

etal-free tannages are becoming more and more prevalent in a move towards what some brands and consumers perceive as being more sustainable tanning systems. For millennia, tanning using vegetable tannins was the norm. In the modern arena, where high performance leathers are required to go above and beyond what these traditional tannages can offer, combination tannages are often used. By combining tannages, the characteristics of the leather can be adapted to give the best results, drawing on properties from the individual tanning agents. In many cases, the combination of tannages includes the use of chrome (III). While scientific studies, including REACH regulations, prove that the use of the trivalent form of chromium, when used in properly managed tanning systems, presents no danger to the manufacturer or the end user, there has been growing demand for chrome-free alternatives.

In reacting to this demand, wet white leathers made using glutaraldehyde have become popular. For almost 30 years, the use of glutaraldehyde as a pre-tanning system has been used to good effect with subsequent wet-end work undertaken to impart the physical and chemical characteristics of the final leather. There are certain difficulties in using glutaraldehyde, for example with manual handling or wastewater treatment. Again, a modern well managed tannery will be equipped to handle these aspects. In most cases, whether the leather is wet blue (made using chrome) or wet white, it is the public perception that is mostly the driving force for change. To this point, Silvateam developed Ecotan PAP, a metal-free, aldehyde-free tanning product using a modified hybrid, extracted from gallnuts,

chestnut and tara.

Being members of the hydrolysable group of tannins, these naturally dispersed ellagic/gallic pyrogallols tend to exhibit good light-fastness properties with a pale colour – essential for high-performance leathers.

In creating this hybrid, the highly anionic nature of the tannage, one that exhibits an abundance of negative charges on the collagen polypeptide chains, was found to be improved by the use of a cationic ester, Keusol SP EQ, during the tanning stage. This enabled the leather to exhibit more amphoteric properties leading to high levels of dye and fatliquor exhaustion, and low COD in the final effluent. (see panel 1)

The Silvateam metal- and aldehyde-free tanning product launched in 2017 but it was the first covid-19 pandemic lockdown of 2020 that ignited a more involved project looking at ways in which this new system could be better implemented. Introducing synthetic polymers to the range for the other retanning additives, these non-toxic compounds are so safe that they need no REACH registration. Leathers made with this system are said to not only be fully functional but also beneficial to health, as published in *World Leather June-July 2020: Antibacterial properties of leathers, natural tannins, and their interactions with shoe bacteria.*

The final piece of the puzzle came through the company's partnership with Biofin, part of Gruppo Biokimica. Biofin, a partner of Silvateam's for more than 10 years, has an intimate knowledge of the metal-free range offered by the company and also has a close link to the fashion world, where sustainability is a driving force for new business.



Why metal-free?

Any metal in the finishes, be it with the dyes or pigments, would give rise to issues with the breakdown products in the waste treatment of the leather. In leather colouring, premetallised dyes, also known as metal-complex dyes, are commonly used. The metal of the dye complex often consists of copper, cobalt, nickel or chromium. Providing metal-free alternatives enabled a strategic breakthrough in the ability to create a complete metal-free offering with sustainability and circularity at its core.

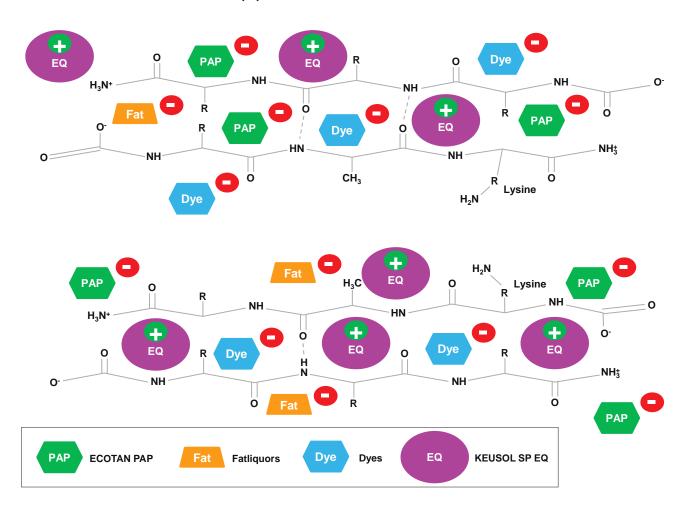
Tanners can now sign up to use the Ecotan system but, on doing so, they must comply with several aspects that will ultimately lead to their trimming and shaving waste being converted into fertiliser. In theory, recycling the leather will also be an option for the end consumer at the end of the product lifecycle. The facility for this to take place is currently unavailable but the technology allows the chain to be put in place in the future. Silvateam is keen to point out that this is not a biodegradability system but a recycling system in which the biocircular element can then be used in a cycle in which farmers can use the fertiliser on the grasses that feed the animals that will ultimately become meat and provide the hide.

In conjunction with Fertilizzanti Certaldo, a fertiliser manufacturing company established in 1931, the leather waste is assigned a regulatory waste code, having been subjected to analysis and RSL substance assessments.

Following this acceptance, the leather undergoes a process of acid hydrolysis, using sulfuric acid. The hydrolysis, a breaking down of the protein chains, whereby the peptide bonds are broken, results in an organic matrix that is more receptive to the subsequent addition of nutritive elements. Additions of micronised natural phosphate leads to the solubilisation of phosphorous by the free acidity in the system and, depending on the final product, other components to enrich the fertiliser can be blended with, and bound to, the organic matter. This allows for the effective adjustment of availability and constitutes an effective regulation for nutrient transfer, granting a slower release, which best synchronises with the absorption by plants. Speaking to World Leather, Fertilizzanti Certaldo technical manager, Luigi Petralli, has explained that as a raw material, vegetable-tanned leather has numerous advantages for production. Aside from the absence of chrome, coming from an industrial cycle it is much more stable and reliable than other organic substances of natural and non-natural origin. It has the constant and significant presence of organic nitrogen and it performs well in the hydrolysis process.

Current EU regulations stipulate that contaminants in an organic fertiliser must not exceed 2mg/kg for chrome VI, with a total chrome limit of 2000mg/kg, 50mg/kg for nickel and 300mg/kg for copper, all based on dry matter. The European Commission foresees a replacement of regulation (EC) number 2003/2003, expanding its scope to secondary raw

Panel 1: Chrome free tanned leather — peptide chains





material-based, that is recovered and bio-based fertilising products. The new EU Fertilising Products Regulation (EU) 2019/1009 was approved by the European Parliament and the Council of the European Union on 5 June 2019 and is expected to come into force in July 2022.

Further sustainability is assured with Programme for the Endorsement of Forest Certification (PEFC) registration. This certification of the tannins tracks forest-based products from source to the final product, demonstrating that each step of the supply chain is closely monitored through independent auditing to ensure that unsustainable sources are excluded. For example, the coppicing of the chestnut woods that are the source of some of the tannins means the trees renew themselves naturally after cutting, and there is no need to plant more – as published in *World Leather* April-May 2019.

Speaking on behalf of one of the tannery partners to have signed up now to use Ecotan system, JBS Couros, sustainability manager, Kim Sena, says: "The sourcing of the vegetable tannins such as chestnut or quebracho is PEFC-certified and recognised for its sustainable approach, which guarantees that the biosphere is being respected and the environmental impact is minimal." Another early adopter, Maurizio Casini, chief executive of Tuscan tannery Conceria La Scarpa, says: "In our 57 years' experience in vegetable tanning, our company's philosophy has always revolved around respecting the environment and future generations. This is why we decided to join the Ecotan project, dedicating ourselves fully to the mission of creating recyclable leather articles."

For his part, the sales manager at Conceria Volpi, Giuseppe Volpi, has said: "With this process it has been possible to obtain leathers with specific and improved characteristics in terms of hand feel and softness for a vegetable leather. Adding these to the minimal content of metals and eco-friendly approach of this procedure, we think it is going to become a new benchmark for our section of the leather industry."

While applicable to almost all leather types, shoe leather is ideally suited to the biocircular system, as shoes have a relatively short lifespan. Collectively, the tannery partners that have signed up to Ecotan have already used it to make all leather types, some to fully finished leathers but in the case of automotive upholstery, to crust (finishing is still challenging here). Turkish tanning company Sepici Grubu has over 30 years' experience working with Silvateam to produce vegetable-tanned leathers for shoes, garments, belting and sole, and have added the biocircular line to their developments, with products now coming through scale-up operations. "We were excited to add the biocircular concept to work that we had already begun in the beamhouse," says one of the group's owners, Mehmet Sepici. "Combined with our knowledge and formulations using reduced salt and water, the Ecotan system adds further credentials in terms of traceability and sustainability."

In more general terms, although Ecotan PAP is seen as the major player in high-performance leather manufacture, any pure form of vegetable tanning can also be assigned the Ecotan brand. "Sole leather and harness leather can be labelled Ecotan, full vegetable-tanned leather is already Ecotan," Silvateam sales director, Eric Poles, tells World Leather. "What we have done with the new range is to work on modernising the traditional vegetable tannage to make formulations that perform well."