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# HAIR-SAVE UNHAIRING METHODS IN LEATHER PROCESSING

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*This is a revised version of an earlier printed document.*

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## ANNEXES

# 1. INTRODUCTION

Up until the 1880's, only hair-save methods (straight lime or sweating) were used for unhairing. These methods required subsequent mechanical unhairing. Originally this was done by hand on a beam; unhairing machines were introduced at a later stage. From the 1880's onwards, hair-destroying unhairing processes using lime and sulphide were used in tanneries: a practice that has since been generally adopted in most countries. Given that it renders mechanical unhairing superfluous, it saves both labour and time. It also ensures a clean pelt and opens up the hide substance to a satisfactory degree.

The above advantages notwithstanding, dissolving the hair results in high organic pollution in the wastewater. With increasingly stringent environmental requirements, it has become necessary to reduce the pollution load in wastewater as much as possible. This may be done by treating the wastewater biologically: an expensive undertaking. Moreover, wastewater treatment generates a large amount of sludge posing disposal problems. For this reason, hair-save unhairing has taken on renewed importance. Today, it is a well-established practice, especially in industrialised countries. In the interest of maintaining high productivity, the mechanical unhairing process used formerly has to be avoided as it would be too expensive today.

Tanneries must decide for themselves on the basis of cost-benefit analyses whether it is advantageous to adopt hair-save unhairing techniques (See Chapter 5). Outside industrialized countries hair-save unhairing is still not all that common; however, the ever-increasing environmental costs (related to treatment, disposal and tax) and external pressures will serve as an incentive to use the method on a broader scale.

Adopting hair-save unhairing techniques may help a tannery to acquire a green label (eco-label) for the leather it produces.

## 2. THE MECHANICS OF HAIR-SAVE UNHAIRING

Skin (or hide) is usually considered to comprise three layers (Figure 1). On the surface of the intact skin lies the keratinous epidermal layer comprising the epidermis and its appendages (hairs, hair root sheaths, etc). Immediately below it, the basement membrane is to be found, attaching the epidermal layer to the underlying dermis (or corium). In the tannery, the corium is transformed into leather. In hair-save unhairing, the epidermal layer must be removed from the dermis without damaging the hair. A further component of raw skin (or hide) is the subcutaneous layer (connective tissue and fat) which is removed by fleshing. That layer, however, is of no relevance to unhairing except when applying the painting method.

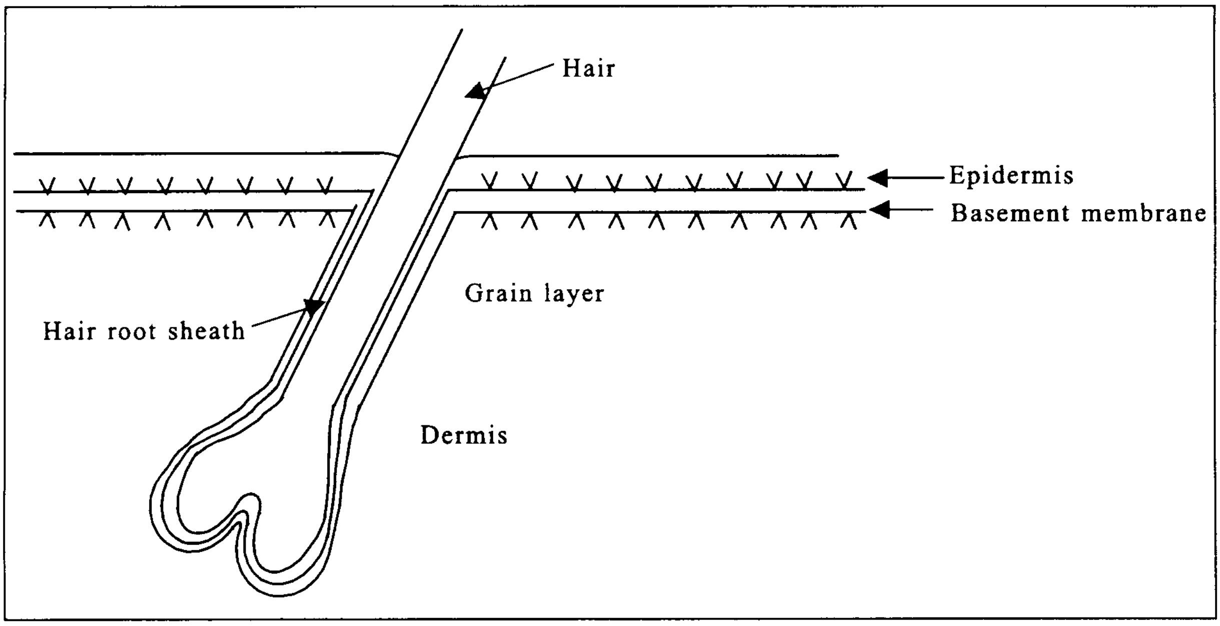

**Figure 1. Schematic diagram of the skin layers**

Keratin is stabilised through disulphide bonds (-S-S-). 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: treatment with an alkali, but without sulphide (2) (3). 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.

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.

The basement membrane is a thin layer (50-100 nm) between the epidermal layer (including the hair roots) and the dermis. It is attached to the surface layer (grain) of the dermis. It consists of a special type of collagen as well as various glycoproteins and proteoglycans (protein-carbohydrate compounds) which are interlinked in a close network. 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 (See Chapter 3.6).

Breaking the corium-epidermis junction is achieved by destroying or modifying the basal cell layer of the epidermis, the hair bulb and root sheaths and/or the basement membrane network. In most hair-save methods, the hair breaks in the pre-keratinous zone above the hair bulb.

Ground and fine hair (hair still growing) are more deeply anchored in the dermis than fully developed hair. Normally, treatment with a small amount of sulphide is necessary to remove these hairs completely. Commercially viable hair-save systems include the use of a certain amount of sulphide.

If the swelling needed to open up the hide structure does not occur during unhairing, it must be induced subsequently by using an alkali (usually lime). An appropriate dose of sulphide can be added during re-liming (see Annex 2).

When processing sheepskin, it may be preferable to unhair without lime or sulphide. This holds all the more true in those instances where the wool is more valuable than the leather, since both alkali and sulphide damage the wool.

## 3. CURRENT METHODS

### 3. 1. General remarks

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. Modern 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)1.

Almost all methods in use entail immunising the hair, re-liming and using some sulphide. All processes claim to offer environmental benefits, as well as enhanced leather properties and improved area yields.

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).

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1 A general survey of unhairing methods was recently published by H.P.Germann (46)

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 (5), the upper limit being the temperature at which risk of damage to the hide substance is incurred. Temperatures up to $30^0$C are considered safe, whereas at $35^0$C the hide substance is drastically damaged, especially in the grain layer (6).

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

### 3. 2. Straight lime

In many countries, tanneries use hair-save unhairing with straight lime, normally in pits. Slow alkaline hydrolysis of the corium-epidermis boundary layer leads to a loosening of the hair after 3-5 days. In addition, slow degradation of the hide substance occurs, attaining a significant level after approximately 8 days. The optimum unhairing time is thus 4-6 days.

Re-use of old lime liquors after strengthening, as often practised, renders unhairing more effective because of the unhairing effect of the amines yielded by protein hydrolysis (See Chapter 3.7).

Advantages of this technology are that it is simple to control and requires practically no energy input. Its disadvantages are the incipient attack on the hide substance leading to loose grain, the long processing time and the need for mechanical unhairing. In all probability, this method will fall into disuse, given the industrialisation of leather production.

### 3. 3. 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 $S^{--}$ per tonne salted raw hide (2).

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 (5). Approximate limits, based on laboratory scale trials, are as follows (2):

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

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 $S^{--}$ per tonne raw hide. Normally, a dosage ranging between 1.5 and 3% (equivalent to 3.7-7.4 kg $S^{--}$ per tonne raw hide) is used.

Industrial-scale hair-save unhairing trials using lime-sulphide were conducted in a major European tannery (7). Unhairing was carried out in batches of 1.2-6 tonnes raw hide using a mixer or a drum equipped with recirculation and a hair-separation sieve.

The recipe in summary was as follows:

Immunisation: Max. 150% water
1.5% lime
45 min. (15 min. rotation)

Unhairing: + 1.5 % sodium sulphide flake (60% $Na_2S$ )
After $1^{3/4}$-2 h filtration

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

In order to obtain a perfectly clean pelt grain, a minimal amount of enzyme was added to the reliming liquor. Both the pelt and the leather produced (upper leather) were comparable with the reference production.

For the hair-destroying unhairing process, the factory used 2% sodium sulphide flake (60 % $Na_2S$). For the hair-save unhairing process, a dosage of 1.3% flake would have been quite adequate, but for reasons of safety a dosage of 1.5% was chosen.

Two commercial methods are based on lime-sulphide unhairing: **Sirolime** and **Blair Hair**.

### 3.3.1. Sirolime

The Sirolime method was developed in 1981 by CSIRO (Commonwealth Scientific and Industrial Research Organization) Leather Research Centre, Australia. The method is currently used in tanneries in Australia and New Zealand, as well as elsewhere.

The original version of the method consisted of impregnating the hair with a sodium hydrosulphide solution, without any further additives. The relatively low pH value (decreasing from approximately 11.5 to approximately 8.6 in the course of the process) ensures that the hydrosulphide has an immunising effect, yet does not attack the hair. The hydrosulphide associated with the external hair is subsequently eliminated through oxidation with calcium hypochlorite, whereas the hydrosulphide absorbed in the hair follicle remains. A subsequent addition of lime activates the remaining hydrosulphide which attacks the hair-roots, thus loosening the hair. The unhairing liquor is recirculated through a filter in order to separate the hairs as soon as they become loosened. After unhairing, the pelts are relimed.

The method was modified at a later stage since the original version incurred the risk of hydrogen sulphide being generated during impregnation. This occurs when the pH drops below the limit critical for the generation of hydrogen sulphide (pH 9). It proved possible to avert that risk and at an even later stage, the method was modified once again in order to simplify the process. It is claimed that recycling offers a range of possibilities for saving water and chemicals. Waste liquor from the impregnation step can be re-used after sedimentation; any surplus can be used in the wash after impregnation. Waste liquor from hair loosening and liming can be used during re-liming. Consequently, fresh water is needed only for the wash after impregnation and for immunisation.

An outline of the modified version with recycling of waste re-liming liquor only (4) is given in the box below. The modifications are said to improve the unhairing effect.

### OUTLINE OF MODIFIED VERSION OF SIROLIME UNHAIRING(4)

In drum

**Immunisation**: 100% water (28°C)
Reducing agent
1.5% lime
1 hour

**Hair loosening**: + sulphide, e.g. 1% NaHS (60%)
1 hour
Start recirculation and filtering of the hair
3 hours

**Re-liming**: + 0.5% $Na_2S$ (60%)
0.75% lime
60% recycled liquor
Overnight
Drain

Liquor recycled, excess liquor to sewer

Net consumption with the Sirolime method is claimed to be as follows:

| | **Original version** | **Modified version with recycling** |
|---|---|---|
| Water | 250% | 100% |
| Sulphide flake (60% $Na_2S$ ) | 1-1.5% | 0.5% |
| Hydrosulphide flake (60% NaHS) | 1% | 1% |
| kg $S^{--}$ per tonne raw hide | 5.9-7.1 | 4.7 |

The advantages of the method are:

- No proprietary products are used; the chemical costs are thus low.
- The process can be delayed between individual steps, if advantageous or necessary.

- Minimal risk of over-immunisation.

It is stated that a clean grain is obtained, thus making the pelts suitable for aniline leather production. The risk of drawn grain is low and growth marks are not pronounced.

The disadvantages are:

- Somewhat complicated process/procedures.
- With large batches of hides, risk of insufficient unhairing in patches.
- Given the heavy use of sulphides, total sulphide consumption is high. If organic sulphur compounds are used as reducing agents, sulphide consumption decreases, but chemical costs increase.

### 3.3.2. Blair-Hair

The Blair Hair method (12) (13) was developed in 1985 by Rohm and Haas Co. in co-operation with Eagle Ottawa Leather Co. The method is currently used in tanneries in the United States, Mexico and Korea.

The main features of the method are as follows: lime treatment is used to immunise the hair. After immunisation, sodium hydrosulphide is added and the hairs gradually loosen. When hair loosening is complete, the liquor is pumped out and filtered. The subsequent re-liming is carried out by the means of lime, hydrosulphide and an auxiliary: Unhairing Assist FR-62. This product is an aliphatic amine which helps to complete the action on hair roots and epidermis and prevents further immunisation or (by means of a pH increase) generation of hydrogen sulphide. (see Chapter 3.7 for use of amines in unhairing). The recipes are given in the two boxes below.

**BLAIR HAIR UNHAIRING IN CEMENT MIXER**[1]

Adjust to 27-28°C after soak.

| | |
|---|---|
| **Immunisation**: | 150% water (27°C)<br>2.5% lime<br>Run 10 min. (4 r.p.m.), rest 50 min. |
| **Hair loosening**: | + 1.5% NaHS (flake)<br>Run 10 min. (8 r.p.m.), rest 20 min.<br>Run 10 min., rest 20 min.<br>Run 10 min., rest 20 min[2]<br>Run 10 min, rest 20 min.<br>Run 10 min (90% of hair is loose and patches will drop off). |
| **Hair removal**: | Pump out hair; refloat and wash through for 1 h. If pump out exceeds pump in, stop mixer and refill. |
| **Re-liming**: | 150% water (27°C)<br>2.5% lime<br>0.5% NaHS<br>1.25% Unhairing Assist FR-62<br>0.25 Anionic surfactant<br>Run 10 min. (4 r.p.m.), rest 50 min<br>Run 14 times |

1)Information from the supplier

2)If hair is not loosening at this point, extend the 30 min cycle. If by error the temperature drops to 21-24°C, run mixer constantly until hair has dropped off or the heat in the mixer reaches 27°C.

**BLAIR HAIR UNHAIRING IN DRUM**[1]

| | |
|---|---|
| Adjust to 27-28°C after soak. | |
| **Immunisation**: | + 2% lime (to soaking liquor)<br>Run 5 min. , rest 25 min.<br>Run 5 min. , rest 25 min.<br>Run 5 min. (28°C) |
| **Hair loosening**: | + 1.5% NaHS (flake)<br>Run 10 min., rest 20 min.<br>Run 10 min., rest 20 min.<br>Run 10 min. (Hair is 90% removed from skin; adhering hair is easily removed by hand rubbing) |
| **Hair removal**: | Wash 28-29°C (running water for 30-45 min.) |
| **Re-liming**: | 2% lime<br>0.5% NaHS<br>1% Unhairing Assist FR-62<br>0.2 Anionic surfactant<br>Run 10 min.<br>Run 5min/h for 8 h. |

1) Information from the supplier

As the hair is only separated once hair loosening is complete, the drums do not need to be fitted with recirculation equipment. The liquor used to loosen the hair can be re-used after mending. Total unhairing time is approximately 18.5 hours. Unhairing entails only a limited number of liquor changes. It is claimed that a clean pelt and wet blue can be obtained and that grain draw and growth wrinkles are minimised.

The method requires a high level of control, as process temperatures and times are critical. Over-immunisation leading to hair patches is a real risk. Not all the hair is entirely removed during the hair removal stage; any hair roots remaining and other residue must be eliminated during re-liming. Washing with running water leads to excessive water consumption. This, however, could probably be avoided by installing a recirculation system.

Sulphide consumption is high; 2% hydrosulphide flake Na HS, equivalent to 10.9 kg $S^{--}$ per tonne raw hide; however, lower dosages seem possible.

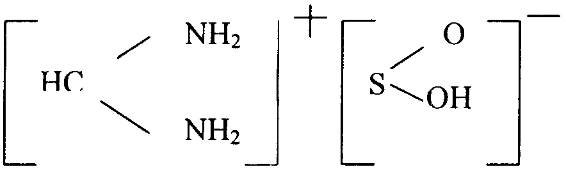
### 3.3.3. Painting

Painting (2)(5)(14) is a traditional hair-save method for calf, sheep or long-haired goat skins. It is used in cases where the hair/wool is valuable. The 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. Normally, the paste contains 5-15% sodium sulphide and 40-70% water, with a density of 15-40% Bé.

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, although some attack at the end of the hair root end may be discernible. Mechanical unhairing and re-liming are necessary.

### 3. 4. Unhairing with organic sulphur compounds

Three types of organic sulphur compounds are used in commercial unhairing systems:

| | |
|---|---|
| Mercaptoethanol | $CH_2SH \cdot CH_2OH$ |
| Salts of mercaptoacetic acid (thioglycolic acid) | $CH_2SH \cdot COONa$ |
| Formamidinesulphinic acid |  |

All three types 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 than sulphides. Owing to their high price, these products are mostly used in instances where effects other than environmental improvement are sought (2) (5) (15). For example, liming with these compounds yields a lower degree of swelling than using lime and sulphide only. This may be expected to have a positive effect on the area yield and the smoothness of the grain. The positive effects can be enhanced by adding enzymes or other proteolytic agents to the soak.

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.

#### 3.4.1. With mercaptoethanol-based products (Mollescal)

Of the commercial methods, the BASF Mollescal method is based on mercaptoethanol. Of the two mercaptoethanol products, Mollescal SF and Mollescal LD 6025, the latter also contains unhairing auxiliaries based on thio - and amino- compounds. The method is used in various countries in Europe and Asia. A vessel with recirculation and hair filter is required. Although preferably a drum, mixers or paddles can be used.

The whole process (immunisation, unhairing and re-liming) is carried out without any change of liquor. The thio compound is added first in order to degrade the hair roots and epidermis so as to avoid their being immunised afterwards. Subsequently, immunisation is effected by adding lime. After immunisation, sodium sulphide and/or hydrosulphide is added in order to induce hair loosening which takes place after 90-120 min. The recipe is given in the box below.

### MOLLESCAL UNHAIRING1)

In drum

**Immunisation/unhairing/reliming** is carried out in the same float

| | | |
|---|---|---|
| | 40-60% water (28°C) | |
| | 1.0-1.2% Mollescal LD 6025 | |
| | | run 60 min. |
| + | 0.8% lime | |
| | | run 60 min. |
| | | pH appr. 11.5 |
| + | 1% $Na_2S$ (60%) | |
| | Start of filtration after 90-120 min. | |
| + | 1.6% lime | |
| | | run 30 min. |
| + | water until 80-100% float (28°C) | |
| | | run 30 min. |
| | | run 5 min, rest 30 min. for 10-12 h. |

**Rinsing**: Twice at 28°C

1) Information from the supplier

Some advantages of the method are:

- No risk of hydrogen sulphide generation and total oxidation of mercaptoethanol to harmless end-products.
- No unloading or liquor changes throughout the process.
- Low sulphide consumption (only 2.5 kg $S^{--}$ per tonne raw hide).

The final rinsings consume too much water, but can probably be substituted by washing in a closed drum. Another possibility would be to use a mercapto product, Mollescal HW, in the soak. Subsequent unhairing would be effected using sulphide without mercaptans. A recipe for this method, as practised in a Scandinavian tannery (16), is given in the box below.

## UNHAIRING WITH MOLLESCAL HW IN THE SOAK

In drum

| | | | |
|---|---|---|---|
| **Soaking** | | Water (30°C) to the axle of the drum | |
| | | 0.2% sodium carbonate | |
| | | 0.2% Borron T (detergent) | |
| | | | run 60 min. |
| | | drain | |
| | | 150% water (25°C) | |
| | | 0.8% Mollescal HW | |
| | | 0.5% sodium carbonate | |
| | | | run 10 min, check pH and temperature |
| | | | run 5 h |
| | | drain | |
| **Immunisation, unhairing, re-liming** | | | |
| | | 80% water (26°C) | |
| | | 0.3% $Na_2S$ | |
| | | | run 40 min. |
| | + | 2% lime | |
| | | | run 45 min. |
| | + | 0.2% NaHS | |
| | | 1.3% $Na_2S$ | |
| | | | run 15 min, start filtration |
| | | | run 90 min., until hair is eliminated |
| | + | 1.5% lime | |
| | | | run 10 min. |
| | + | 60% water (25°C) | |
| | | | run while filling |
| | | | run intermittently overnight |
| | | drain | |
| **Rinsing (twice)** | | | |
| | | water (26°C) | |

In this version, sulphide consumption is higher than in the other version (Mollescal LD) described above: 5.1 kg $S^{--}$ per tonne raw hide.

Mason (18) found a higher degree of hair breakdown using the Mollescal SF method than in hair-save lime -sulphide unhairing. Screenability of the hair was not affected, but in Mollescal unhairing the need for immediate dewatering and drying of the hair was more pronounced.

### 3.4.2. With mercaptoacetic acid-based products (Erhavit HS, Carpetex 2 WS)

The Erhavit HS process (17), based on a salt of mercaptoacetic acid (thioglycolic acid), was developed in 1986 by Röhm GmbH, now TFL Ledertechnik GmbH & Co. KG (TFL). The procedure can be carried out in a drum, mixer or paddle, equipped with recirculation and hair filter.

Lime and Erhavit HS at pH 12.0-12.3 are used to impregnate and immunise the hair. Hair loosening takes place in the same float after adding sodium hydrosulphide. After separating the hair, the pelts are re-limed with lime and sodium sulphide or sodium hydroxide. Re-liming may be carried out in the same float or after fleshing and splitting. The recipe is given in the box below.

### ERHAVIT HS2 UNHAIRING1)

**Immunisation- unhairing**

70-100% Water (26°C)  
1.2-1.5% Erhavit HS2  
1% lime  
run 60-90 min.  
pH 12.0-12.3  
\+ 0.9-1.2% NaHS (72%)  
run 60-90 min.  
Hair-loosening begins after appr. 30 min.  
Hair separation

**Re-liming**

\+ 70-80% water (26°C)  
0.3-0.5% $Na_2S$ (60%) <u>or</u>  
0.3-0.5% Sodium hydroxide (33%), diluted 1:2  
2-3% lime  
0.03-0.05% Rohagit 3995 (slip agent)  
run 30 min.  
run 1 min. per hour for 16-18 h.  
pH 12.3-12.5, t = 26-28°C

drain

**Washing (twice)**

200% $H_2O$ (26°C)  
run 15 minutes/h  
drain

1) Information from the supplier

The advantages and disadvantages of the method are the same as for other methods based on thio compounds. In this method, sulphide consumption is estimated to be approximately 5 kg $S^{--}$ per tonne of raw hide, depending on variations in the recipe (lower dosages are possible).

The Carpetex 2 WS system is also based on using a thio-compound as the unhairing auxiliary. A recipe for the system (bovine hides, in drum) is given in the box below. With slight modifications, the recipe may also be used for unhairing in paddle.

**HAIR-SAVING CARPETEX 2 WS UNHAIRING, BOVINE HIDES1)**

| | | | |
|---|---|---|---|
| In drum | | | |
| **Impregnation**: | | 80% water<br>1.0% Merpin 8018 (reducing unhairing agent)<br>0.1% Merpin 8020 (magnesium oxide product) | |
| | | | Run 20 min |
| **Immunisation** | + | 1.0% lime | |
| | | | Run 30-40 min. |
| **Hair loosening**: | + | 1.2-1.5% $Na_2S$ (60%)<br>filtration | |
| | | | Run 1 h 40 min. |
| **Re-liming**: | + | 2.0% lime | |
| | | | Run 60 min. |
| | + | 30% water<br>0.1% Hydrophan 8076 (detergent)<br>overnight | |

1) Information from the supplier

Sulphide consumption is 3.0-3.7 kg $S^{--}$ per tonne raw hide (in drum) or approximately 4 kg per tonne (in paddle).

In a comparative test of many different hair-save unhairing processes, Simoncini yielded the best results using a method based on mercaptoacetic acid and sodium hydroxide, supplemented by a small amount of sulphide (19). The method, however, does not seem to enjoy any significant application.

### 3.4.3. With formamidinesulphinic-acid based products (Depilor,Erhavit FS)

Formamidinesulphinic acid is a stronger reducing agent than either sulphides or thio-compounds, and a salt derived from the acid is the basis of two commercial methods.

The Depilor method (14) (20) (21) was developed by the Österreichische Chemische Werke GmbH/Degussa Austria GmbH in 1985. It is used in some Italian tanneries. The process involves no change of float. After immunisation with lime, sodium sulphide and Depilor are added in order to loosen the hair. After separation of the hair, lime is added for re-liming.

A recipe for the method is given in the box below.

**HAIR-SAVE DEPILOR UNHAIRING, BOVINE HIDES**[1]

In drum (5 r.p.m.)

| | | | |
|---|---|---|---|
| **Immunisation** | | 70-100% water (26°C)<br>2.5% lime | |
| | | | Run 5 min, rest 25 min.<br>Run 5 min, rest 55 min. |
| | + | 0.8-1.2% $Na_2S$ (60-62%)[2]<br>0.3% sodium carbonate | |
| | | | Run 10 min. |
| | + | 0,7% Depilor | |
| | | | Run 1-2 h (pH 12.6) |
| | + | 50-70% water (28°C) | |
| | Recycling, filtration: 60-90 min.' | | |
| | | | Run 5 min, rest 55 min. |
| **Re-liming:** | + | 2% lime<br>overnight | |

1) Information from the supplier
2) For calf skin 1.0-1.3% $Na_2S$ (60-62%)

Sulfinic acid derivatives have a pronounced bleaching effect. The process is odourless. Sulphide consumption is low: 2.0-3.0 kg $S^{--}$ per tonne raw hide for bovine hides, 2.5-3.0 kg per tonne for calfskins. It is claimed that the resulting pelt is clean, smooth and bright, yielding a uniformly coloured leather. Increased area yield is also claimed. The chemical costs are rather high; it is said that this unhairing process is 2-3 times more costly than lime-sulphide unhairing.

TFL also supplies a formamidinesulphinic acid-based product, Erhavit FS. The product is used more or less in the same way as Erhavit HS (see above).

### 3. 5. 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.

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.

Partial putrefaction occurs during the sweating process when storing hides in a hot and humid room until the hair is loosened. Sweating is followed by mechanical unhairing. The process, however, is very difficult to control. A middle course must be steered between insufficient hair loosening and excessive degradation of the hide substance. Today, sweating is thus hardly used anymore: an exception being old-fashioned tanneries, especially those processing sheepskins, where the wool is more valuable than the skin.

An unhairing process using commercial enzyme preparations (2) (5) (6) was first introduced in 1910 by Otto Röhm who sought a process that was easier to control than sweating.

That notwithstanding, a high level of control will always be necessary when using enzymatic unhairing, because in all likelihood it will never be possible to develop proteolytic enzymes that specifically target proteins in the epidermis, hair roots and basal membrane. Commercial preparations containing proteolytic enzymes attack the collagen of the grain layer to a certain degree, thus leading to looseness of grain and grain sueding (45). Bacterial putrefaction is also intensified by enzymatic treatment. Furthermore, enzymes alone cannot eliminate the ground and fine hair completely. In all probability, an unhairing process exclusively based on the use of enzymes will never be practically possible. Enzymes, however, can be used in combination with other unhairing agents. Alkaline immunisation, alkaline swelling and sulphide treatment to eliminate ground and fine hair, are component parts of both enzymatic and other hair-save unhairing processes.

Enzyme preparations are expensive. In most cases, the environmental benefits they offer are an insufficient incentive for introducing enzymatic methods.

Enzyme unhairing is especially attractive when good wool or hair quality has high priority. For decades, 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. Sheepskins are considerably more sensitive and the wool is inevitably damaged somewhat during the essential alkali treatment.

Since enzyme unhairing was first introduced, enzyme preparations have significantly improved, although the difficulties mentioned above still persist. Interest has focused on the use of enzymes which achieve maximum effect in a highly alkaline medium. The enzyme input into enzyme-assisted chemical unhairing is far less than in unhairing based mainly on enzymes; the risk of grain damage is thus considerably lower.

Several commercial methods exist:

### 3.5.1. Cromogenia method

Cromogenia-Units, S.A markets a method developed in 1990 that is based on an enzyme, an amine auxiliary and sodium sulphide (22) (23). The method is currently used in several Spanish tanneries. The unhairing is carried out in a drum with recirculation and filter; the complete process (from immunisation to re-liming) entails no change of float.

After a dosage of amine compound and immunisation using lime, hair-loosening is induced by adding the enzyme product and sodium sulphide. The enzyme (supplied by Novo Nordisk A/S) is stable in an alkaline, reducing medium. During re-liming, additional sodium sulphide is added after filtration of the hair.

A recipe for the process is given in the box below. According to the recipe, sulphide consumption is 4.0 kg $S^{--}$ per tonne raw hide.

**ENZYME ASSISTED UNHAIRING, CROMOGENIA**[1]

In drum

80% water (28°C)
0.2% Ribersal PLE (amino compound)

Run 15 min.

\+ 1.5% lime
Run 30 min.

\+ 1.2% $Na_2S$

0.05% Riberzym MPX (enzyme product)
after 2 h, the hair loosening is total
recycling and filtering

\+ water until 180% (28°C)
1.5% lime
0.4% $Na_2S$
Run 60 min
Run 5-10 min/h overnight

[1] Information from the supplier

The costs of chemicals are reported to be 0.6-0.65 USD per square foot.

### 3.5.2. Novo-Nordisk method

Novo-Nordisk A/S produces an alkali-stable protease, NUE 0.6 MPX, for use in enzyme-assisted chemical unhairing. A recipe recommended for enzyme-assisted lime-sulphide unhairing is presented in the box below. Trials with the enzyme, conducted by the BLC Leather Technology Centre (BLC), are described in the literature (24). Using the enzyme permits a reduction in the chemical dosage and/or process time. More recent trials, likewise conducted by BLC, showed that it is possible to produce a commercially acceptable upholstery leather by using the enzyme in hair-save unhairing. The total consumption of lime and sodium sulphide was reduced to 1.5% and 1.0%, respectively.

**ENZYME ASSITED LIME-SULPHIDE UNHAIRING, NOVO-NORDISK[1)]**

| | | |
|---|---|---|
| | 110-300% water (24-28°C)<br>2% lime | |
| | | Run 60-75 min. |
| + | 1.5% $Na_2S$ | |
| | | recirculate and filter for 1-2 h. |
| + | 0.1-0.15% NUE 0.6 MPX | |
| | | Run 45 min.<br>Run automatically overnight |

It may be necessary to reduce the process time for re-liming as the hides open up faster when the enzyme is present.

1) Information from the supplier

The product is used in many tanneries around the world. The process can be carried out in a drum, mixer or paddle equipped with recirculation and filter. The sulphide consumption is 3.7 kg $S^{--}$ per tonne raw hide, according to the recipe, or 2.5 kg/tonne corresponding to the trials referred to above.

A third process of this type is the Enzyme Shower process developed by TFL (15). In this process, sulphide consumption is 1% sulphide flake (60 % $Na_2S$), corresponding to 2.5 kg $S^{--}$ per tonne of raw hide. Another process developed by TFL Ledertechnik GmbH combines an enzyme (Erhavit MC) with formamidinesulphinic acid (Erhavit FS). This process can be implemented with or without sulphide (15).

It was established that adding enzymes to the first stages of the Sirolime process accelerates unhairing (25).

In various parts of the world such as India or Nigeria, vegetable matter containing proteolytic enzymes is used for unhairing (5) (26).

### 3. 6. Lyotropic unhairing

The unhairing effect of lyotropic agents, i.e. substances which break hydrogen bonds, has been known for many years (27). By attacking the basement membrane, these substances cause the epidermis and hair to loosen. Normally, this type of unhairing takes some days, but by combining the enzymes which, in some cases, may be derived from the hide itself, it is possible to achieve a practicable method.

Since the 1950's, a method of this kind, based on acetic acid and autolytic enzymes from the skin, has been in commercial use in Australia for dewooling sheepskin (4) (28). The method used is a combination of painting (with acetic acid plus salt) and sweating. It is reported that this method is more easily controlled than classical sweating; that notwithstanding, the method is most suitable when the grain layer is not used. Subsequent lime-sulphide treatment is necessary.

Heidemann has developed an analogous method, based on lactic acid and enzymes (as enzyme preparations or microorganisms) and carried out in a drum. (29).

### 3.7. Amine unhairing

It has been known for many years that amines accelerate unhairing in combination with straight lime (see Chapter 4.2). More than 70 amino compounds have this effect to a greater or lesser degree (6).

For several years, a method for hair-save unhairing in a paddle was used in the United States; it was based on the use of dimethylamine sulphate and sodium hydroxide after previous immunisation (30). However, given that it might generate carcinogenic nitrosamines in the beamhouse air, DMA is no longer used as an unhairing auxiliary.

It has since proved possible to avoid the generation of nitrosamine. None the less, the method will probably not be reintroduced.

Amino compounds which do not generate nitrosamines, such as hydroxylamines or certain alkanolamines, enjoy widespread use as unhairing auxiliaries (2) (5) (15). They are used in unhairing processes based on sulphide, organic sulphur compounds or enzymes.

### 3. 8. Others

TFL has developed an unhairing agent, Erhavit AF, without any thio or amino groups. The product is based on modified polysaccharides. A recipe for its use of the product is given in the box below.

### ERHAVIT AF UNHAIRING[1]

| | | |
|---|---|---|
| **Main soak** | 150% water | |
| | 0.2% Pellvit S (enzyme) | |
| | 0.3% Borron A (detergent) | |
| | 0.05% Aracit DA (bactericide) | |
| | 0.5% sodium hydroxide (33%), diluted 1:3 | |
| | | run 4 h |
| | | pH 9.2-9.5. Temperature 27-29°C |
| | drain | |
| **Immunisation - hair removal** | 80% water (28°C) | |
| | 1.3% Erhavit AF | |
| | 0.1% Borron A | |
| | 1.2% lime | |
| | | run 60 min. |
| + | 1.2% NaHS (72%) | |
| | | run 90 min. |
| | | after 30 min hair separation |
| + | 70% water (28°C) | |
| | 2% lime | |
| | 0.5% sodium hydroxide (33%), diluted 1:3 | |
| | 0.1% Borron A | |
| | 0.1% Erha GM 3034 (slip agent) | |
| | | run 30 min. |
| | | run 5 min/h in 16-18 hours. |
| | | pH 12.2-12.5. Temperature 26-28°C |
| **Washing (twice)** | 200% $H_2O$ (26°C) | |
| | | run 15 min. |
| | drain | |

1) Information from the supplier

According to the recipe, sulphide consumption is 4.9 kg $S^{--}$ per tonne of raw hide.

## 4. 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. Drums equipped with recirculation as well as temperature and pH regulation are commercially available. The float is pumped out of the drum laboratory box and fed back in again through a hollow axle.

A recirculation and filtering system can be fitted on existing drums provided that the drum axles that can be used for float circulation.

As for mixers, the filtering unit is fitted into the exisisting recirculation system. Recirculation in a mixer may release greater quantities of gas than recirculation in a drum. Methods which entail the risk of generating toxic or malodorous gases should not be carried out in a mixer. It is necessary to install a filtering unit in each vessel. Alternatively, if one and the same filter is to serve several vessels (at most two or three), unhairing should be carried out in the individual vessels with a time lag of approximately two hours (the time needed for hair-loosening and recirculation).

Another solution is filtration after collecting the drained float in a pump sump and then collecting the filtered float in a tank, whence it can be pumped back to the unhairing vessels. In this case, it is possible to use one filtering unit for several vessels. This set up is simple to install; it can also be used for paddles, provided that space is available for the tanks (a length of blocked sewer can also serve as a pump sump).

In addition to degrading the hair, a further disadvantage is that production must be homogeneous in order to avoid cross contamination of the liming systems.

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. It should be mentioned that in one tannery, sieving through a cloth filter (hessian) has proved adequate. The float may be pumped to the sieve through the vessel's existing circulation pump or via separate pumps.

A relatively simple device is a 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. The cost of a static wedge wire screen is approximately US$ 5,500-8,500; a vibrating screen costs twice as much.

In a rotating drum sieve, the cylindrical surface serves as a filter. The surface is either perforated with holes or comprises a wedge wire screen.

Two basic types of drum sieve exist. In the more common type, 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. The drum may be connected direct to a screw press where the hair is dewatered. Most sieves supplied to tanneries are of this type; a unit may cost approximately US$ 12,000.

In the other type, 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.

A rotating disc sieve consists of a series of narrow cylindrical drums (discs) connected by a rotating axle. The float is pumped into the drums through the axle; the filtered float is drained off through the filter cloth at the base of the drum surface. The hairs pass through the other end of the axle.

With suitable filtering equipment, up to 90% of the loosened hair can be recovered.

Mason (18) conducted comparative trials with a vibrating sieve (1.0 and 0.2 mm mesh gauge), a static wedge wire screen (the gap width had to be at least 0.5 mm in order to avoid clogging) and a rotating wedge wire screen (0.25 mm gap width without any clogging). His conclusion was that the rotating wedge wire screen was the most efficient of the three units. Cleaning and maintaining the screen proved straightforward.

Dewatering separated hair is not always easy, but it can be important for further handling. Some of the screening systems on the market are combined with dewatering devices.

## 5. ECONOMIC ASPECTS

A cost-benefit analysis of hair-save unhairing focuses on the following items:

**Additional costs**

1. Chemicals
2. Energy
3. Hair disposal
4. Running, interest, maintenance and depreciation
5. Labour

**Savings and additional income**

6. Savings in environmental costs (waste water treatment, sludge disposal, and raw water costs)
7. Improved leather quality
8. Increased area yield (purported)
9. Income from sale of hair.

The analysis must be made for each individual tannery. The economic impact of single items can vary widely from tannery to tannery. Of the individual items, it can be noted that:

| | |
|---|---|
| Item 1: | Chemical costs are relatively easy to calculate. |
| Item 2: | Energy costs increase in relation to the more intensive use of mechanical unhairing processes. In most cases, however, the energy costs are of minor importance. |
| Items 3 & 9: | These items are governed by the manner in which the hair is utilised or disposed of. |
| Item 4: | Capital and maintenance costs depend on the amount of new equipment needed, if any, and current interest rates. |
| Item 5: | In most cases, labour costs will increase given the need to screen the hair and other operations. However, in some cases, labour cost savings might be possible. |
| Item 6: | This item depends entirely on local conditions, such as the type of waste water treatment and degree of purification needed or whether a treatment plant exists or has to be constructed. The charges levied as well as local construction and wage costs vary considerably. |
| Items 7 & 8: | Only experience will show whether any improvements in leather quality or increases in area yield are possible in the individual tannery. |

Moreover, tannery size has a significant impact on the analysis.

A decision to introduce hair-save unhairing does not hinge on economic considerations alone. In some countries, the introduction of hair-save unhairing may be required by the local environmental authorities.

Some comparative cost calculations are available:

In a UNEP report (32), a comparison was drawn between the chemical costs for Sirolime unhairing and those incurred by conventional hair-dissolving (pulping) unhairing for a tannery processing 40 tonnes raw hides a day:

| **Hair-dissolving unhairing** | **US $/tonne raw hide** |
|---|---|
| Sodium sulphide | 16.35 |
| Lime | 2.50 |
| Total | 18.85 |
| **Sirolime unhairing** | |
| Sodium hydrosulphide | 2.40 |
| Calcium hypochlorite | 1.25 |
| Lime | 2.50 |
| Sodium sulphide | 2.73 |
| Total | 8.88 |

The savings in terms of chemicals offered by Sirolime unhairing are thus US$ 9.97 /tonne raw hide (equivalent to US$ 399/day or US$ 87,780/year). Coincidentally, a drum with recirculation and filter (capacity 10 tonnes raw material) also costs US$ 87,780. As four drums are needed, the payback period is four years (32)

In 1992 in a Scandinavian tannery (processing 16.5 tonnes raw hide a day) the following balance was drawn up (33):

| **Hair-dissolving unhairing** | **US$/tonne raw hide** |
|---|---|
| Unhairing costs | 46.6 |
| **Erhavit HS unhairing** | |
| Unhairing costs | 73.8 |
| Hair disposal costs | 9.9 |
| Total costs | 83.7 |
| Additional costs | 37.1 |
| Savings, waste water treatment | 33.4 |
| Net additional costs | 3.7 |

The total $BOD_5$ discharge from the tannery was reduced from 60 to 48 kg/tonne raw hide, corresponding to 19.6%. The economic break-even point corresponds to a BOD reduction of 21.8% (47 kg/tonne raw hide) and to a COD reduction of the same magnitude. Since 1992, hair disposal costs have been substantially reduced.

In a Kenyan tannery processing dried skins, a comparison was drawn between hair-dissolving and hair-save unhairing processes (34):

| | **Costs of chemicals** | |
|---|---|---|
| | **US$/1000 dried skins** | **US$/tonne green weight (approx.)** |
| Hair-dissolving | 79.3 | 56.6 |
| Hair-save | 97.2 | 69.4 |
| Additional costs | 17.9 | 12.8 |

In the Czech Republic (7) and Denmark (35) cases are on record where the costs of chemicals for hair-save and hair-dissolving unhairing are of the same magnitude. In the one case, it was lime-sulphide hair-save unhairing, in the other enzyme-assisted unhairing.

Elsinger et al. (20) estimate the costs of conventional lime-sulphide unhairing to be approximately 1% of total production costs: probably a reasonable estimate. At the time, total costs for unhairing with thio compounds, sulfinic acid derivatives, enzymes or dimethylamine were estimated to be 2-3% of the production costs. Heidemann states that unhairing using thio compounds is 2-5 times more expensive than lime-sulphide unhairing (2). In a Norwegian tannery using hair-save unhairing, industrial scale experience showed that the cost of the Mollescal process was approximately the same as for the hair-dissolving lime-sulphide process, whereas the Erhavit HS process was 56% more expensive than the two other processes.

The price for the Mollescal products was reported (August 1997) to be approximately US$ 1600/tonne for Mollescal SF and US$ 1500/tonne for Mollescal LD 6025, while the price of sodium sulphide was approximately US$ 910/tonne. This corresponds to chemical costs of approximately US$ 25 per tonne raw hide for the recipe given earlier (Mollescal unhairing).

The costs of the Cromogenia enzyme unhairing is reported to be US$ 0.046-0.0529 per square foot of leather (22), corresponding to approximately US$ 83-95 per tonne of raw hide.

The requisite equipment costs (excluding installation costs) are as follows:

| | |
|---|---|
| Drum with recirculation (3.5 x4 m) | approx. US$ 70,000 |
| Rotating drum filter | approx. US$ 12,000 |

Fitting an existing, reasonably modern drum of the same size with the requisite recirculation and filtering outfit would cost approximately US$ 27,000. As mentioned in Chapter 4, a static wedge wire screen offers a cheaper solution than a rotating drum filter (price US$ 5,500-8,500).

## 6. SCOPE FOR HAIR UTILISATION OR DISPOSAL

Two useful surveys on the possible use and disposal of hair are available (37) (38).

Once recovered, hair presents the tanner with the problem of coping with yet another solid by-product. Finding a suitable outlet for the hair, preferably some kind of use, thus becomes an important factor when considering the introduction of hair-save unhairing. It so happens, however, that for economic or political reasons, many tanneries use hair-save unhairing processes, even though they have to unload the hair recovered in a waste dump. After dewatering to 35% dry matter, the hair does not give rise to any odour when deposited as waste.

Numerous speculative proposals for hair utilization have been advanced. This report, however, only addresses applications that are currently in use or have a reasonable chance of being introduced. Furthermore, the report does not address the issue of processing and marketing wool.

The quantity of hair recovered in relation to the weight of raw hide depends on hair length and hide thickness. Typical figures are cited in the table below (from (39)):

| | **% drained hair** | **% hair dry matter** |
|---|---|---|
| Heavy bovine hides | 10-15[1)] | 3-5[1)] |
| Light bovine hides | 15-20[1)] | 5-7[1)] |
| Calf skin | 20-40[1)] | 10-13[1)] |
| Sheep or goat skin | 60-90[2)] | 20-30[2)] |

1) Calculated on salted weight
2) Calculated on dry weight

According to the above figures, the dry matter content of the drained hair is approximately 33%. The dry matter content of the hair discharged at the end of the process is 15-20%.

The hair must be dewatered as swiftly as possible: for example, by means of a screw press or by draining it in a perforated container. Containers that can be used for both draining and subsequent transport are commercially available. Failure to act swiftly results in very rapid putrefaction of the proteinaceous matter in the water adhering to the hair (17). The sulphide content in fresh, wet hair is approximately 80-100 ppm (37). Sulphide, however, oxidises easily; within three to four hours, the sulphide content is less than 10 ppm. After a day, the sulphide has totally disappeared (17)(39). Sodium ions and lime must be eliminated by washing, a prerequisite for some hair uses.

In the past, hair from the hair-save unhairing of bovine hides, for example, was used in felt production. One of the reasons for the disappearance of hair-save unhairing was that following the introduction of synthetic fibres, the use of animal hair as a raw material became obsolete. Furthermore, at that time hair was recovered by mechanical unhairing, whereas notwithstanding immunisation, the hair recovered from modern unhairing processes is degraded somewhat through chemical and mechanical action in the drum or mixer. Its fibre strength is thus reduced. Given the competition from synthetic fibres, this means that scope for its use as a fibre material is relatively limited while in industrialised countries its use for felt production is out of the question.

According to Heidemann (40), degradation, even of immunized hair, takes place at a dosage of more than 0.75% sodium sulphide, corresponding to 1.9 kg $S^{--}$/tonne raw hide. Degradation is significant at a dosage of 1% sodium sulphide, corresponding to 2.5 kg per tonne raw hide.

The two most promising applications for hair recovered from hair-saving processes are: agricultural fertiliser and animal feedstuffs.

Given its properties as a source of slow-releasing organic nitrogen, hair is a valuable soil conditioner. As mentioned above, it will be necessary in some cases to reduce the sodium content of the hair before use (39). Trials in Germany have shown that after 18 weeks only 6% of the nitrogen present in the hair has dissolved (38): a factor governed by the character of the soil. As the amount of hair-based fertilisers is insignificant compared to total fertiliser consumption, it must of necessity be marketed as a special product. Hair-based fertilisers are especially useful in orchards, market gardens, nurseries and private gardens. In some cases, partial hydrolysis of the hair, for example by heating, may serve a useful purpose prior to formulation of the commercial product. Adding phosphorus may also increase the fertilising effect.

An Italian company, Giuseppe Sala & Co. s.r.l. in Arzignano, has marketed an organic nitrogen fertiliser (Ecolfert), prepared from partially hydrolysed, pelleted hair (37) (41). In Australia, a pelleted, hair-based, organic nitrogen fertiliser is also being marketed. The product has yielded excellent results in plant-growth trials (8). Low grade wool fibre has also been used commercially as a fertiliser.

Hair recovered from a Scandinavian tannery has been used in conjunction with bark in the cultivation of spruce trees; the results have been positive.

AIICA in Igualada (Spain) has conducted trials over a two-year period on the use of hair mixed with other organic material as a fertiliser. In toto, 10,000 tonnes dry hair were processed. The product yielded good results with various types of vegetables (47). Furthermore, TFL has carried out trials on the use of partially hydrolysed and granulated hair as a fertilizer. Here again, the results were positive.

The agricultural value of the hair can be increased by composting, a process involving the accelerated aerobic degradation of organic waste materials by natural micro-organisms. In order to grow, the micro-organisms need a specific carbon-nitrogen ratio in the substrate. The optimum value is approximately C:N = 25-35:1. In hair, this ratio is 3-4:1 (17) (37) (38). This means that the 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. Composting trials have been carried out in a Czech tannery with reasonably good results (7).

In a Swedish tannery, a mixture of the following composition is being composted in windrows:

| | | |
|---|---|---|
| Hair, drained | 4.5 | % |
| Fleshings (drained) | 14.5 | % |
| Sludge (municipal) | 6 | % |
| Wood chips and bark | 75 | % |

Temperatures in the windrows reach 80°C within a few days, and after two months the windrows are turned. Turning the windrow promotes aeration and homogenisation of the mass, in addition to being conducive to uniform temperature distribution throughout the material.

TFL has carried out extensive composting trials using a mixture of 33% hair (in humid state) and 67% organic household and garden refuse (the carbon source). The trials yielded excellent results; and the compost has a long-term fertilising effect.

One Danish tannery sends the hair it recovers to a biogas plant together with fleshings and other organic waste. The plant input is mainly agricultural waste, but it also uses various kinds of industrial waste. Most probably, the hair is only degraded to a minor extent and contributes insignificantly to the production of gas. However, as mentioned earlier, the hair content increases the long-term fertilising effect of the solid residue when spread on farming land.

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 (18) (38). Owing to its high cysteine content, it is especially valuable as an ingredient in poultry feed, in all respects comparable to feather meal. (17) (18) (37) (38). The use of hair protein in feedstuff presupposes hydrolysis at high temperature and pressure (17)(37), preferably carried out in a rendering plant.

A Dutch company uses waste hair from a German tannery as an ingredient in the animal feed it produces.

Waste hair from a Czech tannery has been processed on an industrial scale in a rendering plant (pressure hydrolysis at 130° C) with good results. The product proved suitable for use as a feedstuff supplement (7). In Sweden hair hydrolysis trials were carried out in a special rendering plant designed for poultry (mostly feather) waste. Owing to the special properties of the raw material, the hydrolysis temperature was above 140° C.

In England, waste hair has been used since 1995 in the production of biologically degradable flower pots.

Hair hydrolysate has also been used in the production of cosmetics, pharmaceuticals or cysteine, but the market is very limited. To a limited extent, hair has been used in the production of foaming agents for fire-extinguishers.

The Central Leather Research Institute (CLRI) at Chennai (India) has developed a method using keratin hydrolysate derived from hair or feathers as an additive in chrome tanning or retanning in order to increase the degree of chromium exhaustion (42). Hydrolysed keratin has been used as a casein substitute in finishing (37).

Waste hair could possibly be used as thermal or acoustic insulation material. However, according to (38), this would only be economically viable, were the tanner to pay US $ 80-110 per tonne of hair: an unrealistic prposition.

## 7. ENVIRONMENTAL CONSIDERATIONS

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 table below presents a considered evaluation of what can be achieved in practice:

| | **Discharge from hair-save unhairing[1)]** **kg/tonne raw hide** | **% reduction compared to hair-destroying unhairing** | |
|---|---|---|---|
| | | **In unhairing liquor[1)]** | **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 ($S^{--}$) | 0.6-1.2 | 50-60[2)] | 50-60[2)] |

1) Including waste water from washing
2) The percentage reduction of the discharge is greater than the corresponding reduction of the dosage

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.

It is evident from the table 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, $BOD_5$ and COD . 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.

The sulphide dosages for various hair-save methods are to be found in Annex 2. The lowest dosage in practice is 2.0 kg $S^{--}$ per tonne raw hide, while that for unhairing based solely on lime-sulphide is approx. 3.7 kg $S^{--}$ per tonne raw hide. In several hair-save methods, sulphide dosages are higher than those found in some hair-destroying unhairing processes. This is partly due to the immunisation of the hair and partly to the fact that some of the sulphide is only added once the hair has been filtered off.

As mentioned in Chapter 6, degradation of hair, including also post- immunisation degradation, occurs at dosages higher than 1.9 kg $S^{--}$ per tonne raw hide. It becomes significant at dosages higher than 2.5 kg per tonne. This underscores the need to separate the hair at the earliest possible juncture.

The greater part of the sulphide added disappears during the unhairing process, mostly through oxidation, but to some extent through reaction with the hair. As the amount consumed is only partially dependent on the sulphide dosage, the percentage consumed is greater for small dosages and the percentage discharged consequently less.

Processing in a short float and/or in a mixer increases the intensity of oxidation and consequently reduces the percentage discharged. The percentage of sulphide discharged is normally 50-80%, depending on processing conditions.

Even at the lowest dosages, subsequent sulphide oxidation process is often necessary. In this connection, it must be recalled that some of the sulphide in the unhairing liquors is oxidised by mixing with waste water emanating from other segments of the production. Sulphides are relatively easily oxidised by catalytical oxidation and/or during biological waste water treatment. However, even when the waste water is treated biologically, the sulphide discharge from the processes has to be kept as low as possible in order to: (i) avoid the sewers corroding and (ii) guard against the sulphate generated by sulphide oxidation contributing to the discharge of neutral salts (TDS) in the waste water.

It is possible to re-use the waste re-liming liquor and, to some extent, other waste liquors as well. Such recycling systems are described for Sirolime unhairing (4)(10), (see Chapter 3.3) and by Cantera et al. (44) for Erhavit HS unhairing.

It is thus possible to save water and sulphide, thereby reducing the sulphide output, but the discharge of organic substance remains unchanged.

For Erhavit HS unhairing, the savings are assessed as follows:

| | **Consumption without recycling** | **Net consumption with recycling** | **Savings** |
|---|---|---|---|
| Water | 300% | 160% | 140% |
| $Na_2S$ (60%) | 1.5% | 1.2% | 0.3% |
| Lime | 2.5% | 2.0% | 0.5% |
| kg $S^{--}$/t raw hide | 3.75 | 3.0 | 0.75 |

It is questionable, however, whether savings such as these justify the necessary installations (tanks, pipes and pumps) and careful analytical control.

Another possible advantage of the hair-save method is that it is often easier to dispose of waste hair than waste sludge. Several hair-save methods also incur a lower risk of releasing toxic or odorous gases.

## 8. CONCLUSIONS

1. 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 local conditions (internal and external).

2. The starting point in any consideration should be a cost-benefit analysis encompassing: savings in environmental costs; possible improvements in leather quality and increases in area yield; marketing possibilities (□eco-leather□, eco-labelling); possible additional costs of the method selected; and, last but not least, the economic implications of hair disposal.

3. In evaluating a method, occupational safety and health must also be taken into consideration.

4. In the course of introducing hair-save unhairing, other processes in the tannery should, as far as possible, remain unchanged.

5. 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.

6. 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.

7. 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').

8. 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 completely replace end-of-pipe technologies.

9. Hair-save unhairing must be seen as a partial, but important element in the general optimisation of the production, incljding environmental aspects and better housekeeping.

10. As mentioned in Chapter 7, hair-save unhairing processes also discharge sulphide with the waste water; in some cases the amount discharged may be even higher than in hair-burn unhairing.

11. If needed, sulphide elimination can be achieved through an end-of-pipe treatment: for example, catalytic oxidation.

12. 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).

13. 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.

14. 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.

15. 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.

## *Acknowledgments*

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## ANNEX 1

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## ANNEX 2

## SULPHIDE DOSAGES IN VARIOUS UNHAIRING METHODS

| | **Dosage kg sulphide ($S^{=}$) per tonne raw hide** |
|---|---|
| Hair-dissolving lime-sulphide unhairing., minimum dosage | 2.5-4.0 |
| Hair-dissolving lime-sulphide unhairing., normal dosage[2] | 3.7-7.5 |
| Minimum dosage for sulphide unhairing | 0.6-1.2 |
| **Hair-save lime-sulphide unhairing**: | |
| European tannery (7) | 3.7 |
| Sirolime[1] | 4.7 |
| Blair Hair[1] | 10.9 (5.4-8.1)[3] |
| **Thio compounds** | |
| Mollescal[1] | 2.5/5.1 |
| Erhavit HS[1] | 5.0 (3.7-6.2) |
| Erhavit HS, Argentinian tanneries (44) (45) | 3.7-3.8 |
| Erhavit HS, with recycling (44) | 3.0 |
| Simoncini (19) | 2.4 |
| Depilor, bovine hides[1] | 2.0-3.0 |
| Depilor, calf skins[1] | 2.5-3.3 |
| Carpetex WS 2[1] | 3.0-3.7 |
| **Enzyme-assisted unhairing** | |
| Cromogenia[1] | 4.0 |
| Novo-Nordisk[1] | 3.7 (2.5)[3] |
| Enzyme-assisted unhairing, Argentine tannery (45) | 3.8 |
| TFL Enzyme Shower (15) | 2.5 |
| **Polysaccharides** | |
| Erhavit AF[1] | 4.9 |

1) According to recipe in this report
2) Good housekeeping
3) Stated elsewhere

# ANNEX 3

## SUPPLIERS OF COMMERCIAL SYSTEMS MENTIONED IN CHAPTER 3

BASF AG, Textile and Leather Dyes and Chemicals,
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[1] HAIRSVF3