



A new green leather

Stefan Marx, Jens Zotzel, Heinz-Peter Germann and Stefan Banaszak
N-Zyme BioTec GmbH, Germany



A natural plant tanning agent has been developed from olive waste

About 90% of the world's cultivated area of olive trees is found within Europe. Here, with approximately 12 million tons of olives produced annually, and with a growth rate of 3.5-4% per annum, the olive industry is considered the fastest growing agro-food sector. Approximately 30 million tons of olive residue (including brine and olive-mill wastewater) from oil and table olive production are generated in the Mediterranean area every year. In practice, the yield as olive oil is approximately 20%, the balance being 50% liquid and 30% solid residue.

The leaves and twigs that are inevitably gathered during olive harvesting is about 5-10% of the total weight, especially, when modern mechanical harvesting techniques are applied. There are also leaves which accumulate during pruning of olive trees in spring time. Up to now, these leaves are mostly deposited or burned leading to a negative environmental impact.

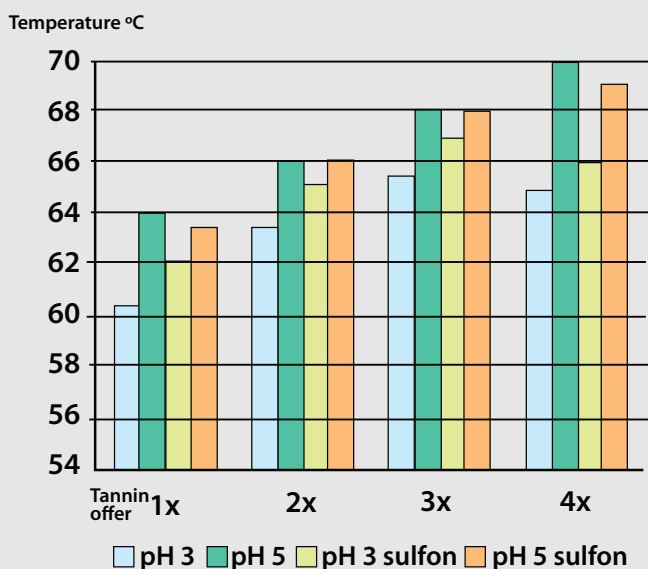
However, it has been shown that based on an aqueous extraction process, these olive by-products contain precursor

Panel 1: 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



Panel 2: Optimisation trials - Wet-green tannage Standard Pickle/Sulfonic Acid Pickle



molecules, and these can be transformed by a catalytic reaction into an activated molecule. This can form chemical combinations with the collagen of hides and skins. [Legend 1, 2 & 3]

As a result of close cooperation between N-Zyme BioTec and LGR (Lederinstitut Gerberschule Reutlingen), a tanning process has been developed and optimised on bovine hides of South-German origin using different activated olive residues. This extract is derived from olive leaves, and the processing is performed in conventional tanning vessels without the need for new additional process chemicals. This novel leather – known as Wet-green® – shows good shaveability and a shrinkage temperature $\geq 70^\circ\text{C}$. This forms an excellent basis for the production of different kinds of crust leather [ref 1].

To define the best possible techniques for using this new tanning agent, many variations of pickling or conditioning systems have been trialled. These have been based on knowledge and experience from the field of wet white (free-of-chrome) and vegetable tannage, an example of which is shown in *Panel 1*.

The most important result from these studies is that Wet green production can be carried out based on a relatively wide range of pelt preparation techniques. One objective of the initial trials was to determine the optimum tannin offer to best suit shrinkage temperature as well as samming and shaving requirements. These findings are given in *Panel 2*.

In these early investigations, the shrinkage temperatures of the different leathers ranged from $64\text{--}70^\circ\text{C}$ in the case of lab-scale experiments. Also, the colour varied from yellow-brown to grey-green depending on the type of acids and pH applied in the pickle.

But other further investigations were then made at the conventional acid/salt pickle stage, and included tanning at a higher pH directly after deliming and bating. This provided the advantage of avoiding any addition of acid or salt – both major steps in terms of rationalisation and avoiding the salinity issues stemming from the conventional acid/salt pickle stage. Moreover, a tendency was found where higher hydrothermal stability (shrinkage temperature) was observed when the process was performed at less acidic pH values.

At the same time, pilot and small technical scale trials were carried out to investigate the reproducibility of the new tanning system and up-scale for commercial application. In this situation a tendency towards better tanning behaviour and further improvements in shrinkage temperature could be observed.

The properties of Wet-green

In general it has been found that:

- A new leather possessing excellent sammability and shaveability can be produced.
- In common with vegetable tanned leathers there is a certain susceptibility to iron staining (i.e. blue-grey to black dots caused by contact with iron implements/rust) hence a possible requirement of an appropriate masking agent [2].
- When stored for periods greater than two to three weeks an application of fungicides is required as with other types of wet leathers, such as wet blue and wet white.
- Retannage of the new product is mainly comparable with wet white. However, a reduction in retanning agents such as syntans and/or vegetable tanning and filling agents seems to be possible.
- The dyeing intensity is higher when compared to that of leathers on the basis of commercial wet white. It is possible to save dyestuff in leather dyeing, thus reducing costs and protecting the environment.

Crust material and final leathers have also been produced to evaluate their suitability for manufacturing different leather articles. In general, the crust from Wet green fulfils all relevant requirements concerning physical test parameters, and is comparable in those terms with chrome-free crust from wet white.

In addition, some industrial tanneries have been involved in these studies to provide commercial opinions and technical feedback. So, for example, in the case of upholstery leather based on Wet green, the scope for conversion into leather covers for high quality upholstered furniture could be demonstrated. For automotive leather all essential technical requirements on full-grain leather set by automotive producers could be met.

Advantages of a new crust intermediate

Another issue that has been investigated is that a delay in processing at both the wet blue or wet white stage can lead to mould growth, hence a potential loss in quality and value. Effective preservatives are needed in these situations, but there is a growing interest in avoiding these chemical agents mainly on behalf of consumer protection.

For this reason, investigations based on this new product included the direct development of a crust intermediate stage that requires no preservatives/fungicides. In particular, this product should allow drying and subsequent wetting back without any problem.

This requires an appropriate stabilisation to provide an increase in the shrinkage temperature to withstand shaving. It should also ensure sufficient “fibre separation” (usually achieved by the filling effect of certain tanning agents or fatliquors) to enable drying without sticking within the fibrous collagen structure [3,4].

Trials at the pretanning stage, first using a wide range of organic (aldehydes, syntans, polymers, other types of resins)



Panel 3: Generation of leaves and twigs during manual, and especially, mechanical olive harvesting



Manual olive harvesting

Panel 4:



Mechanical olive harvesting

and inorganic products (aluminium salts, phosphates, wasserglass) individually, and then in promising combinations – were conducted at LGR.

Over and above variations in shrinkage temperature, significant differences concerning fibre separation effects became clear. First promising findings were developed based on the new plant tanning agent from olive leaves, especially, in combination with syntans.

Accordingly, crust leathers have been produced and evaluated in terms of dyeability, touch and area yield, for comparison with crust obtained by standard processing. This new approach still need optimisation, but the findings are extremely promising.

Summary of developments

- Wet-green technology produces a natural high quality leather product. This is based on a truly sustainable pre-tanning process where conventional chemical tanning

agents are replaced by a natural plant tannage based on residues from table olive and olive oil production.

- This technology has been developed into full scale commercial manufacture of upholstery leather, and the potential for other types of leather are under evaluation.
- The tanning process can be carried out in conventional process vessels and there is no need for any additional new process chemicals.
- Pilot studies have also shown that the amount of chemicals in post-tanning steps can be reduced, hence scope for savings in materials consumed and less waste for effluent treatment.
- Residual floats, sludge, shavings and trimmings from Wet green process are free from chrome, aldehydes and other reactive organic substances. For this reason, solids as by-products from leather manufacture and from effluent treatment could be integrated in material or thermal applications.
- There is the possibility of producing a new commodity in the form of a dry leather intermediate (“green crust”) that can readily be wetted back for targeted retannage, dyeing and fatliquoring. This product would avoid the problems associated with preservatives/fungicides, and provide a new and flexible alternative to storage in the pretanned/tanned wet state. ©

Legend

- 1] This is a condensed version of the paper entitled “A natural plant crosslinker from olive waste for leather tanning” presented by H.-P. Germann (“Heidemann Lecture”) to 31st IULTCS Congress, Valencia, Spain, 2011.
- 2] N-Zyme BioTec is the inventor of the new tanning agents 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)
- 3] The extraction process totally avoids any organic solvents. The extract is concentrated and could be transported to tanneries without any safety instructions. The solid residues from processing can be used either for composting or biogas production.

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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”

References

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