Sustainable Leather Management: A mass balance bench mark of different chromium tanning technologies

Dietrich Tegtmeyer, Leverkusen, Germany

Hitherto, there is no better alternative to the chrome tanning salts (CTS) for stabilize the collagen matrix. A non-chrome system needs additional retanning chemicals to compensate for this but then, exhibits a different crust performance. This justifies the 85% of the world’s leather demand being still based on Chrome tanned leather for over 100 years. Decades of research have helped understand the complex chemistry of chrome tanning. As a result today's chrome tanning process is a stable and safe operation also with a resulting safe and high performing technical substrate. In order to further improve chrome tanning in general and especially from a sustainability point of view a closer look at two important aspects are needed. First: Process rules (already established) to avoid the formation of Cr VI in leather and generate a stable crust. Second: Process concepts to increase the utilization of CTS further in order to reduce the release of chromium into the effluent to an absolute minimum. A simple mass balance shows, that there are alternative process technologies such as high exhaustion and hybrid technology (wet white pretanning in combination with rechroming), which significantly reduce the current discharge of chrome into waste, and which can be done with standard operating equipment in every wet blue tannery worldwide. These alternative technologies also mean that similar retanning recipes for a leather with comparable crust performance.

Advances in Bio-based Polyurethanes for leather finishing

Michael Costello, Director of Sustainability at Stahl

Recent advances in biotechnology have allowed a new class of polymers, aqueous polyurethanes that demonstrate superior film performance to their fossilfuel based predecessors. It is now possible to formulate high performance polyurethanes using polyols derived from plant-based oils. Stahl has been researching bio-based polyurethanes for several years and recently have obtained high performance characteristics in these bioproducts. Films made with the latest bio-polyurethane technology (Biobased EXP-1 and Biobased EXP-2) are more resilient than previously studied polyester and polyether-based alternatives. In fact they are closer to the level of polycarbonate-based polyurethanes, considered the gold standard for automotive finishing. We strongly believe that polyurethanes can be developed with higher biocontent and even higher performance in the future.
How relevant do you think the theme of the present congress (Science and Technology for Sustainability of Leather) to the global leather industry?

Let me borrow the words from Dr. Tegtmeyer, who said the trinity people, planet and profit as the important elements to be considered for attaining sustainable growth. Therefore, sustainability shall address the society, environment and economy while aiming at growth. If that could be done then the growth that is attained would not only be significant but sustainable. Increasing financial compensations for the workforce of leather industry, need for compliance with environmental requirements and decrease in the economic returns are the challenges. Whereas all these are not technological challenges, science and technology could certainly provide remarkable solutions to these challenges. Therefore, I expect this congress will set the tone for efforts to come forward for a global alliance.

Apart from bring the stakeholders together, what other benefits do you envisage from the congress?

Different research groups have been working in different parts of the world trying to develop solution to similar problems. Nevertheless, the congress could bring together the research community closer; it is high time that the organic linkage between the research groups and institutions may be established. This global networking will not only just bring about outstanding knowledge products, but the outcome could be reaped in shorter span of time with minimum resources. And I strongly believe that sustainability of global leather industry is not a tall task if such amalgamation of minds and efforts could be achieved.

What is the striking difference you see between the congress held earlier in India and now?

It was in 1999, when the congress was held, the Tamil Nadu industry had been limping back to normalcy from the agony of closure. Nevertheless, even at this point in time the Indian leather industry is facing enormous pressure on account of environmental management, the Indian leather industry is confident in overcoming the challenges. The present congress is different from the one that had been conducted in 1999 in several ways. To indicate the striking one, I may say that the professionalism that is demonstrated in conducting the present congress in the one aspect that comes immediately could come to my mind. It does not ever mean that there is no scope for improvement.

What is the likely strategic direction of leather research in future, say in another 15 years?

The world leather industry is expecting a lot from the research community. The immediate direction can be on development of technological measures for enabling the industry to attain sustainability. The long-term focus will be on development of technologies for the production of high-value products not wasting any constituent material of the hide or skin. Having said that let me once again reiterate that global networking could bring about all the desired results in a much short span of period with lesser resource input.

What is your message to the participants of the congress?

I wish all the success to all the participants in their present and future endeavors. I also would like to welcome all the research groups to come forward for a global alliance.
Tanning strategies for sustainable leather production
Heinz-Peter Germann, Reutlingen, Germany

In the field of leather production, the patented wet-green® tanning technology constituting a really sustainable alternative to conventional tanning methods is based on a purely aqueous olive leaf extract that allows production of high-quality leathers for the diverse applications. Conventional tanning agents are totally eliminated and hence, a new benchmark for sustainability. The olive leaf extract combines the merits of organic synthetic reactive agents by creating stable covalent chemical bonds with those of the usual vegetable tanning. The deposition of vegetable polyphenols additionally generates a better fiber separation and filling effect as well as a pleasant round feel. As this is sans traditional pickling process, it also permits reduction of salt content in the effluent. Thus, considerable savings of retanning products and dyes are possible over wet-white technology. Its human safety aspect has been awarded the Cradle to Cradle® certificate in Gold as well as Material Health certificate in Platinum. Olive leaf tanned leather has myriad uses and the wet-green® system also results in more flexibility and eliminate fungicides.

Waste to wealth approach: Adhesive from the unused goat head skin
Md. Abulhashem, Khulna, Bangladesh

In the case of goats and sheep, the head skins are disposed of without proper environmental management leading to gaseous emissions. Water body and soil are also being polluted by the waste. In Bangladesh, the head skins of all 30 million goats annually slaughtered are disposed of without utilization for any commercial product. In this investigation to explore glue production, goat head skins were soaked and heat treated to extract the collagen in soluble phase. The extracted solution was dried and obtained glue was investigated for commercial application. The produced glue could be used in the packaging industry, furniture, plumbing, shoe making, book binding, etc. Glue was prepared from the goat head skins by using simple and easy technique with a few chemicals. It was estimated that Bangladesh could produce 270 MT glue per year only from the unused goat head skins.

Fabrication of Antibacterial Casein-based ZnONanocomposite for Leather Finishes through in situ Route
Wang Yanan*, Ma Jianzhong, Xu Qunna Xi’an, China

A casein-based ZnO nanocomposite leather finishing material was fabricated through in-situ polymerization, aiming to improve the antibacterial activity of casein films. The structure and size of the nanocomposite were characterized while the tensile strength, water absorption and antibacterial activity of the films were measured. DLS measurement result showed that the size of nanocomposite latex particles was approximately 260nm. The composite film displayed superior mechanical property, high water resistance and excellent antibacterial activity against S. aureus and E. coli. This natural polymer-based nanocomposite antibacterial film is simple to prepare and has great potential for many applications.

Ionic Liquids: New age “designer” chemicals for leather processing
N Nishad Fadhima, Chennai, India

Ionic liquids (ILs), help instigating desired effect on proteins due to the easy tunability of cation and anion. The conformational stability of collagen at the molecular level, thermal and dimensional stability at the interfibrillar level and fibre structure at skin matrix level using different types of ILs viz., imidazolium, choline, ammonium and phosphonium as cations with different anions have been studied in detail. Almost all ILs with the exception of choline destabilized collagen at fibrillar and skin matrix level. Choline based ILs stabilised collagen and hence tanning with choline salts was attempted. Thus, ionic liquids were found to have both stabilising and destabilising effects on collagen and accordingly exploited for various applications in leather processing. Future leather production will evince interest in the use of ionic liquids as advanced chemicals for cleaner and greener leather processing.

A New Age Chromium-Melamine Syntan : Towards Quality Upgradation of Lower - end Raw Materials
M Sathish, Chennai, India

Chromium syntan is employed during the rechroming process for uniform chromium content and also to impart fullness. During belly filling, however, more amount of melamine-formaldehyde condensate is used in the subsequent retanning process. Liberation of free formaldehyde is one of the major limitations of the conventional synthetic tanning agent. Hence, an attempt has been made to prepare a novel formaldehyde free chromium-melamine syntan and use in rechroming process. The product imparts selective filling/grain tightening effect on loose area/belly region and also increases the thickness without affecting the area yield. The product yields good dye levelling, excellent buffability with natural sheen, uniform milling pattern and improved cutting value.

Novel surfactants – in Leather Processing
Vijayabaskar, Chennai, India

Surfactants – polymerisable surfactants prepared from renewable resources can be used in processing of leathers. A facile method was developed in-house using a dispersion of a stable emulsion copolymer and substantially free from organic solvents. They impart light fastness characteristics, reduce fogging and minimize Cr(VI) a carcinogenic generation in leather. This polymer binds the free crome on to the collagen and Cr (VI) was below detectable limits on leather on ageing.

Tanning with a Gallic extract in combination with a cationic ester for the production of high performance leathers
Eric Poles, San Michele Mondovì (CN) Italy

A new metal free tanning system that can be associated with vegetable tanning systems was developed by using a modified hybrid extract from Gall nuts and Tara in combination with a cationic fatty ester. The hybrid extract obtained has self tanning properties with a shrinkage temperature of over 80°C, a very light colour and strong light / heat fastness. The levels of exhaustion of retanning agents, dyes and fatliquors obtained are very high as well as low COD and high biodegradability of the final effluent. The systems reaches equilibrium after two batches which guarantees consistency of quality. By varying the retanning / fatliquoring all types of leathers can be obtained. The systems works well both on bovine and small skins. A study on the effluent of the system was carried out and the biodegradability tested in a pilot tannery effluent plant.

Study of the variation of chromium VI content inside the leather
Jean-Claude Cannot, Villeurbanne, France

If the process of tanning is not perfectly mastered, some free Cr III radicals can be transformed into hexavalent chromium (CrVI). Four different bovine leathers viz., one with best practice followed, using unstaturated fat liquors, tanning without best practices and without best practices but with vegetable tanning. The variation of Chromium VI was monitored for several months. Best practices have shown a great impact.
Intelligent real time leather defect detection system using image processing technique
Malathy Jawahar, Chennai, India

Manual inspection of leather quality is highly subjective leading to inaccuracy and inconsistency and further to dispute between the buyer and the seller. An intelligent automatic leather defect detection using image processing technique is proposed and features such as Entropy, Energy, etc are determined. The normal and defective leathers are classified using an artificial neural network features.

Analysis of characteristic odor compounds in leather by GC-MS and GC-Olfactometry
Hirohiko Washiya, Hyogo, Japan

More than 20 volatile compounds especially hexanal, heptanal, octanal, nonanal, heptanol, octanol, 2-ethoxyethanol, and 2-butoxyethanol were identified by GC-MS while aldehydes such as octanal and alcohol were characterized by GC-O. In contrast, solvent such as 2-ethoxyethanol was not characterized by GC-O.

Method for determining the optimized exhaustion of fat liquors to minimize the ETP-inflow
Dirck von Behr, Nijverheidslaan, Weesp

The proposed amendment of the German regulation for the treatment of tannery waste waters emphasizes the minimization of the pollution burden and a verifiable reduction of the polluting load before the water enters the treatment system. Each product has a specific affinity to the tanned hide and an individual environmental imprint that can be used for targeted reduction of the inflowing pollution burden. This study is a starting point for setting up an own methodology and a detailed level of reporting, to understand a fat liquor's true affinity towards the leather and to minimize the environmental impact of their processing.

Artificially induced collagen fibril orientation affects tear propagation in leather
S J Kelly, Palmerston North, New Zealand

Ovine leather with only half the strength of bovine leather is not suitable for high value applications such as shoes. The extent of collagen fibril alignment (orientation index) is closely correlated with the strength of the leather and this understanding was used to test whether biaxial stretching for the duration of tanning or compressing pickled pelts prior to tanning the ovine skins could increase the orientation index of the collagen fibrils and the strength of the final product. It was possible to increase the collagen fibril orientation, yielding direction-specific tear strength increase rather than an overall increase in the tear strength.

Chrome-free Tannage: Suede Garment Leathers from Rural Vegetable Sheep Crust Leathers
Ali Elnaeim Musa, Khartoum, Sudan

Retanning of vegetable tanned leather with metals can elevate the shrinkage temperature (T_s) in a process known as semi-metal tanning. Semimetal tanning systems have gained importance in recent times as an alternative for chrome tanning. In this study, an attempt has been made to manufacture of semi-alum garment leathers from sheep rural garad tanned crust leathers. The physical and chemical characteristics of experimental leathers are comparable to control leathers yielding very soft and flexible leathers with high tensile strength. Shrinkage temperature of 102°C was observed with 2% NaOH, and acidylated into acyl chloride group, then reacted with collagen, to fix it on the PAN fiber through covalent bonding. IR spectrum and SEM confirmed this. The water absorption property of the modified fiber improved by 93.6%, moisture absorption improved by 280 %, rate of dye-uptake improved to 91% and the specific resistance reduced by 99.2%. The performance of PAN fiber is improved to a great degree after surface modified by collagen protein.

Effect of binder selection on topcoat property retention after accelerated weathering
Joseph Hoefler, Collegeville, USA

Dow Leather Solutions has developed acrylic topcoat binders with an exceptional balance of performance properties when combined with conventional PUD binders. Retention of properties in seating materials in accelerated weathering conditions is critical. The performance of fully finished automotive upholstery leathers after they were subjected to heat, hydrolisis, and several xenon-arc chamber conditions was assessed. Certain classes of PUD binders were preferred depending on the weathering specification. A strong moderating effect was noted in many PUD-acrylic blend systems indicating that the two chemistries produce a measurable synergetic effect when used together in leather upholstery topcoats.

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Enzymatic unhairing: Permeability assay of bovine skin epidermis with fungal enzyme extracts
Galarza Betina, Gonnet, Argentina

Laboratory isolates of various keratinolytic fungi previously were cultivated in solid-state conditions using hair waste. Enzyme extracts were characterized for keratinolytic activity, proteolytic activity and protein content. Bovine skins were placed in a pressing-device, incubated at 25°C and 40 rpm in contact with different solutions on the epidermis side: fungal enzyme extracts with commercial tensioactives (0.1%, 0.5%), biocide 0.2% w/w (wet skin) for 4 h (soaking) and 24 h (unhairing). SEM revealed enzymatic alteration of the epidermis through the detachment of corneocytes and empty hair follicles while the patterns of hair cuticle and collagen fibres were preserved. The strongest depilatory effect was showed by Trichophyton ajelloi.

Preparation and characteristics of surface modified PAN fiber by collagen protein
Ding Zhiven, Beijing, China

The combination of collagen with PAN fiber on the surface can improve the latter’s properties compared to wool. The cyano-group on PAN fiber surface is hydrolyzed into carboxyl-group by NaOH, and acidylated into acyl chloride group, then reacted with collagen, to fix it on the PAN fiber through covalent bonding. IR spectrum and SEM confirmed this. The water absorption property of the modified fiber improved by 93.6%, moisture absorption improved by 280 %, rate of dye-uptake improved to 91% and the specific resistance reduced by 99.2%. The performance of PAN fiber is improved to a great degree after surface modified by collagen protein.