



ALTERNATIVE LEATHER MANUFACTURING PROCESS - 2. ASSESSING THE LEATHER'S ECO-FRIENDLINESS

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Abstract: *It is the aim of this paper to assess the eco-friendliness of a bovine leather, obtained by an improved process that consists in pretanning with an oligomer resin, followed by low-offer chrome tannage. Namely, the leather tendency to release the tanning chemical auxiliaries was tested. The following analyses were performed to quantify the auxiliaries from aqueous leather extracts: total dissolved solids, organic and inorganic soluble matter, UV-VIS spectroscopy, HPLC chromatography. Experimental data indicated high release rates of oligomer and resorcin from the pre-tanned leather, which proves the reversibility of the pretanning process. The release rates of the same compounds after trivalent chrome tanning and retanning was about 4 times lower. This is due to the supplementary complexation effect of the oligomer resin and resorcin upon the trivalent chrome. Pretanning with oligomer resin and resorcin determined the decrease of chrome salt consumption by 50 ÷ 60 % as compared with the conventional chrome tanning technology, and advanced exhaustion of spent floats. Low-offer chrome tanning preceded by pretanning can contribute to the obtaining of eco-friendly leather, mainly due to lower Cr(III) content of finished leather. Consequently, the occurrence in leather of hexavalent chrome Cr(VI), which is one of the most restrictive indicators for leather eco-friendliness, is mitigated.*

Keywords: *leather tanning, clean technology, syntans, melamine-formaldehyde resins, wet-white*

1. INTRODUCTION

At present, about 80-85 % of the worldwide leather production is tanned with Cr(III) salts and, except some leather types with special applications, chrome basic sulfate cannot be replaced by salts of other metals if high quality products must be obtained. Regular chrome offer in conventional tanning processes is about 2% Cr₂O₃. In order to reduce chrome consumption in the tanning operation and chrome-tanned leather waste, mechanical operations such splitting and shaving must be performed as early as possible in the manufacturing process. Both effects can be achieved during the pretanning operation, performed with different chemical auxiliaries such as: Al, Zr, Ti or Mg basic salts, synthetic organics, silicates or combinations of them; modern leather manufacturing technologies demands that splitting and shaving are not performed on wet-blue leather, but on pre-tanned leather, which is categorized as wet-white leather [1-4]; thus, finding new pretanning agents is of interest for clean technologies with low chrome salts consumption.

Basically, the insertion of pretanning is beneficial to the manufacturing process, because it results in important saving of chrome tanning salts in the tanning operation and in chrome-free



leather wastes resulted from the shaving operation, which mitigates the environmental impact of the tanning industry.

It is the aim of this paper to assess the suitability of using an oligomeric resin as pretanning agent of a bovine leather obtained by an improved process, which consists in pretanning with an oligomeric benzenesulfonate melamine-formaldehyde resin (BSMF), followed by low-offer chrome tannage and conventional wet-end operations. Namely, the leather tendency to release the chemical auxiliaries used during pretanning, tanning and retanning in aqueous solution was tested.

2. EXPERIMENTAL

Dry-salted cattle hides not exceeding 12 kg, previously processed to reach the delimed pelt state, were used as raw material for the pretanning-tanning-wet finishing-crusting processing flow, as described in Table 1.

Table 1: Alternative leather manufacturing process that includes pretanning

Operation	Process description
Pretanning step with oligomer resin	
Input: delimed pelt from dry-salted cattle hides not exceeding 12 kg	
Pretanning with oligomer resin and resorcin	100 % float, 40 °C; stirring for 10 minutes + 5 % Densotan A (1:2); stirring for 10 minutes + 10 -15 % Oligomer resin; stirring for 120 minutes + 1.0 % Resorcinol; stirring for 60 minutes + 5 % salt; stirring for 15 minutes + 5 % Eskatan GLS; stirring for 30 minutes + 1-1.2 % formic acid (1:10); stirring for 20 minutes Control float pH = 3.5; float exhaustion
Washing	100 % float, 40 °C; + 1 % Boron SE; stirring for 10 minutes; float exhaustion
Horse up after pretanning	Leathers are piled on the fleshing beam and covered with polyethylene foil, for 36 hours;
Setting out and sammying	On the setting-out and sammying machine
Splitting	On the splitting machine
Shaving	On the shaving machine
In-process product: Pretanned wet-white leather	
Tanning with low-offer basic chrome(III) sulfate	
Acid treatment	200 % float, at 25 °C; + 8 % salt; + 10 % HCl solution stirring for 10 minutes
Tanning with basic chrome salt	In the same float at 25 °C; + 1 % Cr ₂ O ₃ , stirring for 4 hours; Basification with NaHCO ₃ solution; + 5 % ESKATAN GLS, emulsion; Stirring for 60 minutes; Control float pH = 4.2; float exhaustion;
Horse up after chrome tanning	Leathers are piled on the fleshing beam and covered with polyethylene foil, for 36 hours;
Setting out and sammying	On the setting-out and sammying machine
In-process product: Wet-blue obtained by a combination tanning	
Wet finishing sub-process	
Washing	100 % float at 40 °C; + 0.5 % BORRON SE; stirring for 10 minutes; float exhaustion



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Neutralization	200 % float at, 40 °C; + 1.5 % NaHCO ₃ (1:20); stirring for 3 hours; control; 200 % float at 40 °C; stirring for 15 minutes; float exhaustion.
Rinsing I	200 % float at 40 °C; stirring for 15 minutes; float exhaustion
Retanning	75 % float at 40 °C; + 4 % DENSOTAN A (1 : 2); stirring for 20 minutes; + 5 % mimoza extract; stirring for 60 minutes; + 3 % ESKATAN GLH; stirring for 30 minutes;
Dying and fatliquoring	In the same float: + 4 % LUGANIL Braun NR (1 : 2); + 4 % LIPODERM liquor PSE; + 2 % LIPODERM liquor SLW; stirring for 60 minutes + 1% formic acid solution 10 %;stirring for 20 minutes; float exhaustion.
Rinsing II	200 % float at 40 °C; stirring for 15 minutes; float exhaustion.
In-process product: dyed leather	
Leather crusting sub-process	
Setting out and sammying	On the setting out and sammying machine
Air Drying	In the tunnel dryer
Toogle Drying	In the toggle dryer;
Conditioning /Rewetting	On the water spray machine
Milling tumbling	In the milling drum;
Staking	On the staking machine;
Horse up	Piled on the beam for 5-6 h ;
Buffing on the flesh side	On the buffing machine;
Dedusting	On the dedusting machine;
Chemical grain correction	Spraying on the grain side with an aqueous solution of 1 g /L ammonia, 0.5 g / L BORRON SE and 6 g /L ethanol
Natural air drying	On the overhead air dry chain conveyor
Mechanical grain correction	On the hot plate machine
Intermediate product: crust leather ready for any dry finishing process.	

Leather samples were withdrawn at different moments of the manufacturing process, as given in Table 2. Aqueous extracts were prepared with a leather: water mass ratio of 1:20, under stirring for 6h. The following analyses were performed on the aqueous extracts of leather samples, in order to quantify the auxiliaries released from the in-process leather: solid matter content, UV-VIS spectroscopy, HPLC chromatography. Solid matter content, expressed as total dissolved solids, and organic and inorganic soluble matter, was determined gravimetrically. The UV-VIS spectra of the aqueous extracts were recorded on a Jasco 550 with the following characteristics: 1 mL quartz cuvette, wavelength range 190÷600 nm, scan speed 200 nm/min, resolution 1 nm. A Zorbax SB-C18 (4,6 x150 mm) column, provided with a programmable Varian 9010 ternary pump, Waters 717plus autosampler and a Waters 486 UV-VIS detector, was used to record the extracts chromatograms; the HPLC system working conditions were as follows: MeOH solvent/water = 50/50 (v/v), solvent flow 0,5 mL/min, maximum absorbancy wavelength = 254 nm.

The UV-VIS spectra were processed with a dedicated SpectraManager software and the chromatograms were processed with the OriginLab 7.5 software.

3. RESULTS AND DISCUSSION

The results of gravimetric determinations of solid matter released from leather samples are given in Table 2.

Table 2: The soluble solids content of aqueous leather extracts

Leather sample (aqueous extract)	Sample label	Total soluble matter %	Maximum acceptable concentration MAC*	Inorganic soluble matter %	Organic soluble matter %
Pretanned with 10 % BSMF 1 % resorcin (wet-white)	BSMF10	1,44	max. 1,5 %	0,35	1,09
Pretanned with 15 % BSMF 1 % resorcin (wet-white)	BSMF15	2,38		0,8	1,58
Pretanned with 15 % BSMF, 1 % resorcin, tanned with 1 % Cr ₂ O ₃ , retanned with 5 % mimosa extract (wet-blue)	BSMF15T	0,77		0,5	0,27

*certifies the absence of adverse effects on users, assigned by TÜV Rheinland, Fresenius Institut, Prüf- und Forschungsinstitut Pirmasens e.V. (PFI),

Experimental data indicate high release rates of oligomer and resorcin from the pre-tanned leather. This means that, when conventional chrome-tannage must be performed after organic pretanning and mechanical operations, the resin can be removed from the wet-white cross-section, and leather can be tanned with regular offer of Cr(III) basic salt.

Leather samples tanned with BSMF in the presence of resorcin have a pronounced tendency to release organic chemicals, which increases with the tanning oligomer initial offer. Instead, leather sample tanned according to the novel technology (BSMF15T) exhibit significantly lower release of solubles from its structure, which confirms the strong binding of the chemical auxiliaries to the collagen matrix.

The organic compounds released by the leather samples processed in accordance with the recipes given in Table 2 were identified on the UV-VIS spectra and HPLC chromatograms of the corresponding aqueous extracts.

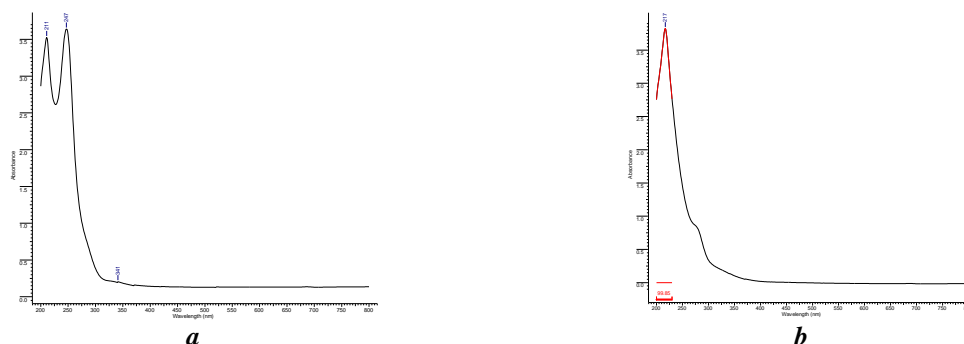


Fig. 1: UV-VIS spectra of leather aqueous extracts: **a)** Pretanning with 15% BSMF and 1% resorcin (BSMF15); **b)** Pretanning with 15% BSMF and 1% resorcin, tanning with 1% chrome(III) oxide, retanning with 5% mimosa (BSMF15T).

The UV-VIS spectrum of the aqueous extract of the BSMF15 sample (Figure 1a) points out the release of two organic compounds, with maximum absorbance peaks at $\lambda = 211$ nm and $\lambda = 247$ nm. The first peak, at 211 nm is characteristic to the $-C = O$ chromophore group of the carboxylic function of the formic acid. The second peak, at 247 nm, can be assigned to the chemical compound resulted from the reaction between the BSMF resin and resorcin, more precisely to the m-disubstituted benzen cycle reacted with the 1,3,5 triazine cycle.

The UV-VIS spectrum of the aqueous extract of the BSMF15T sample (Fig. 1b) indicates the presence of only one peak at $\lambda = 217$ nm [5-8], and the absence of the peak at 247 nm, which may indicate the absence of the reaction product between BMSF and resorcin in the tanned leather.

Two peaks are recorded on each of the HPLC chromatogram of aqueous extracts, corresponding to the two injection times (Fig. 3). The peak maximum corresponds to a certain retention time, which is the qualitative characteristic of the organic compounds found in the analyzed solutions. The peak height (h) and area (A) account for the amount of the analyzed compound in the sample.

The HPLC chromatograms are consistent with the UV-VIS spectra and with the theoretically predictable composition of the aqueous extracts. Comparative chromatograms of the BSMF resin, resorcin and aqueous extracts of BSMF 15 and BSMF 15T samples are given in Fig. 4. The experimental retention times are as follows: resorcin, 4.53 min; BSMF resin, 2.81 min; aqueous extract of the BSMF15 sample, 3.26 min and aqueous extract of the BSMF15T sample, 3.31 min.

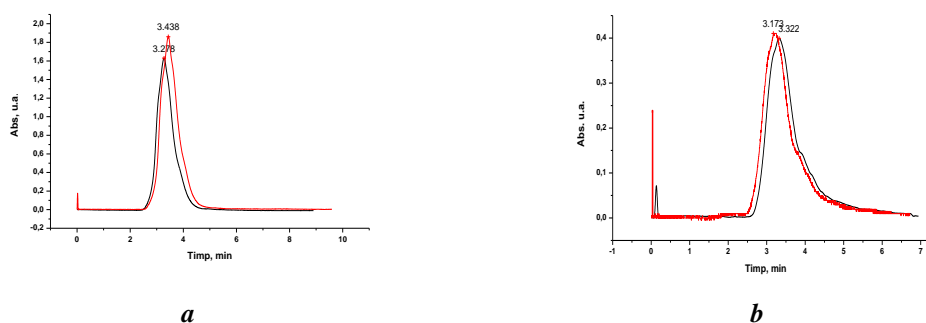


Fig. 3: HPLC chromatograms of leather aqueous extracts: (a) Pretanning with 15% BSMF and 1% resorcin (BSMF15); (b) Pretanning with 15% BSMF and 1% resorcin, tanning with 1% chrome(III) oxide, retanning with 5% mimosa (BSMF15T);

The values of retention time and maximum absorbancy indicate that leather pretanned with the BSMF oligomer in the presence of resorcin as cross-linking agent have the tendency to release the chemical auxiliaries entered into the collagen matrix cross-section, which proves the reversibility of the oligomer –collagen interaction.

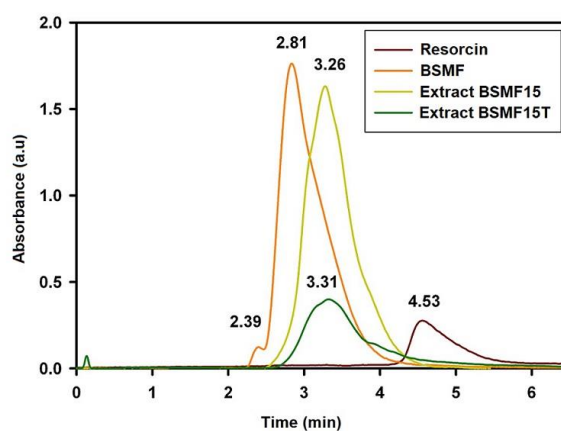


Fig. 4: HPLC chromatograms of resorcin, BSMF, and aqueous extracts of tanned leather



If pretanning is followed by conventional tanning and retanning, the amount of released organics is four-fold lower. The stronger binding of tanning agents to the collagen matrix is due to supplementary complexation effect that BSMF and resorcin exert on the chrome complex salt.

4. CONCLUSIONS

Experimental data indicate high release rates of oligomer and resorcin from the pre-tanned leather, which means that the pretanning process alone is a reversible process.

The oligomer resin and resorcin are extremely versatile complexing agents, and their use in the tanning process result in the reduction of chrome salts offer by 50-60% and an advanced chrome exhaustion in the tanning spent floats.

Pretanning with the oligomeric benzenesulfonate melamine-formaldehyde resin can be applied through different processes, depending on the desired leather type and degree of "eco-friendliness" requested to the final product.

Even if for most leather types chrome- tanning can not be replaced by any other alternative, pretanning allows a low-offer chrome tanning not exceeding 1% Cr₂O₃, which results in high exhaustion of spent floats and low chrome content of finished leather. At the same time, the appearance in leather cross-section of hexavalent chrome Cr(VI), which is one of the most restrictive indicators for leather eco-friendliness, is considerably reduced.

The pretanning operation complicates the overall manufacturing process, but this disadvantage is counterbalanced by technological and environmental benefits.

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