

Bating: gaining area while retaining cutting values

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It is almost 100 years since Otto Röhm introduced the first industrial application of an enzymatic product. This was the bating process of animal hides within leather production, the enzymes being derived from pancreatic glands. This can be seen as the start of modern biotechnology.

New enzymes have since been developed from bacteria and fungi. Thanks to modern biotechnology and genetic engineering these enzymes can be manufactured in consistent quality and quantity, from industrial applications to food, the synthesis of new chemical substances, and pharmaceuticals. The bating process has also evolved, including acid bating of pickled skins using a fungal protease, and the treatment of wet blue using acid proteases.

The changing needs of bating enzymes

The most important effects of bating on leather are an increase of area, improvement of inner softness, more uniform dyeing and better physical/mechanical properties. These benefits are sometimes hard to achieve, especially if they are all needed at the same time. This applies especially to area yield (sq.ft.) and cutting yield where gains in one value are often coupled with losses in another.

Moreover, the needs of bating have changed over the years. These stem from important alterations in the composition of animal hides due to different breeds and dramatic changes in feed and raising conditions. This applies especially during the past 20 years.

When raising cattle, one of the main goals is that animals gain as much weight as possible within the shortest time possible. This means that animals reach maturity at an earlier stage.

The collagen matrix of hides is comprised of many different kinds of crosslinks. One of those is the so-called pyridinolin crosslinks between collagen molecules. They are sensitive to alkali treatment and is mainly found in younger, less mature hides. In older or mature animals pentosidine cross-links prevail, being stable to alkali treatment, superseding the importance of the pyridinolin cross-links.

In general, early matured hides have a lower content of mature crosslinks but have a higher amount of reducible crosslinks. They also have a lower content of elastin and a higher content of soluble collagen. All these facts explain the increasing sensitivity of hides towards processing conditions that support faster processing, such as the use of sharpening agents in liming.

The increase of cost pressure in leather making has led to shorter process times, but at the same time the tanner has to strive for the biggest possible gain in area. Area is often expanded at the expense of the fullness and grain tightness of the flank parts, meaning that the usable area of leather is diminished. Nevertheless, inferior parts of the hide are used at prime locations of leather articles. Examples are shown in *Figures 1 & 2*.

The characteristics of enzymes

There are different kinds of enzymes used during soaking, and bating of delimed pelts and wet blues. These play a critical role in speeding up the unhairing and opening of the hide. Enzymes have a direct impact on collagen (mainly type I and III), elastin, keratin and lipids (grease). They can deliver the same effects and cleaving properties that any conventional leather processing chemical can provide.

Understanding the different effects that enzymes can have on hide components in the beamhouse is critical in order to optimise enzymes and their application.

The proteases characterised by exo- and end-peptidases do not act on the collagen helix itself, but on the collagen molecules at their telopeptide ends. They therefore influence the grain character, and depending on how far the degradation of collagen goes, the area yield and softness. In addition the softness is related to the removal of the proteoglycans such as decorin/dermatansulfate, being interfibrillar substances located between collagen molecules. If they are not removed properly they impair the diffusion of retanning chemicals and oils into the micro fibre structure.

The same type of protease removes scud typically consisting of residues of blood, globular proteins and hair roots. For removal of the hair roots a good keratinolytic action is favourable.

Elastases, which are a special kind of protease, work on the elastin fibre protein contained in the grain and walls of veins. Due its elastic properties elastin can extend to double its original size. Elastases therefore have an impact on grain tightness, elongation and mechanical strength, as well as on the area yield and cutting yield of leather.

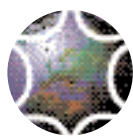
Keratinases will degrade hair and hair roots to improve cleanliness. This is also improved by lipases as these help the release of any triglyceride-type grease left in the hide.

Over and above activity towards globular proteins and proteoglycans, commercially available proteases also have collagenase, elastase and keratinase activity. Proteases distinguish from each other in the different ratios of these single activities.

Proteases with very low collagen and elastin degrading properties usually give reasonably good cleanliness, tight grain and full ▶

Figures 1 & 2: Outcome of using inferior parts of the hide



**Figure 3: Analytical data of different enzymes***Relative units are expressed in relation to LVU activity*

	elastase (rel. units)	Collagenase (rel. units)	Elastase/ Collag. ration	Keratinase (rel. units)	Lipase (FIP)
Modified Pancreatic Enzyme (MPE) (Pancreas- Enzyme RB2)	4.2	1.23	3.4	6.02	22500
Bacillus protease 1	7.8	1.17	6.6	4.3	<100
Bacillus protease 2	8.02	1.50	5.2	3.74	<100
Fungi protease FA	4.78	0.5	9.6	0.55	<100

flanks, and veins are often less pronounced. At the same time there is little improvement in area yield and softness. The grain elasticity, elongation, stitch and grain tear strength are also lower.

Proteases with high elastase and high collagenase activity gives good cleanliness, area yield and inner softness. The grain is more elastic and the tear and stitch strengths are improved. On the downside one needs to watch out for looser grain, emptier flanks and sometimes more visible veins.

The different properties of enzymes and their effects on leather characteristics

The challenge is to find an enzyme preparation that combines the advantages of good area yield and cutting value, whilst keeping unwanted effects at a minimum. The ideal point in

process to apply these enzymes is the bating process since the best diffusion into the hides can take place following the removal of the hair and epidermis.

Insight into the outcome of using enzymes with different properties was gained in a series of investigations. Here the analytical data of a Modified Pancreatic Enzyme (MPE), a Bacillus Protease 1, Bacillus Protease 2 and Fungi Protease FA in relative enzyme units is shown in *Figure 3*. The values shown almost correspond with the practical outcomings shown in *Figure 4*.

Bating conducted with the MPE gave very good relaxation of the entire hide (indication for area gain), the flanks remained full and crust leather had very good softness. The grain was smooth and visibly not damaged.

Bacillus Protease 1 was derived from a Bac.Subtilisin strain,

**Figure 4: Practical results on crust leather**

	cleanliness	relaxation/area gain	fullness flanks	softness	veins
Modified Pancreatic Enzyme (MPE) (Pancreas- Enzyme RB2)	++	+++	++	+++	+
Bacillus protease 1	-	+++	-	+++	-
Bacillus protease 2	+	++	+	++	-
Fungi protease FA	++	0	++	-	++

with a higher elastase activity than RB 2 but similar collagenase activity. Here area gain and good softness was observed, but at the expense of fullness of the flanks.

Tests with Bacillus Protease 2 distorted the picture somewhat. Although this enzyme showed high elastase and collagenase activity there was not so much relaxation seen after bating, and the area gain was less than expected. The flanks were fuller than with Bac. Protease 1, but the softness was rather less than found with the MPE or Bac. Protease 1.

The fungal protease FA with medium elastase and very low collagenase activity gave full flanks but poor inner softness.

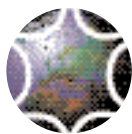
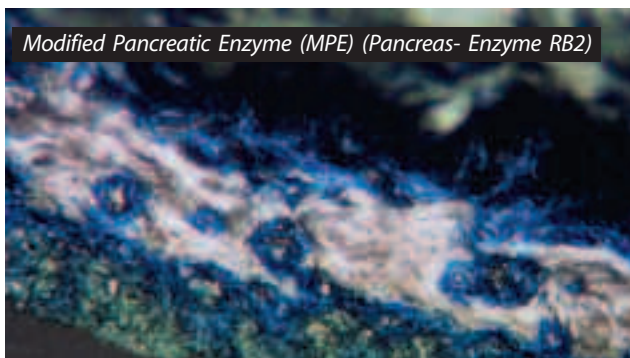
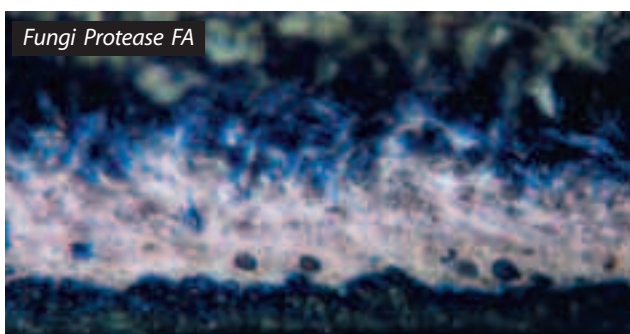
GAINING AREA AND RETAINING FULLNESS

If we form a ratio between elastase and collagenase activity, the correlation between analytical values and practical results

becomes more obvious.

A low figure as we see in the case of the MPE is the ideal, that is the best balance between area yield and full flanks on one hand, and grain tightness and inner softness on the other. The high keratinase and lipase activity explains the excellent surface cleanliness achieved by this enzyme. This is reflected in less LVU units needed to achieve the same degree of scud loosening. In practical tests, when compared with other enzymes, the 'mild' fungal protease FA needed the highest amount of LVU in order to achieve same loosening of the scud.

When comparing the physical-mechanical properties of the MPE with the fungal protease—the two enzymes which represent very different elastase/collagenase ratios—the two provide similar tensile strength. However in terms of tear and stitch tear strength, and to lastometer figures, the MPE shows ►

**Figure 5: Penetration of dyes***Modified Pancreatic Enzyme (MPE) (Pancreas- Enzyme RB2)**Fungi Protease FA*

Improved dye penetration due to better opening of the grain and corium structure by the MPE.

far superior values. In addition, these leathers show better opening of the grain and corium structure, and dye penetration than the fungal protease FA. This can be seen in the larger undyed zone in *Figure 5*. In this situation it is assumed that elastin as a hydrophobic protein blocks the penetration of the dye, although the removal of proteoglycans may have a role.

Elastin is a fibre protein that is difficult to degrade. This can clearly be seen in histological studies where elastin fibres were treated with the high elastase-containing enzyme Bac. Protease 1. Even after six hours extended treatment the fibres are still present although much weakened and thinner. This is shown in *Figure 6*.

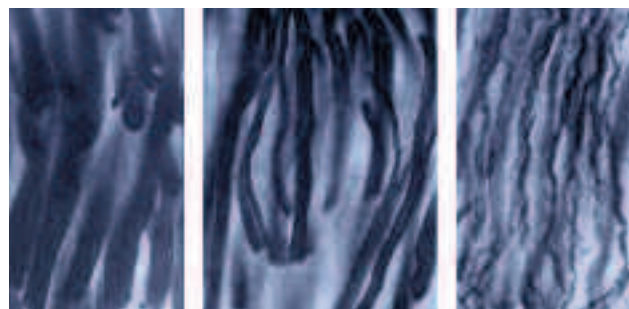
Based on these comparative studies, we can assume that the fibre proteins collagen type I and III and elastin that make up the papillary layer work in an antagonistic way. It is possible to increase area and keep flanks full and grain tight if the dense network in the grain is weakened by degradation of both proteins to a similar extent. In this situation the collagen in the reticular layer or corium will follow the relaxation process of the grain.

Bating of wet blues

If wet blues undergo poor beaming processing a significant amount of elastin can be left in the grain. Proteases, which have a pronounced elastolytic effect, can remove or degrade these fibres and thus improve the relaxation of the wet blue. Depending on the type of retannage an increase in area yield can be achieved.

There is a risk of a looser grain break and reducing the grain strength, but these risks can be minimised by controlling running time, pH and dosage and using appropriate retanning and fatliquoring agents. As chrome only fixes to the collagen and does not affect elastin fibres, there is no or little risk of grain attack.

When the process was pioneered in the 1980s acid proteases derived from fungi were used. These covered an application pH

Figure 6: Elastin degradation

0 hrs

3 hrs

6 hrs

Degradation of elastin fibres with Bac. Subtilisin protease 1 (magnification 1000x)

range of 3 to 7, so depending on the final leather requirements they can be applied during the neutralisation process for two hours or even overnight. Over and above an improvement of area, a better cleanliness and more uniform dyeing can be noticed in many cases. Over time these enzymes were further optimised, those with a high elastase/collagenase ratio showing the most pronounced effect regarding grain relaxation.

Maximising benefits

Regardless of whether enzymes are applied in soaking or liming, the use of carefully developed pancreatic enzymes in bating provides a safe way to gain improvements in terms of quality, yield and physical performance. However, the LVU activity should not be used as the only practical guideline—the dosage needs adjusting according to the end needs.

If the character of the pancreatic enzyme is balanced correctly, it will be both versatile in application and cost effective. Moreover, the opening of the hide structure should not be at the expense of grain tightness and fullness of flanks. In order to maintain these valuable properties whilst achieving good inner softness, it is best to use the enzyme at a lower dosage and extend the running time.

It is also recommended to treat the bated hide gently in the subsequent pickle and chrome tannage. This means avoiding high mechanical action and high temperature in pickle, and the use of very reactive basifying agents in chrome tannage.

Bating with a selected pancreatic enzyme under the right conditions completes the opening and cleaning provided by beamhouse processing before commencing chrome tannage. Regarding the enzyme treatment of wet blue, although attention is needed to avoid possible side effects, this can be seen as a valuable process to redress the effects of deficient beamhouse processing. It should, however, be remembered that a single component of the hide can only be removed once. If these components are removed correctly before tannage it eliminates the need for further bating of wet blue stock. ●

Legend

TFL products:

- 1) OROPON O range (OXX, OR, OO, ON 2)
- 2) OROPON DVP, WB, SAN

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