



Technologies to improve the useful area of leather

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The manufacturing of leather is facing diverse challenges nowadays including pressure from the eco-toxicity point of view. This is in the form of new stringent regulations regarding emissions into the environment, or the possible release of potentially harmful substances from the finished leather or leather article. The measures necessary to deal with these issues add to the cost pressures that tanners are experiencing.

Leather-making is a relatively complicated and labour intensive process, based on a rather expensive raw hide material, and chemicals linked to increasing crude oil prices. Furthermore, we are seeing vast improvements in so-called 'artificial leather', where new materials not only come close in terms of mimicking the look and feel of leather, but also show excellent performance. These materials can be made to the same quality, and can often be produced at much lower costs.

Cost reductions by tanners have often gone in the wrong direction. Many compromises were made in the quality of the leather, and examples typical of brand name 'high end' articles are shown in *Panel 1*.



Panel 1: Leather articles with problems



The problems start with poor tear strength, through the use of leather, from loose flanks or loose grain, to leathers in the upholstery area which feel like a piece of plastic. If we further pursue this direction, leather certainly will not win the battle.

In future, it will be critical to focus on quality, and thus sell leather as a luxurious material with a unique look, feel and properties, and at a price it really deserves.

In order to improve the quality of leather, emphasis should not only be put on technologies to increase the area yield (square footage), but rather focus on the usable area of leather. Technologies which increase square footage, either chemically or mechanically, are often linked with sacrifices in grain tightness, fullness of the flank area, or even in physical mechanical properties.

So what does the useful area (or cutting yield) of leather mean? By definition the usable area of leathers is influenced by following three parameters:

- Area (square footage)
- Area which has most uniform grain break, softness, and fullness
- Area with the minimum amount of surface defects

Focusing on the useful area means finding the optimum balance between opening up the hide structure and retaining important leather characteristics such as grain break, fullness, softness and strength of the leather.

Raw hides and skins

Knowing that raw hides and skins are the most important cost factor in leather production, special attention has to be taken in the processes that change, modify or degrade the hide structure. These are mainly the liming processes, processes where enzymes are being used, pickling/tanning and, to a certain extent, retanning.

During the last few decades significant changes in hide structure have been apparent. Cattle are being raised in a more industrialised manner, meaning that a maximum live weight has to be achieved within a short time.

Cattle now reach maturity at an earlier stage, and the hide structure has fewer crosslinks and assumes a more sponge-like character than found previously. These younger animals also carry more alkali sensitive pyridinolin crosslinks, which were previously transferred into the more alkali stable pentosidine crosslinks during ageing. This means that, in general, early matured hides become more sensitive to processing conditions such as the use of alkali, enzymes and hydrotropic chemicals. This results in a looser grain, emptier flanks and more abraded grain. ➤



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Use of enzymes

Proteolytic enzymes in soaking, liming and bating play an important role in opening up, increasing area yield, or even the usable area of leather. For this reason the selection of the most specific enzymes is crucial to achieve the best useful area of leather.

Studies carried out using enzymes of different specificity give a better understanding about how leather characteristics and analytical values such as collagenase, elastase and keratinase activity are interrelated as shown in *Panels 2* and *3*.

Panel 2: Analytical data of enzymes

	Elastase (rel. units)	Collagenase (rel.units)	Elastase/ Collag. ratio	Keratinase (rel.units)	Lipase (FIP)
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
Pure elastase	562	0		0	0

Relative units are expressed in relation to LVU activity

Panel 3: Leather characteristics of different enzymes

	Grain enamel	Relaxation/ area gain	Fullness flanks	Softness	Veins
Pancreas- Enzyme RB2	0	+++	++	+++	+
Bacillus protease 1	0/+	+++	—	+++	—
Bacillus protease 2	+/-	++	=	++	—
Fungi protease FA	+	0	++	—	++

Enzymes which show pronounced elastolytic activity often create leather with good area (sq.ft.) and inner softness, but with looser grain and emptier flanks¹. On the contrary a fungal enzyme with medium elastolytic activity, but almost zero collagenolytic activity, gives leather with a tight grain and full flanks, but poor area gain.

This indicates that the elastolytic activity alone is not enough to relax the hide structure and to improve yield. A certain collagenase activity is needed too.

The elastase works mainly on grain relaxation, and the collagenase partly disintegrates the collagen structure by breaking the crosslinks in the telopeptide region of the collagen helix. This does not mean that proteoglycans—that act as the 'glue' between the fibres—aren't removed at the same time by these enzymes. Their removal or breakdown certainly contributes to the opening up effect, and eventually to a gain in area yield².

A well-balanced ratio between elastase and collagenase activity is found in new modified pancreatic enzyme complexes³. Applying these enzymes in bating leads to an optimum cutting yield by relaxing the hides, but avoids problems with loose grain or empty flanks. The conditions during bating are almost ideal for the optimal penetration of these enzymes, the opening up process being steered by controlled adjustment of temperature, running time and enzyme concentration. Another unique aspect of the pancreatic enzyme complex is the high content of keratinase and lipase activity. The keratinase helps in the removal of scud and residual hair, and the lipase improves the degreasing effect.

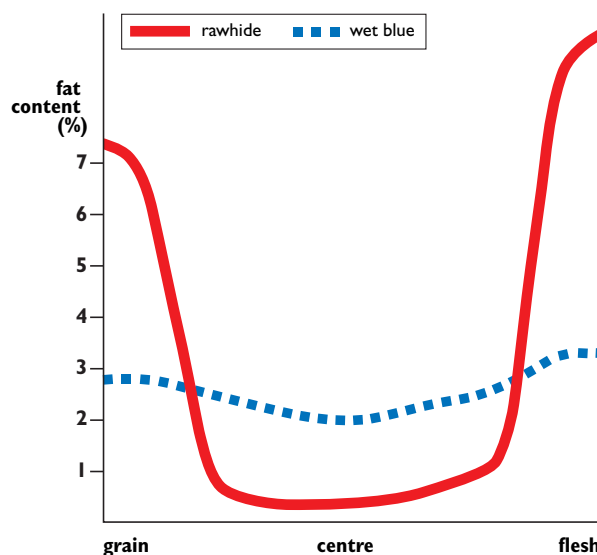
If enzymes are applied in all of the steps such as soaking, liming and bating, one needs to keep in mind that the enzymatic actions are accumulative, and the hide components can be modified or removed beyond the degree that was originally desired. If less specific enzymes are applied, the risk of problems with loose leather and abraded grain is increased.

A hide which is opened up either too strongly or inadequately is much more susceptible to form draw from high mechanical action, a too reactive chrome tannage, or within basification. If a problem with loose grain and empty flanks is created in the beamhouse, it is not easily cured by a stronger retannage or the use of selective fillers.

Degreasing

Next to collagen, fat is the single biggest component of hides and skins. By degreasing, we actually mean partially removing and partially redistributing the grease across the entire cross section as indicated in *Panel 4*.

Panel 4: Grease distribution in raw hide and wet blue



The grease of a raw hide is mainly located on the flesh side, and in the sebaceous glands surrounding a hair follicle, whereas little grease is found in the centre. However, at the wet blue or wet white stage, grease is found to be distributed more or less evenly across the hide section.

Depending on the character of the surfactant, the extracted grease is emulsified in a more or less stable emulsion. The more stable this emulsion, the more likely it is to achieve a natural fatliquoring effect, with the grease driven towards the centre ➤



of the hide. In such cases, the resulting leather is softer, but also shows looser grain, emptier flanks, and poorer waterproofing and fogging values.

For the best cutting yield, the use of an appropriate surfactant⁴ during the beamhouse processes is critical. The surfactant should show the right ratio between fat extracting power, emulsifying power, and emulsion stability. The best stage for the use of surfactants is in soaking, and especially in the deliming and bating process.

Very interesting results for maximising the useful area of leather have been achieved with a new type of soaking additive. Here, in combination with an inorganic alkali, a good wetting back effect is assured, and an optimised distribution of the grease. The flanks, however, remain much fuller through temporary incorporation of salts of fatty acids. A positive side effect of this action can be observed in the subsequent liming step, where swelling is much more controlled and uniform. This greatly helps to minimise the draw.

A similar effect can also be achieved by products based on specially formulated alkaline lipases¹⁰. They are applied in soaking and deliming/bating, and turn the triglycerides based part of the hide fat into a semi-stable fat emulsion. In cases of very greasy hides, the addition of small amounts of surfactants may be necessary to increase the emulsion stability. Lipases applied in soaking and liming can also improve the cleanliness of hides and mitigate the problem of fine or short hair.

Pickling and chrome tanning

CHASER TANNAGES

In recent years we have seen a renaissance of the so-called 'chaser' chrome tannage. In these tannages the chrome is basically added at a higher than regular pickle pH. By doing this, the amount of salt can often be reduced, and the alkalinity left in the hide is used as part of the basification stage. The amount of basifying agent is reduced, or can even be completely dispensed with. Chrome fixation and exhaustion are improved, with better grain tightness, fuller flanks and better tear strength. The limitations with 'chaser' tannages are that chrome penetration through thicker parts of the hides is more difficult to achieve, and there is often a loss of inner softness. For these reasons the technology is more interesting for skins and light structured hides.

Penetration can, however, be improved by using complex or low basicity chrome tanning products, or novel penetrating agents⁵. These agents greatly improve the chrome penetration and distribution in the cross section when used as an additive in regular pickle processes. This is because the reactions between the chrome and the fibre happen in a 'smoother' manner.

An optimised pickling/chrome tanning process with a novel penetrating and complexing agent is shown as *Panel 5*.

The improvement in cutting yield with these technologies is mainly attributable to the tannage being performed at a higher fibre angle. This is as a result of either different swelling due to a higher pH, or a lower salt content at the time of chrome addition.

ELECTROLYTIC STABLE FATLIQUORS

In order to manufacture leather with good inner softness, fatliquors are often used in the pickle. They improve the wetting back of wet blue or wet white, and lead to excellent inner softness. Care has to be taken with the amount of fat added, since it can easily lead to a loose grain and flanks. The development of

Panel 5: Grease distribution in raw hide and wet blue

PICKLING	50%	Water 20°C		
	7%	Salt		
	0.5%	Electrologtic stable fatliqur	10'	Bé 6.5-7.0
	0.6%	Formic acid (1 : 5)	30'	
	0.6%	Sulfuric acid (1 : 10)	45'	
	0.6%	Sulfuric acid (1 : 10)	120'	pH 2.8; Bé 6.0-6.5
	0.7%	Penetrating/complexing agent	30'	
TANNING	5.5%	Chrome salt 26/33	60'	
	0.2%	Fungicide	120'	
	0.5%	Sodium formate	30'	
	1.0%	Basifying agent	10 hrs	pH 4.0; Temp 45°C
WASH	100%	Water 20°C		
	0.05%	Fungicide	45'	
		Samm		

electrolyte stable fatliquors⁶ with excellent penetrating power deserves special attention. This leads to an improved separation of fibres, good inner softness, and a tight grain. In addition to this, there is improved tear strength, excellent rewetting power, and good dimensional stability of the leather. These benefits have an important role in the subsequent wet processing.

Improved retanning technology

When considering the impact of wet end operations on the useful area of leather we need to differentiate between two situations:

- One is dealing with wet blue stock which has a 'built-in' looseness arising from too strong an opening up in beaming operations, or from raw hides with an 'immature' collagen fibre structure. These wet blues are not easy to retan, and special efforts are needed to fill them—especially in the flank area—and to avoid grain looseness.
- The other situation is the retanning of wet blues whose basic hide structure is tight, and where the structure has been opened up insufficiently.

Since most tanners try to achieve the maximum possible area yield (sq.ft.), the majority of wet blues are well opened up, but tend to have the problem of loose grain and empty flanks. The processing of these 'loose' wet blues poses quite a challenge.

To achieve good inner softness and fullness a good penetration of all wet end chemicals is a must. A key factor is good neutralisation of the wet blue and in many cases a stronger retanning and the use of selective filling agents is critical.

But neutralisation increases the risk of looser grain, and too much retanning may cause a deterioration in the physical strength of the leather. A careful balance is needed, and the question is, can the neutralisation step be avoided but, at the same time, guarantee good chemical penetration to ensure inner softness and fullness?

The answer is possible through a retanning technology⁷ that is conducted at a much lower pH. A lower pH in retanning is an important prerequisite to achieve good grain tightness and full flanks, however, these leathers are usually not as soft and also have poorer dye penetration. The key is to improve penetration but at a lower pH, and this needs special acid retanning and ►



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dispersing products⁸. If these are applied instead of the usual neutralising agents, the pH can remain lower with values below pH 4. Normally a change of pH does not necessarily mean a change of the IEP (iso electric point), however, this approach lowers the IEP of the wet blue from between 6.5 and 7.0 to values around 4.

Since penetration is best if the pH value during application is close to the IEP of the wet blue, the retanning /fatliquoring and dyeing operations can be conducted at low pH and still achieve good penetration. A typical formulation of an acid retannage is given in *Panel 6*.

Panel 6: Upholstery leather formula Acid retanning technology (AR)

RETANNING/	150	Water, 30°C		
FATLIQUORING	6	Acid Retanning Agent	40 min.	pH: 2.5-3.5
	3	Acrylic Copolymer	20 min.	
	5	Tara		
	5	Syntan	60 min.	
	2	sodium formate	30 min.	pH: 4.0-4.5
	100	Water, 50°C	10 min.	
	12	New Type fatliquor	60 min.	
	1	Formic acid, 85%	30 min.	pH: 3.5
WASHING	200	Water, 30°C	10 min.	
DYEING	100	Water, 30°C		
	0.5	Ammonia		
	0.5	dye fixing agent	10 min.	
	2	Dyestuff	40 min.	
	1	Formic acid, 85%	20 min.	pH: 3.5
WASHING	200	Water, 30°C	10 min.	
Horse up, set out, toggle, condition, stake				

Although the technology works with most types of retanning and fatliquor chemicals, differences can be noticed in penetration and performance. This may be linked to the stability of the products at low pH but also to the chemical character of the product itself. This is especially true when it comes to fatliquors and syntans.

A proper application of products in acid retanning technology (AR) leads to simple recipes, bearing the possibility of reducing chemical and water use, and time in process. The main advantage, however, is to improve the useful area of hides and skins with loose structure.

New finishing technology

Over and above problems that can arise from the collagen structure, surface defects influence the profitability of leather-making and present one of the biggest challenges to the tanner.

We need to differentiate between the various types of defects. With a traditional finishing the small-sized defects such as stains, small bacteria damage, and open and scuffed grain can be covered very well. Large defects such as holes, deep open scars, brand marks and severe bacterial damage need a manual stucco application. But the most problematic defects are medium-sized defects such as tick and insect bites, small open scars and medium-sized bacterial damage.

Roll coating machines that can apply the finish coat in reverse mode on very soft leathers have changed things, enabling the

application of finishing materials based on micro-sphere technology and high performance polymer resins. Advanced helicoidal roller design has complemented the technology, allowing the finishing of large volumes of leather with small- to medium-sized defects.

At the heart of this new finish technology from the chemical side are polymer products⁹ suited for reverse mode finishing on both full grain or buffed leather. A typical application is given as *Panel 7*.

Panel 7: Typical application of pre-bottom coat with RRC

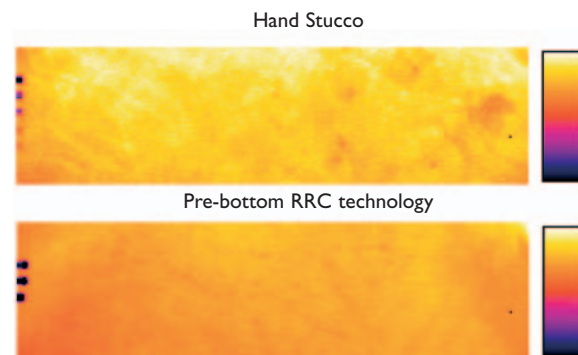
Process	Products	Quantity (full grain)	Quantity (corrected)
Application on	RODA CARE 5622	600	500
RRC machine	RODA CARE 5616	400	500
(Reverse Roll Coating)	RODA CARE Pigments	0-20	0-20
full grain: 2-3 g/sqft			
corrected: 4-6 g/sqft			
dry, rest 6-12 hrs, continue with next operation: for strong defects buff again			

The combination of finishing chemistry with specific machine settings is the key to successful application. In particular:

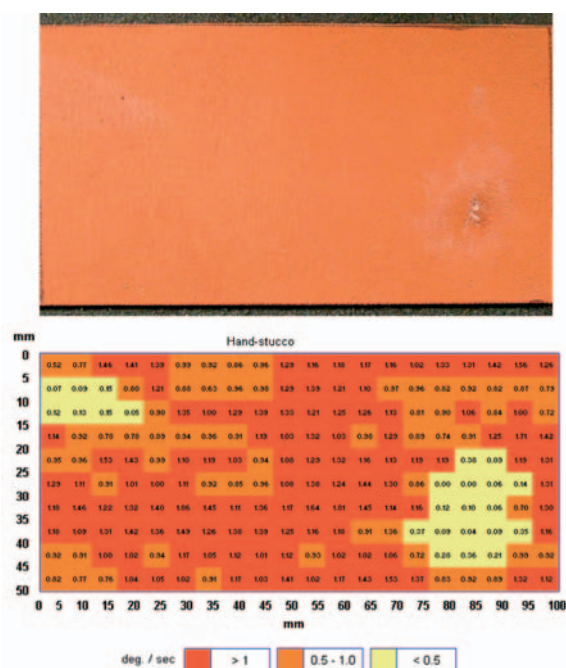
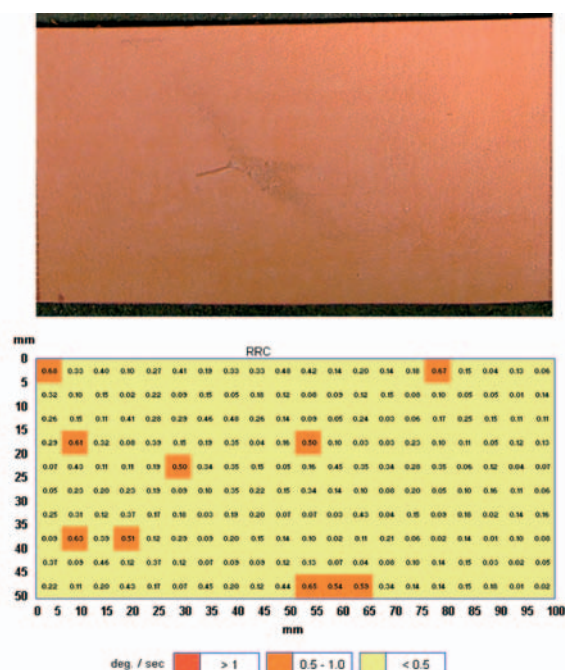
- A high speed application roller (up to 60 RPM), has a 'cleaning' effect on the surface. Defects and cavities will be filled selectively, leaving only a fine film on the undamaged part of the surface.
- A steep feeding belt angle increases the cleaning effect of the grain.
- A tight gap, in combination with the soft conveyor belt, allows selective filling effect.
- The conveyor belt speed (8-10 m/min) facilitates selective filling at high throughputs.

When compared with hand stucco application, this technique provides an almost continuous thin film on the surface. The differences between these pre-bottom coatings and hand stucco application can be assessed by means of Impulse Thermography images, as shown in *Panel 8*. ➤

Panel 8: Impulse thermography images



Raw thermal images after impulse do not show defect structures

**Panel 9: Surface tension maps - Hand Stucco****Panel 10: Surface tension maps - pre-bottom RRC**

This uniformity is also shown in *Panel 9* and *10*, where surface tension figures and dynamic contact angles were measured across the surface of a coated hide. The pre-bottom coat applied by reverse roller coat shows a more homogenous surface tension pattern. The low figures indicate the surface uniformity with no excessive spill-over outside of the defects as found with hand stucco application. A much more selective filling of small- and medium-sized defects is achieved.

Because of this uniformity of absorbency, the following base coat application can be reduced by up to 25%. More natural finishes can be achieved, resulting in a finer break for both full and corrected grain articles, hence an increase in cutting value.

Conclusion

Modern technologies allow tanners to better cope with deteriorating leather quality, and can help to add value to the final leather article. No single technology will do the job, but

attention to a combination of several criteria is essential. The goal is to add maximum value at competitive costs, thus keeping unique characteristics and performance, and prices at viable levels that provide a reasonable profit to the tanner.

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7. *Acid Compact System*
8. *SELLATAN AR*
9. *RODA CARE 5616 and 5622*
10. *VL 3118*

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