

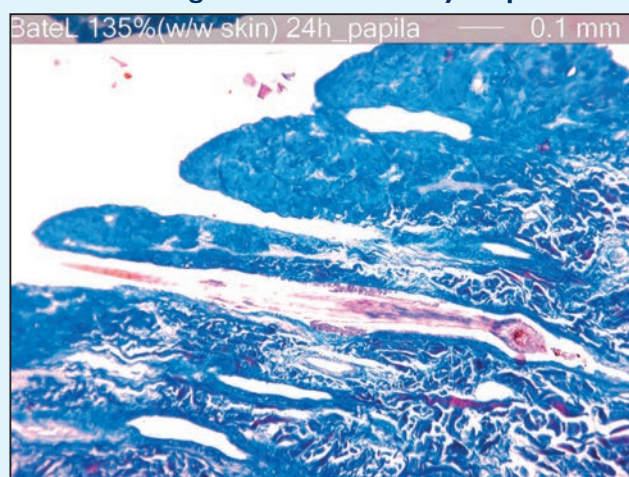
Innovation in the beamhouse

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The conventional sulfide/lime system for unhairing and as part of the fibre-opening process has been in its existing form for approximately 150 years. However, appropriate treatment is required to avoid considerable pollution, and this is at the expense of the tanner. Moreover, the presence of sulfide restricts the use of by-products, and limits the way that effluent treatment can be rationalised.

A new process is very desirable, and a new technique has been investigated. This is outlined in this paper together with the potential advantages that might be gained by a sulfide-free unhairing system, and the route that must be followed if rationalised processing is to be achieved.

Panel 1: Clean grain from DMB/enzyme process



The current status of chemical processing throughout the beamhouse can be summarised as follows:

- Soaking:** Requires surfactants +/- enzymes, bases for pH adjustment.
- Liming:** Requires 2% sodium sulfide, 3% lime +/- mercaptoethanol, urea and amines.
- Deliming:** Requires 2% ammonium sulfate or carbon dioxide, propylencarbonate and dicarboxylic acids.
- Bating:** Requires bating agents (ammonium sulfate) and enzymes (proteases).

At the end of these operations, in addition to unused chemicals, the following waste products result:

- Soaking:** Salts and dung.
- Liming:** Hair, sulfide, soluble proteins, fats, fleshings, calcium hydroxide.
- Deliming:** Calcium salts, ammonia, hydrogen sulfide.
- Bating:** Ammonia, salts, soluble proteins, fats.

The usage of water in these initial beamhouse operations is considerable when compared to the general water requirement throughout the whole leather manufacture. Moreover, the

generation of COD from these beamhouse operations is very high when compared to the whole leather making sequence. These values are generalised in *Panel 2*:

Panel 2: Water consumed in leather manufacture

BASED ON 25m ³ / 1000/kg RAW HIDE		
Operation	Water consumed %	Generation of COD %
Beamhouse	54	66
Tanning and dyeing processes	23	22
Finishing operations	11	4
General washings	12	8

Against this background a typical cost allocation for leather production is given in *Panel 3*:

Panel 3: Process analysis: cost allocation for leather production

Components of manufacture	Percentage allocation
Raw hides	55
Manufacturing costs	15
Labour costs	12
Chemicals	10
Waste disposal	5
Energy	3

Over and above fluctuations in the value of raw hides, and the differences in labour costs that are found between different regions, the costs for waste disposal continues to rise. This is because of environmental laws and controls that are continuously becoming more stringent, and the rising costs of waste management.

The scale of the waste generated from leather manufacture is illustrated in *Panel 4*:

**Panel 4: Evaluation of waste for leather manufacture**

RAW HIDES: 10 Million tons > LEATHER: 2.5 Million ton	
Waste generated	Million tons/year (worldwide)
Effluent	10 x 25
Solid residues	6.1
Effluent sludge	5.0
Chloride	1.8
Sulfate	0.8
Solvents	0.1

The demands of the sulfide/lime unhairing/liming system

Although there have been many new developments in the way that leather is manufactured - new products, better controls, improved equipment, reduced throughput times, etc. - the basic sodium sulfide/lime unhairing/liming process remains largely unchanged. This originated approximately 150 years ago, and cannot be considered an eco-efficient beamhouse process due to the high:

- Volume of water consumed
- COD in the final effluent
- Salts generated
- Volume of sludges generated
- Residual sulfide in the effluent, being partly released during deliming as hydrogen sulfide
- Nitrogen content (from ammonium sulfate and hair) in the effluent

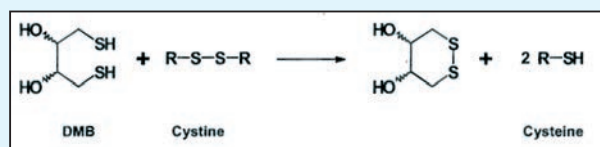
The avoidance or a reduction in these items would significantly reduce the costs of waste treatment and disposal. It may enable better use of some waste products as new raw materials.

An alternative to sulfide unhairing

The first target for basic innovation in the beamhouse is the replacement of the sodium sulfide/lime unhairing/liming system. This demands an alternative reducing agent for hair removal that is safe to use, and does not lead to the development of hydrogen sulfide during unhairing or when the pH is lowered in subsequent processing.

One product that is technically suitable is the reducing agent 1,4-dimercapto-butan-2,3-diol (DMB). If this is reacted with cystine it produces 4,5-dihydroxy-1,2-dithian which is odourless; there is no evolution of hydrogen sulfide.

A 2-step mechanism for hair removal is possible using DMB. First, a reduced cleavage of the disulfide linkage in keratin as indicated in *Panel 5*:

Panel 5:

This is followed by cleavage of the peptide linkage using protease and alkali, and leads to complete hair destruction

into a gel-like form.

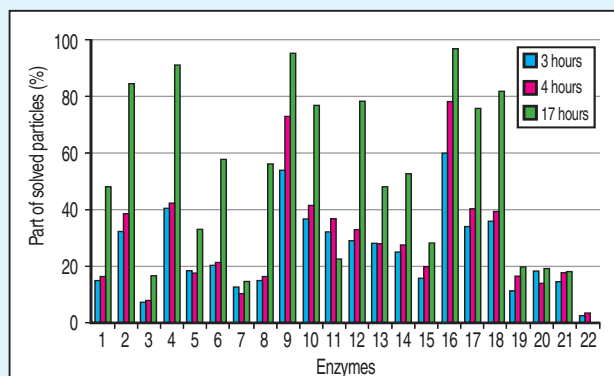
The viability of DMB within an unhairing system

The manufacture of DMB is based on simple raw materials - butadiene, hydrogen peroxide and hydrogen sulfide. The synthesis requires several steps to bisepoxide, then reaction with hydrogen sulfide to DMB.

However, at the moment no pilot plant exists for the manufacture of DMB. Accordingly it remains an expensive product, the present price being €1,000/kg for technical grade. Nevertheless, it is considered that if the creation of a pilot plant was feasible, then the manufacturing cost could be reduced to €20/kg for technical grade.

If the process is to become viable, then the usage of DMB must be reduced as far as possible. For this reason proteolytic enzymes are required for the removal of the residual hair that has been partially reduced by the DMB. Under test conditions 0.5% DMB for 6 hours + enzymes in a buffer solution at pH 9.5 for 18 hours caused complete dissolution.

Many enzymes were investigated for their suitability and three were found suitable, being Savinase (Novozymes), Esperase (Novozymes), and Papain-brands (India). The typical performance of some enzymes in the hair dissolution stage after treatment with DMB is indicated in *Panel 6*:

Panel 6: Comparison of the enzymes after 3, 4 and 77 hours**The potential of DMB/Protease technology**

It is clear that DMB/Protease technology is not a simple combination process that is ready for full-scale trials and application. DMB is not available commercially in bulk, and even if a pilot plant were viable, the cost/kg as a specialised chemical would remain high. However, the amount of DMB is low compared to sodium sulfide, and there are many possible advantages and cost savings. For example:

- Fast and complete hair destruction
- Complete dissolution of melanines
- Low process pH. Between pH 12 and pH 10 with sodium hydroxide.
- No lime required
- Fast and complete deliming
- The possibility of no bating

Because of the absence of sulfide in the system it is estimated that the process would generate approximately 60% less effluent. For example, acid precipitated unhairing floats could be used for:

- Presoak and main soaks. The effluents from soaks can be



discharged directly to the effluent treatment plant.

- Deliming floats.
- The pickle bath.
- Fresh water would only be required for liming, bating and washing processes.

In addition, the process offers a better usage of existing by-products from manufacture such as fleshings, lime splits and trimmings. The residual hair and solubilised proteins in the effluent are sulfide free. This means that simple acidification is possible to precipitate these proteins in an uncontaminated and odour free form for different applications, or energy generation.

This route would cause a considerable reduction in the volume of sludge for treatment and disposal compared to conventional processing. Moreover, the viability of acid precipitation means that there can be a considerable reduction of soluble protein carried over into effluent treatment. It is calculated that the COD can be reduced by approximately 60%, with the opportunity for rationalisation and cost saving in effluent treatment.

Limitations for DMB technology

Over and above price consideration there are the following barriers to take into account:

- Consistent results have not been yet obtained under large-scale test conditions.
- There is a breakdown of the skin on some occasions.

- Cost savings where common effluent treatment plants are used are not sufficiently attractive for tanners.
- Long test periods are needed for suitable leather making process development, optimised effluent treatment and recycling, and waste management.
- Investments for a production plant for DMB without an upscale in trials is not acceptable.

The outlook for eco-efficient beamhouse processing

- The problems of unhairing and other beamhouse processes are not yet solved.
- Innovation cannot be achieved by simple replacement of product against product due to cost reasons.
- Organic chemistry cannot solve these problems: the biochemistry of collagen needs to be researched and better understood.
- Cooperation is needed by the international research and development community to find solutions for developments in this difficult area.
- Basic research and development is a common task: Medical research and development could support collagen research.

Acknowledgements

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