

The structural upgrading of leather: A new micro-sphere application

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Tanners often comment that there has been a lack of real innovation in the wet end, at least for the last decade. However, the same old problems they have always been facing are getting much worse as the quality of raw hides and skins continues to decrease.

The use of thermo-expandable micro-spheres in the retanning process for structural upgrading of collagen is a technology that opens up completely new possibilities. These opportunities include improvement in leather quality, and in turn achieve higher yields in terms of area utilisation with a more regular surface appearance.

This new technology is an intelligent combination of chemistry and physics. It consists of a new functional product, a special polymer dispersion that contains the micro-spheres, and a new, customised expansion technology.

This polymer dispersion—known as Levotan X-Cel—contains compact micro-spheres of an average diameter between approximately 5 and 20 μ . These spheres, which are filled with a liquid gas, can expand up to 40 times their original volume size into much bigger micro-cells by a thermal activation treatment.

The use of this polymer dispersion that contains micro-spheres always has to be followed by an expansion step. During this expansion process the liquid gas in the unexpanded micro-sphere converts into the gas phase. The pressure inside the sphere becomes reduced, and the density of the particle changes significantly from ca. 1000 g/dm³ in the unexpanded form to ca. 30 g/dm³ in the expanded form. It is important to know that in both the unexpanded and expanded form the shell of the micro-cells is absolutely impermeable. The gas cannot escape without the destruction of the cell itself.

Micro-spheres and the expanded micro-cells in both forms have a high resistance to chemicals such as retanning and finishing polymers. Furthermore, the expanded form of the cell is not hard, but highly flexible and resilient.

For a better understanding of dimensions, you can compare this process of expansion with the following macroscopic picture: it is like immediately transforming a tennis ball, which is filled with a liquid gas, into an elastic gymnastic ball. These expanded spheres can reach dimension of 100 - 200 μ m and are perfectly suited to fill loose areas and defects. They fill open areas and defects without increasing the density of leather and have an elastic structure.

The incorporation of the micro-spheres in leather

One of the main reasons for the use of micro-sphere technology in the leather making process is the upgrading of the

internal structure of leather. This completely new application for the leather industry gives the tanner a lot of new opportunities to upgrade lower quality leather—something tanners have long wished for.

This new application consists of:

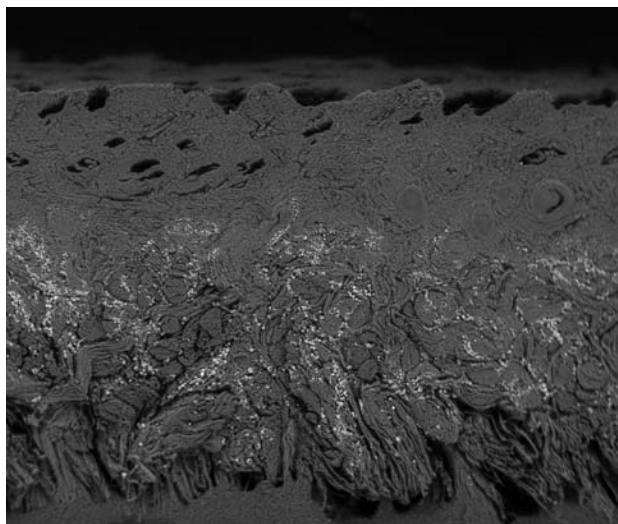
- the addition of a special polymer containing the unexpanded micro-spheres in the wet end process.
- an expansion step of the leather at a later point in the process with a customised, new expansion technology.

The micro-cells, through expansion, can fill open and loose areas inside the leather. It can be described as a type of “internal stucco” to upgrade the structure of leather.

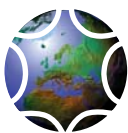
The polymer containing micro-spheres is added in the retanning step at a relatively early stage of this wet end process. It is a combination of several parameters—the right size of the micro-sphere, the right product formulation and the right penetrating polymer dispersion—that results in a high exhaustion rate of the micro-spheres of more than 95%.

Conventional processing, with normal pH and temperature conditions, and equipment are used to produce the usual leather types such as furniture, automotive, shoe upper and leather goods. Due to the relatively long but normal running time in the drum during the retanning process, the micro-spheres ➤

Panel 1: Penetration of micro-spheres into the leather structure during retannage

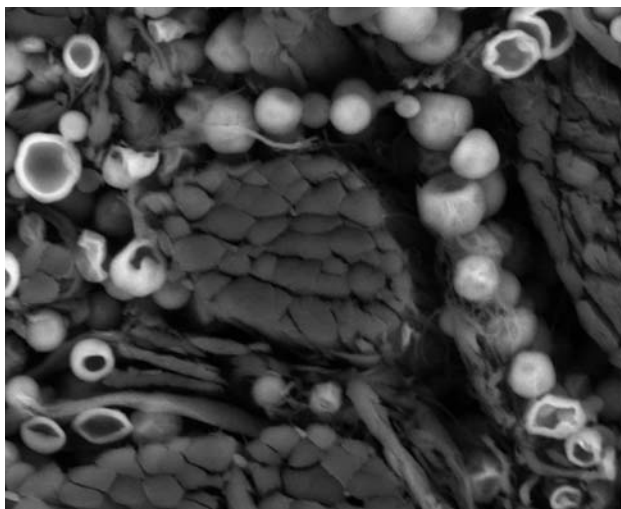


Unexpanded micro-spheres penetrate from the flesh side, through the more open structure, towards the blood vessels and other voids.



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Panel 2: Micro-spheres in open spaces in the corium layer

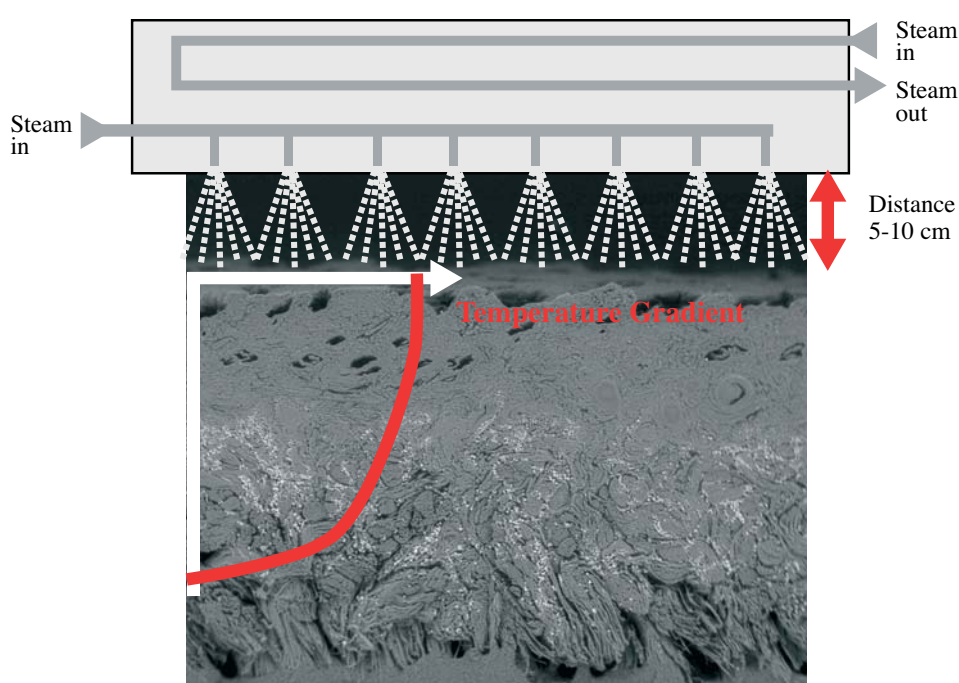


Magnification of Panel 1; still unexpanded micro-spheres in open spaces in the corium layer.

penetrate deep into the leather and reach their optimal distribution. Their distribution is based on a normal physical diffusion process and it has been shown that the unexpanded micro-spheres end up predominantly in loose areas and voids such as blood vessels. This is shown in *Panels 1 and 2*.

In comparison to conventional retanning chemicals, which are usually fixed chemically by functional groups to the collagen, the distribution of these micro-spheres is by diffusion. This means, their final distribution in the leather is complementary to that of conventional retanning chemicals. Therefore, through expansion they can “fill” areas inside of the leather in a manner that cannot be achieved by syntans, retanning polymers or resins.

Panel 3: Activation of micro-spheres by applying steam



Once the micro-spheres have been added to the process, retanning and drying processes follow as usual. Investigations have clearly shown that no significant expansion happens to the micro-spheres inside the leather during these subsequent steps under normal conditions. One can conclude that the temperature inside the leather is not high enough to activate the micro-spheres at this stage.

Activation of the micro-spheres in leather

Since the standard drying process through vacuum or toggling is not sufficient to activate the unexpanded micro-spheres, an additional process step is required for activation. This is performed using a special machine where the dry crust leather is passed through a channel where it is treated with a hot, saturated steam for several seconds only. This is indicated in *Panel 3*.

The hot steam penetrates into the leather without making it wet, and the humidity transports the temperature within seconds inside to the unexpanded micro-spheres. These special conditions of humidity and temperature lead to a softening of the shell of the micro-spheres, and they expand immediately to form the much larger micro-cells.

The size of expansion depends on the structural environment of the particle. If it sits in a loose area, it will increase in size significantly (up to 40 times), if it is in a tighter area, the expansion will be much more moderate.

Once the micro-spheres are expanded, they can not be removed, and permanent elastic filling has been achieved as indicated in *Panel 4*. The voids, veins, and loose parts in the corium are filled with the micro-cells, but without making the leather heavy and hard.

Increase in thickness of final leathers

Depending on the amount of micro-spheres offered during retanning, open areas are not only filled after expansion, but there is also a significant increase in the overall thickness of the final leather. The leather can be ‘pumped up’, and an increase in thickness of between ca. 0.2 mm to 0.8 mm (from 1.2 mm up to 2.0 mm) in thickness is possible.

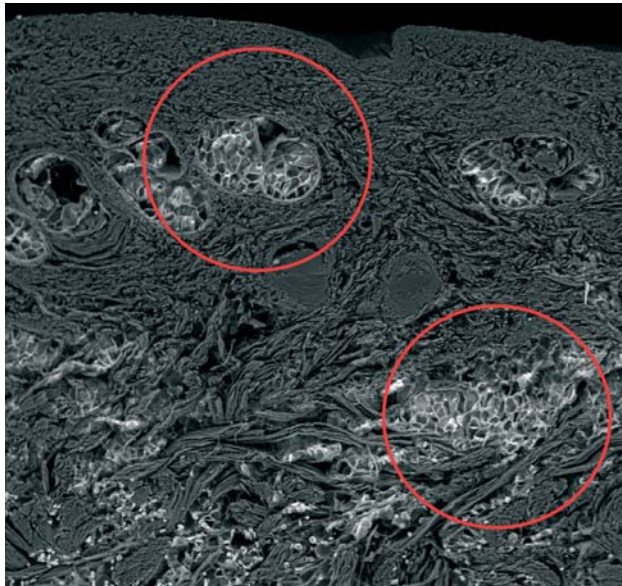
The magnitude of thickness increase depends very much on the type of leather—mainly the tightness of the fibre structure—as well as pre-treatments, such as milling of the leather, before expansion. This is shown in *Panel 5* in the two curves for two different types of leathers. While adding the same amount of 6% X-Cel, the resulting increase in thickness was respectively 20% and 60% of the two original crust leathers. The thickness increase can be controlled by adjusting the expansion conditions and by varying the quantity of X-Cel applied.

A significant increase in thickness, if desired, can lead to a reduction in

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Panel 4: Open areas, blood vessels and other voids inside leather are selectively filled with expanded micro-cells

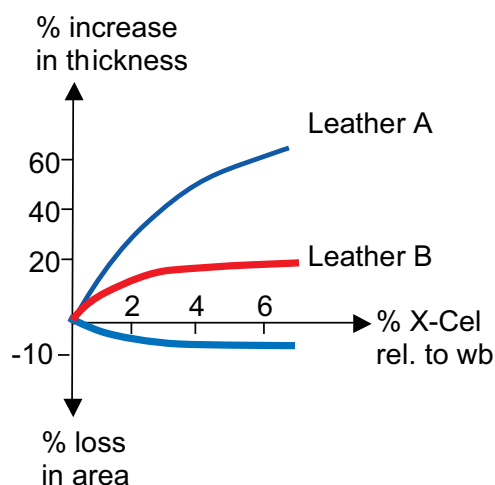


area. A reduction of between 2% and 10% of area reduction has been observed at a thickness increase of 60%. However, if focussing on just upgrading, and not thickness increase, the area can be maintained.

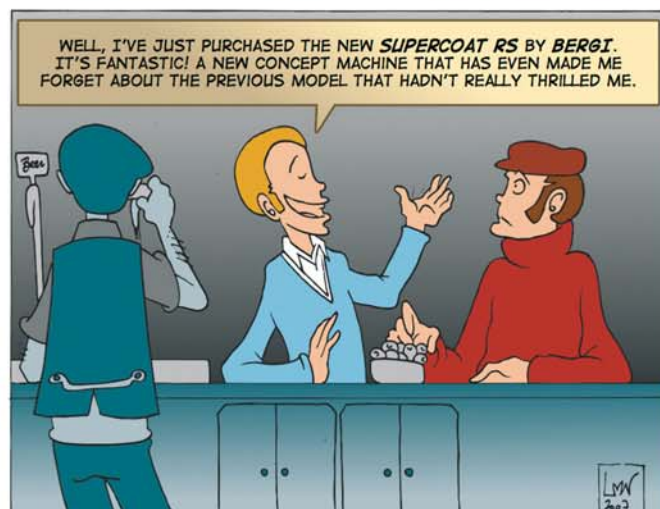
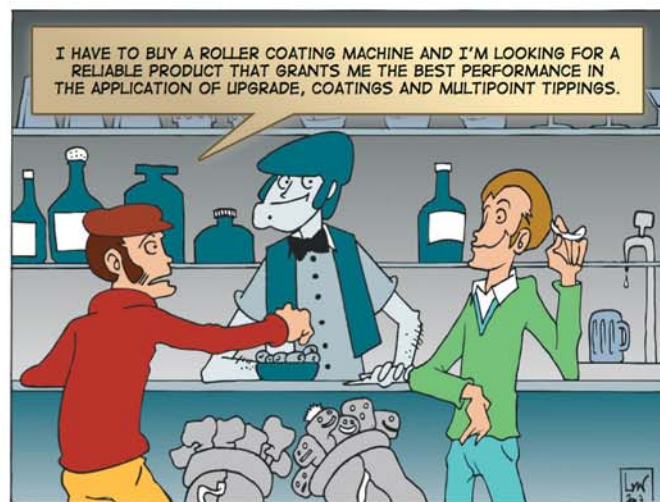
The absolute values for tear strength of leather does not decrease with the increase in thickness. The leather keeps its strength, with the tear strength in relation to the thickness becoming smaller. Other important values, such as water transmission and water absorption will be improved by filling the voids and small holes with micro-cells.

Moreover, since open areas are filled evenly and the soft and elastic micro-cells are not fixed inside with a binder, the leather becomes soft after milling while maintaining the increase in the thickness and filling effect. ➤

Panel 5: The thickness increase of two different leather samples



The increase in thickness of samples. A correlates with a loss in area of between 2 and 10%



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It is noted that the expansion step can be performed at a later or earlier point in the process, say, after finishing or prior to drying the crust. Milling of a dried leather, especially prior to expansion, has led in some cases to a significantly better structural filling. Both the right point of process stage and the right parameters for this expansion step have to be evaluated case by case, and depend on the article and the specific upgrading requirements required.

New opportunities in leather-making

This new technology has been tested in many areas of leather application. Wet blue from zebu, cows and bulls were used and compared, with expansion performed on both split and full grain leather. Many main leather articles were tested, including finished and milled articles, etc. Not everything turned out to be successful, but the focus has been on three main applications:

- The elimination of veininess
- The reduction of looseness
- The general increase in substance

After the optimisation of parameters such as micro-sphere concentration and expansion conditions, it has been clearly demonstrated the system can be of significant value to the leather industry. Many other applications can be envisaged and need to

be studied carefully, for example:

- Firm, waterproof applications
- The substitution of other filling chemicals such as vegetable tanning agents.
- The substitution of products which show problems in terms of yellowing.
- The repair of "off spec" material in tanneries, such as leather with inadequate substance.

Micro-sphere technology is an innovation, which opens up completely new possibilities for the tanning industry. It can be used as an internal, structural upgrading of lower quality leather: this can lead to a tremendous value increase of the final article due to the increase of cutting yield, increase of thickness and improvements of certain characteristics.

Micro-sphere technology will be seen in a decade from now as a real milestone in the history of wet end technology. 🌐

Acknowledgement

We wish to thank Mr Phillip Schaefer, who has made the breakthrough for this new wet end technology by his initial invention of expanding micro-spheres by hot steam for finishing applications. The encouraging discussions with him throughout the development phase of this wet end technology at Lanxess were more than helpful, and have encouraged us to stay on track and reach a successful result.

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