals. Rohm and Haas Company.
14. V. Olip, K.H. Munz: Ideas on liming. UNIDO Expert Group Meeting on Pollution Control in the Tanning Industry in the South-East Asia Region, Madras, India, 15-17 February 1991.
15. J. Christner: Low sulphide liming systems. Internat. Cleaner Technology Seminar, Birmingham 22-23/5 1995.
16. J. O. Borge: Hair save unhairing from a practical point of view. International Cleaner Technology Seminar, Birmingham 22-23/5 1995.
17. J. Christner: Quality improvement and reduction of the wastewater pollution with a new hair-save unhairing process. Das Leder 41, 177 (1990).
18. I.G. Mason: A hair recovery process for hides. JSLTC 68, 93 (1984).
19. A. Simoncini et al: Hair preserving unhairing. Cuoio, Pelli, Mat. Conc. 62, 95 (1986).
20. F. Elsinger et al: Method for unhairing and opening-up without sulphides. Das Leder 38, 143 (1987).
21. V. Olip: Practical experiences with a new liming chemical. Proceedings of the International Workshop on Chemistry and Technology of Tanning Processes, San Miniato (Pisa) 21-23/6 1988. Cuoio, Pelli, Mat. Conc. 66, 360 (1990).
22. M. Asensio: Ecological soaking and hair-save unhairing. Internat. Cleaner Technology Seminar, Birmingham 22-23/5 1995.
23. NN: Ecology in the beamhouse. Leather, July 1995, 37.
24. K.T.W Alexander: Enzymes in the tannery - catalysts for progress? JALCA 83, 287 (1988).
25. R.W. Cranston et al: The use of the Sirolime process in the production of wet-blue leather. IULTCS XX Congress, Philadelphia 15-19/10 1989.
26. R.O. Adewoye; S. Bangaruswamy: Use of pulped fruit of Adenopus Breviflorus (Tagiri) as an unhairing agent and characterization of the enzymes extracted from the fruit. JALCA 79, 446 (1984).
27. K.H. Gustavson: Depilatory Action of Urea. JSLTC 33, 162 (1949).

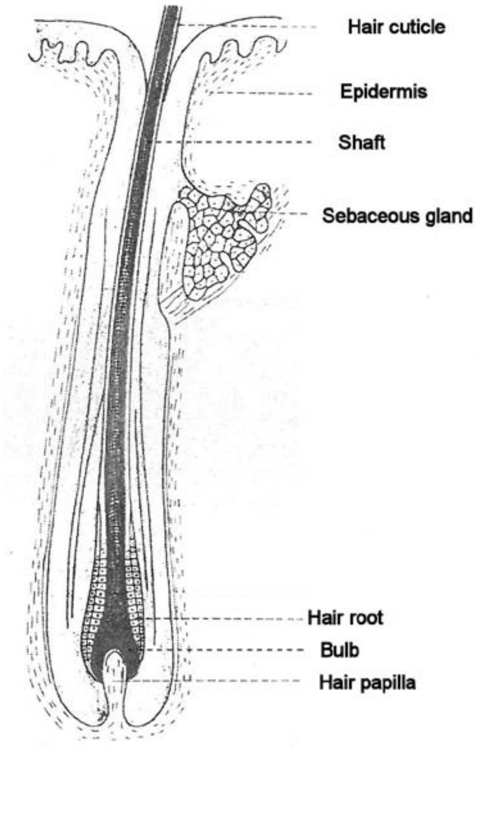
28. *S.C. Hawkins, J. Wassenberg: Endogenous enzyme fellmongering. Skin structure and properties. IULTCS XXIV Congress, London 11-14/9 1997.*
29. *W. Keller, E. Heidemann: Investigations of the mechanism of the lactic acid unhairing. Das Leder 41, 1 (1990).*
30. *I.C. Somerville et al.: Rapid Unhairing with Dimethylamine. JALCA 58, 254 (1963).*
31. *A.A. Fadel, M. Speranza: Hair recovery liming. Leather July 1995, 33.*
32. *Cleaner Production in Leather Tanning. A Training Resource Package. Preliminary Edition. UNEP, Paris, February 1995.*
33. *W. Frendrup. IUE Commission Meeting, Athens 14-16 April 1992*
34. *C.M. Maranges: Introduction of a Cleaner Technology. The Hair Saving Method. UNIDO, Vienna, 1996.*
35. *B. Stentebjerg-Olesen: Enzymes, environmentally friendly compounds in the manufacture of leather. Proceedings of the Workshop on Topical Questions of the Environment Protection in the Leather Manufacturing. Partisanske, Slovakia, 1996.*
36. *R.M. Davies: Setting of consent limits for tanning industry trade effluents. JSLTC 81, 32 (1997).*
37. *C.S. Cantera, J. Buljan: Hair - a new raw material. World Leather 10, No. 7, 51 (1997).*
38. *K. Hellinger, R. Mühlbach: Hair-preserving liming - What can we do with the hair obtained ? Leder- u. Häutemarkt 48, Nr. 9, 116 (1996).*
39. *B. Cortese: Hair-save unhairing with the Röhm HS process. Cuoio, Pelli, Mat. Conc. 66, 350 (1990).*
40. *E. Heidemann: What will be the future of the wet processing in the leather industry? Das Leder 37, 79 (1986).*
41. *C.A. Money: Tannery Waste Minimization. JALCA 86, 229 (1991).*
42. *G. Ramamurthy et al: Improved uptake of basic chromium salts in tanning operations using keratin hydrolysate. JSLTC 73, 168 (1989).*
43. *E. Heidemann: Clean technology - what does that mean for the leather industry? Das Leder 43, 262 (1992).*
44. *C.S. Cantera et al.: Unhairing technology involving hair protection. Adaptation of a recirculation technique. JSLTC 79, 12 (1995).*
45. *C.S. Cantera et al.: Hair-save enzyme-assisted unhairing, influence of enzymatic products upon leather quality. JSLTC 80, 83 (1996).*
46. *H.P. Germann: The evolution of the unhairing process as influenced by technological, economic and ecological considerations. 1997 J.A. Wilson Memorial Lecture. JALCA 92, 84-92 (1997).*
47. *S. Rydin: Evaluation of job creation by LIFE projects in tanneries. Report to the European Commission, Dir. Gen. XI., May 1997.*
48. *EU – Best Available Technologies Reference Document (BREF) 2012.*
49. *A. Zissel: Arbeiten der Wasserwerkstadt bei der Lederherstellung, Bibliothek des Leders, 1989.*
50. *Z. Bayer, Sirova koža, Zagreb, 1978.*
51. *H. Grgurić, T. Vuković, Ž. Bajza, Tehnologija kože i krzna, Zagreb, 1985.*
52. *BASF, From collagen to leather, 2007*
53. *BASF, Pocket Book for the Leather Technologist, Third edition.*
54. *I. Kral, Hair save liming, PPT presentation, Chennai, India, 2011*
55. *Utilization of bovine hairs recovered from the hair-save unhairing process for preparing the filling agent for retanning: environmental and economic considerations, Liu Wentao, Li Guoying, XXXI IULTCS Congress, Valencia, 2011*
56. *Equipment manufacturers Italprogetti, SC* Costruzioni Meccaniche*, Nuove Energie,, Vallero,* ewuenviron - *information, drawings and photos available on Internet.*

Annex 1 Process diagram of hair-save soaking-liming with float recirculation

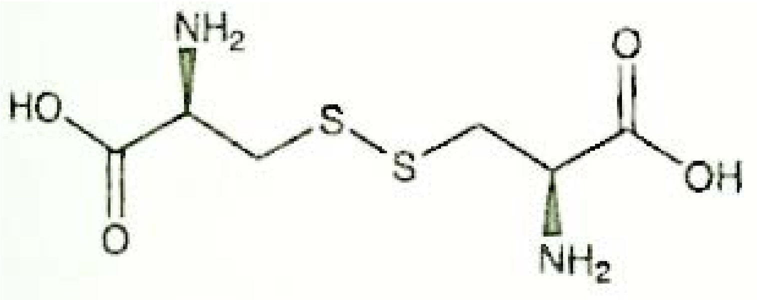


Annex 2 Schematic cross-section of bovine hide; the structure of individual hair



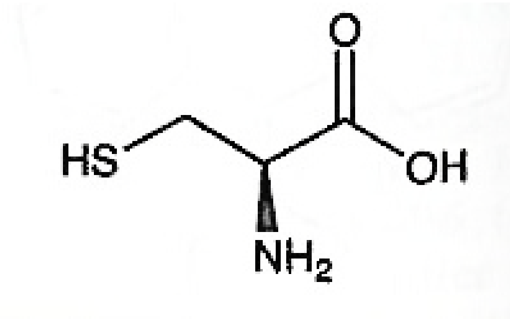


Annex 3 Amino acids in keratin of special importance in unhairing



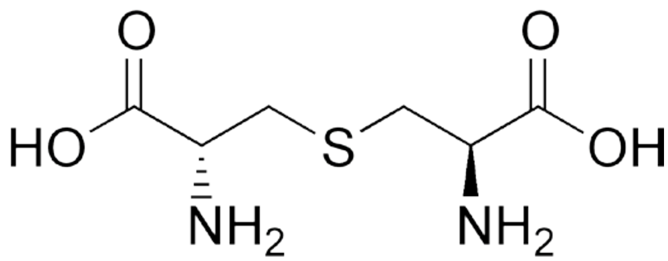
Cystine

Following the attack by strong reducing compounds such as sodium sulphide (Na_2S) in alkaline medium the bisulphide bond (-S-S-) is broken; one molecule of cystine gives two molecules of cysteine:



Cysteine

Sometimes, it happens that cystine is only converted to lanthionine:



Lanthionine

Annex 4 Organic sulphur compounds used in commercial unhairing

The formulae of three types of organic sulphur compounds used in commercial unhairing systems:

Mercaptoethanol

$$CH_2SH \cong CH_2OH$$

Salts of mercaptoacetic acid (thioglycolic acid)

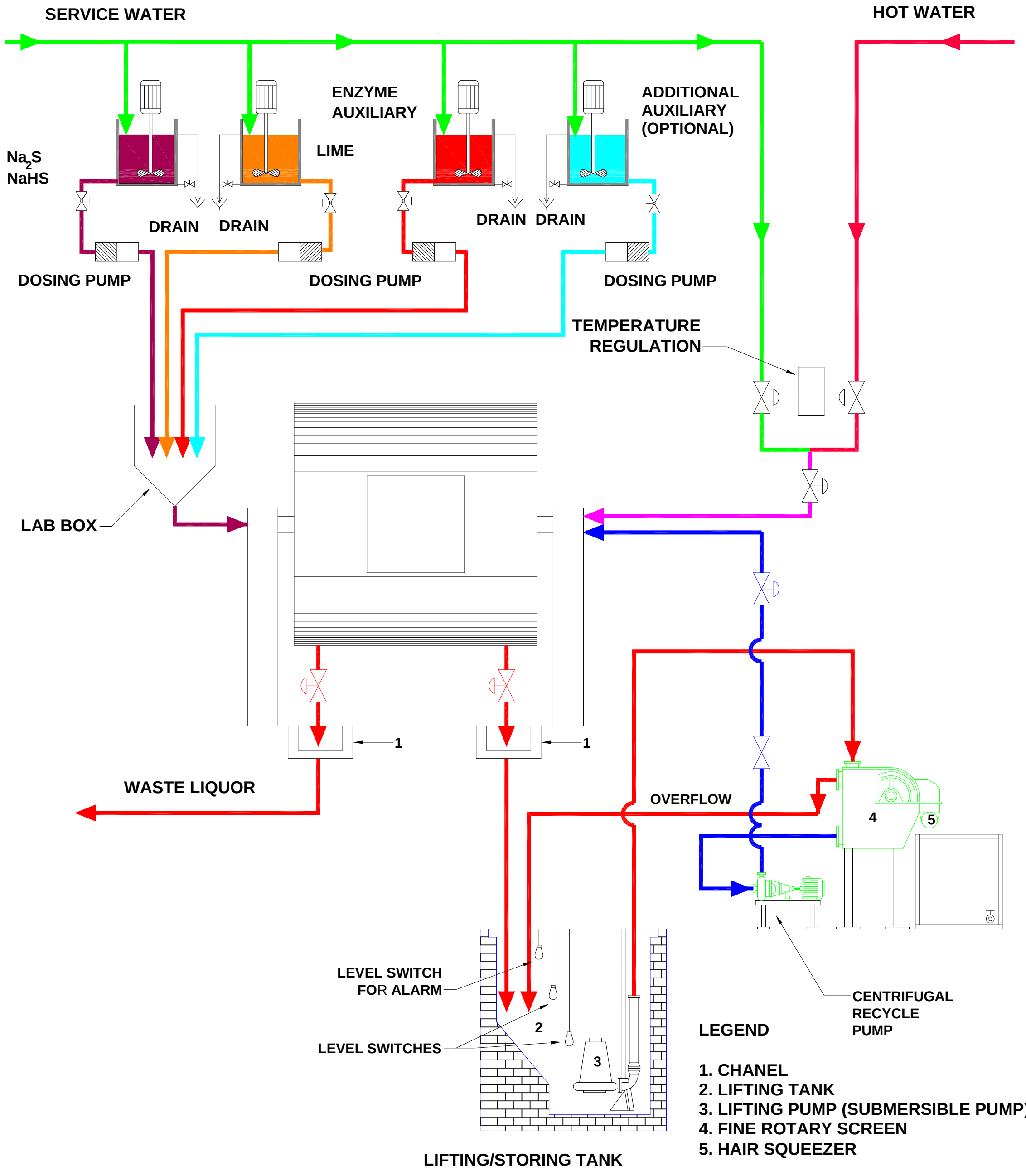
$$CH_2SH \cong COONa$$

Formamidinesulphinic acid

$$(CHNH_2NH_2)^+ \ (SOOH)^-$$

Annex 5 Schematic flow-chart of the hair-save unhairing process

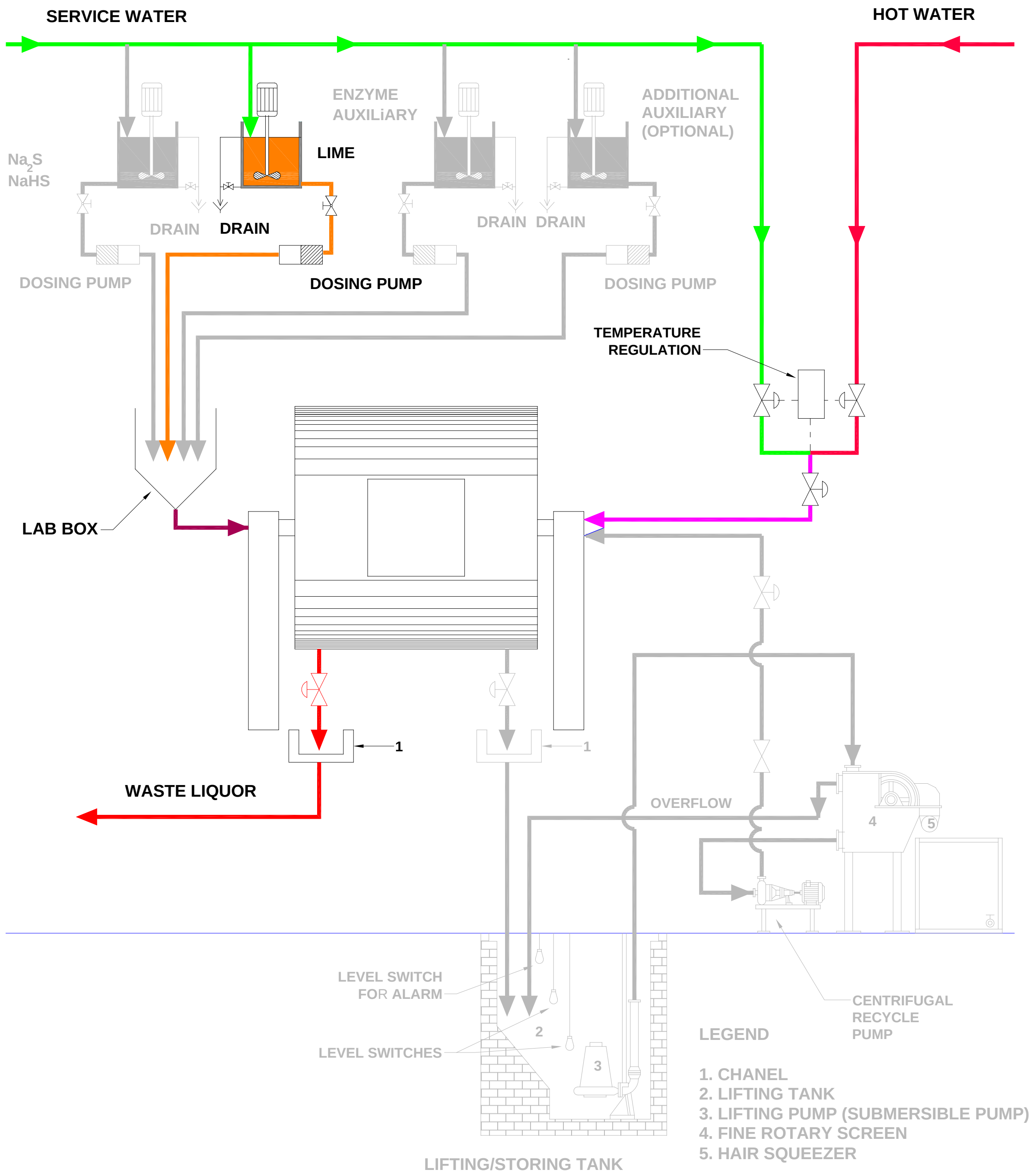
OVERALL SET UP



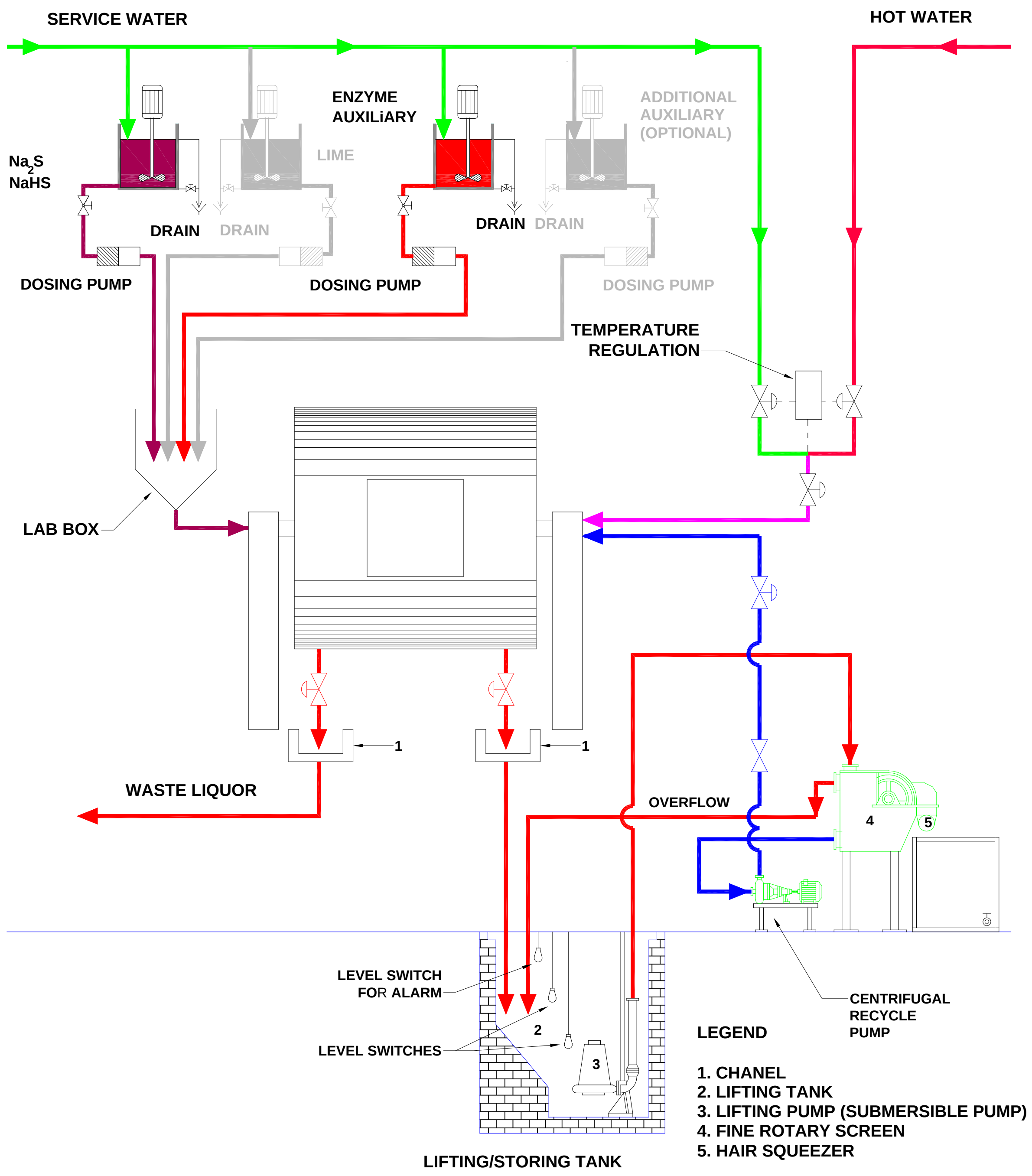
LEGEND

1. CHANEL
2. LIFTING TANK
3. LIFTING PUMP (SUBMERSIBLE PUMP)
4. FINE ROTARY SCREEN
5. HAIR SQUEEZER

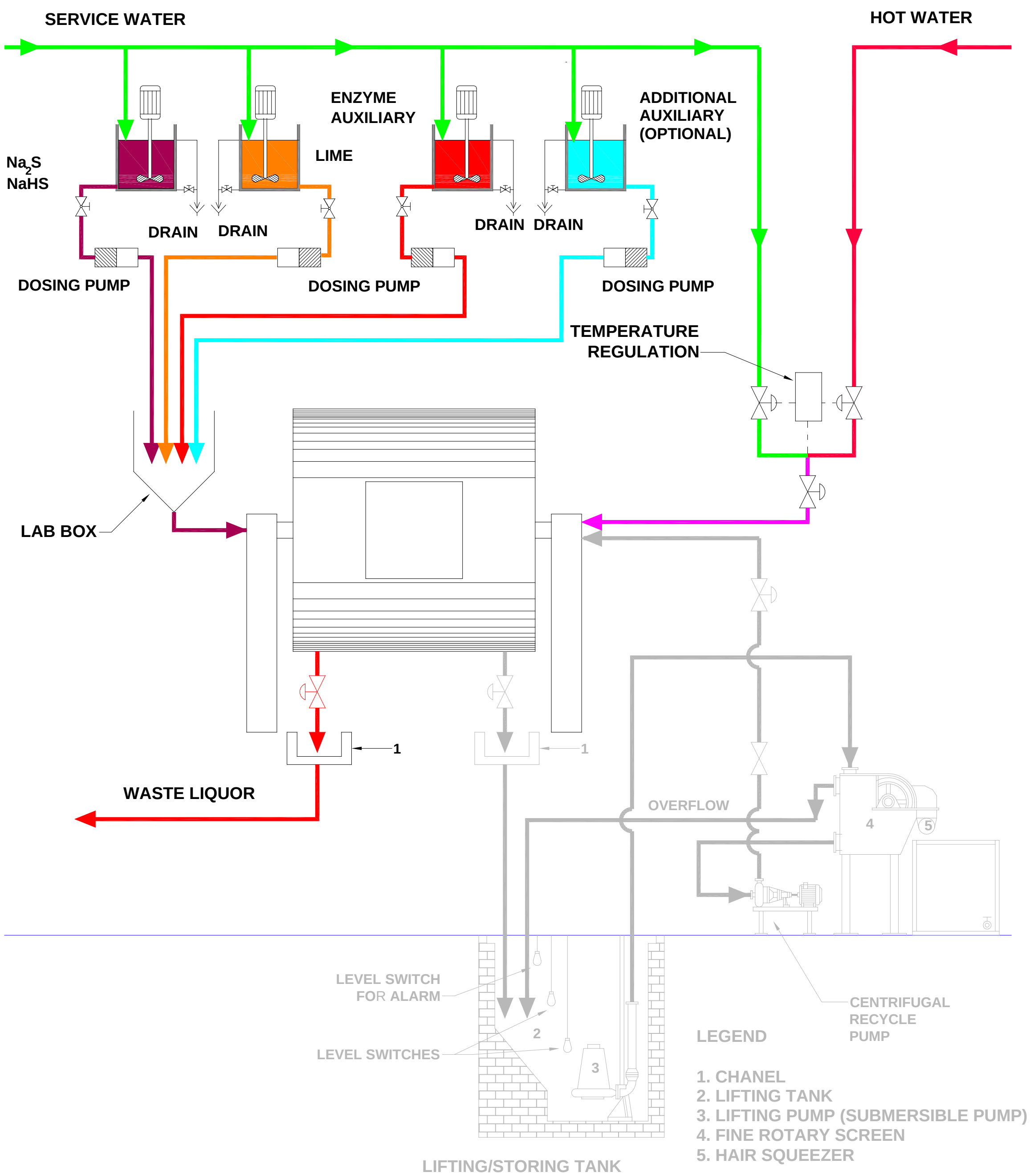
IMMUNISATION STAGE



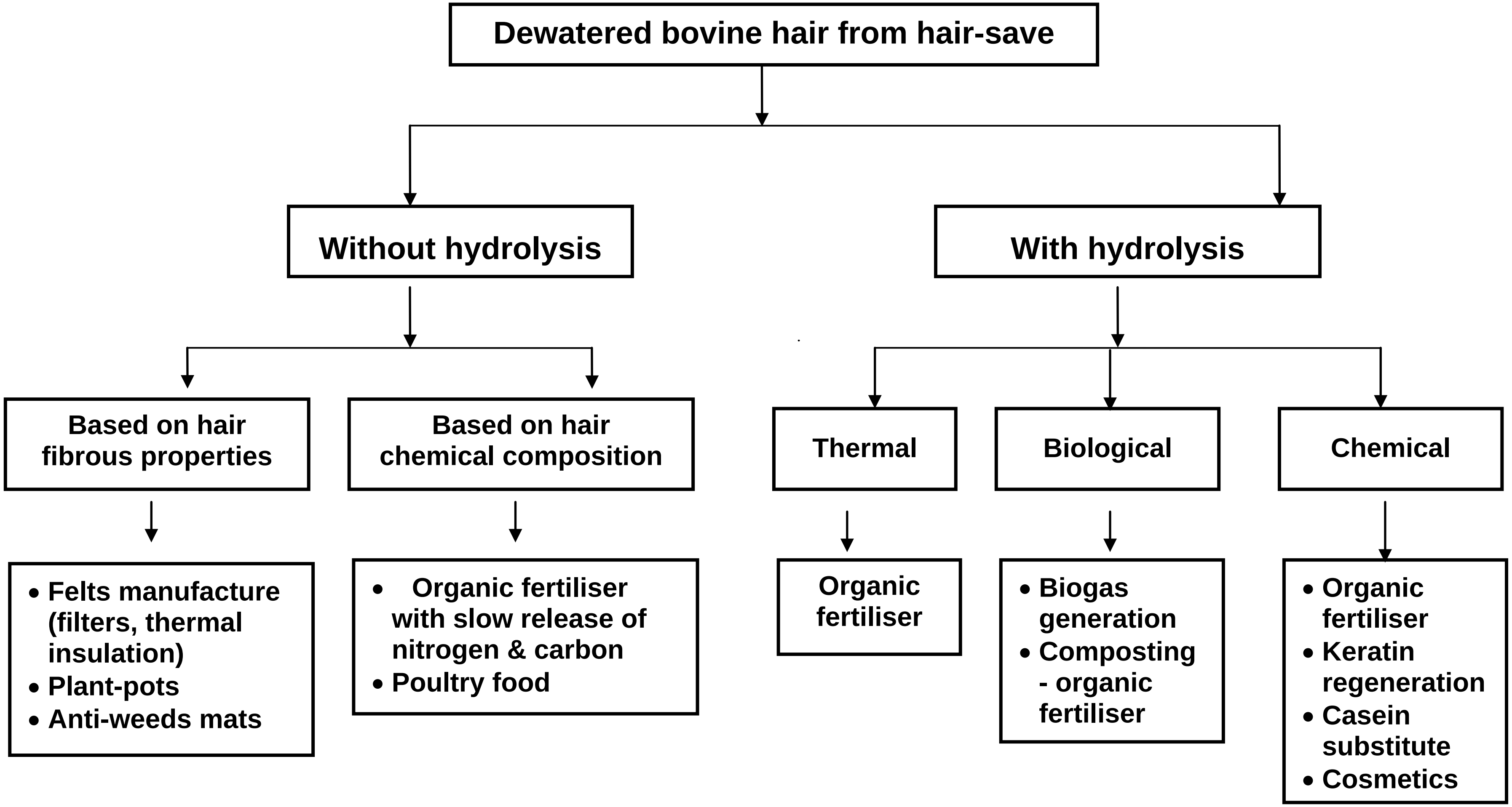
UNHAIRING STAGE



RELIMING STAGE



Annex 6 Potential categories of utilisation of bovine hair



Annex 7 A case study: The filling agent for retanning from the hair-save unhairing process[4]

1. Introduction

The objective of this work was to report an application of the bovine hairs from hair-save unhairing, i.e., preparing the filling agent for retanning, and the environmental and economic aspects of this utilization were discussed.

2. Recovery of Bovine Hairs with a Hair-save Unhairing Method

Fig.1 shows the hair-save unhairing method used in Zhaofu Leather Product Co., Ltd., Nanhai, Foshan, China. The lime-sulphide unhairing was carried out in a drum, where the hair was loosened by mechanical action and the friction among pelts during the chemical unhairing process that only attacked the hair roots. Then the unhairing liquor containing hair was discharged and filtered to obtain the bovine hairs and the filtrate which was recirculated after sedimentation. It should be noted that a self-developed machine was used to recover the bovine hairs with a high recovery ratio of above 97% (Fig.2).

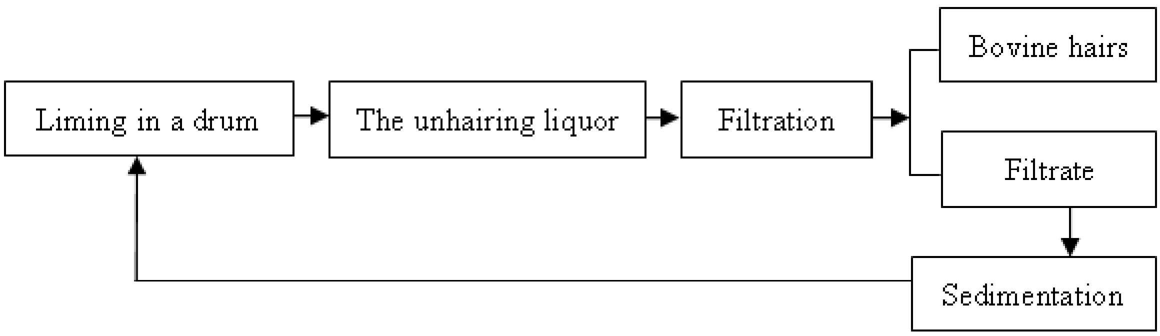


Fig.1 The hair-save unhairing process

3. Pilot-Scale Preparation of the Filling Agent for Retanning Using Bovine Hairs

Fig.3 indicates the use of bovine hairs for preparing the filling agent for retanning. The bovine hairs recovered from the unhairing process were firstly washed until a neutral or faintly basic pH was achieved and then the hairs were dehydrated by using a perforated container. Next, the hairs were subjected to a series of pretreatments and then hydrolyzed and filtered to obtain the filtrate, which was modified before concentrating and drying. The final product is powder and has a coffee appearance (Fig.4). Up to now, approximately 1200 tons of bovine hairs from hair-save unhairing were processed and about 380 tons of filling agents were prepared in Zhaofu Leather Product Co., Ltd., Nanhai, Foshan, China. Fig.5 shows the newly built workshop for preparing the filling agent for retanning by use of bovine hairs.

---

4 *Extract from the paper by Liu Wentao and Li Guoying XXXI IULTCS Congress, Valencia, 2011*

Fig.2 The self-developed machine for recovering bovine hairs in Zhaofu Leather Product Co., Ltd., Nanhai, Foshan, China

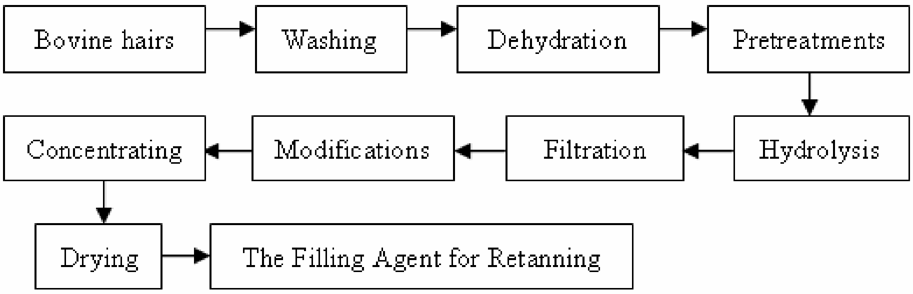


Fig.3 The use of bovine hairs for preparing the filling agent for retanning

Fig.4 The filling agent for retanning prepared from bovine hairs

Fig.5 The newly built workshop for preparing the filling agent for retanning in Zhaofu Leather Product Co., Ltd., Nanhai, Foshan, China

4. Pilot-Scale Leather Retanning with the Filling Agent

The filling agent prepared from bovine hairs was applied for retanning the wet blue in several tanneries. The retanning results showed that the fullness, softness and elasticity, as well as the thickness of the leather retanned with this filling agent were increased, and the retanned leather had fine and tight grain. Furthermore, the filling agent had assistant dyeing properties, and the tensile strength and tearing strength of the retanned leather were improved.

5. Environmental and Economic Benefits Analysis

Due to the recovery of bovine hairs, the concentration of suspended solids, total nitrogen, sulphide and chemical oxygen demand were reduced in wasted unhairing-liming liquor, resulting in an easier handling of the tannery wastewater. The testing of the unhairing liquor showed that chemical oxygen demand and total nitrogen were respectively reduced for 0.9094 ~ 0.9579 kg and 0.1179 ~ 0.1237 kg when recovering 1 kg bovine hairs on a dry weight basis. As far as the recovery of 1200 tons of bovine hairs is concerned, about 430 tons of chemical oxygen demand and 58 tons of total nitrogen were avoided discharging into the environment. In addition, the wastewater treatment charge decreased RMB 1.0 and the transport charge for tannery sludge was also reduced. Up to now, the environmental benefits amount to about RMB 750,000 has been produced as a result of the adoption of hair-save unhairing method in Zhaofu Leather Product Co., Ltd., Nanhai, Foshan, China.

The 380 tons of filling agents prepared from bovine hairs were all used in Zhaofu Leather Product Co., Ltd. to replace with the plant protein filling agent, which was purchased from the market with the price of RMB 12,000 per ton. Subtracting the production cost (about RMB 1,000 per ton) for preparing the filling agent from bovine hairs, the economic benefit of approximately RMB 4,200,000 has been brought for Zhaofu Leather Product Co., Ltd. due to the use of bovine hair protein filling agent for retanning.

6. Conclusions

This work has demonstrated that the bovine hairs recovered from hair-save unhairing could be used to prepare the filling agent for retanning with good filling effect. The pilot-scale utilization of bovine hairs presented here could produce relative considerable environmental and economic benefits, and would be beneficial to the widespread use of hair-save unhairing methods in leather industry.

References

[1] W. Frendrup. *United Nations Industrial Development Organization*, 2000, US/RAS/92/120, 3-32
[2] H. Germann. *J. Am. Leather Chem. Assoc.*, 1997, 92, 84-92
[3] E. Heidemann. *Das Leder*, 1986, 37, 79
[4] C. S. Cantera and J. Buljan. *World Leather*, 1997, 10, 51-54
[5] K. Hellinger, R. Mühlbach. *Leder- u. Häutemarkt*, 1996, 48, 116