RETANNING CHEMISTRY MADE FROM TANNERY BY-PRODUCTS

Catherine Gabagnu, Dr. Jens Fennen, Volker Rabe, Dietrich Tegtmeyer

TFL Ledertechnik GmbH, Dietrich.Tegtmeyer@tfl.com

ABSTRACT

The production of leather generates a not inconsiderable amount of by-products; only about 25% of the incoming raw material weight (cattle hides) is finally commercialized as genuine leather. The rest are protein containing by-products, such as hair, lime leather, shavings, etc., which can and should serve as valuable raw material for other products. In particular, a production of retanning chemicals from these raw materials would make sense, as it would allow an interesting value creation on the one hand and avoid many unnecessary logistics on the other hand. It also will increase the bio content of the chemistry used for leather making.

TFL is working on various conceptual approaches; this presentation will give an overview of the state of the art and developments, as well as introduce an economically and ecologically feasible, decentralized production possibility with an "INSITU concept".

Keywords: biobased retanning chemicals, decentralized production, INSITU

1. General

In recent decades, the leather industry has focused almost exclusively on its main product, "leather". On the one hand, this is of course obvious, as this has always been the actual purpose of a tannery, and on the other hand, it also generates by far the greatest added value. The costs to produce leather in the form of machines, personnel costs, energy and the necessary disposal costs for the by-products generated during production are not insignificant here and are increasing more and more. The latter costs are not negligible, especially because the actual amount of by-products to be disposed is quite high. According to a simple mass balance[1)] for chrome-tanned leather - which was established a good 20 years ago but is still essentially valid - only about 25% of the taken rawhide (wet salted) is sold as finished genuine leather in the dry state. According to this mass balance, 195 kg of finished leather and 60 kg of split leather are produced from 1 ton of hide and 637 kg of solid by- products such as Fleshings, Trimmings, shavings, cuttings etc. are produced. All these by-products contain protein and are much too good to be simply disposed of. According to a rough calculation and today's market prices for finished products containing fat or protein, such as biostimulants or retanning agents, each ton of this by-product mix contains a value of about €100. Although this is only a small fraction of the value of leather, it is nevertheless interesting to note that the disposal cost center of a tannery can be transformed into an upcycling profit center because of the volumes involved.

In addition to the pure cost consideration, the manufacturing process of the leather is also playing an increasingly important role. Thus, in addition to the quality of the finished leather, sustainable production methods are increasingly coming into focus. Here, the entire by-products can serve as a source, for example, as a substitute for energy suppliers such as petroleum or as a raw material to produce chemicals based on renewable material,

which can replace synthetic chemicals based on fossil origin. From a sustainability point of view, upcycling and recycling should be therefore considered anyway.

2. Decentralization

One reason why the recycling of these by-products has often not been tackled is the relatively high transport costs. All the by-products accumulate with at least 50% water content and also have unfavorable transport conditions: Either the by-products, such as Fleshings and Trimmings, are perishable or they have a very low bulk density, such as the Shavings. Both are difficult for transport and central processing over long distances.

For this reason, we believe that a decentralized reprocessing approach is the better way to go. In this article, we will focus purely on the recycling of shavings into retanning materials that can be reused directly in the tannery, where the by-products are also generated. Alternatively, if the retanning chemicals cannot be fully utilized, decentralized processing of shavings into intermediates such as protein hydrolysate (amino acid mixture) would already be a good first alternative. These intermediates can be transported more easily and at lower cost, even over longer distances, and then processed centrally for further applications.

2.1 Recycling

In the recycling concept considered in this article, by-products are reprocessed at the tannery into chemicals which can also be directly reused there, thus reducing chemical purchases.

Such a concept was piloted at the HELLER-LEDER tannery in cooperation with TFL (formerly LANXESS) over several years 2). Different products, such as various retanning agents, softening or water workshop chemicals were produced in a pilot plant on a ton scale.

On the basis of the pilot tests, it was shown that above a certain throughput of approx. 1,000 t/a production volume in the mix of the entire portfolio, the overall concept also becomes very interesting economically, since the manufacturing costs of the recycled products for the tanner can fall below the market prices of comparable commercial benchmark products.

The pilot plant at HELLER-LEDER has a scale of 1 m3 bins, i.e. one batch produces 1 m3 of INSITU retanning end product. This is a perfect scale to produce samples for production trials and to determine the best process conditions. Based on this experience, a full size production plant was designed. This plant has a batch size of 8 m3; if one batch per day is produced, this means a capacity of about 1,600 t/a of liquid products for 200 working days; this is well above the minimum commercial limit of 1,000 t/a mentioned above. The 1,600 t/a of chemicals not only replaces chemicals that the tanner would normally have to buy in but also saves on transportation, packaging, etc. .

For one batch of INSITU product between 2-4 tons of Shavings (depending on product type) have to be fed. This means that per year a quantity of about 400-800 t/a can be recycled and does not have to be disposed of.

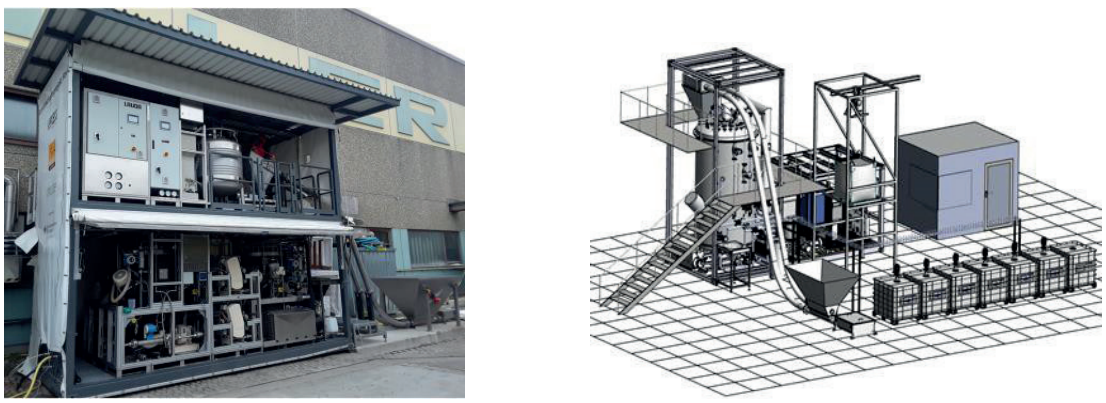


Fig.1: the INSITU pilot plant at HELLER-LEDER and the conceptual design of a 8 m3 batch production plant

2.2 Upcycling

Upcycling is an opportunity for the amount of by-products, which cannot be used in the recycle pathway. In order to minimize logistics it makes sense to do certain parts of the process even on-site. On average we have found out, that a tannery can about 1/3 of their shavings recycle for its own use; more shaving based retanning chemicals can't be incorporated during retanning in the according amount of shaved weight intermediate. In

order to generate value out of the entire amount of shavings, products for other uses need to manufactured, for other industries e.g. fertilizer, bio stimulants or raw materials for glue production. This process is considered to be an "upcycling", which is not part of this paper.

3. Manufacturing process

The manufacturing process for the tested product range is divided into 2 main production steps. In the first step, the shavings are hydrolyzed until they form a homogeneous solution. This can be done either in a fairly short process in a strongly alkaline medium at higher temperatures - pH >10 and approx. 90°C - or enzymatically, which takes longer. All raw materials used are integrated into the finished product, so that no new by-products are generated in this recycling process - the process is therefore emission-free. The corresponding production plant should be able to be automated as far as possible, so that production can be carried out independently by trained personnel. Both facts are an important requirement to make a decentralized on-site production (=INSITU) possible.

This intermediate is mixed with starch solution, and then graft polymerized with a monomer. The starch addition serves for better penetration and more uniform fullness. The monomers - usually acrylates - polymerize to form chains grafted onto the protein core, and serve to improve fixation in the leather matrix.

The principle of the product design is in most cases similar, however based on different types of monomers, on different ratios of starch hydrolysate vs. protein hydrolysate, the final product performances will vary. This concept ensures the need of a minimal amount of needed chemicals for production.

Even both - wet white shavings and chrome shavings - can be used in the production process. In the case of chromium-containing shavings, the chromium is suspended as Cr2O3 during hydrolysis. The simplest way is to simply leave the chromium oxide in the finished retanning agent; tests have shown that the chromium oxide is almost quantitatively absorbed in retanning by the leather. The amount of added chromium recycled in this form is a relatively small fraction (about 0.5%) compared to the amount of chromium bound in the leather by a chrome tanning process. Alternatively, the chromium can also be separated on a filter press. The dechromed hydrolysate is then further processed in the same way as the hydrolysate of a wet white tanning agent. The retanning chemicals produced in this way have a residual chromium content of <50 ppm. Wet White shavings produced with different tanning systems - Glutardialdehyde, Easy White, Zeolite, X-TAN) could all be used as raw material for X-Biomer; the differences in the final application were insignificant as the main component – is still protein independently of the the tanning technique.

One big advantage of an On-Site manufacturing (=INSITU) is, that products can be also produced in higher dilutions. Since transportation is not a factor anymore, and the application in retanning is anyhow in a drum full with water, energy intensive concentration steps are not necessary anymore. This saves cost and keeps the process simple. Another advantage of On-Site production is, that even a preservation of the product is not necessary, if the tanners is only producing for his near future demand. This saves cost for biocides as well.

4. Product portfolio

In order to be able to achieve maximum plant utilization, a whole range of products with different properties has been developed, all of which can be produced in the same plant. As mentioned above, the difference comes from the different selection, combination and ratio of the 3 main ingredients: protein hydrolysate, starch hydrolysate and a monomer. Even the hydrolysis grade – the resulting molecular weight distribution – is playing an important role. The best results have been obtained with a broad range of distribution, which can be achieved by running the right process conditions in terms of time and pH.

4.1 Resins

In the resin segment, the largest amounts of shavings hydrolysate can be recycled and processed, since the protein

part gave a good Fullness. The dependence on the type of monomer used has a great influence on the properties of the final products. For example, cationic monomers can significantly improve the exhaustion of anionic auxiliaries such as dyes, or sterically flexible polymer chains can positively influence softness. All these products can be produced from both chrome and wet white shavings.

4.2 Softening auxiliaries

Another category of auxiliaries used in larger quantities in retanning formulations are softening chemicals. Since oils are not soluble in water, they must be dispersed as an emulsion. It has been shown that this dispersion can be achieved with a protein hydrolysate grafted by acrylates and the minor addition of specific emulsifiers.

According to this principle, a lecithin softener was produced which has >90% organic content in the solids. Other combinations are also conceivable.

4.3 Polyacrylates

By increasing the amount of monomer, products can be obtained which, on the one hand, show comparable applications to acrylate binders and, on the other hand, still have a bio content of 50%. In this way, the effluent values of retanning liquors are significantly better biodegradable compared with liquors of pure polymer tanning agents.

4.4 Syntan Hybrid

All the products mentioned so far have no tanning power, i.e. they can only be exchanged for a syntan or a vegetable tanning agent in a formulation to a limited extent. For this reason, the INSITU product range was extended by a hybrid in which a Syntan Precurser is the "monomer" condensed with protein hydrolysate. The resulting product is a true hybrid, has a bio content of about 50% based on solids, and has the desired tanning effect. It behaves differently from a simple mixture of separate components.

4.5 Deliming agent

The development of an ammonium salt-free deliming agent takes advantage of the amphoteric character of protein hydrolysates, which imparts a certain buffering property to the product, as well as the complexing ability of polyacrylates towards calcium ions. The combination of these two properties in a graft polymer ensures the partial or complete replacement of ammonium salts during the deliming process. This not only replaces an inorganic product, the production of which requires a relatively large amount of energy, with a renewable agent, but also reduces the frequent problem of existing effluent limitations for ammonium nitrogen in tannery wastewater.

5. General Product Performances

Normally a disadvantage of natural based products are the lack of certain fastness performances. However, in this process due to the polymerization the opposite is the case. All products are characterized not only by good filling effects and color intensity; also lightfastness and heat-yellowing values after polymerization were very good, which is particularly interesting for an application in the field of automotive leather. Due to the process all products have very limited amount of salt, which is an environmental benefit in many regions of the world.

Even the formaldehyde (FA) residue is zero, because no formaldehyde is used during the entire process. All results compared to peer products summarized in fig. 2 for the example of Resin types:

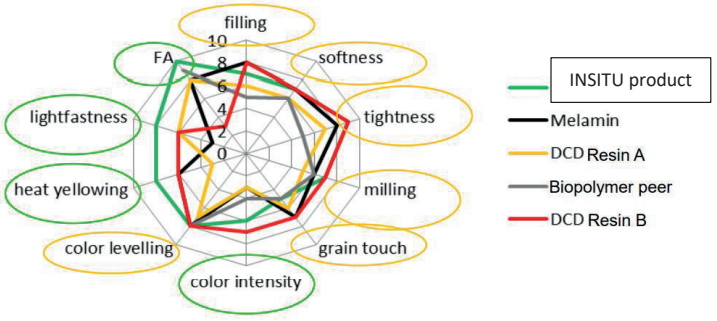


Fig.2: Performance on leather of recycled INSITU product versus peers

Due to the high biocomponent, all products are significantly more biodegradable than their synthetic peers. While, for example, sulfone- or phenol-based syntans are only approx. 25% degraded after 28 days, the INSITU products are classified as "readily biodegradable" according to the OECD test:

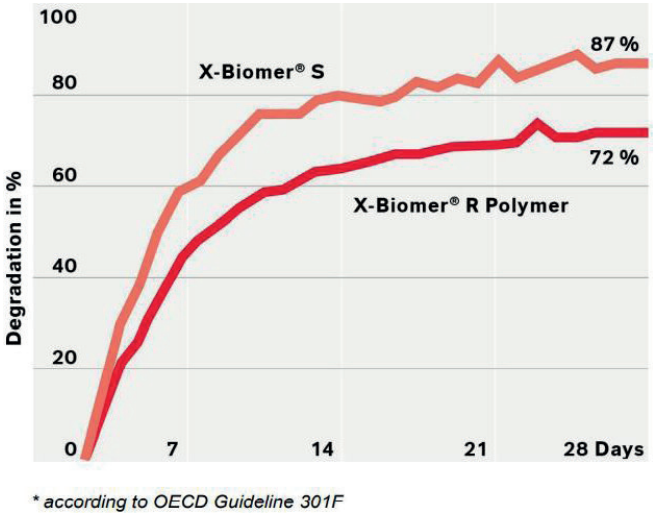


Fig. 3: Biodegration results of the two types of INSITU products: Resin (A) and Polyacrylate (B)

6. Conclusions

As a conclusion we believe, the tanning industry should broaden its scope of leather making and be encouraged to discover new way of operations. In order to minimize logistics and packaging decentralized on-site solutions (=INSITU) can help a lot and are opportunities to reduce cost and generate additional value. The pilot study mentioned above has proven the technical and economic feasibility. A range of products out of shavings have been developed and tested in many applications with promising results. About 1/3 of shavings can be recycled in a On-Site production of retanning chemicals replacing products, the tanner otherwise has to purchase. The manufacturing process can be kept relative simple and easy, no separations, no concentrations, no preservation is necessary, if the products get directly used again.

References

MASS BALANCE IN LEATHER PROCESSING, J. Buljan, G. Reich, J. Ludvik, UNIDO, US/RAS/92/120; 9.8.2000

WHAT MAKES THE DIFFERENCE BETWEEN AN INTERESTIN INNOVATION AND A DISPUTIVE INNOVATION, Dietrich Tegtmeyer, World Leather, August/September 2017

Note