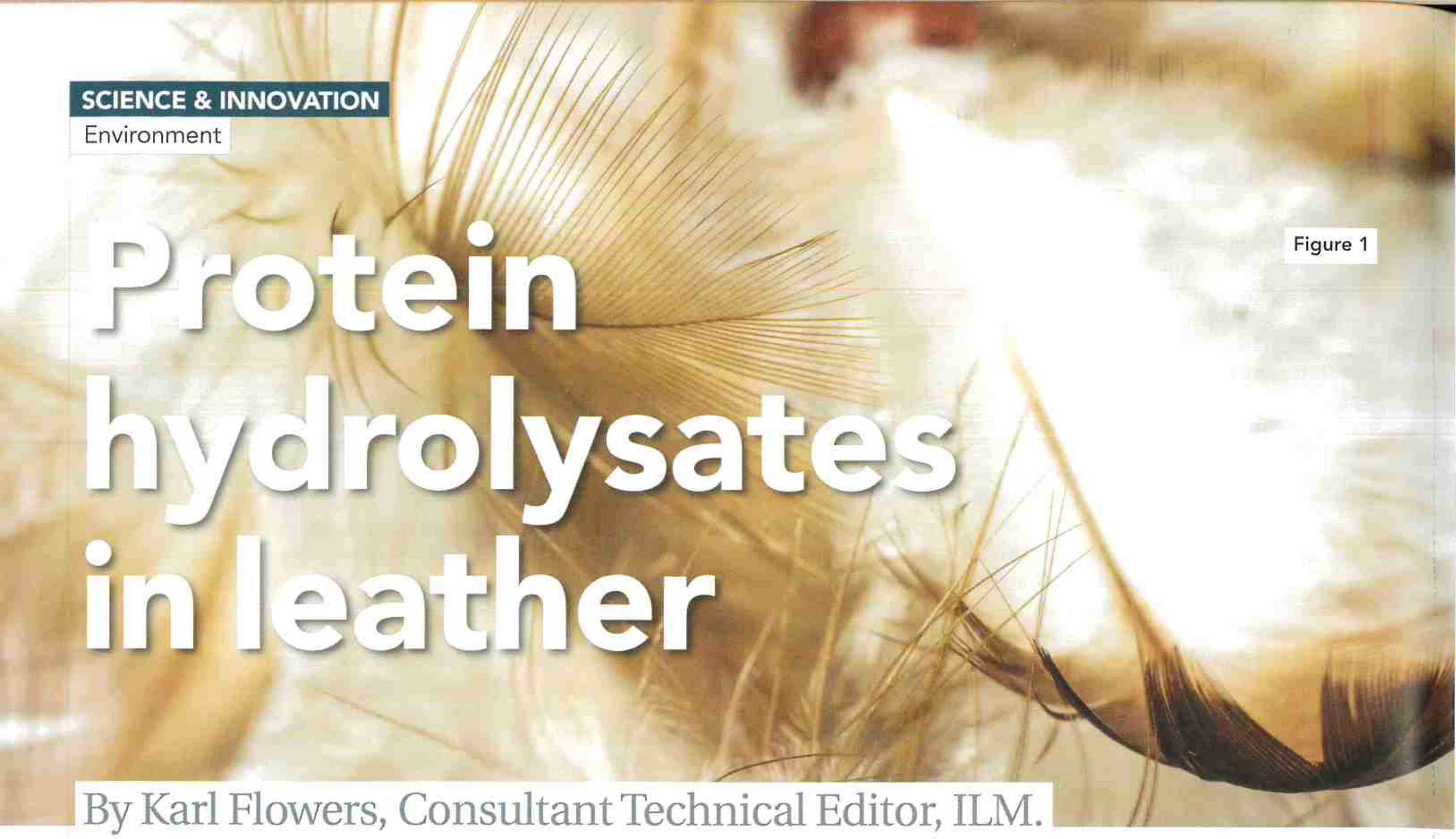

Figure 1

Protein hydrolysates in leather

By Karl Flowers, Consultant Technical Editor, ILM.

At the 7th Leather Days held in Freiberg on June 14, Dr Dietrich Tegtmeyer, Lanxess, and Brendan Wynne, Heller-Leder, reported on the scaling up of the inclusion of protein hydrolysates into the upholstery leather produced at Germany based tanners, Heller-Leder. The reason this should be news to everybody is that the technology is not going to go away and makes better use of all starting raw materials that are going in to the leather industry – a positive trend the leather industry needs to embrace.

The permissible re-allocation of upstream carbon footprint from a primary product to a co-product, depends on whether the co-product has value or not. In other words, is it a waste, a non-determining (by-product) or determining product? Upstream carbon footprint cannot be allocated to wastes, which is one of the reasons why leather does not compete as favourably with alternative materials.

Leather waste, potentially recyclable, could be sold to a third party, potentially unlocking re-allocation of the upstream carbon footprint. This inclusion of the recycled product in the leather making process (as you would another chemical) would then add the chemical's production carbon footprint to your leather process. Of course, you would be lowering the production footprint of the final leather by a net sum of:

- reduction to the process carbon footprint (due to re-allocation),
- the reduction of an amount due to the loss of a chemical displaced by the recycled chemical
- an amount added from the new production carbon footprint of the recycled chemical.

The sharp eyed among you may state that the full re-allocation should not take place if the recycled material re-enters the leather process, except that partial allocation does not fall within the rules of ISO 14067: 2014, so re-allocation would not be allowed.

What are the hydrolysates?

Hydrolysates have been used in the industry for a very long time. Casein and gelatine-based hydrolysates have been applied onto leather as finishes, as have proteins used as fillers in sole, shoe upper, upholstery, and leather goods leathers. Since the 1970s, the emergence of using breakdown products of feathers and removed hair has been typical. Initially used as a chromium saver (increases the uptake of chromium) and later as a filler in the leather.

The early 2000s saw protein hydrolysates from the dairy industry (whey protein) being used in the retanning of many leather types (Karthikeyan et al., 2007). More recently, an increasing number of chemical companies have included a selection of collagen hydrolysates in their ranges. Typically, the companies would take waste shavings from large tanneries and they would digest the materials into a soluble hydrolysate, which could be included into the leather to help with filling (Ramamurthy et al., 1989). No increase in shrinkage temperature would be seen so the product added could not be called a tanning agent.

Interestingly, the idea of using the wastes of the tanning process, which comprise largely of proteinaceous substances that are re-processed in the tannery into a filler, is the next step in improving the sustainability; more specifically, the biodegradability of the leather. Tanneries can quite easily convert trimmings, hair, connective tissue (from fleshings), and chromium-free shavings/buffing dust into protein fillers that can be added as filling chemicals. The use of chromium-containing solid wastes will need to make use of a chromium extraction method first. These methods would often use detanning (by alkali, enzyme, or thermal methods) prior to hydrolysis. In many cases, these pre-treatments may enhance the yield of the breakdown process. The conversion of the proteinaceous wastes into useful hydrolysate will never be 100%, and there will always be some residual product that will need to go into a composting process.

> "Tanneries can quite easily convert trimmings, hair, connective tissue (from fleshings), and chromium-free shavings/ buffing dust into protein fillers that can be added as filling chemicals."

How do they work?

The proteins from which all the hydrolysates are derived are generally large proteins that are structural and complex in their composition. The proteins are then attacked using (separately or in combination) enzymes, heat, acids, or alkalis (Colantoni, et al., 2017). These agents begin to weaken the proteins, generally on the peptide backbone, resulting in fragmentation of the protein into smaller peptide sections. The molecular weight of the resulting fragments is randomly created, and the hydrolysates would show a normal or binomial statistical distribution. The chemistry resulting from an uncontrolled hydrolysis would produce a variable quality, that would not be described as a technical grade. Performance of the hydrolysate may need to be standardised if the product consistency is to be predicted.

Figure 2

Functionality

The protein functionality depends on the origin of the protein. The amino acid content of the hydrolysate will be different if obtained from hair, whey, collagen, or feather. In general, the amino acids will contain acidic side chains and basic side chains that will be of interest for the tanner. Like the leather collagen, these amino acid sidechains can form increased binding sites for the tanning chemicals. The peptide fragments will show an increasing number of terminal carboxyl and amino groups that increase the hydrolysis proceeds, giving smaller fragments.

As a chromium saver, the keratin hydrolysates have a high number of aspartic acid groups and this can bind increasing amounts of chromium (Ramamurthy et al., 1989). The amino groups on the hydrolysate will bind to dyes, retanning agents and fatliquors, as well as the anions already bound to the leather collagen. Recently, these hydrolysates have been reported to give excellent results in the scavenging of antioxidants (Sedliacik, 2018).

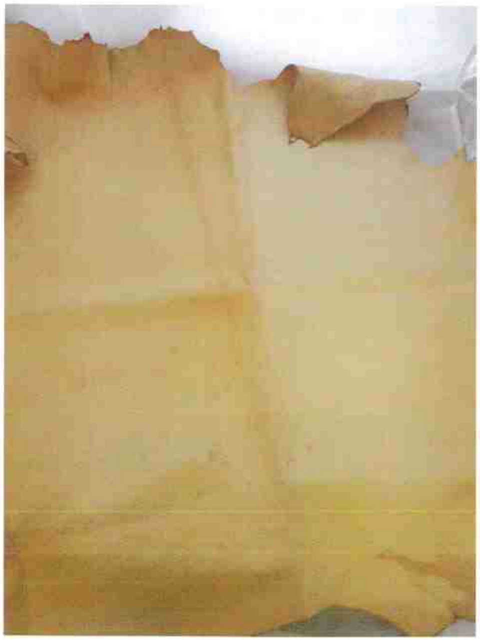

Figure 3. The presence of poor lightfastness in the skin due to inferior tanning and retanning products.

Protein hydrolysates, if partially hydrolysed to the extent that they are barely soluble, can have a molecular weight that could be described as high. These molecules can penetrate inside the leather, particularly into the open areas, and could result in increased filling. Consequent treatments that cross-link the hydrolysate, or a treatment that precipitates the hydrolysate, will result in an interpenetrating network of a hydrolysate inside a leather network.

How do these materials increase leather sustainability?

The inclusion of a hydrolysate must be done carefully. Hydrolysates can result in a higher organic content of the final leather. Leathers with a higher organic content require higher levels of fungicide. The hydrolysate themselves, if made off site, will include a biocide (generally a fungicide) that ensures their shelf life and prevents putrefaction of the product (and the smell this may produce in the final leather). If made on-site, this restriction may be less but the degradation of the resulting leather at the end of its life may be expedited.

Another major consideration of the hydrolysate is that they may be prone to heat or lightfastness problems, but some do not have this issue. Careful testing and a deeper understanding of the protein feedstock may help prevent this. Keratin hydrolysates have good resistance to UV and they could be used to boost the light properties of the leather.

If placed into water, several potential issues could arise for water resistant leathers. Depending on the hydrophilic/lipophilic balance (HLB) of the hydrolysate, the leather may lose dynamic resistance; even if the HLB value is lower, the static water uptake may be affected by the small number of hydrophilic groups are present. Future progress in hydrolysate development may include molecular sieving/ selection for particularly hydrophobic fragments and the improvement in the grade of hydrolysate (lowering yield).

A final note on the use of hydrolysates in finishing. The use of hydrolysates; casein, whey (lactoglobulins, lactoalbumins, albumins), soluble collagens, keratins, gelatines, or zeins, are undoubtedly the future of fast-fashion finishes. Petroleum-based polymers may still have a limited future in performance leathers, until new technologies can disrupt them. The protein plays several functions in modern finishing:

- to increase naturalness
- to help with flow out
- to provide gloss increase
- to give/assist with burnish/polish effects
- if cross-linked can help with film forming functions

Future applications of protein hydrolysates in finishes will be to provide UV protection, soft points in film degradation (end-of-life), give a waterproof surface coating and allow thinner, more natural finishes that are an extension of the leather rather than a non-protein coating that is viewed as a plastic layer, which remains in the compost after biodegradation. ◘

References: Karthikeyan, R., Balaji, S., and Sehgal, P.K. (2007) Industrial applications of keratins – A review. J. Sci. Ind. Res. India 66: 710-715.

Ramamurthy, G., Sehgal, P.K., and Mahendrakumar (1989) Improved uptake of basic chromium salts in tanning operations using keratin hydrolysate. J. Soc. Leath. Technol. Chem. 73: 168—171.

Sedliacik, J. (2018) Antioxidant activity of keratin hydrolysates studied by DSC. Proceedings of the 114th ALCA Convention June 19-22, Itasca, Illinois, USA. American Leather Chemists Association (ALCA), Texas, USA.

Colantoni, A., Recchia, L., Bernabei, G., Cardarelli, M., Rouphael, Y., and Colla, G. (2017). Analysing the environmental impact of chemically-produced protein hydrolysate from leather waste vs. enzymatically-produced protein hydrolysate from legume grains. Agriculture-London 7: 62-71.