Heidemann Lecture

A natural plant crosslinker from olive waste for leather tanning

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Ladies and Gentlemen,
This lecture has been instituted by IULTCS to honour the memory of Professor Dr. Eckhart Heidemann, who always supported the idea and objectives of IULTCS and who created a special session on fundamental research and collagen – also known as "Heidemann Symposium" – which used to precede the other congress program, for many years. Therefore, I feel deeply honoured and pleased by the invitation of the Scientific Committee and Organizers of the XXXI IULTCS Congress to give the Heidemann Lecture 2011.

Indeed, it is much more than a privilege for me as a scientist and teacher in tanning technology to be the speaker today, not least because I came to the area of leather technology via late Prof. Eckhart Heidemann, my supervisor at the Technical University of Darmstadt, where I took my doctoral degree, in 1986, exactly, at the leather research department once founded by Prof. Edmund Stiasny, who was followed by Prof. Adolf Kuentzel and later by Prof. Heidemann. As a result of the process of shrinking of the German leather industry, the world-renowned university department of "Protein and Leather Research" was closed down with the retirement of Eckhart Heidemann in 1990. Now, just 21 years later, Lederinstitut Gerberschule Reutlingen had to close down as well, basically, for the same reasons. However, considering still growing world-wide leather manufacture and questions raised e.g. in connection with sustainability, fundamental and applied research on leather is required to continue.

On the other hand, I also cannot imagine any place in the world fitting better than Valencia/Spain for presenting a paper entitled "A natural plant crosslinker from olive waste for leather tanning", as Spain is well-known to be the world's leading producer of table olives and olive oil.

1. Introduction

Having a look some hundred thousand years back when stabilized animal skin by chewing (principle of chamois tannage) and smoke tannage (following to the discovery of fire) were discovered by mankind, this type of leather making and using resources could certainly be considered an environmentally acceptable process.

And also the "Iceman", a human being from Copper age, found in the European Alps in the frontier area between Italy and Austria who has been reported as wearing fur clothes "tanned" by a special fatliquor procedure that has to be seen as an "impregnation" rather than a tannage [1], could still be seen as acting in the same line.

But in those early times the (main) interest of mankind had been the stabilisation of hides and skins – available from animals hunted for the need of nourishment – just for their effective use in personal protection; although, from today's scientific perspectives, this could possibly be considered as the first attempt for pollution prevention and control by avoiding uncontrolled rotting of hunting/slaughtering waste in the environment.

And, indeed, leather manufacturing is in itself recycling – or as mentioned first by IULTCS Past President Elton Hurlow: *"Leather is a sustainable environmental solution to the very real disposal problem of a large volume of hides and skins that originate from the meat industry …"* [2].

Within the last years, *sustainable development* more and more has become a major guideline concerning our life and industrial production.

The term which was used by the World Commission on Environment and Development (Brundtland Commission) coined what has become the most often-quoted definition of sustainable development as *"Development that meets the needs of the present without compromising the ability of future generations to meet their own needs".*

By IUCN, "The World Conservation Union" [3], it has been shown that the field of sustainable development can be conceptually broken into three constituent parts: environmental sustainability, economic sustainability and socio-political sustainability (Fig. 1).

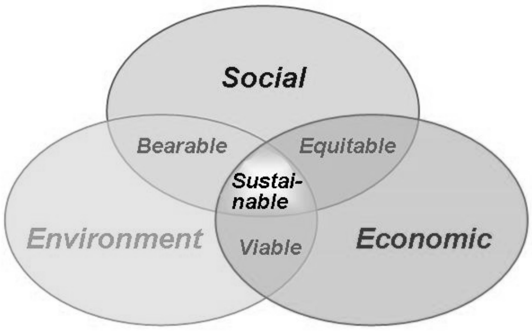


Fig 1. Scheme of sustainable development – at the confluence of three constituent parts

Sustainability can be related to different levels of consideration, i.e. it can be considered as a local, regional, national or global issue. While it is increasingly considered as a global issue from an ecological point of view, the focus of economic and socio-political sustainability is often a national one.

Practical approaches to realizing the idea of *sustainable development* in manufacturing companies, in general, are followed up by *cleaner production* which includes

- reduction of energy use,
- minimization of water consumption
- use of renewable resources, *a n d*
- reduction of waste generation.

These objectives are valid also for future development in leather manufacturing. Leather production, like many other industrial processes, does indeed involve the generation of polluted waste water and solid by-products or wastes, so that an appropriate effluent treatment and waste management are the subject of a must, nowadays. This also includes the reuse of valuable by-products, which does not cause too many problems in the case of untanned material like e.g. splits or split off-cuts that can be used in the production of gelatine and sausage casings [4], and also fleshings that e.g. can be used in biogas production or directly to replace the fuel for energy generation after separation of fat, as demonstrated by Suedleder GmbH & Co. KG, a leading German contract tannery. In Suedleder tannery [5] this has resulted in 50% CO_2-reduction (savings of 4,500 t/a CO_2).

Of course, some thousand years ago, by-products such as connective tissue should not have created any problems since they were most probably consumed as food. However, factors like fashion, commercial interests and globalisation had not existed yet. Also preservation in today's sense should not have played a major role; skins were either used freshly enough after separation from the animal body *or* certain defects resulting from putrefaction were probably considered as normal. Today, in the preservation of hides and skins common salt is still the most extensively used agent, although the 30-40% sodium chloride which is needed for this process is causing serious problems, especially, in countries with warm and dry climate, where fresh water resources are at a premium.

Obviously the best solution from the environmental point of view is the use of fresh (green) uncured or chilled hides for processing wherever the proximity of the tannery to the slaughterhouse is given. In other words, this will always be restricted by the respective slaughtering and flaying conditions as well as the climate in the place of processing. However, looking for a really sustainable leather manufacture, the sourcing of hides and skins becomes of equal importance to controlling the manufacturing process. This will always call for processing of raw hides at the place of origin [6].

Regarding the tanning process itself, in the pre-industrial period lasting nearly till the end of the 19th century, vegetable tannage or tanning with Aluminium (tawing) have been the techniques employed depending upon the intended use of the resulting leather – i.e. based on the leather characteristics required.

Following the discovery of the tanning effect of chromium salts by the German Friedrich Knapp in the 1850's [7] and further development of the process by M. Dennis (1893) [8] who brought it into a practical system, chrome tannage represented a major step towards industrialisation, and it became the worldwide accepted standard method of tanning during the last century.

As a result of an increasing sensitivity to the ecology and health concerns by the majority of people, different approaches for an improved chrome management were developed, within the last decades. This has involved chrome-recycling techniques, a better understanding of the individual and combined influences of process parameters as well as the development of high exhausting chrome tanning systems.

Today's "greener" way of thinking brings about new requirements on process-chemicals and -technologies in leather manufacturing. Moreover, this way of thinking has been much intensified by an increasing number of press reports and television programmes raising questions concerning the environmental burden and consumer health. In addition, there are the increasingly stringent requirements of governing tannery effluents as regards to their chrome content and also certain issues involving the disposal or utilization of by-products containing chrome for which chromium tannage, in particular, has come under criticism.

Considering, on the other hand, the worldwide consumption of 350.000-400.000 tons/annum chrome tanning agents used for the manufacture of ≥80% of the world's leather production and the consumption of vegetable tanning agents of approximately 200.000-250.000 tons/annum, it becomes more than evident that a (complete) replacement of chromium by vegetable tannins is not realistic. Increasing the production of vegetable tannin extracts by the necessary factor, in the case of wild growing trees like Quebracho, would immediately decimate their existence and in the case of e.g. mimosa grown in plantation, the required cultivation area would not be available; *or in other words:* extending the plantation area of tannin producing plants to the debit of agricultural food production may not in the least be considered as sustainable – in a world where lots of people are still suffering from hunger.

Although different studies showed that chrome tanned leather produced in accordance with the 'best available technique' principle can be classified as environmentally compatible, there is an increasing share of chrome-free tannages besides 80-85% of worldwide leather production being based on chromium tannage, today [9]. This is mainly due to the growing demand for so-called free-of-chrome leathers ("FOC-leathers") in the automotive industry where the current share of FOC-leather is about 25-30%.
The principle of FOC-leather production is based upon a wet-white pre-tannage, which is followed by a retanning using polyphenols (vegetable and syntan tanning agents) and other organic-synthetic retanning agents. Today, wet-white production is achieved mainly by e.g. glutaraldehyde tanning agents (partially modified), THPS, chlorotriazines or other reactive organic compounds.

However, initially, the idea of "wet-white" pre-tannage as an alternative to wet-blue that was followed e.g. by E. Heidemann, implied the use of aluminium salts [10]. Resultant white leather intermediate products showed a good shaveability and could be stored for an appropriate duration. At the same time, unfortunately, the leather character was already fixed (firmer leather type with poor fullness) more than desired for the case of a flexible intermediate product. Moreover, aluminium shows a high leachability and therefore, problems could be arising in post-tanning.

Compared to chrome leathers advantages of today's FOC-leathers include

- the absence of "heavy metal",
- less problems in solid waste disposal (*including sludge*) and
- improved performance in dry-shrinking behaviour.

On the other hand, well-known disadvantages include

- higher COD in the effluent,
- reduced fixation of dyestuffs and fatliquoring agents,
- extremely difficult hydrophobing,
- more difficult "handling" in production and processing,
- lower stability and mould resistance of semi-finished products *(wet-white)*.

In principal, the course of tanning in modern processing can be divided in 2 steps:
1. The pre-tanning or main tanning stage for the stabilisation in order to permit mechanical treatment (sammying, shaving) and the production of a storable and transportable semi-finished leather product (wet-white, wet-blue) *and*
2. The retanning/filling process for adjustment of the required leather characteristics (e.g. fullness, shape-retention ability, grain firmness, embossability, buffability).

However, neither wet-blue nor wet-white production can be considered as sustainable processes in the proper sense, since both chromium salts and glutaraldehyde (or any other reactive organic-synthetic tanning agent) are non-renewable raw materials.

2. Materials and methods

More recent research concerning ecologically beneficial methods of pre-tanning or stabilising the skin (collagen matrix) include

- wasserglass stabilisation [11-13],
- enzymatic crosslinking [14, 15] *and*
- application of natural plant crosslinkers [16, 17]

There are three main objectives of these studies:

- To establish an innovative, sustainable and environmentally friendly tanning system – as an appropriate complement to the existing tanning methods

- Stabilisation/pre-tanning of the skin material – under the avoidance of conventional chemical tanning agents – so that a satisfactory mechanical processing (sammying/splitting and shaving) can be achieved
- To obtain by-products/waste (shavings) enabling practically unlimited usage

Skin stabilisation by wasserglass results in a white, stable and shaveable material that proved to be storable for months. However, there is no significant increase in the shrinkage temperature, and therefore reluctance for technical application.

Basis of the idea of a biotechnological tanning system is the application of an enzyme from the group of transglutaminases for which technical applications already exist in the field of food-technology. The effect of crosslinking results in the formation of high-molecular protein aggregates with modified characteristics (e.g. increased thermal stability). This is achieved by irreversible crosslinking by covalent isopeptide bonds between glutamine- and lysine-side chains.

In a cooperative research project entitled "Enzymatic crosslinking of skin in leather manufacturing" and funded by the German Federal Ministry of Education and Research (BMBF), the application of transglutaminases in tanning was studied [18]. Unfortunately, the enzyme transglutaminase could not provide either sufficient stabilisation or a significant increase in the shrinkage temperature as required for leather manufacture, although transglutaminase produces irreversible crosslinking with denaturated collagen (gelatine).

Therefore, on the basis of existing protein-crosslinking know-how of our project partner N-Zyme BioTec, complementary crosslinking- and tanning-experimentation with special plant extracts were carried out. In these trials, the application of an (enzymatically) activated extract from olive solid waste material proved to be successful.

As a consequence of this, a new research project entitled "Production of a natural plant crosslinker from olive waste for leather tanning" has been set-up as a cooperative project under EUROSTARS Program [19].

Olive solid waste material includes leaves – originating from olive harvesting – as well as the effluent and residues from olive oil- and table olive production. In Europe (about 95% of world cultivation area for olive trees) 12 million tons of olives are produced, annually, and with a growth rate of table olive and olive oil-production being 3.5-4% per annum, olive industry is considered the fastest growing agro-food-sector.

Approximately 30 million tons of olive-residues from oil and table olive production are generated in the Mediterranean area every year (Fig. 2).

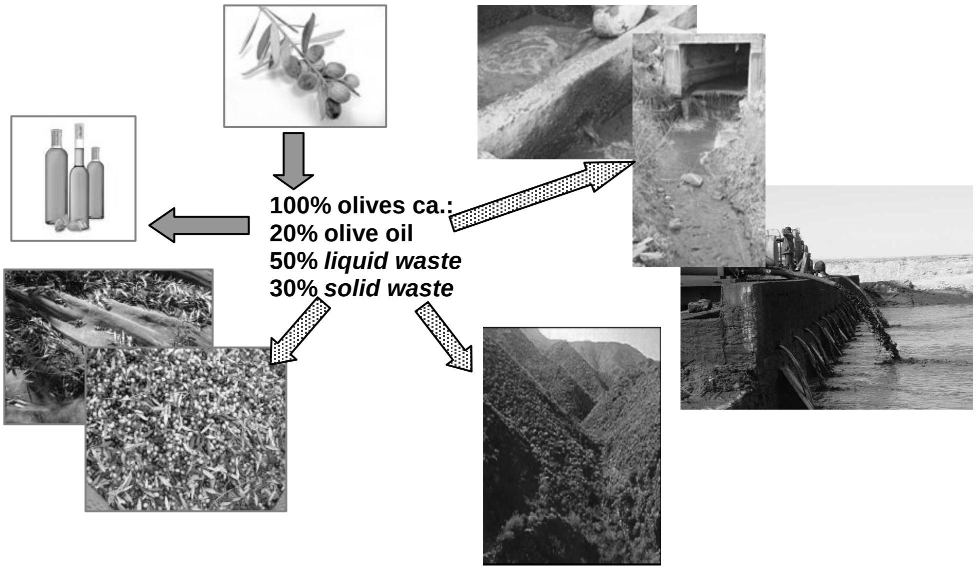
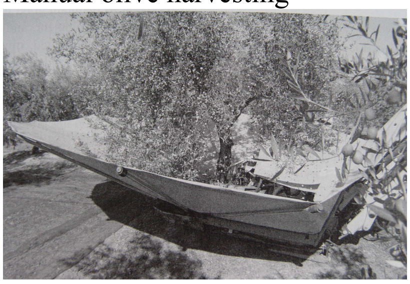


Fig. 2 Olive residues from oil and table olive production

The generation of leaves and twigs, merely, during olive harvesting is about 5-10% on total weight, especially, when modern mechanical harvesting techniques are applied (Fig. 3). At an olive mill where olives delivered are separated from leaves, some tons of leaves are collected per day. In addition, there are leaves which accumulate during trimming of olive trees in spring time.


Manual olive harvesting


Mechanical olive harvesting

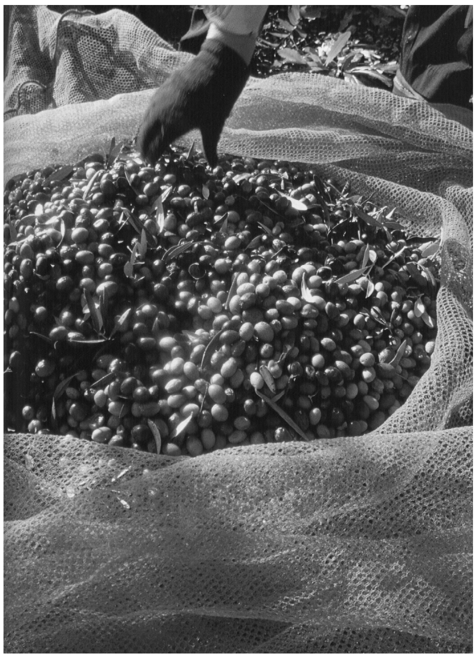


Fig. 3 Generation of leaves and twigs during manual and especially, mechanical olive harvesting

It has been shown that olive by-products of the olive industry contain precursor molecules, which can be transformed by a catalytic reaction into an activated molecule, which can covalently crosslink the collagen of hides and skins. N-Zyme BioTec is the inventor of the new crosslinker and the owner of the patent WO 2009/065915 [20]: *Agent and methods for tanning skins and pelts* and of the international trademark *wet-green*® (WIPO 1012351) [21].

The wet-green® technology which was developed together with LGR uses a new and innovative tanning agent based on an aqueous olive leaf extract. The extract is produced from olive leaves that accumulate in huge amounts as waste during the olive harvest and the trimming of the trees in the Mediterranean countries without any valorisation today. Up to now, the majority of the leaves is deposited or burned leading to a negative environmental impact.

Together with a sub-contractor, N-Zyme BioTec developed and industrialized an efficient aqueous extraction process totally waiving any organic solvents. The extract is concentrated and could be transported to the tanneries without any safety instructions. The solid leave residues are given to a local farmer who uses the organic material either in composting or biogas production.

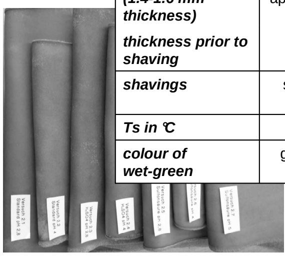
Using the activated extract, at LGR series of tanning trials in lab- and pilot-scale have been carried out mainly, on bovine hides of South-German origin. The novel (pre-)tanning process is carried out in conventional process vessels (i.e. tanning drums) and there is no need for "new" process chemicals besides the innovative natural plant crosslinker.

3. Results and discussion – conclusions

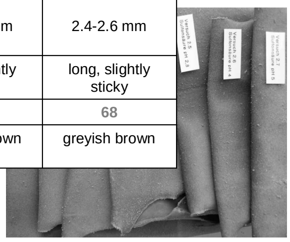
The overall objectives of the German-Spanish cooperation project have been the production of a new tanning agent derived from olive by-products and integration of the new tanning agent into the complex process of leather manufacturing. Therefore, in close cooperation of LGR with N-Zyme BioTec, the activation and leather tanning process have been constantly improved and optimised by using different activated olive residues, mainly derived from olive leaves.

Application of an activated extract from olive leaves (OLE) produced a novel stable leather intermediate – "wet-green®" – with good shaveability and a shrinkage temperature of >70°C. This new leather intermediate forms an excellent basis for the production of different kinds of crust leather [22].
In order to define the best possible preparation of skin material for pre-tanning with the new plant crosslinker – and also from the viewpoint of salt reduction in tanning – tanning trials with variations of pickling or conditioning systems have been conducted (Fig. 4). Systems applied in these investigations were essentially based on knowledge and practical experience from the field of (free-of-chrome) wet-white tannage and vegetable tannage. Measured shrinkage temperatures of the resulting wet-green® varied from 64-73°C (whole range) and 64-68°C in the case of lab-scale experiments. Wet-green® colours varied from yellow-brown till greyish green depending on the type of acid(s) and pH applied in the pickle.

Fig. 4 Investigation of *wet-green®* pickling variations



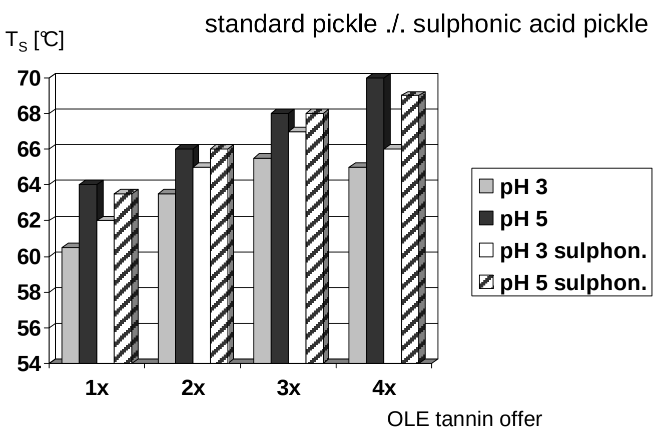
	Trial 2.5 Sulphonic acid	Trial 2.6 Sulphonic acid	Trial 2.7 Sulphonic acid
pickle	pH 2.8-3	pH 4	pH 5
pH-adjustment	pH 5.5	pH 5.5	pH 5.5
sammability	good	good	good
shaveability (1.4-1.6 mm thickness)	good, native appear. backside	good, native appear. backside	good, native appear. backside
thickness prior to shaving	2.6 mm	2.4-2.6 mm	2.4-2.6 mm
shavings	short, slightly sticky	long, slightly sticky	long, slightly sticky
Ts in °C	64	67	68
colour of wet-green	greyish brown	greyish brown	greyish brown



However, the most important result from these studies is the fact that wet-green® production can obviously be carried out in a relatively wide range of ways of preparing the pelt: with or without pickling treatment or conditioning by acid salts. As a tendency, obtaining of higher hydrothermal stability (shrinkage temperature) has been observed in the case of applying the crosslinker at less acidic pH value.

Another main objective of serial trials carried out in laboratory scale has been the determination of the required (minimum) amount of crosslinker applied if conduction of the processes of mechanical de-watering (sammability) and correct adjusting of thickness (shaveability) has to be kept on high-quality level, as required in industrial leather manufacturing (Fig. 5). As a result of these experiments, the crosslinking agent offer required for achieving sufficient skin stabilisation could be reduced by 50% with respect to amounts used, initially.

Fig. 5 Optimisation trials – *wet-green®* tannage



In the meantime, also both numerous tanning trials in pilot scale and various small-technical scale trials have been carried out at LGR, in order to investigate mainly, reproducibility of the new crosslinking system and transferability into process vessels of larger scale. In these trials, results obtained from laboratory scale experiments could be principally confirmed. However, as expected due to increased mechanical drumming action in larger scale, a tendency towards even better tanning behaviour and higher shrinkage temperature could be observed.

Such batch production of wet-green®, in general, yields a leather intermediate possessing excellent sammability and shaveability. As known in the case of vegetable tanned leathers, wet-green® leathers also show a certain susceptibility to iron staining (i.e. blue-grey to black dots caused by contact with iron implements / rust) and, therefore, they may require the application of an appropriate masking agent [23].

Wet-green® storage over a longer period (e.g. a couple of weeks) requires application of fungicides similarly to the case of other types of wet leather intermediates like wet-blue and wet-white.

Retanning trials carried out so far, revealed that the retannage of the new intermediate is principally comparable with wet-white. However, a reduction in retanning agents – like syntans and/or vegetable tannins – and filling agents seems to be possible, in most cases.

Moreover, dyeing experiments showed that dyeing intensity is higher as compared to that of leathers on the basis of commercial wet-white. Therefore, it will probably be possible to save dyestuff in leather dyeing, thus reducing costs and protecting the environment.

In addition, from LGR's side, crust material and final leathers have been produced on the basis of wet-green® in order to evaluate the suitability of the new intermediate for manufacturing different leather articles. In general, it could be observed that crust from wet-green® fulfils all relevant requirements concerning physical test parameters – comparable with chrome-free crust from wet-white.

Partially, some interested leather manufacturers (e.g. industrial tanneries) have been included in these studies by receiving wet-green® samples to gather some first knowledge and experience on the new material and give their feedback together with general impression. In this way, e.g. in the case of upholstery leather based on wet-green®, the principal processability into leather-covers of high-quality upholstered furniture could be demonstrated. For automotive leather all essential technical requirements on full-grain leather set e.g. by automotive producers could be fulfilled.

The wet-green® technology uses a new and innovative tanning agent based on an extract produced from olive leaves that accumulate in huge amounts as waste during olive harvest and trimming of the trees in the Mediterranean countries without any valorisation today. So, wet-green®-technology addresses a natural high-quality leather product based on a real sustainable pre-tanning process in which conventional chemical tanning agents are replaced by a natural plant crosslinker.

Residual floats, sludge, shavings and trimmings from wet-green® process do not contain usual tanning chemicals (chrome, aldehydes and other reactive organic substances) and, therefore, these by-products could be integrated either in material or thermal applications.

The tanning process is carried out in conventional process vessels and there is no need for new process chemicals besides the novel natural plant crosslinker. In contrary, pilot studies have shown that the amount of chemicals in the post-tanning steps could be reduced which is in scope with the sustainable approach.

Another issue to be dealt with is the undesirable problem of mould occurring in the wet leather intermediate stage. A delay of further processing in the wet-blue or wet-white stage can lead to mould growth and hence a potential loss in quality and value. Avoiding such losses includes the use of effective preservatives in the (pre-)tanning system. Although our former investigations showed that the initial fungicide content is reduced significantly by post-tanning operations and finishing, there is an interest in avoiding the presence of those chemical agents mainly on behalf of consumer protection.

Therefore, further investigations at LGR included the development of a universal intermediate stage (pre-/tanned) that requires no inclusion of preservatives / fungicides. I.e., in addition, this product should allow drying, and subsequently wetting-back without any problem.

This requires an appropriate stabilisation/crosslinking and sufficient increase in the shrinkage temperature to enable sammying and shaving as well as appropriate “fibre separation” (e.g. by the filling effect of certain tanning agents or fatliquors) to enable drying without sticking within the fibrous collagen structure [24, 25].

Within the scope of a research project, different series of pre-tanning trials – at first, with the application of a wide range of individual products having organic (e.g. aldehydes, syntans, polymers, other types of resins) and inorganic (e.g. aluminium salts, phosphates, wasserglass) nature, and then with a large number of their promising combinations – have been conducted at LGR [26].

In these investigations, besides variations in shrinkage temperature, significant differences concerning “fibre separation” effects became visible. The most promising experiments have been those on the basis of either the novel plant crosslinker from olive leaves or glutaraldehyde, especially, in combination with syntans.

Best combinations found in lab-scale trials have been selected for pilot-scale experiments. These experiments in larger scale using half sides, have been carried out in order to establish the characteristics of resulting leather intermediates regarding hydrothermal stability, shaveability and wetting-back behaviour. Finally, crust leathers have been produced from the selected intermediates and evaluated in terms of dyeability, touch and area yield, in comparison with crust obtained by standard processing. Although the new technology suggested will still need some optimisation, results are extremely promising and giving inspiration about a further increase in the sustainability of leather manufacture.

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(I) “Production of a natural plant crosslinker from olive waste for leather tanning”

(II) “Generation of a universal intermediate stage requiring no preservation”

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