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DEVELOPMENT OF A TANNING TECHNO-LOGY WITH TANNING AGENTS FROM LIGUSTRUM VULGARES

INTRODUCTION

The sole use of vegetable tanning agents for pre-tanning as an alternative to synthetic or chromium-containing tanning agents is one way of improving sustainability and ecology in leather production. In recent years, a new group of secondary plant compounds, the iridoids or secoiridoids, has been discovered for use as tanning agents. The reaction mechanism is similar to the cross-linking mechanism of collagen with glutaraldehyde [1]. Currently, a tanning agent from olive leaves with cross-linking active substances deriving from the secoiridoid Oleuropein is commercially available [2]. In order to extend the product range of alternative vegetable tanning agents with covalent cross-linking mechanism by indigenous raw material, we screened a number of further plants for such covalently cross-linking active substances. Extracts from privet leaves showed a particularly high crosslinking activity. Privet belongs to the Oleacea family and is common in Asia with several species. In Europe, the species Ligustrum vulgare can be found everywhere, especially as a hedge plant for gardens. The main Secoiridoids in privet leaves are Oleuropein, Ligustalosid A and Ligustrosid [3]. The goal of this work was to explore, if tanning agents from privet leave can be used for production of leather. The following topics were considered in the development of tanning technology:

chemical properties of the crusts were tested with standardized testing

norms.

The diffusion and binding progress was estimated by determination of the denaturing temperatures in dependence of the tanning time.

- use of privet leaf extracts vs. ground privet leaves
- assessment of concentrations of the tanning agent and the pH control of the tanning process in lab scale
- investigation of the interaction of diffusion and binding of the tanning agent to skins on a pilot plant scale
- production of leathers with various retanning technologies and

RESULTS

ADJUSTMENT OF CONCENTRATION ON PELTS IN LAB SCALE

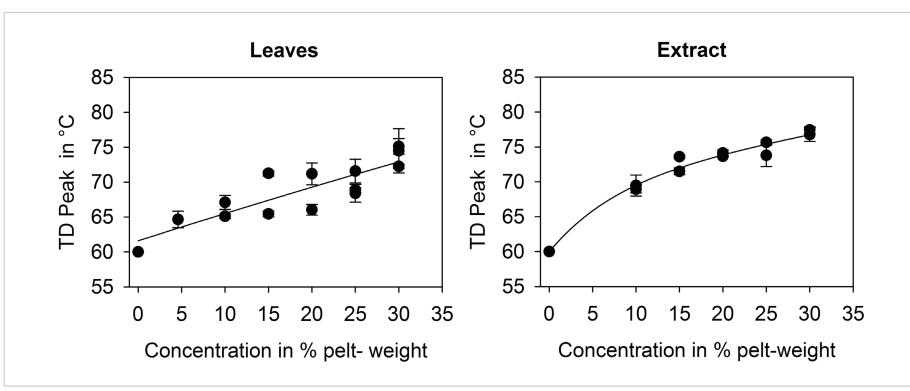


Figure 1: Denaturing temperatures (TD Peak) inside the tanned pelts with extracts from privet leaves and ground leaves as a function of concentration (pH pickle 3.5, pH end 4.1)

Acceptable denaturation temperatures inside the pelt (TD Peak > 70 °C) are achieved at concentrations of 25 % extract based on pelt weight and 30 % ground leaves, resp (Figure 1). The tanning is not perfectly uniform in most cases. The reproducibility of the tanning results is significantly better with extracts than with ground leaves. the power demand was regarded in Fig. 5. There it could be shown that the RF heating process is an efficient and energy saving technological alternative to common hot air processes.

ADJUSTMENT OF PH IN PICKLE ON PELTS IN LAB SCALE

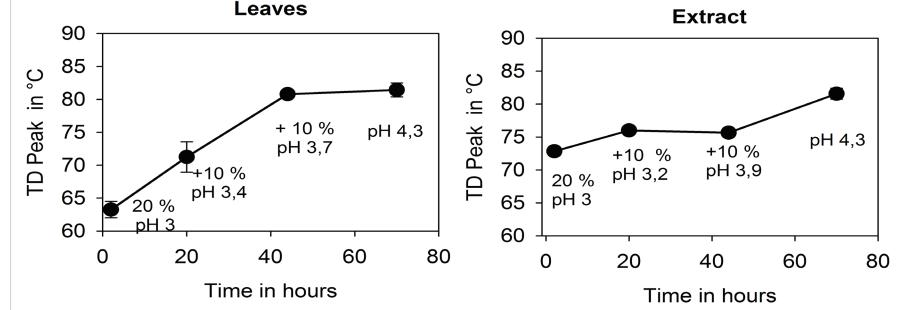
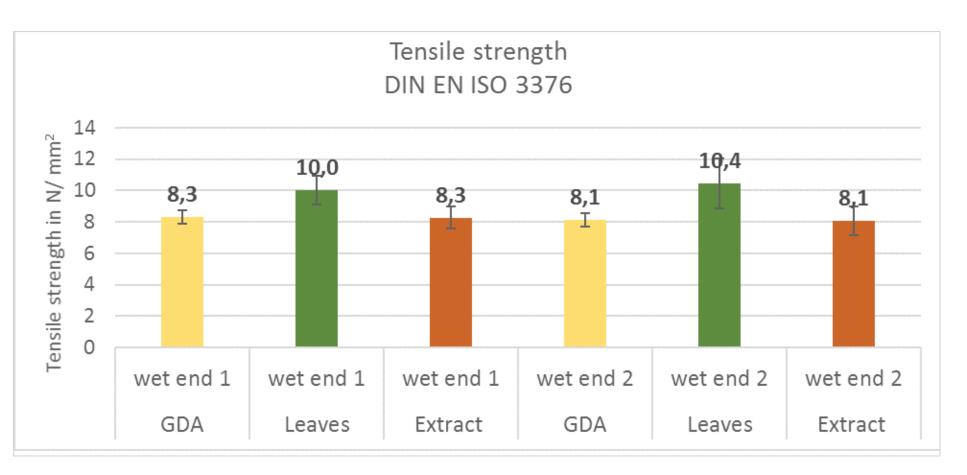


Figure 4: Time course of the denaturing temperatures (TD Peak) of the hide during tanning with privet leaves finely ground and extracts, numbers represents the addition of different amounts of tanning agent as denoted and the pH during tanning

The leathers show good mechanical properties comparable to Glutaraldehyde- tanned leathers. Some properties such as tensile strength are even better for the leathers tanned with the finely ground privet leaves compared with leathers tanned with privet leave extract or Glutaraldehyde (Figure 5).



testing of its mechanical properties.

METHODS

EXTRACTION OF PLANT MATERIAL

The plant material was collected from the cut of garden hedges and dried. The Extracts were produced according to a process developed by numerous optimization trials. The target parameter was a high cross-linking activity, which was tested on hide powder. The leaves were ground in a turbo-rotor-mill.

TANNING TRIALS IN LAB SCALE

Appr. 200 g pelt (limed cattle hide, standard liming protocol) were treatetd with privet-leaf-extracts or finley ground leaves in a parallel dyeing machine (diameter approx. 50 cm). Pelt mass, treatment time (36 h) and float volume were kept constant. Concentration of tanning agent and pH of pickle were varied.

The tanning results were evaluated by determination of denaturation temperature (TD Peak) of the cross-linked pelts with differential scanning calorimetry (DSC) (n = 3 DSC-measurements per sample)

Before DSC-measurement, samples were thoroughly washed with water and buffered to pH 7 to ensure comparability of the denaturation temperatures.

PRODUCTION OF LEATHERS

Crusts were produced in a 1 m-diameter tanning drum (Dosemat). Half croupons (cattle hides of mass class 20-25 kg) were used After liming pre-tanning was carried out with privet leaves extracts and finely ground leaves at constant concentrations. To estimate diffusion behavior samples were analyzed with DSC at different times. Crusts with two different wet-end technologies from the automotive sector were produced. Leathers with glutaraldehyde pre-tanning with the same wet end technology were produced as references. The mechanical and

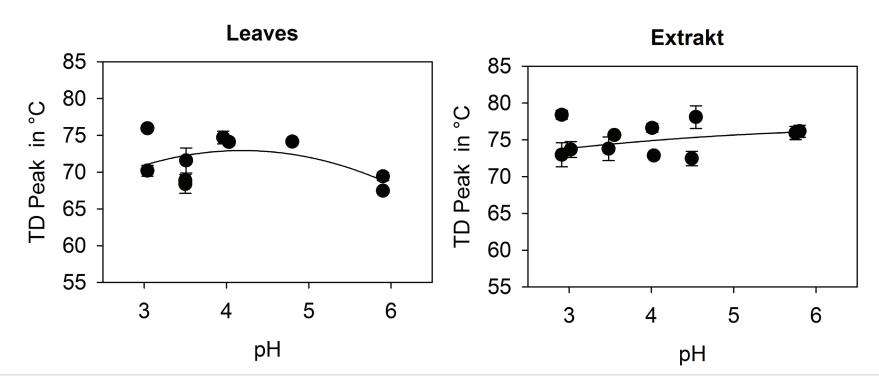


Figure 2: Denaturation temperatures inside the tanned pelts (TD Peak) with extracts from privet leaves and ground leaves depending on the pH of the pickle, C Extract = 25 %

The pH of pickle has only minor influence on the cross-linking results as shown by the denaturing temperature of the semi-finished products when considering the variation of the results from triplicate tests. During the production of the leather, however, dead-tanned leather with partial grain breakage could result if the process was carried out without pickling or with a high starting pH. The pH value has an influence on the intensity of the coloring of the semi-finished products: the higher the pH value, the darker the color and the more pronounced the grain. If extracts are used, the color of the pelts is brown, if ground leaves are used, the color of the semi-finished products is green (Figure 3).

Privet Leave Extract



Figure 5: Tensile strength of Leathers tanned with prive leaves privet leaf extract and Glutaraldehyde (GDA), wet end 1 and wet 2

CONCLUSIONS

Tanning agents from privet leaves contain Secoiridoids, which can be used to produce leather. It has been shown that privet leaves that are finely ground are just as suitable for tanning as extracts from ground leaves. This offers economic and ecologic advantages. Some mechanical properties like the tensile strength could be improved by tanning with the finely ground leaves.

REFERENCES

- [1] M. Schroepfer, M. Meyer, Investigations towards the binding mechanisms of vegetable tanning agents to collagen, Res J Phytochem, 10 (2016) 58-66.
- [2] J. Zotzel, A.C.-D.-. Sarafeddinov, S. Marx, H.-P. Germann, Agent and methods for tanning pelts and skins, in: WO Patent WO/2009/065,915, 2009.
- [3] A. Romani, P. Pinelli, N. Mulinacci, F.F. Vincieri, E. Gravano, M. Tattini, HPLC analysis of flavonoids and secoiridoids in leaves of Ligustrum vulgare L(Oleaceae), J. Agric. Food Chem., 48 (2000) 4091–4096.

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Figure 3: Color of tanned pelts with extracts from privet leaves and ground leaves depending on the pH of the pickle, C Extract = 25 %

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