



Oisterwijk, venue for Freiberg Leather Days.

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The 2017 Freiberg Leather Days took place in June in the southern Dutch city of Oisterwijk. World Leather reports on some of the interesting developments that were presented during the two-day conference.

Diverse programme at sixth Freiberg Leather Days

More than 200 delegates descended on the site of the former Royal Leather Factory (KVL) in Oisterwijk, the Netherlands from June 20-21 to attend the 2017 edition of the Freiberg Leather Days. The conference, jointly organised by the German Leather Technicians and Chemists Association (VGCT) and Forschungsinstitut für Leder und Kunststoffbahnen (FILK), was taking place outside of Germany for the first time.

Those in attendance included representatives from across the automotive leather supply chain, as well as tanners who work closely with the footwear and leathergoods industries. Several important German and European leather chemical manufacturers were also present. Opening the event, Martin Heise, chairman of the VGCT executive board, said the only two continents not represented were Asia and Antarctica. He emphasised the need for even more research and development in the leather industry, insisting there are “still lots of interesting things to discover”.

Sustainability challenges

The conference's technical programme was opened by Dr Martin Kleban, head of the management team of the leather business unit of chemicals manufacturer Lanxess, who offered an overview of current sustainability initiatives. He explained that growing demand from the public for transparency “compels” the industry to work harder to

address sustainability challenges. He warned that this is easier said than done because there are so many different aspects to take into account.

All members of the leather supply chain have a responsibility to help make the industry more sustainable, Dr Kleban insisted, and chemicals manufacturers should be making “substantial efforts” of their own to tackle the issues.

Away from sustainability, Dr Kleban was critical of the way the media depicts the leather industry, lamenting that it is frequently the bad news stories and negative imagery that appear first when the word ‘leather’ is entered into an online search engine. He called on the industry to “question our own values” and do more to promote the positive things about leather.

Probiotic alternatives

The global marketing manager for Stahl's wet-end division, Juan Carlos Castell, presented one potential solution for making the leather manufacturing process more sustainable. His talk focused on his company's use of probiotic chemicals as an alternative to some leather chemicals.

Probiotic chemicals are “compatible with all chemicals used in the leather-making process”, he explained, and there would be no need to alter the temperatures or pH of conventional leather manufacturing processes in order to accommodate them. He added they could be employed to



eliminate, or at least reduce, a range of substances, including wetting agents, enzymes, degreasers, dispersing agents and dye auxiliaries. Their ability to activate the ionic groups in the protein chains of compounds could improve finished leather quality by optimising the uptake of tanning and processing substances.

Mr Castell revealed that tanners in Igualada, Spain, have expressed concerns about how the use of probiotic chemicals would affect their wastewater. Stahl's research in response to these concerns has shown that these chemicals are 100% biodegradable and will not negatively impact the toxicity of tannery wastewater.

The missing link?

Dr Valentina Beghetto spoke in her capacity as founder and president of Crossing Srl, a start-up company established to develop a new class of active cross-linking agents (ACLs) suitable for use on an industrial scale. The structure of the compounds allows them to be easily modified to offer different activity levels, performance, or speeds of action. One of the possible uses is as tanning agents.

The main challenge facing the project's researchers was bringing down the unit cost of ACLs to make them environmentally and financially sustainable. Dr Beghetto said the "very simple chemistry" behind ACLs means the manufacturing cost is low. She added that the majority of chemical plants have the requirements to make these substances. There would also be no need to adjust the industrial procedures currently used in tanneries to accommodate ACLs. Other advantages include less wastewater, energy is saved as the tanning process takes less time (than for chrome, for example), and it is possible to recycle some of the chemicals used.

Crossing has already developed an extensive library of ACLs suited to different uses, including for the production of automotive leather.

More detail on deep eutectics

A presentation from a PhD student at the University of Leicester, Omaymah Alaysuy, captured the attention of even the most senior technical experts and representatives of the global leather industry at Oisterwijk. Originally from Saudi Arabia, Ms Alaysuy is in her third year of PhD studies in Leicester. At the conference, she spoke about her work on how deep eutectic solvents (DES) can be used in leather production.

She explained that she has spent time recently at the tannery that the University of Northampton runs as part of its Institute for Creative Leather Technologies putting her ideas to the test on materials including sheepskin. She evaluated the performance of DES in tanning, retanning, fatliquoring and dyeing. Ms Alaysuy described DES as a mix of two simple salts that combine to form a liquid. "The main concept is to place an active ingredient, with high concentration and low waste, inside the hide," she explained. "We can take a piece of hide or skin, apply our mixture to the surface and see the hide absorb it with no apparent loss of the collagen structure."

Obvious benefits include a large saving in water and a large reduction in the amount of effort and expense required to manage tannery waste. Fielding a lengthy series of questions from the floor, Omaymah Alaysuy assured delegates that the DES will not rinse out during processing



Saudi Arabian doctoral student, Omaymah Alaysuy, told the conference deep eutectic solvents will allow tanners to save large volumes of water and reduce the amount of effort and expense required to manage tannery waste.

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and produces material with an attractive, soft touch. She also said using DES will not hinder the use of other important leather chemicals, including basifying agents.

She confirmed that work is ongoing to increase the shrinkage temperature of the hides and skins processed using DES, which is currently around 80°C compared to around 100°C for chrome-tanned leather produced in the traditional way. A major leather chemicals firm told *World Leather* at the event that it has signed a non-disclosure agreement to work with the University of Northampton on deep eutectic solvents.

Innovative tannins

Eric Poles, global sales director for Silvateam's leather division, gave details of a new tanning system it has developed using Gallic/Ellagic Dispersed Tannins (GEDT). The tannins are made using a modified hybrid extract from gallnuts and the pods of the tara tree.

Mr Poles explained that these materials are readily available. In fact, there is enough supply for this method to fully replace chrome tanning, he claimed. When used on pickled pelt, the system gives a near white colour, good light fastness, good heat fastness, good penetration and medium softness.

Silvateam incorporated a cationic ester into the process to improve the physical and organoleptic properties of the leather. It was added to improve the reactivity of the leather with dyes and fatliquors. The use of GEDT means the tanned leather has lots of anionic charges; this inhibits its reaction with anionic fatliquors and dyestuffs, which are mostly anionic. Without the cationic ester, it would be difficult to fix the dye shades, he said.

To make the tanning process more sustainable, the company designed the system so that a partial recycling of the main tanning liquor is possible. Furthermore, the high exhaustion of the product results in nearly zero discharge.

Examining exhaustion

Chemicals manufacturer Trumpler recently carried out an extensive dyehouse product exhaustion study, the findings of which were presented at the conference in Oisterwijk by Dr Jeffry Guthrie-Strachan, the company's product communication and promotion manager.

A key aim of the research was to investigate improvements in chemical oxygen demand (COD) that Trumpler's current product range can offer. It tested 35 fatliquors, 30 syntans and vegetable tannins, and nine acrylics and polymers to identify the products that exhaust well. This is designed to help technicians and customers with product selection and the design of dyehouse application processes. It managed to report reliable exhaustion and COD results for a "significant number" of products from its range based on standard recipes.

Through the study, Trumpler sought to establish a theoretical effluent COD mass balance based on practical exhaustion data. This would help inform the chemical selection for dyehouse recipes by being able to predict the COD loading of the effluent stream. It used the data it had gathered to identify product ranges and components that may contribute to high or reduced product exhaustion. Dr Guthrie-Strachan told those in attendance that the results were "a lot more promising than we ever would have expected".

Trumpler shared its spot at the seminar with rival leather chemicals manufacturer Smit & zoon, whose newly appointed strategic leather specialist, Dirick von Behr, said his company has also been examining the relationship between fatliquor exhaustion and the "pollution burden" of tannery waste. "We started to look at this closely in 2014," Mr von Behr said. "We looked at COD and BOD because we wanted to know what impact our products have on wastewater. In our industry, we have always simply hoped that our wastewater treatment plants would be able to deal with the chemicals we were using." He added that it's unfair for tanners to have to pay once to use a chemical product and then pay again to remove the excess material from sludge or from wastewater.

However, he said it wasn't easy to tell which fatliquors will be the best products to use in processing particular types of leather. "The most important thing for me," Mr von Behr concluded, "is that what we are really talking about is better fixation. What we have found is that the fixation of many products is reversible and, to make sure we really have higher exhaustion, the big challenge is to make the fixation irreversible."

Formaldehyde standards

Dr Sara Cuadros, from the Spanish National Research Council (CSIC), discussed the results of a two-part study into the use of formaldehyde in leather manufacturing. More specifically, it focused on its role in the synthesis of syntans and resins for use in the retanning process.

The presence of formaldehyde in leather is not a minor problem, according to a recent report from the A3 Chair in Leather Innovation at the Polytechnic University of Catalonia (UPC). Of the leather footwear from Asia it tested, 16% failed to meet the formaldehyde content requirements of major brands. This rose to 30% for double face skins.

CSIC examined whether there was a need to revise the current official standard for the determination of formaldehyde content in leather (ISO 17226). It studied the



The audience at the sixth Freiberg Leather Days.

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possibility of using different chromatographic conditions to improve on the method.

The second part of the study investigated how the addition of different dyes affects the formaldehyde content of leather and how it evolves over time depending on the dye used. Dr Cuadros concluded that the results from the dyes were very good, even though the research is still at an early stage. CSIC is working on how vegetable extracts could be used in dyes to reduce the formaldehyde content of leather.

Understanding collagen structures

Researchers from the New Zealand Leather and Shoe Research Association (LASRA) have been studying how small-angle X-Ray Scattering (SAXS) can be used to better understand tanning mechanisms. LASRA scientist Dr Sujay Prabakar gave more information about it in Oisterwijk.

The studies were carried out on lamb pelts during tanning. The use of SAXS allowed LASRA to obtain molecular-level information about the collagen structure of the hides and how this changes during the tanning process. They were able to see the intermolecular space within the structure, which provided insight into the electrostatic interaction between tannins and the collagen during the tanning process, and the size and arrangement of the collagen fibres, which influences the feel of the leather.

Dr Prabakar claimed the mechanisms involved in the tanning process are "very poorly understood". LASRA believes using SAXS to get a better understanding of them could help tanners reduce the amount of chemicals they use, which would bring down costs and reduce effluent.

One aspect that was studied was how the use of chrome affects shrinkage temperature. The researchers found that although a high chrome concentration delays the onset of shrinkage, there is a point at which increasing the concentration no longer affects the collagen structure on a molecular level. As a result, there is no further improvement in shrinkage temperature.



Efficient drying

Bavaria-based tanner Südleder has been using a new overhead vacuum drying system devised by Dutch tanning machinery supplier IM since 2016. Marc Oomens, owner of IM, and Dr Beate Haaser of Südleder, shared the stage to extol the benefits of the tunnel drying technology.

They explained that the system is conveyor based and so results in gradual, progressive drying as the material moves through the different zones. A low drying temperature, around 35-40°C, prevents any loss of yield and quality. The total drying process takes four to five hours.

They also highlighted how easy it is to manage the process, which is controlled by a Siemens PLC system. It has the option to programme recipes for different articles. An algorithm calculates the humidity of the leather based on several parameters and this is used to select the most suitable drying process.

The Therna Dry Tunnel is more efficient than current drying methods, they revealed, both in terms of total process time and the manpower it requires. Standard batch drying requires six staff, but the new system needs just five. IM estimated that it allows for more than twice as many pieces to be dried each day compared to batch drying.

Working with wet white

Spanish leather chemicals manufacturer Cromogenia has conducted a study to assess the effect of different fatliquoring products on the physical and organoleptic properties of wet white tanned leather. Olga Ballús, a member of the company's tanning laboratory team, said it was undertaken to address a shortage of information about the relationship between fatliquors and wet white.

Cromogenia tested 12 fatliquors from its range on Spanish cattle hides processed to the wet white stage. The fatliquors fell into five categories: sulfated, sulfochlorinated, sulfited, lecithin and polymer.

After applying the fatliquor to the leather, the researchers measured a range of properties, including softness, thickness, tear load, grain firmness, extractable matter and fogging characteristics. They also evaluated the COD of the residual bath.

In her conclusions, Ms Ballús explained that the factor that has the most influence on the fatliquoring ability of a fatliquoring product is the nature of the product itself. The study concluded that the lipophilic/hydrophilic balance of a fatliquoring product is a determining factor in the degree of softness of the final leather. It also found that fatliquors with a lower stability have better properties in wet white. The ultimate conclusion was that sulfated and lecithin fatliquors, which have a low stability, provide the best softness results for wet white.

Leather lamination

Ramon Weren, operational sales director of French adhesive specialists Protechnic, explained the advantages of using prestructured thermoplastic adhesives, one of the products the company offers, in leather lamination.

He described the limitations of the current adhesive systems available. One option is thermoplastic powder, which is sprinkled on the surface of a substrate. Mr Weren said this powder sometimes penetrates into the material, causing stiffness. There is also a risk that some of the powder remains on the surface of the material if it is not activated

correctly, which would affect the feel of the leather. Regular thermoplastic hotmelts can also cause stiffness if the melted granulate penetrates the substrate's surface.

Prestructured thermoplastic hotmelt adhesives are a valid alternative, he told the attendees. Protechnic offers these in the form of films, webs or nets. They can be designed to have different activation temperatures or pressures, and the adhesive structure can be altered to suit different materials. He said Protechnic's web adhesives provide good adhesion as its fibres are spread over the surface of a substrate in a "homogenous way". This means less adhesive is needed, reducing the cost. The close-knit structure of its adhesive webs reduces the risk of delamination, he added.

A shaving revolution?

Hanns Peter Spaniol, the general manager of fleshing and shaving blades maker Heusch, offered details about the company's new "wave tooth" shaving blades. The blades, which it calls 'New Wave', are embossed rather than milled. They are inspired by chef's knives; Heusch realised that chefs use different knives for different purposes and wondered why this could not also be applied to shaving blades.

Mr Spaniol explained that the blades offer a variety of advantages, including stable thickness and uniform surface quality. He added that they result in an "open surface" of the hide, making it better prepared to receive post-tanning agents. The new blades have "markedly lower" wear than those currently available, he said, meaning they have a longer lifespan. Heusch believes they are suitable for use on all types of leather.

Heusch has carried out trials of the blades with some of its customers, including those in the Santa Croce tanning cluster in Tuscany. It is planning to carry out further tests to optimise the process and is seeking more partners to determine their full potential. It hopes to bring the technology to market some time in 2018. Although the blades are currently just used for shaving, Heusch is to conduct fleshing trials in the coming months.

Conductive leather

A team at the Leather Industry Development Institute (LIDI) in Addis Ababa, Ethiopia has devised a method for producing conductive leathers through in-situ polymerisation of pyrrole. Wegene Demisie Jima, a senior researcher at the institute, alluded to leather being an electrically insulating material as the main reason why it has so far failed to find any applications in wearable electronics.

A common solution to this problem is to stitch conductive wires into the leather, but LIDI's method doesn't require any materials beyond the leather itself. It involves immersing the leather in a solution containing pyrrole and a dopant. After 30 minutes, an oxidant is added to start the in-situ polymerisation. This creates a conductive coating of polypyrrole on the material.

The researchers measured the electrical resistance of the leather and carried out experiments to find the optimum treatment conditions for conductivity.

LIDI also conducted bulk trials of the method on sheep nappa in the white crust stage. It says the process does not require any additional equipment in the tannery as the tanning drum can serve as the reaction bath. There is no need to use dyes because the polymerisation process generates colour. Pyrrole generates black, but other monomers could be used to generate different colours. ●