

Advances in the degreasing of hides

J.T. Pelckmans, J. Fennen, J. Christner,
TFL Ledertechnik AG, Switzerland

A new lipase degreasing product⁽¹⁾ is described that provides good degreasing when compared to the use of standard surfactants. It provides additional benefits such as improved grain tightness, better flatness, cleanliness of the hide, improved dyeing levelness, and has the potential to reduce fogging characteristics and improve hydrophobing. In addition, the replacement of surfactants by lipase offers significant ecological benefits within the degreasing process and in the subsequent treatment of wastewaters.

Natural grease

The amount of natural grease in hides and skins differs widely depending on the breed, origin, gender and age of the animal. It also varies with season. A fat content of 5 - 10% is found for pre-fleshed bovine hides, whereas pig skins may show fat contents of up to 30%.

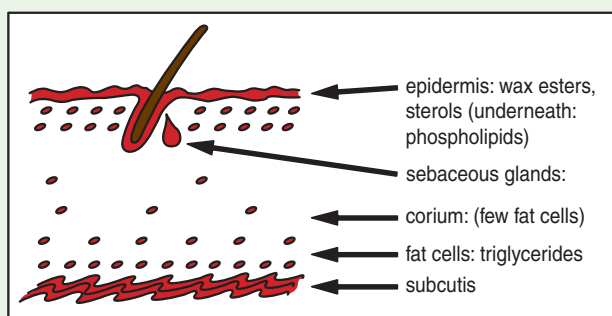
The main components of natural grease found in bovine hides are triglycerides, phospholipids, wax esters and free fatty acids, with a typical ratio as given in *Panel 1*.

Panel 1: Fat in fresh pre-fleshed US cattle hides

triglycerides	53%
phospholipids	21%
wax esters	11%
free fatty acids	10 %

The greatest part of this grease is located on the flesh side of the hide, and also in the grain around the hair follicles (*sebaceous glands*). Significantly lesser amounts are found in the corium, the general distribution throughout the cross-section, being indicated in *Panel 2*.

Panel 2: Location of grease (red) in the hide



Degreasing technology

Many studies and evaluations of different degreasing technologies have been made^(3 - 9), where the efficiency of the degreasing has been found to be closely linked to the residual fat

content of the raw hide.

In practice, an almost complete removal of natural grease is not always beneficial in terms of the quality of the resulting leather. The typical effects of a too strong degreasing are looseness, coarseness of the grain, and a decrease in physical properties such as tensile strength and tear resistance. Removing too much natural grease also means that the wastewater of the degreasing process is unnecessarily loaded with fatty substances, and this adds to the BOD/COD value.

On the other hand, a variety of problems are caused by insufficient removal of natural grease. This includes fatty based stains, bad odour, poor preservation and lack of inner softness. Any successful degreasing technology therefore has to be efficient regarding the removal of grease, but also flexible enough to avoid too weak or too strong degreasing.

Before the fat can be removed from the hide, it first has to be made accessible, and this requires the membranes of the fat cells to be broken down.

In fresh or properly chilled hides the fat cells are still intact and the fat is not easily accessible. Salt or brine curing opens the fat cells due to their hydrotropic effect, and therefore the amount of moveable grease becomes significantly greater. Hides which are pre-fleshed retain a lesser amount of moveable grease due to the removal of the high fat containing tissue on the flesh side and the fat pockets that would otherwise remain clinging to the hide. Increased temperature and the addition of proteolytic enzymes in soaking are also used to break down fat cells and make more grease accessible.

Degreasing with surfactants

In a standard process, the grease can be mobilised and effectively emulsified using a non-ionic surfactant. The addition of an appropriate second surfactant (*co-surfactant*) can help to stabilise this emulsion.

Examples for non-ionic surfactants are the environmentally questionable nonylphenol-ethoxylates, and more recently available fatty alcohol ethoxylates as these avoid the formation of problematic by-products as they degrade. Typically, non-ionic surfactants used for degreasing have an HLB (*hydrophilic-lipophilic balance*) of around 11 - 12 (*the HLB scale ranges from 0 for extremely lipophilic to 20 for extremely hydrophilic surfactants*). The co-surfactant used to keep the grease in a stable emulsion



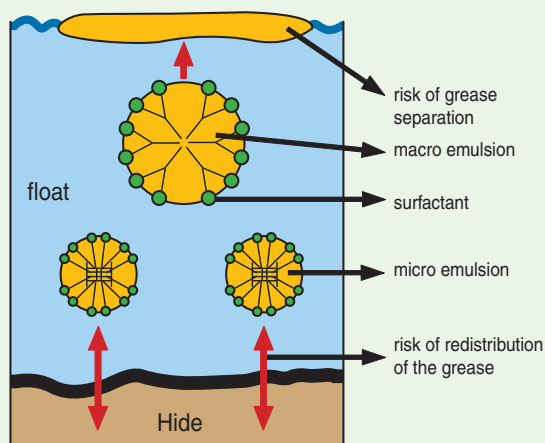
ideally would have a higher HLB value with a more hydrophilic character. Alkaline conditions, increased temperature and mechanical action support this degreasing process.

The latest generation of surfactants for degreasing combines the effects of fat extraction and very good fat emulsification. An effective degreasing of hides with normal fat content can therefore be achieved with one single surfactant⁽²⁾, although very greasy hides may need a co-surfactant or the use of more alkali.

In all cases it is important that the dosage of the surfactant is adapted to the amount of fat present in the substrate. In addition to the potential problems associated with the removal of too much grease, as previously described, an over dosage of surfactant may also lead to the formation of a finer particle sized and more stable emulsion. The effect is that this grease is then re-distributed through the cross-section of the hide. As the grease is not properly fixed to the collagen (*unlike a fatliquoring agent*) it may interfere with subsequent leather processing; for example, by forming chrome soaps or fat stains via migration to the grain surface.

On the other hand, a too low dosage of surfactant leads to improper degreasing and/or an unstable emulsion, and this can cause a separation of grease. This then becomes a layer on top of the float, or settles on the hide surface, drum walls and drain pipes as indicated in *Panel 3*.

Panel 3: Different degrees of emulsification



Lipase based degreasing

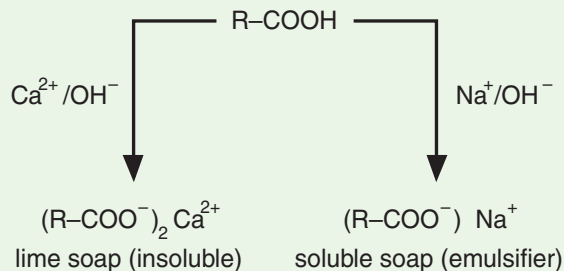
Alkalinity is a very decisive factor for degreasing, even in a standard process with surfactants. Under alkaline conditions the free fatty acids—typically about 10% of the natural fats—are transformed into soluble soaps which then act as co-emulsifiers. However, in the presence of calcium or other divalent ions these fatty acids are converted into insoluble soaps as shown in *Panel 4*.

Saponification of the triglycerides—constituting about 50% of the natural grease in the hide—also occurs under alkaline conditions. Hydrolysis of the ester bonds leads to the formation of diglycerides, monoglycerides, glycerol and free fatty acids as shown in *Panel 5*.

These additional fatty acids can be converted to soluble soaps (as shown in *Panel 4*), thus increasing the amount of emulsifier in the system.

However, under the conditions of a standard degreasing process, the hydrolysis of the triglyceride ester bonds as shown in

Panel 4: Formation of soaps from free fatty acids



Panel 5 is a slow reaction with a low turnover rate. For comparison, the traditional process of making soap involves high amounts of caustic soda and a temperature at boiling point.

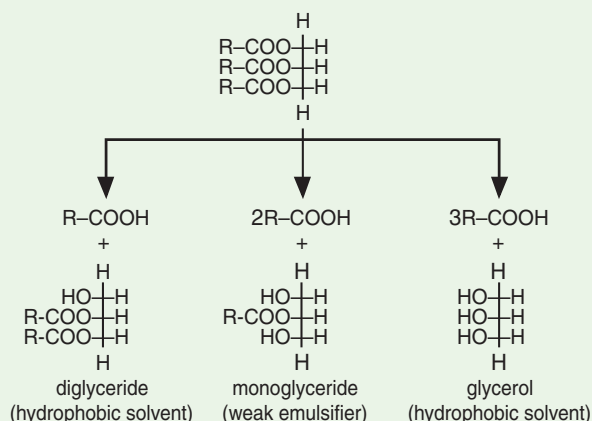
For efficient processing a selective lipolytic enzyme product⁽¹⁾ is needed as a biocatalyst to lower the activation energy of this reaction path, and thus speed up the saponification of triglycerides. This is illustrated in *Panel 6* where the turnover rate of the saponification of triglycerides is tremendously increased.

Although the possibility of using lipases for degreasing has been explored for many years⁽⁵⁾, so far the technology has not been widely adopted. It was often thought that lipases have to be used together with surfactants and only break down triglycerides and do not have a direct effect on the other grease components such as phospholipids, wax esters, or free fatty acids.

But the hydrolysis of the triglyceride ester groups, catalysed by lipase, creates chemical species with surfactant properties. Over and above the soluble soaps (*emulsifiers*) originating from the release of the free fatty acids (as described in *Panel 4*), these are mainly monoglycerides. This is because the lipase attacks selectively at the 1st and 3rd position of the triglyceride, leaving the 2nd position unchanged. These monoglycerides show surfactant-like properties, and can facilitate the removal of grease from the hide, provided that sufficient alkalinity is available. Under normal conditions, a degreasing of hides with lipase can be achieved without the addition of further traditional surfactants.

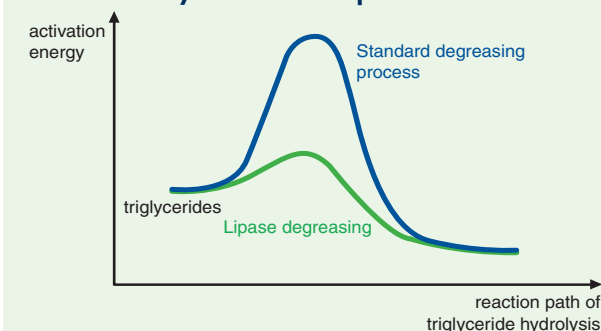
If surfactants and lipase are used together they compete, and this makes the fat less accessible for lipase attack. Accordingly, it is recommended that the lipase be used on its own with sufficient amount of alkali. In this event it is very important that the lipase tolerates alkalinity and has its maximum activity within a

Panel 5: De-esterification of triglycerides





Panel 6: Catalytic effect of lipase



pH-range of 8 - 11. Surfactant is only needed when processing very greasy hides⁽³⁾.

It is important to recognise that due to the catalytic effect of the lipase degreasing product, there is no linear relationship between the dosage and the final degreasing effect. The lipase degreasing process is intrinsically self-supporting, because a greater amount of grease results in the formation of more reaction products with surfactant properties.

This principle does, however, only work within certain limits as in practice biocatalysts 'wear out' during process. Furthermore, every enzyme molecule can only assist in the breakdown of a certain number of triglycerides within a given time frame. The turnover rate is therefore dependent on the quantity offered, so the quantity of lipase required must be adjusted according to the amount of moveable grease.

Application of lipase degreasing in soaking

The lipase degreasing agent can be used very effectively in the soaking operation as this is the step in the leather making process with the highest amount of natural grease present. And to be effective it is important to ensure a sufficient level of alkalinity. The higher the amount of moveable grease, the more alkali is needed to neutralize the fatty acids being formed and to keep the pH in the desired range between 9 and 10.

A pH between 9 and 10 can be achieved initially by using sodium hydroxide or sodium carbonate. However, the stabilisation of alkalinity can be assisted by the addition of alkaline earth metal oxides like lime. Alkaline earth ions will convert free fatty acids into insoluble soaps, but this can be beneficial as the temporary formation of a certain amount of insoluble soaps can improve the leather quality.

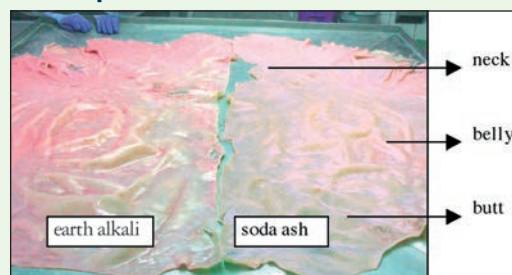
A comparison was made between two sides, both degreased with lipase in soaking. One side used soda ash to provide alkalinity, whereas an alkaline earth was used for the other side. After splitting in three layers the middle split was stained with oleophylic sudan red pigment. The belly part of the side where the alkaline earth was used to provide the alkalinity showed a darker coloured red, and this is shown in *Panel 7*.

This can be attributed to the insoluble soaps accumulating in the belly area, where they may have a stabilising effect on these looser parts against the mechanical action applied in liming. These temporarily formed soaps are removed by thorough washing after liming, or after deliming bating, and when suitable dispersing agents can be added.

Use of lipase in other process steps

Lipase has also been used at the beginning of the unhairing process, and at the start of the deliming process before the pH was lowered by the addition of the deliming agent. This enabled

Panel 7: Temporary accumulation of insoluble soaps in loose structured areas



the degreasing to be improved, but this improvement mainly depends on the amount of fat that still remains for degradation from the preceding stage.

The ability to use this product in the three processing steps described helps to eliminate the use of surfactants. In turn this reduces the degree of fogging in final leathers, and improves the waterproofing properties.

Benefits of using new lipase product

When used in soaking the lipase product provides:

- A faster and more uniform penetration of liming chemicals. This results in less draw, fat wrinkles, and cleaner hides. In addition, the levelness of dyeing is greatly improved.
- An improved distribution of natural fat, achieving a tighter grain leather with fuller bellies. This will provide better cutting values and thus higher profitability.
- Elimination or largely reduced use of surfactants. This results in processing floats where the greasy substances separate more easily, hence easier and more efficient removal via recycling within the process, or from the discharged process float.
- Significantly lower COD and also BOD values than a standard degreasing process. This is particularly helpful for tanneries which run their own biological waste water treatment plant.
- A very cost effective processing auxiliary for the beamhouse.

This information has been obtained by studies using bovine hides, and these advantages also apply for the processing of skins. However, conditions may vary, especially in the processing of pickled skins, and accordingly the degreasing of skins will be elaborated upon in a later publication. 🌐

Acknowledgements

D. Herta, A. Lenglar, M. Hess and G. Renner and other colleagues in TFL for their valuable contributions.

References

- 1) BORRON® DL registered trademark of TFL Ledertechnik GmbH, Germany.
- 2) BORRON® DN, BORRON® DNC
- 3) V. Addy, *BLC Journal*, 1996, 39, pp 81-83
- 4) R. Palop, *World Leather* 1998, 11, pp 76-81; *World Leather*, 9, pp 48-51
- 5) D. Ivanova et al, *JSLTC*, 2004, 88, 161-163
- 6) R. Nowak, *IULTCS Congress, Barcelona*, 1975, pp.58 ff
- 7) D.T. Didatto, C.F. Watson, *IULTCS Congress*, 1992, pp. 135-142
- 8) J. Christner, *JALCA*, 1992, 87, pp128-139
- 9) J. Christner, *World Leather*, 1995, 6, pp 60-62