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HAIR-SAVE UNHAIRING METHODS IN LEATHER PROCESSING

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I. INTRODUCTION

Until the 1880's, only hair-save methods (straight lime or sweating) were used for unhairing. These methods necessitated a subsequent mechanical unhairing, originally manually on a beam; later on with an unhairing machine. From the 1880's onwards, hair-destroying unhairing with lime and sulphide was introduced in the tanneries and it has been generally adopted in most countries.

It saves manpower and time by rendering the mechanical unhairing superfluous, and can ensure a clean pelt and a satisfactory opening-up of the hide substance.

However, dissolving the hair substance entails a high load of organic pollution in the wastewater, and as the environmental demands have grown acute, it has become necessary to reduce the wastewater pollution load as much as possible. This may be done by a biological treatment of the wastewater, which is expensive. Furthermore, the wastewater treatment generates a large amount of sludge which has to be disposed of. For this reason, hair-save unhairing has gained renewed importance and is today a well-established practice, especially in industrialized countries. In order to maintain a high productivity, it is necessary to avoid the formerly used mechanical unhairing which would be too expensive today.

Whether or not the implementation of hair-save unhairing is an advantage to the individual tannery must be decided on the basis of a cost-benefit analysis (See Chapter V). Hair-save unhairing is far from being general practice as yet, but in the future the increase of environmental (treatment, disposal and tax) costs and pressure from outside will be an incentive to a more widespread use of the method.

The use of hair-save unhairing may facilitate the obtaining of a green label (eco-label) for the leather produced.

This report has been prepared under the project: Assistance in Pollution Control in the Tanning Industry in South-East Asia. (1)

II. MECHANISMS INVOLVED IN HAIR-SAVE UNHAIRING

The skin (or hide), properly spoken, consists of three layers (Figure 1). On the surface of the intact skin lies the keratinous epidermal layer consisting of the epidermis and its appendages (hairs, hair root sheaths, etc). Below this is found the basement membrane attaching the epidermal layer to the underlying dermis (or corium) layer, which in the tannery is transformed into leather. In a hair-save unhairing the attachment of the epidermal layer to the dermis must be broken without damaging the hair. A further component of the raw hide is the subcutaneous layer (connective tissue and fat) which is removed by fleshing. This layer is, however, not relevant for the unhairing.

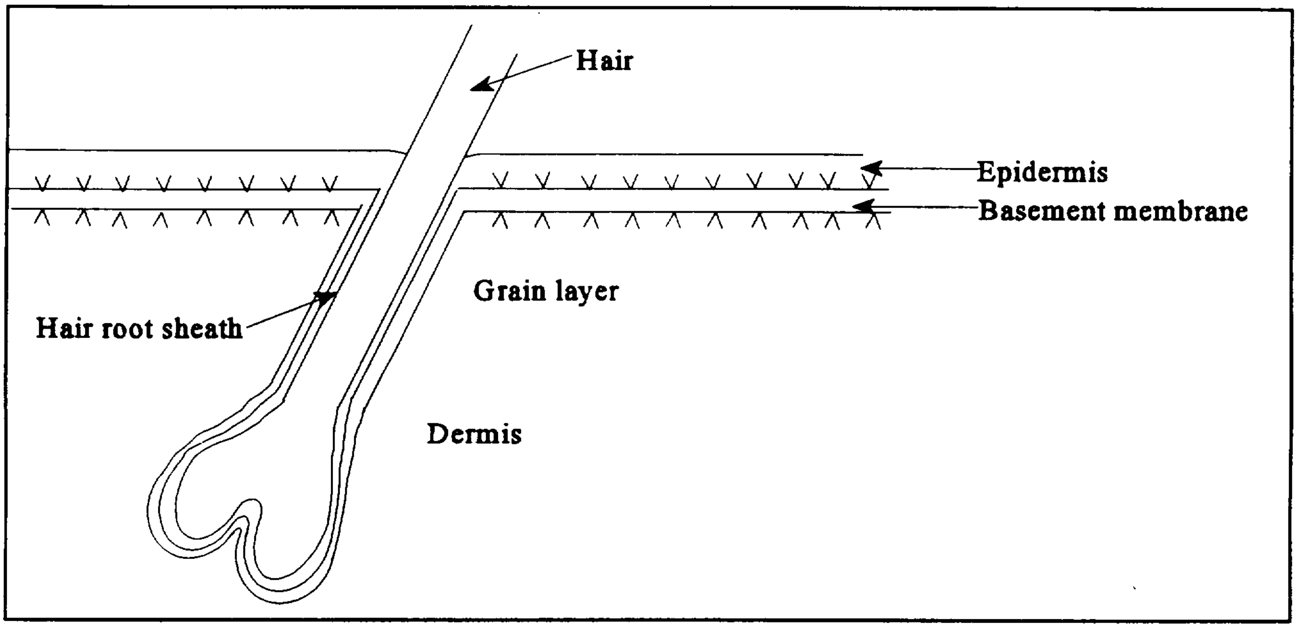


Figure 1. *Schematic diagram of layers of the skin discussed*

The keratin is stabilized through sulphur crosslinks (-S-S-). The fully developed keratin in hair, nails and the upper layer of the epidermis is very resistant towards chemical or biological attack (except from sulphides which break the sulphur crosslinks) whereas the immature keratin of hair roots, hair root sheaths, and the lower layer of the epidermis is more easily degraded and dissolved.

The resistance of the hair keratin towards chemical degradation can be substantially increased by immunization, i.e. by a treatment with alkali without sulphide (2) (3). The alkali transforms the S-S-crosslinks into other, very resistant, crosslinks. The mature keratin is immunized much more easily than the immature keratin in hair roots, root sheaths, and epidermis. Thus, the difference in solubility between hair and hair roots is increased and consequently, the hair-save unhairing becomes easier.

To obtain the immunization, sodium hydroxide, lime or calcium hydroxide may be used. The time necessary is typically 1-1.5 hours. Most commercial systems for hair-save unhairing are based on immunization.

The balance between insufficient immunization and over-immunization must be carefully maintained. In the case of an over-immunization, the hair cannot be loosened satisfactorily in the subsequent unhairing.

The basement membrane is a thin (50-100 nm) layer between the epidermal layer (including the hair roots) and the dermis. It is attached to the surface (grain) layer of the dermis. It consists of a special type of collagen and various glycoproteins and proteoglycans (protein-carbohydrate compounds) which are connected in a tightly interwoven network. The structure of the basement membrane and consequently the corium-epidermis junction is mainly based on protein-protein bindings, although also protein-carbohydrate interaction and a few sulphur bridges play a role. This makes the basement membrane a target for selective proteolytic enzymes. An attack on the basement membrane is important in enzymatic and lyotropic unhairings (See section III.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.

The ground and fine hair (hair still growing) is anchored deeper in the dermis than the fully developed hair. Normally, a treatment with a small amount of sulphide is necessary for a complete removal of this hair, and the commercially viable hair-save systems include the use of some amount of sulphide.

If the swelling necessary for opening up the hide structure is not achieved during the unhairing it must be carried out in a subsequent alkaline treatment, normally using lime. The sulphide can suitably be added during this re-liming. (For amounts of sulphide typically used in practice see Annex 2).

In sheepskin processing, unhairing without lime or sulphide may be preferred if the wool is more valuable than the leather, as both alkali and sulphide damage the wool.

III. METHODS USED IN PRACTICE

III. 1. General Remarks

Whereas hair-save unhairing of hides by straight lime in a pit system or of skins by sweating has been used from time immemorial, and the hair-save lime-sulphide unhairing dates from the 1880's, the modern commercial methods have been developed in the period 1980-1990, after the necessary equipment (mixers or drums with equipment for recirculation and for separation of the loosened hair) became available.

A general survey of unhairing methods has been recently prepared by H.P.Germann (46).

Almost all methods used in practice include an immunization of the hair, a re-liming, and the use of some amount of sulphide. A common feature is that not only the environmental aspect but also the possibility for improvement of leather properties and increase in area yield is claimed in the marketing.

In all modern methods, a separate mechanical unhairing step is left out and the hair loosening results from the intensive mechanical action during the chemical unhairing process. This mechanical action implies a risk for grain damage by abrasion and suitable measures must be taken in order to prevent this (for example, addition of slip agents).

To obtain the minimum wastewater pollution, the hairs must be separated from the liquor as soon as they have loosened. Prolonged staying in the unhairing liquor may cause a certain degree of dissolving of the hair substance, leading to a higher organic pollution of the wastewater than necessary and a poorer filterability of the hair.

The unhairing is accelerated by temperature increase. The effect on the layers relevant for hair-save unhairing depends strongly on the temperature (5). An upper limit is given by the risk of attack on the hide substance. Temperatures up to 30°C are considered safe, whereas at 35°C the hide substance is drastically damaged, especially in the grain layer (6).

In tropical countries where the fresh water temperature may be higher than 30°C, it may be necessary to use paddles instead of drums for the unhairing, or to add ice in order to avoid heating because of friction.

III. 2. Straight Lime

Hair-save unhairing with a straight lime, normally in pits, is still used in (mostly small) tanneries in many countries.

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. Thus, the optimum unhairing time is 4-6 days.

Re-use of old lime liquors after strengthening, as it is often practiced, renders the unhairing more effective because of the unhairing effect of amines, resulting from the protein hydrolysis (See section III.7.).

Advantages of this technology are that it is easy to control and needs practically no energy input. Disadvantages are the incipient attack on the hide substance leading to a loose grain, the long processing time and the necessity of mechanical unhairing.

In all probability, this method is going to disappear, as a consequence of the industrialization of the leather production.

III. 3. Hair-save Lime-Sulphide Unhairing

The minimum sulphide dosage for obtaining a 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 sulphide dosage corresponding to the transition between unaffected hair and destroyed hair depends on several variables: the length of the float, the lime dosage, pH, temperature, process time, intensity of mechanical action and hair length (5). Approximate limits, based on laboratory scale trails, 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

The minimum figures for a hair-destroying drum unhairing in industrial practice is approximately 200% float and 1.5% Na_2S flake, corresponding to 3.7 kg $S^{=}$ per tonne raw hide. Normally, a dosage between 1.5 and 3%, corresponding to 3.7-7.4 kg $S^{=}$ per tonne raw hide, is used.

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

The recipe in outline was as follows:

Immunization:	Max.	150% water
	1.5% lime	
	45 min. (15 min. rotation)	
Unhairing:		+ 1.5 % sodium sulphide flake (60% Na_2S)
	After 1¾-2 h filtration	
Reliming:		+ water until 180-200%
	2% lime	

For ensuring a perfectly clean pelt grain, a very slight quantity 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 in the factory 2% sodium sulphide flake (60 % Na_2S) was used. For the hair-save unhairing, a dosage of 1.3% flake was fully sufficient, but for reasons of safety a dosage of 1.5% was chosen.

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

The Sirolime method was developed in 1981 by CSIRO (Commonwealth Scientific and Industrial Research Organization) Leather Research Centre, Australia.

The method is used in practice in tanneries in Australia and New Zealand, as well as in some tanneries elsewhere.

The original version of the method consisted in an impregnation of the hair with a sodium hydrosulphide solution without any further additions. The relatively low pH value (decreasing during the process from approximately 11.5 to approximately 8.6) ensures that the hydrosulphide immunize without attack on the hair substance. Afterwards, the hydrosulphide associated with the external hair is 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 the unhairing the pelts are relimed.

Later, the method was modified:

In the original version, there was a risk of hydrogen sulphide being generated during the impregnation step, as a consequence of pH falling below the critical limit for hydrogen sulphide generation (pH 9). The risk could be avoided by addition of alkali to raise the pH to 10.5 before the draining.

Subsequently, the method was further modified in order to simplify the process.

Based on the original version, it was claimed that there are several possibilities for saving water and chemicals through recycling:

Waste liquor from the impregnation step could be re-used after sedimentation; any surplus could be used in the wash after the impregnation.

Waste liquor from hair loosening and re-liming could be used in the re-liming.

Consequently, fresh water was needed only for the wash after impregnation and for the immunization.

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

OUTLINE OF MODIFIED VERSION OF THE SIROLIME UNHAIRING (4)

In drum

Immunization: 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

The net consumptions with the Sirolime method were claimed to be as follows:

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

Advantages of the method are:

- No proprietary products are used; consequently the chemical costs are low.
- The process can be delayed between individual steps if advantageous or necessary.
- Minimal risk for over-immunization.

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

Disadvantages are:

- A somewhat complicated process procedure.
- With large batches of hides, there is a risk of insufficient unhairing in patches.
- Because of the dominant use of sulphides, the total sulphide consumption is high. If organic sulphur compounds are used as reducing agents, the sulphide consumption decreases, but the chemical costs increase.

The Blair Hair method (12) (13) was developed in 1985 by Rohm and Haas Co. in cooperation with Eagle Ottawa Leather Co.

The method is used in tanneries in USA, Mexico, and Korea.

The main features of the method are the following:

The hair is immunized by a lime treatment. After the immunization, sodium hydrosulphide is added and the hair gradually loosen. When the hair loosening is completed, 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 to prevent further immunization or (by means of a pH increase) any hydrogen sulphide generation. (Concerning use of amines in the unhairing, see section III.7.).

BLAIR HAIR UNHAIRING IN CEMENT MIXER[1)]

Adjust to 27-28 °C after soak.

Immunization:	150% water (27 °C) 2.5% lime Run 10 min. (4 r.p.m.), rest 50 min.
Hair loosening:	+ 1.5% NaHS (flake) Run 10 min. (8 r.p.m.), rest 20 min. Run 10 min., rest 20 min. Run 10 min., rest 20 min[2)] Run 10 min, rest 20 min. Run 10 min (90% of hair is loos and patches will push 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) 2.5% lime 0.5% NaHS 1.25% Unhairing Assist FR-62 0.25 Anionic surfactant Run 10 min. (4 r.p.m.), rest 50 min Run 14 times

1) Information from the supplier
2) If hair is not loosening at this point, increase running time of the 30 min cycle. If temperature is 21-24°C by error, run mixer constantly until hair is off or heat mixer to 27°C

BLAIR HAIR UNHAIRING IN DRUM[1)]

Adjust to 27-28 °C after soak.

Immunization:	+ 2% lime (to soaking liquor) Run 5 min. , rest 25 min. Run 5 min. , rest 25 min. Run 5 min. (28 °C)
Hair loosening:	+ 1.5% NaHS (flake) Run 10 min., rest 20 min. Run 10 min., rest 20 min. 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 0.5% NaHS 1% Unhairing Assist FR-62 0.2 Anionic surfactant Run 10 min. Run 5min/h for 8 h.

1) Information from the supplier

As the hair is separated only at the end of the hair loosening, recirculation equipment for the drums is not necessary. The used hair loosening liquor can be re-used after mending. The total unhairing time is approximately 18.5 hours. The unhairing comprises only a few liquor changes.

It is claimed that a clean pelt and wet blue can be obtained and that grain draw and growth wrinkles are minimized.

The method requires a high level of control, as process temperatures and times are critical. Over-immunization leading to hair patches is a very real risk. Not all hair substance is eliminated at the hair removal stage; remaining hair roots etc. must be eliminated during the re-liming. The washing with running water implies a too high water consumption. However, this can probably be avoided by use of a recirculation system.

The sulphide consumption is high; 2% hydrosulphide flake Na HS, corresponding to 10.9 kg $S^{=}$ per tonne raw hide. (Lower dosages seem possible, however).

For enzyme-assisted lime-sulphide unhairing, see section III. 5.

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, and has a density of 15-40% Bé.

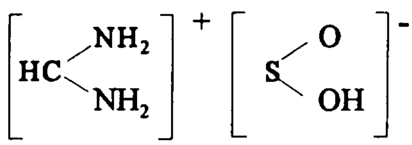
After painting, the skins are stacked in a pile, hair side against hair side. The unhairing chemicals penetrate the skin from the flesh side and destroy the hair roots. The hair, which is not in contact with the unhairing chemicals, are easy to scud off.

The hair is practically intact, although some attack in the hair root end may occur.

Mechanical unhairing and re-liming are necessary.

III. 4. Use of 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)	$CH_2SH \cdot COONa$
Formamidinesulfinic acid	

All three types are strongly 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.

Due to the high price, these products are mostly used in cases where effects other than the environmental improvement are sought for (2) (5) (15).

The use of mercapto products presupposes the same occupational health 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 the free mercaptanes, higher boiling point of the mercaptanes, the risk of giving off mercaptane vapours to the airs is considerably lower than is the case for hydrogen sulphide).

A consequence of the high oxidability of thio-compounds is that as soon as they are added a thorough mixing is necessary.

Liming with these compounds gives a lower degree of swelling than the use of 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 may be enhanced by the addition of enzymes or other proteolytic agents to the soak.

Of the commercial methods, the Mollescal method of BASF 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 a filter for the hair is required; this is preferably a drum, but mixers or paddles can be used.

The whole process (immunization, unhairing, and re-liming) is carried out without any liquor change. At first, the thio compound is added in order to degrade the hair roots and epidermis so that they are not immunized afterwards. Subsequently, the immunization is carried out by an addition of lime.

After the immunization, sodium sulphide and/or hydrosulphide is added in order to bring about the hair loosening, which takes place after 90-120 min. After separation of the hair, lime is added for the re-liming.

MOLLESCAL UNHAIRING[1)]

In drum

The immunization-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 by 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 during the whole process.
- Low sulphide consumption (only 2.5 kg $S^{=}$ per tonne raw hide).

The final rinsings are too water consuming but can probably be substituted with washing in a closed drum.

Another possibility is the use of a mercapto product, Mollescal HW, in the soak and a subsequent unhairing with sulphide without mercaptans. A recipe for this method, as practised in a Scandinavian tannery (16), is given below.

UNHAIRING WITH MOLLESCAL HW IN THE SOAK

In drum

<u>Soaking</u>	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	
<u>Immunization, unhairing, re-liming</u>		
	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	
<u>Rinsing twice</u>		
	(water 26 °C)	

In this version, the sulphide consumption is higher than in the version described above, namely 5.1 kg $S^{=}$ per tonne raw hide.

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

The <u>Erhavit HS process</u> (17), based on a salt of mercaptoacetic acid (thioglycolic acid), was developed in 1986 by the company Röhm GmbH, now TFL Ledertechnik GmbH & Co. KG.

The procedure can be carried out in a drum, mixer or paddle, equipped withrecirculation and a filter for the hair.

Impregnation and immunization of the hair is carried out with lime and Erhavit HS at pH 12.0-12.3. The hair loosening takes place in the same float after the addition of sodium hydrosulphide. After separation of the hair, the pelts are re-limed with lime and sodium sulphide or sodium hydroxide. The re-liming may be carried out in the same float or after fleshing and splitting.

ERHAVIT HS2 UNHAIRING[1)]

Immunization- 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%) or		
	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.

The sulphide consumption for the method can be calculated to be approximately 5 kg $S^{=}$ per tonne raw hide, dependent on variations in the recipe (lower dosages are possible).

The Carpetex 2 WS System, too, is based on a thio compound as unhairing auxiliary. A recipe for the system (bovine hides, in drum) is found below. The recipe may also, with minor modifications, be used for unhairing in paddle.

HAIR-SAVING CARPETEX 2 WS UNHAIRING, BOVINE HIDES[1)]

In drum

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

1) Information from the supplier

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

In an investigation of many methods for hair-save unhairing, Simoncini obtained the best results with a method based on the use of mercaptoacetic acid and sodium hydroxide supplemented with a small amount of sulphide (19). The method seems not to be used in practice to any significant extent.

Formamidinesulfinic acid is a stronger reducing agent than sulphides or thio compounds. A salt of this acid is the basis of two commercial methods:

The Depilor method (14) (20) (21) was developed by Österreichische Chemische Werke GmbH/Degussa Austria GmbH in 1985. Depilor is used for hair-save unhairing in Italian tanneries.

The process is carried out without any change of float. After immunization with lime, sodium sulphide and Depilor are added in order to loosen the hair. After separation of the hair, lime is added for the re-liming.

A recipe for the method is found below.

HAIR-SAVE DEPILOR UNHAIRING, BOVINE HIDES[1]

In drum (5 r.p.m.)

Immunization		70-100% Water (26 °C) 2.5% lime	
			Run 5 min, rest 25 min. Run 5 min, rest 55 min.
	+	0.8-1.2% Na_2S (60-62%)[2] 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 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. The 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 and smooth with a bright colour and that the colour of the leather is uniform. An increased area yield is said to be possible.

The chemical costs are rather high; it is said that the cost of this unhairing is 2-3 times the corresponding costs of a lime-sulphide unhairing.

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

III. 5. Enzymatic Unhairing

Any putrefaction of hide leads very soon to a loosening of the hair, due to enzymes from the putrefactive bacteria and from degradation of the hide itself. This phenomenon is seen most often in connection with storage of insufficiently conserved hides in a hot climate.

At first, the bacteria attack the basement membrane and the basal cell layer of the epidermis, leading to the hair loosening, but subsequently the attack is extended to the hide substance itself.

Partial putrefaction was used in the sweating process where hides were stored in a hot and humid room until the hair was loosened. The sweating was followed by a mechanical unhairing.

However, it is very difficult to control the process, steering a middle course between insufficient hair loosening and attack on the hide substance. For this reason, sweating is hardly used anymore, except in old-fashioned tanneries, especially those processing sheepskins whose wool is more valuable than the skin.

Unhairing by the use of commercial enzyme preparations (2) (5) (6) was first introduced in 1910 by Otto Röhm with the purpose of achieving a process easier to control than sweating.

However, a high level of control will always be necessary when using enzymatic unhairing, because highly specific proteolytic enzymes, targeting proteins in the epidermis, hair roots and basal membrane exclusively, will probably never become a reality. Commercial preparations of proteolytic enzymes attack the collagen of the grain layer to some extent, leading to looseness of the grain and grain sueding (45). Also, bacterial putrefaction is intensified by enzymatic treatment. Furthermore, enzymes alone cannot eliminate the ground and fine hair completely. Thus, an unhairing process exclusively based on the use of enzymes will probably never be practically possible.

However, enzymes can be used in combination with other unhairing agents. An alkaline immunization step, an alkaline swelling, and a sulphide treatment to eliminate ground and fine hair, form part of enzymatic as well as other hair-save unhairings.

Enzyme preparations are expensive and in most cases environmental advantages alone are not a sufficient incentive for the introduction of the method.

Enzyme unhairing is especially attractive when good quality of wool or hair has a high priority. Enzyme unhairing has been used for decades for long-haired goatskins, as goatskins are more resistant to enzymatic attack on the grain layer than skins or hides from other species. Sheepskins are considerably more sensitive and to some extent the wool is damaged in the unavoidable alkali treatment.

Since the introduction of enzyme unhairing, a significant improvement of enzyme preparations has taken place, although the difficulties mentioned above still exist. The interest has concentrated in enzymes which have their maximum effect in a highly alkaline medium, to be used for enzyme assisted unhairings.

Enzyme assisted chemical unhairing requires much less enzyme than unhairing based mainly on enzymes, thus, the risk of grain damage is considerably lower.

Several commercial methods exist:

Cromogenia-Units, S.A markets a method, based on an enzyme, an amine auxiliary, and sodium sulphide (22) (23), developed in 1990. The method is used in several Spanish tanneries.

The unhairing is carried out in a drum with recirculation and filter; the whole process from immunization to re-liming is carried through without changing the float.

After dosage of the amine compound and immunization with lime, hair-loosening is brought about by an addition of the enzyme product and sodium sulphide. The enzyme (supplied by Novo Nordisk A/S) is stable to strong alkali in reducing medium. In the re-liming, after filtration of the hair, more sodium sulphide is added.

A recipe for the process is given below. The sulphide consumption according to the recipe corresponds to 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 chemical are reported to be 0.6-0.65 USD per square foot.

Novo-Nordisk A/S produces the alkali-stable protease NUE 0.6 MPX to be used for an enzyme assisted chemical unhairing. A recommended recipe for an enzyme assisted lime-sulphide unhairing is presented below. Trials with the enzyme, carried out by British Leather Confederation, are described in (24). The use of the enzyme makes it possible to reduce the dosage of chemicals and/or the process time. Recent trials, also by the BLC, showed that it is possible to produce a commercially acceptable upholstery leather by using the enzyme in a hair-save unhairing. The total consumption of lime and sodium sulphide was reduced to 1.5% and 1.0% respectively.

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

	110-300% water (24-28 °C) 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. Run automatically overnight

It may be necessary to reduce the process time for the 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 a 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 TFL Enzyme Shower process (15). The sulphide consumption in this process is 1% sulphide flake (60 % Na_2S), corresponding to 2.5 kg S^{-} per tonne of raw hide.
Another process, developed by TFL, combines an enzyme (Erhavit MC) with formamidinesulphinic acid (Erhavit FS). This process can be carried out with or without sulphide (15).

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

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

III. 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 loosening of the epidermis and hair. Normally, this type of unhairing takes some days, but by the combination of enzymes, which in some cases may be derived from the hide itself, it is possible to achieve a usable method to be used in practice.

A method of this kind, based on acetic acid and autolytic enzymes from the skin, has been used commercially in Australia for dewooling of sheepskin since the 1950's (4) (28). The method is carried out as a combination of painting (with acetic acid plus salt) and sweating. It is stated that this method is easier to control than the classical sweating, but nevertheless, the method is most suitable when the grain layer is not used. A subsequent lime-sulphide treatment is necessary.

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

III.7. Amine Unhairing

It has been known for many years that amines accelerate the unhairing with straight lime (see section IV, 2). More than 70 amino compounds have this effect at a higher or lower degree (6).

A method for hair-save unhairing in a paddle, based on the use of dimethylamine sulphate and sodium hydroxide after a previous immunization (30) was used for several years in USA. However, due to the possibility of generation of carcinogenic nitrosamines in the beamhouse air, DMA is not used for unhairing any more.

Generation of the nitrosamine can be avoided but nevertheless the method is probabaly not going to be reintroduced.

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

III. 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 the use of the product is given 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	
Immunization - 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

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

IV. EQUIPMENT

For a modern hair-save unhairing , equipment for recirculation of the float and separation of the hair is essential.

The separation of the hair is preferably carried out simultaneously with the hair loosening, in order to minimize the degradation of the hair substance. Drums equipped with recirculation and temperature and pH regulation are commercially available. The float may be pumped out from the laboratory box of the drum and returned through the hollow axle.

It is also possible to install a recirculation and filtering system in existing drums provided that these have axles to be used for the float circulation.

In the case of mixers, the filtering unit is fitted into the exisisting recirculation system. The recirculation in a mixer may release greater quantities of gas than the recirculation in a drum. Methods, where a risk of generating toxic or odorous gases exist, should not be carried out in a mixer. It is necessary to install one filtering unit for each vessel or, if the same filter is to serve more vessels (maximum two or three), to carry out the unhairing in the individual vessels with a time lag of approximately two hours (the time necessary for the hair-loosening and recirculation).

Another solution is filtration after collection of the drained float in a pump sump, and collection of the filtered float in a tank, from where 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 easy to install, also applicable to paddles, provided that space for the tanks is available. (To function as a pump sump, a length of blocked sewer may do).

One disadvantage, besides the degradation of the hair substance, is that it is necessary to have a homogeneous production to avoid cross contamination of the liming systems.

The flow capacity of commercial recirculation - filtering systems are typically 600-1000 l/min. Various types of sieves can be used for separation of the hair. It should be mentioned that in one tannery sieving through a filter cloth of hessian does suffice.

The float may be pumped to the sieve through the existing circulation pump of the vessel or with separate pumps.

A relatively simple device is a static wedge wire screen. The filtered float flows through the screen plate whereas the hair slide down the screen plate and finally fall into a container. A suitable gap width is 0.5-1.0 mm.

Static wedge wire screens are used in many tanneries for separating chrome leather fibres or hide fibres from the waste water. Vibrating wedge wire screens are also available.

The cost of a static wedge wire screen is approximately 5,500-8,500 USD, but double that amount for a vibrating screen.

In a rotating drum sieve, the cylindric surface serves as a filter. The surface may be perforated with holes or consist of a wedge wire screen.

The drum sieve exists in two types. In the most common type, the float is fed into the inside of the drum. The filtered float flows through the cylindrical surface, and the hair is conveyed through the drum by gravity (an inclined drum) or, more effectively, by a screw conveyor and is collected into a container at the end of the drum. The drum may be connected directly to a screw press for dewatering the hair. Most sieves supplied through tannery machinery suppliers are of this type.The cost of one unit may be approximately 12,000 USD.

In another type, the float is conveyed to the outside cylindrical surface of the drum. The filtered float flows through the surface into the drum and the hair is scraped from the surface by 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 surfaces of the drums. The hair are let out through the other end of the axle.

With suitable filtering equipment, it is possible to recover up to 90% of the loosened hair.

Mason (18) made comparative trials with a vibrating sieve (1.0 and 0.2 mm mesh gap), 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 maintenance of the screen proved to be straightforward.

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

V. ECONOMY

An economic balance for the implementation of a hair-save unhairing consists of the following items:

Additional costs:

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

Savings and additional income:

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

The balance must be drawn for each individual tannery, because the economic consequences of each single item are highly variable from tannery to tannery.

The individual items can be commented on as follows:

Item 1:	The chemical costs are relatively easy to calculate.
Item 2:	Energy costs increase as a consequence of the more intensive mechanical action during the unhairing. However, in most cases, the energy costs are of minor importance.
Items 3 & 9:	Entirely dependent on how the hair can be utilized or disposed of.
Item 4:	Capital and maintenance costs depend on how much new equipment, if any, is necessary and on the current interest rate.
Item 5:	In most cases labour costs are going to increase because of the screening of the hair etc. However, in some cases, a saving in labour costs might be possible.
Item 6:	This item depends entirely on local conditions; which type of waste water treatment and which degree of purification are necessary; and whether a treatment plant exists or has to be constructed. The level of charges as well as the local construction and wages costs vary considerably.
Items 7& 8:	Only experience will show whether any improvement of leather quality or increase of area yield is possible in the individual tannery.

Furthermore, the size of the tannery has a significant influence on the balance.

The decision about an introduction of hair-save unhairing does not depend on economic considerations only. In some countries, the introduction of hair-save unhairing may be demanded by the environmental authorities.

Some comparative cost calculations are available:

In a UNEP report (32) are compared the chemical costs for Sirolime unhairing and a conventional hair-dissolving unhairing (for a tannery processing 40 tonnes raw hides per day):

Hair-dissolving unhairing:	USD/tonne raw hide
Sodium sulphide	16.35
Lime	2.50
Total	18.85

Sirolime unhairing	USD/tonne raw hide
Sodium hydrosulphide	2.40
Calcium hypochlorite	1.25
Lime	2.50
Sodium sulphide	2.73
Total	8.88

The chemicals savings by Sirolime unhairing are thus 9.97 USD/tonne raw hide, corresponding to 399 USD/day or 87,780 USD/year.

Coincidentally, the cost of one drum with recirculation and filter (capacity 10 tonnes raw material) is also 87,780 USD. As four drums are needed, the payback time is 4 years (32).

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

Hair-dissolving unhairing:	USD/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 is 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, the hair disposal costs have been substantially reduced.

In a tannery in Kenya, processing dried skins, a comparison between hair-dissolving and hair-save unhairing has been carried out (34):

	Costs of chemicals	
	USD/1000 dried skins	**USD/tonne green weight (appr.)**
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) there are cases where the costs of chemicals for a hair-save and a hair-dissolving unhairing are of the same magnitude. The former case refers to a lime-sulphide hair-save unhairing, the latter to an enzyme assisted unhairing.

Elsinger et al. (20) estimate the costs of a conventional lime-sulphide unhairing to be approximately 1% of the total production costs, possibly a reasonable estimate. Total costs for unhairing with thio compounds, sulfinic acid derivatives, enzymes or dimethylamine were, at that time,estimated to be 2-3% of the production costs. Heidemann states that an unhairing with thio compounds is 2-5 times more expensive than a lime sulphide unhairing (2). In a Norwegian tannery which implemented hair-save unhairing, industrial scale experience did show that the cost of the Mollescal process is 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 actual price of the Mollescal products is reported to be approximately US $ 1600/tonne for Mollescal SF and US $ 1500/tonne for Mollescal LD 6025 (August 1997), 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 raw hide.

The necessary equipment costs (excl. 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 necessary recirculation and filtering outfit would cost approximately 27,000 USD.

As mentioned in Section IV, a static wedge wire screen is a cheaper solution than a rotating drum filter (price US $ 5500-8500).

VI. POSSIBILITIES FOR UTILIZATION OR DISPOSAL OF THE HAIR

Two useful surveys of the possibilities are available (37) (38).

The recovered hair represents one more solid by-product to be coped with by the tanner, and the possibility of finding a suitable outlet for the hair, preferably some kind of utilization, is an important factor when considering an introduction of hair saving unhairing. It happens, however, that tanneries, for economic or political reasons implement a hair-save unhairing even though they have to deposit the recovered hair in a waste dump. After dewatering to 35% dry matter, the hair does not give raise to any odour when deposited as waste.

A lot of speculative proposals for utilization of the hair have been put forward. However, only applications which are used in practice or have a reasonable chance to become realized, are discussed in any detail in this report. Neither is processing and marketing of wool discussed.

The quantity of hair recovered in relation to the weight of raw hide depends on the hair length and the thickness of the hide. Typical figures are found 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 figures in the table, 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 soon as possible, e.g. with a screw press or by draining in a perforated container. Containers to be used for draining and subsequent transport are commercially available. Otherwise, putrefaction of the proteinaceous matter in the water adhering to the hair occurs very fast (17). The sulphide content in fresh, wet hair is approximately 80-100 ppm (37). but the sulphide is easily oxidized; after 3-4 h, the content is less than 10 ppm; and after a day, the sulphide has totally disappeared (17)(39). Sodium ions and lime must be eliminated by washing, which is necessary for some uses of the hair.

In the past, hair from the hair-save unhairing of e.g. bovine hides was used for felt production. One of the reasons for the disappearance of hair-save unhairing was that the use of animal hair as a raw material became obsolete, due to the introduction of synthetic fibres. Also, at that time the hair was recovered by mechanical unhairing. The hair resulting from a modern unhairing process is to some extent degraded through chemical and mechanical action in the drum or mixer, notwithstanding the immunization which has taken place, and for this reason its fibre strength is reduced. This fact, in connection with the competition from synthetic fibres, means that possibilities for its use as a fibre material are relatively low and any use for felt production in industrialized countries is out of 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; the 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 the hair substance are agricultural use as a fertilizer and processing into animal feedstuffs.

Hair is a valuable soil conditioner because of its character as a slow-releasing organic nitrogen source. As mentioned above, in some cases it will be necessary 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 been dissolved (38), dependent indeed on the character of the soil.

As the amount of hair based fertilizer is insignificant compared to the total fertilizer consumption it must necessarily be marketed as a special product. A hair-based fertilizer product will be especially useful in orchards, market gardening, and private gardens.

In some cases, a partial hydrolysis of the hair, e.g. by heating, may be useful before the formulation of the commercial product. Also, an addition of phosphorus may increase the fertilizing effect.

An Italian company, Giuseppe Sala & Co. s.r.l. in Arzignano, has marketed an organic nitrogen fertilizer (Ecolfert), prepared from partially hydrolysed, pelletized hair (37) (41). Also in Australia, a pelletized, hair-based, organic nitrogen fertilizer is being marketed. The product has given excellent results in plant growth trials (8).

Low grade wool fibre has been used commercially as a fertilizer.

The recovered hair from a Scandinavian tannery has been used, together with bark, for growing of spruce trees with positive results.

AIICA, Igualada, Spain has carried out during two years trials with the use of hair mixed with other organic material, as a fertilizer. Totally 10,000 tonnes dry hair has been processed. The product was used with good results for various types of vegetables (47).

TFL has carried out trials with the use of partially hydrolysed and granulated hair as a fertilizer. Also in this case, the results were positive.

The agricultural value of the hair may be increased through composting. Composting involves the accelerated aerobic degradation of organic waste materials by natural microorganisms.

For growth, the microorganisms need a well-defined carbon-nitrogen relation in the substrate. The optimum value is approximately C:N = 25-35:1. In hair, this relation is 3-4:1 (17) (37) (38), which means that the hair has to be mixed with other waste materials which act as carbon suppliers (sawdust or wood chips, household and garden refuse etc.) The optimum water content in the mixture for composting 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 a windrow:

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

The temperature in the windrow reaches 80°C within a few days. After 2 months, the windrow is turned.

Turning the windrow helps the aeration and homogenization of the mass and assists in uniform temperature distribution throughout the material.

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

A Danish tannery sends the hair to a biogas plant together with fleshings and other organic waste. The input of the plant is mainly agricultural waste, but also various kinds of industrial waste. Most probably, the hair is only degraded to a minor extent and insignificantly contibutes to the gas production. However, as mentioned earlier, the hair increase the long-term fertilizer effect of the solid residue which is used on agricultural soil.

The hair protein can be used in the production of animal feedstuffs. Because of a deficit of two essential amino acids, lysine and methionine, it cannot be used as the only protein component of the diet. However, it has a high metabolisable energy and is useful as a supplementary feedstuff (18) (38). Because of 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 as feedstuff presupposes hydrolysis at high temperature and pressure (17)(37), preferably carried out in an existing rendering plant.

A company in the Netherlands uses waste hair from a German tannery as an ingredient of an animal feedstuff product.

Waste hair from a Czech tannery has been processed in industrial scale in a rendering plant (pressure hydrolysis at 130°C) with good results. The product was suitable as a supplementary feedstuff (7). Trials with hydrolyzing hair were carried out in a Swedish special rendering plant for poultry waste, mostly feather waste. Because of the special raw material, the hydrolysis temperature was in this case above 140°C.

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

Use of hair hydrolysate in cosmetics or pharmaceuticals or for cystein production is carried out in practice, but the market is very limited. To a small extent, hair has been used for a foaming agent in fire-fighting products.

The Central Leather Research Institute (CLRI), Chennai, India, has developed a method for using a 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). Hydrolyzed keratin has been used as a casein substitute in finishing (37).

A possible outlet for waste hair would be the use as a thermic or acoustic insulation material. However, according to (38), this would only be economically viable if the tanner would pay 80-110 USD per tonne of hair, which is not realistic.

VII. ENVIRONMENTAL CONSIDERATIONS

Much information about the environmental load from hair-save unhairing is available, a great part of these deriving from the suppliers of commercial systems.

In the table below there is a reasoned out evaluation of what is possible to achieve 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 (for a water consumption of 40 m^3 per tonne raw hide).

The discharge with the waste liquor does vary strongly with the process conditions; better or poorer results than given in the table are found in practice.

It is evident from the table that the introduction of a hair-save unhairing is only a partial solution to the waste water problems; in relation to the total discharge from the tannery, reductions are primarily in the amounts of sulphide and suspended solids and, to a lesser extent, in BOD_5 and COD . Even the reduction of the sulphide discharge does not render a subsequent treatment superfluous. Whether under these circumstances introduction of a hair-save unhairing is worthwhile must be decided by the individual tannery. In any case, if a substantial improvement of the waste water discharge is to be achieved, the hair-save unhairing must be accompanied by cleaner technologies in all other stages of the processing.

The sulphide dosages for various hair-save methods used in practice are found in the table in Annex 2.

The lowest dosage found in practice is 2.0 kg S^{-} per tonne raw hide; the lowest dosage for a solely lime-sulphide based unhairing is appr. 3.7 kg S^{-} per tonne raw hide.

For several hair-save methods, the sulphide dosage is higher than found in some hair-destroying unhairings. The reason for this is partly the immunization of the hair, partly the fact that part of the sulphide is only added after the hair has been filtered off.

As mentioned in Section VI, degradation of the hair substance, also after immunization, occurs at a dosage higher than 1.9 kg S^{-} per tonne raw hide and becomes significant at dosages higher than 2.5 kg per tonne. This fact emphasizes the need for separating the hair as soon as possible.

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

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

Even at the lowest dosages, a subsequent sulphide oxidation process is often necessary. In this connection it must be remembered that a part of the sulphide in the unhairing liquors is oxidized by mixing with waste water from other parts of the production. Although the sulphides are relatively easily oxidized through catalytical oxidation or in the biological waste water treatment, a reduction of the sulphide output from the process is required in some cases because of corrosion of the sewers or because the final product of the oxidation, sulphate, contributes to the amount of neutral salts in the waste water discharged into rivers or lakes.

It is possible to re-use the waste re-liming liquor and to some extent also other waste liquors. Such recycling systems are described for Sirolime unhairing (4)(10), (see section III.3.) and by Cantera et al. (44) for Erhavit HS unhairing.

In this way, it is possible to save water and sulphide,thus reducing the sulphide output, but the discharge of organic substance remains unchanged.

For Erhavit HS unhairing, the savings are assessed to be 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 like these justify the necessary installations (tanks, pipes and pumps) and careful analytical control.

Another possible advantage is that, most often, it is easier to dispose of waste hair than waste sludge and that the risk of release of toxic or odorous gases is less for several hair-save methods.

VIII. CONCLUSIONS

1. Introduction of hair-save unhairing is not necessarily an advantage for every tannery; whether it is worthwhile to introduce the method must be decided by the individual tannery as the optimum solution depends on the local conditions, internal as well as external.

2. Considerations of an introduction should start from a cost-benefit analysis including savings in environmental costs; possible improvements of leather quality and increase of area yield; marketing possibilities ("eco-leather", eco-labelling); possible additional costs of the method selected; and, last but not least, economic implications of the hair disposal.

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

4. While introducing a hair-save unhairing, other processes in the tannery, as far as possible, should remain unchanged.

5. Environmental authorities may put forward specific demands. As far as possible, such demands should be envisaged beforehand in order to have the time necessary for implementation of a new method.

6. Before any new technology is introduced, it is important to ascertain whether it is equal, better, or maybe inferior with regard to environment and occupational safety than the technology it is going to replace. Information on toxicity of products must, if necessary, be obtained from the supplier.

7. When evaluating a new technology, also factors not directly related to the tannery (e.g. production of the chemicals) may be taken into consideration ("life cycle thinking").

8. Like all cleaner technologies, the hair-save unhairing presents only a partial solution to the environmental problems of the tannery. A tannery having as its only output the finished leather will forever remain a Utopia, and consequently cleaner technologies will never completely replace end-of-pipe technologies.

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

10. As mentioned in Section VII, a hair-save unhairing process also results in discharge of sulphide with the waste water; in some cases the amount discharged may be even higher than for a hair-burn unhairing.

11. Sulphide elimination, if necessary, can be achieved through an end-of-pipe treatment, e.g. a catalytical oxidation.

12. In some cases there is no need to remove sulphide before waste water treatment, as it is eliminated by a biological oxidation of the waste water.

13. Only 50% at most of the nitrogen content of the waste water is eliminated by the hair-save unhairing. If nitrogen is one of the key problems, the hair-save unhairing must be supplemented with deliming without ammonium salts e.g. with carbon dioxide).

14. Improvement of leather quality and increase of the area yield are claimed for all methods marketed. However, such claims cannot be taken at face value but have to be verified in industrial trials over several months.

15. Collection and filtration of the float after the end of the chemical unhairing is the practice which is most easy to implement in existing equipment and consequently implies relatively low investment costs. Screens can be selected to be as cheap and simple as possible.
On the other hand, this practice is not optimal with regard to hair quality and reduction of the waste water load.

16. At present, the most realistic possibilities for utilization of the hair seem to be its use in improving the agricultural soil or as animal feedstuff.
The slowly degradable hair protein is especially useful for soils in dry regions prone to desertification, as it increases the humus content of the soil.

IX. SPECIFIC RECOMMENDATIONS TO THE PROJECT

1. In order to verify the suitability of various methods for different types of tanneries and working under different conditions it would be useful to carry out demonstration trials in selected tanneries in the South East Asian countries.

2. The whole range of methods, from the most sophisticated to traditional and simple technologies, should be included in the testing programme.

3. The methods selected should be as simple and inexpensive as possible, provided that quality and effectiveness are not endangered. Especially in countries with high interest rates and/or import duties, the investment costs must be kept as low as possible.

4. Most commercial methods imply significantly higher costs of chemicals than the traditional lime-sulphide unhairing. The methods selected for implementation should be assessed with the view of minimizing the cost of chemicals by minimizing the dosage, identifying the optimum combination of chemicals, etc.

5. In clusters of small tanneries with limited technical and economical resources, establishing of common facilities for carrying out the unhairing and probably other beamhouse operations as well, should be encouraged. Common plants of this kind would naturally also include a treatment of the waste water.

6. Alternative possibilities for utilization of the hair, in accordance with local or regional conditions, ought to be sought for.

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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 unh., minimum dosage	2.5-4.0
Hair-dissolving lime-sulphide unh., normal dosage[2]	3.7-7.5
Minimum dosage for obtaining a 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]
Enz.Ass.Unh, Argentinian 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) elsewhere stated

ANNEX 3

SUPPLIERS OF COMMERCIAL SYSTEMS MENTIONED IN SECTION III

BASF AG, Textile and Leather Dyes and Chemicals,
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