

Credit: Taneka/Premiere Vision

Tackling “veininess”, Part two

Christopher Tysoe and Christopher Henzel, Lanxess

The second and final part of a paper from Lanxess examining the best strategy for addressing the problem of veininess in hides. The first part appeared in World Leather December 2016-January 2017.

“PTA” (Preparation and Tanning) HIDE AND/OR SKIN PRESERVATION

Preservation can be relevant to veininess. There are two main processes that start immediately upon slaughter. First, autolytic cell destruction occurs in dying tissue and is initiated by the cells' lysosomes releasing digestive enzymes into the cytoplasm. Second, microbial digestion – as soon as the animal is slaughtered the auto-immune defense system keeping bacteria at bay ceases and the hides or skins are immediately at risk of putrefaction. (Bacterial cells vastly outnumber, by a multiple, animal cells so the risk of putrefaction is both high and immediate unless counter measures are taken). Furthermore, bacteria are ubiquitous (Fig 5) in the environment and will also enter the hide. Sanitation and plant hygiene reduce contamination from the immediate working environment. Water, if not from public source, should be chlorinated.

Adequate preservation is always important, but can be tannery specific. For example, those tanneries in the immediate vicinity of the supplying slaughterhouse can process hides and/or skins without delay and tend to use less preservation. Furthermore, those with a high standard of tannery/plant hygiene and the hides are immediately chilled, which slows down enzyme action, then the need for the addition of chemical preservation agents is also reduced. However, if any unplanned significant delays occur then the hides are immediately liable to putrefaction, and an increase in the appearance of veininess, a costly consequence of omitting preservation agents.

SALTING

Salting is a basic form of preservation, it renders the water that's available for most microbes unusable, although there are exceptions – halophilic bacteria “red heat” (Fig 6).

Furthermore, hides contaminated with manure and/or blood keep poorly regardless of the amount of salt present, so protection with a state-of-the-art antimicrobial is essential. Brine curing of hides will tend to produce cleaner stock, thus easier to preserve.

If measures cannot be taken to avoid veininess up to this point, then the next possibility is in the beamhouse and here the effect can be reduced by:

SOAKING

Effective removal of hyaluronic acid is crucial for a uniform and fast penetration of chemicals during the following process steps. In traditional processing a longer soaking time is considered beneficial. This on the other hand increases the risk of more microbial and proteolytic activity which will lead to more veininess. Damage resulting from microbial activity can be largely avoided by the application of preservatives in the soaking. However, the natural enzymatic proteolytic activity cannot be stopped in soaking. It is therefore necessary to speed up the soaking process to keep the attack on the veins at a minimum. A patented soaking technology⁽⁹⁾ based on a unique glucanase⁽⁶⁾ can reduce the likelihood of veininess compared to conventional processing. Here, the enzyme accelerates the removal of hyaluronic acid by cleaving parts of dermatan sulphate proteoglycan in the fibre structure while not attacking the leather protein collagen (also in blood vessels, more so in veins) and elastin in the leather matrix. This non-weakening of the blood vessels reduces the likelihood of veininess compared to conventional processing.

LIMING

To reduce veininess the control of swelling during liming is crucial⁽¹⁰⁾. Excess swelling accentuates looseness around the blood vessels resulting in their appearance becoming more



obvious. Traditional liming uses a relatively strong degree of swelling for “opening-up” and conditions of high alkalinity (e.g. sodium sulfide) to achieve this. The quantity of sulfide has an impact on alkalinity and thus on veininess⁽¹¹⁾. Swelling can be to some degree controlled by applying regulators commonly based on amine compounds. Organic sulfur compounds like mercaptans were also used to reduce the amount sodium sulfide needed. However, there are downsides to these products including elevated effluent values. A superior environmental and technical solution is available based on a patented enzymatic unhairing system⁽ⁱⁱ⁾⁽¹²⁾ which reduces the amount of sodium sulfide required to the absolute minimum. In turn the alkalinity and swelling is dramatically reduced and so veininess is either avoided or its likelihood of appearance significantly reduced.

BATING

Enzymatic bating has to be carefully controlled to avoid an attack on the blood vessels. Traditionally in bating protease based enzymes have been applied, however, excessive breakdown of the protein elastin will result in voids around veins and thus pronounced veininess. This can be minimised by the application of a special non-elastolytic enzyme⁽ⁱⁱⁱ⁾. Unlike traditional, natural, animal extracted enzymes which contain a “wild mix” of enzymes, it has a high degree of purity of a single selected protease, due to its synthetic engineering and production.

CHROME TANNING

It is critical that all reasonable steps are taken in the beamhouse to minimise veininess before tanning. This next process “fixes” the blood vessels and is decisive in how they will react to subsequent application of retanning chemicals. Collagen of the blood vessels must be tanned to the same degree as the surrounding hide collagen. Uniform chrome penetration is essential before fixation takes place, especially when tanning full substance. The neck area is more commonly affected by less uniform through tanning which can ultimately result in pronounced veininess. In order to mitigate this it is important to have a constant pH course during basification, without pH “spikes”, after an adequate penetration of the chrome has been achieved. This uniform chrome content in the cross-section is easily achieved through the application of a safe, efficient, one-shot and high exhausting basification product^(iv) which has the added advantages of more tightness and more uniform intra- and inter-hide wet blue colour.

“CRU” / “CRUSTING”

(from wet blue to ready-for-finishing crust)

Tanneries not employing the latest enzyme technology in the beamhouse or having to buy wet blue need to consider all options in retanning to minimise veininess if they cannot avoid the problem through sourcing. Pronounced blood vessels either “tanned in” or “under-tanned” in the wet blue stage usually require all weapons at your disposal to tackle them. Wet blue for storage and/or transport should be adequately preserved to avoid any veininess being exacerbated. Here a eutectic preservation^(v) system is recommended due to its known high penetration and distribution thus ensuring that all blood vessels are reached with high efficacy, long lasting effect and broad range spectrum of activity⁽¹³⁾ to give maximum protection from fungal attack at this pH.



Fig 5: Lanxess microbiology labs can detect not only fungal but also bacterial growth.

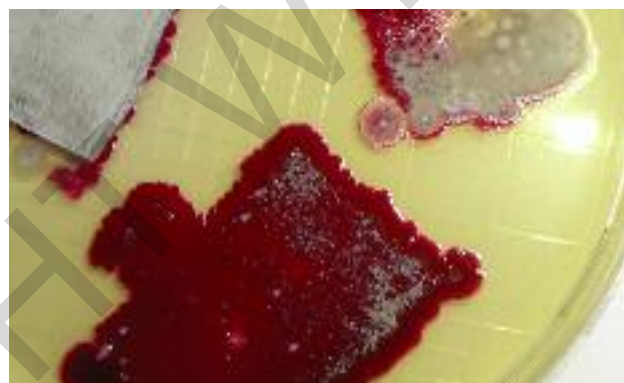


Fig 6: Red microbial growth detected at a Lanxess microbiology lab.

MECHANICAL OPERATIONS

Splitting and shaving, for example, can have an effect on the appearance of the blood vessels which run horizontally on the flesh side. Therefore, with a pack suffering with veininess it is important to consider, if possible, allocating this to an article requiring a substance which will either remove it or not require splitting in this area. This will mainly impact suede leathers. Horizontal blood vessels close to the grain layer, in or near the grain corium junction, obviously present the biggest challenge.

RETANNING

We hear a far higher proportion of complaints referring to chrome tanned leather than, for example vegetable tanned. Chrome tanned leather is more susceptible to veininess since, unlike vegetable tannages, it has no real filling action⁽¹⁴⁾. Chrome tanned leather is a “clean tannage” and you can clearly see the bands on fibrils under an electron microscope, as tannage takes place within fibrils. With a vegetable tanned leather a large amount of material is deposited between fibrils/fibres. A rational interpretation of this is that a higher degree of retanning of chrome leather is beneficial to the reduction of the appearance of veininess. Obviously, for most chrome based articles, it is not possible to simply give a massive vegetable retanning to reduce veininess. However, the tanner now has available a vast array of retanning weapons to help tackle veininess. Filling, in particular, is a critical feature to look for in retanning products; this not only helps to fill blood vessels directly but also is important to support surrounding tissue. Making the leather



less compressible, if the final article allows, and avoiding compression of the leather in finishing if possible, also helps to reduce the likely appearance of this defect⁽¹⁵⁾.

RECHROMING

Traditional chrome syntans have only a minor effect on veininess if a proper chrome tannage was carried out, taking all necessary precautions. However, if a genuine “upgrade” of wet blue is required, as is with veininess affected stock, then the application of a slow acting rechroming product which incorporates reactive complexing and neutralising functionality^(vi) is recommended. Such a product has a strong filling and tightening effect on wet blue, beneficial to the reduction in appearance of veininess. Apart from that the chrome uptake/exhaustion is also improved by fixing unbound chrome coming from the tannage. This rechroming product is completely different to traditional chrome syntans which are more focused on, for example, levelling out surface charge to influence dyeing properties. However, such rechroming product should not be used to substitute a proper chrome tannage, but if buying wet blue it is the best recommended alternative.

SYNTANS

PCS (polycondensed sulphone) syntans, possess key advantages over common phenolic syntans including low residual monomers, high tanning ability, high fastness properties (to both light and heat) and, above all, most relevant for veininess, superior filling effect,⁽¹⁶⁾ due to, at least in part, their relatively high molecular weight. In our experience we have learned that high molecular weight PCS syntans seem particularly promising for a reduction in veininess^(vii). Furthermore, influencing the molecular weight distribution in our next generation syntan can further improve this effect of tackling veininess^(viii). However, with serious cases of the defect, PCS syntans alone obviously may not be sufficient to fill the actual blood vessels themselves, but highly effective in stabilising supporting tissue and should be considered in combination with the following tools.

FATLIQUORS and LEATHER SOFTENING TECHNOLOGY

Fatliquoring helps prevent collagen fibres from sticking together during the drying process. As blood vessels are also composed largely of collagen it is vital that these are equally, adequately and permanently lubricated as the rest of the leather. Inadequate softening will result in more pronounced veininess. Certain softening products can also contribute to filling such as synthetic polymer softeners including PCA-polymer based products^(ix). This technology⁽¹⁷⁾ offers numerous advantages over traditional products, including high and permanent filling effect. Filling, together with lubrication, allowing otherwise stiff blood vessels to flex with the surrounding leather, helps to reduce the appearance of veininess but again alone may not be sufficient to overcome the defect.

RESINS

Genuine resins are most probably the biggest particle sized chemical products on the market today and thus better at selectively filling loose structured areas, including blood vessels, than other classes of products. Veins particularly prominent in the belly regions of dairy cattle would be

preferentially filled by the selective action of such genuine resins. Unfortunately the application of resins in the automotive leather has been reduced in the recent past which limited their application for the tackling of veininess. This was due to two main issues. First, increasing specifications on restricted substances (if formaldehyde is used in their manufacture, there is the risk that traces may be detected in the final product). Second, abuse of inappropriate test methods that liberated formaldehyde through hydrolysis that otherwise would have remained in the structure of the product and/or leather. This problem was solved with the development and introduction of the world's first formaldehyde free resin^{(x)(18)} which now allows us to better tackle veininess with this product class including in automotive.

ACRYLICS

Acrylic polymers not only help to stabilise blood vessel supporting tissues but also – with high enough molecular weight – directly contribute towards filling of blood vessels. It is also possible to select the highest molecular weight products within this large group in order to optimise this filling effect, especially in the vein affected belly regions. Acrylics help preserve the chrome character giving “bounce”/“spring” and help to mitigate the effects of a lone heavy vegetable and/or syntan retanning and potential recovery after compression. Different retanning agents affect the flatness or plumping, as opposed to just filling, of the leather and acrylics are no exception. For example, when plumping is deemed to have a positive effect on the appearance of veininess in a given formulation together with good filling then the addition of a special preparation of polycarboxylic acid polymer^(xi) is recommended. However, as dispersing of higher molecular weight polymers can be a challenge and for veininess where penetration is particularly important, a polyadduct product containing carboxyl groups^(xii) is necessary to ensure the acrylic reaches its target.

NEW CLASS OF RETANNING PRODUCTS BASED ON RENEWABLE RAW MATERIALS

Sustainability is not just a trend but increasingly a necessity for the leather industry. Thus innovative systems not only have to tackle defects like veininess but also to fulfill the latest sustainability and other requirements placed on the industry. An entirely new class of patented retanning products⁽¹⁹⁾ was launched that are not based on oil and formaldehyde is not used as a raw material, nor can it be generated. They are synthesised in a way that no significant neutral salts are generated and feature zero VOC and neutral smell. Residual floats have low COD together with superior biodegradability. These products are not comparable 1:1 to any existing retanning products, but are designed to improve leather quality and performance specially regarding the key performances such as dyeing, tightness, and particularly of relevance to veininess, fullness depending on which product chosen. The one behaving most similarly to a resin^(xiii), due to its high selective filling effect, is particularly recommended to help reduce the appearance of veininess. Furthermore, as a full retannage is more beneficial to the reduction in veininess, as this class of products has a more natural touch, being based on natural raw materials, higher offers can be applied with less negative influence on the final crust character.

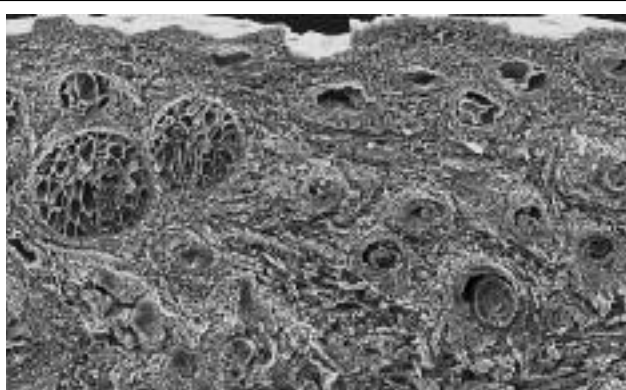


Fig 7: Microspheres in position in blood vessels and thermally expanded to support the grain surface reversing a previous concave veininess effect.

LIGHTWEIGHT HOLLOW POLYMER MICROSPHERES

There are two main classes: (a) Non-expandable (i.e., fixed shape and dimensions) and (b) Thermo-expandable (activated by heat).

(a) **Non-expandable microspheres** can be classed as an "inert filler" and we have been selling these for decades^(xiv) with a particle size starting at about 0.4-0.45 micrometre. This gives them, as opposed to others commonly found in the market, distinct penetration, distribution and ultimately superior direct filling of blood vessel advantages. Although these give excellent filling, especially in the more open looser structures, they cannot replace resins, at least not completely. They reduce the appearance of blood vessels by penetrating the leather mainly from the flesh side and fill all voids big enough to accept them, filling and supporting the vessels so they do not collapse. These microspheres give an optical lightening effect, bright clean dye shades and can replace minerals commonly used like titanium dioxide; thus not only veininess but the appearance of other grain defects and "chalking" can be simultaneously reduced. As these products are effectively inert they can be applied at various process steps, their penetration depending primarily upon mechanical action. However, despite being inert, exhaustion is very high, VOC very low and they are manufactured without ammonia, formaldehyde nor APEO products, so our ideal for tackling veininess even in demanding high specification automotive leather applications.

(b) **Thermo-expandable microspheres:** The first of these products were initially successful in the automotive leather producing industry, a unique "physicochemical". Non-expandable types can reduce the specific weight of the leather by substituting a proportion of products that add weight, but the degree of weight reduction is quite limited. However, thermo-expandable types not only substitute "heavier" products but also have been proven to reduce the weight of leather by up to 20%⁽²⁰⁾. Thermo-expandable microspheres are primarily applied for specific weight reduction in the automotive leather industry currently, but like their non-expandable relatives due to their small initial particle size, they also fill empty blood vessels to avoid their later collapse. The added advantages of thermo-expandable microspheres regarding veininess is that, first, when blood vessels are already collapsed on activation of the product this concave "cave-in" is directly and instantaneously reversed

(Fig 7). Second, this is genuine "selective filling" and on a level unmatched by any other product class, as the microspheres may, depending upon the void size, expand in-situ by approximately 40-50 times their original size. Initial prototypes could admittedly lead to over expansion of blood vessels, however, the latest and successfully selling version^(xv) is applied to milled leather articles under carefully controlled conditions for automotive applications with excellent results. We continue to work on the application for more challenging non-milled articles.

CONCLUSION

Veininess is a complex and very often misunderstood phenomenon and its origins lie in livestock issues. If you cannot avoid the supply of hides or skins with this defect then all the latest innovative technological weapons at your disposal in both Preparation and Tanning as well as in crusting need to be seriously considered and with an increasing eye on sustainability. We have pointed out the numerous key process steps and products that can directly have an influence on this defect but we can only briefly scratch the surface in such an article. Obviously the effect on veininess varies between not only the application of different products but also under which conditions they are applied and so the optimum recipe for this defect resolution needs careful control and we recommend consultation with a competent technical support service. Lanxess is uniquely positioned including with patented products and systems to better attack veininess. ☺

References:

9. Henzel & Tysoe et al World Leather Aug/Sept 2013.
10. BLC / Michel, Leather International Jan 2002.
11. CTC / Hans, Leather International May 2008.
12. Tysoe, International Leather Maker May/June 2014.
13. Rehbein & Tysoe, World Leather April/May 2011.
14. BLC Leather International Oct. 2007.
15. Covington, The Science of Leather 37-38, 2009.
16. Tysoe, Leather International Oct. 2013.
17. Reiners & Tysoe, Leather International Oct., 2008.
18. Tysoe, World Leather April 2007.
19. Tegtmeyer, World Leather Aug/Sept. 2014 and Tysoe Leather international Sept. 2014.
20. Tegtmeyer & Tysoe, World Leather Nov. 2007 and Tegtmeyer & Tysoe World Leather Oct/Nov. 2009 Figs. 2/3 Wikipedia

- (i) Peltec® X-Zyme*
- (ii) Peltec® X-Zyme*
- (iii) Peltec® BG
- (iv) Blancorol® BA
- (v) Preventol® U-Tec G
- (vi) Blancorol® RC
- (vii) Tanigan® VR
- (viii) Tanigan® FT
- (ix) Levotan® L
- (x) Retingan® ZF/Plus
- (xi) Luekotan™ 8090
- (xii) Levotan® C-01
- (xiii) Levotan X-Biomers® RX Liq
- (xiv) Leukotan™ FW-2E
- (xv) X-Lite® Z

*in partnership with Novozymes A/S, Denmark