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ALTERNATIVE LEATHER MANUFACTURING PROCESS - 1. PRE-TANNING WITH A REACTIVE OLIGOMERIC RESIN

PRUNEANU Melinda, BUCIȘCANU Ingrid, MAIER Vasilica, BĂLĂU-MÎNDRU Tudorel

"Gheorghe Asachi" Technical University of Iaşi, Faculty of Textiles, Leather and Industrial Management, Str. Prof. Dr. Doc. Dimitrie Mangeron, No. 29, 700500 Iaşi, Romania, E-Mail: decanat@tex.tuiasi.ro

Corresponding author: Melinda Pruneanu, E-mail: pruneanu_melinda@yahoo.com

Abstract:*This paper presents a non-conventional tanning technology, which uses a benzenesulfonate melamine-formaldehyde resin (BSMF) as pre-tanning agent. BSMF tanning alone can produce white leather, which generates chrome-free leather wastes. A BSMF pre-tanning step can be applied prior to a tanning step with lower chrome offer - 1 % Cr_2O_3, as compared with the conventional chrome tanning technology, which uses around 2 % Cr_2O_3. Thus, low chrome-content leather can be obtained, having the organoleptic properties and physico-mechanical behavior similar to those obtained through conventional processing, mainly as it regards the hydrothermal stability. The cross-section of leather pre-tanned with the BSMF resin is less compact as the cross-section of the conventionally chrome tanned leather, which proves that BSMF tannage alone cannot provide leather with the performances acquired by the chrome tannage. Physical deposition of the BSMF product in the interfibrillar voids and envelopment of collagen fibers, significantly contribute to the fibrilar matrix consolidation, which is the essential condition for splitting and shaving in the tanyard, before chrome tanning and vegetable retanning steps. A BSMF pre-tanning, followed by a chrome tanning with an offer of 1 % Cr_2O_3 and mimosa extract retanning results in leather having the compositional and structural characteristics required by the upper leather type standards.*

Key words*: tanned leather, melamine-formaldehyde resins, wet-blue, wet-white, clean technology*

1. INTRODUCTION

During recent years, there is an increasing concern on the replacement of chrome as tanning agent, due to more stringent restrictions regarding the environmental pollution with chrome-containing wastes coming from tanneries. Efforts to find alternative solutions have been focused on complete replacement of chrome with other tanning agents (basic salts of metals such as Al, Zr, Ti, vegetable tannins,synthetic organics), partial chrome replacement, alternative technologies based on low-offer or high chrome exhaustion [1-5].

Synthetic tannins, also termed as syntans, are reactive chemicals whose action is based on chemical reactions with the collagen functional groups. Sulfonated condensation products of aromatic compounds with low-molecular weight aldehydes are a class of syntans commonly used as retanning agents, but little investigation has been done on their use as pre-tanning agents [6,7].

Chemically modified condensed triazine, known as sulfonated melamine-formaldehyde resins (SMF) showed satisfactory pre-tanning or even tanning effects [8,9], but has at the same time several shortcomings, such as low storage stability, low solubility in the processing float, high hydrophilicity imparted to leather, high prices. Studies on the use of benzenesulfonated melamine-formaldehyde (BSMF) resin as pre-tanning agent showed that its tanning effect is based on its uniform diffusion in the leather cross-section, and on its ability to envelope the collagen fibers and to fill the interfibrillar voids within the collagen fibrous matrix. Tanning practice showed that, as compared with other SMFs, BSMF is able to raise the shrinking temperature of the processed leather, allowing a lower offer of basic chromium salt in the tanning operation [10].

This paper is dealing with a novel tanning technology of cattle hides, which consists of a pre-tanning step with the benzenesulfonated melamine-formaldehyde resin, a low-offer chrome tanning stage and a final vegetable retanning, in order to obtain low chrome-content finished leather that meets the quality requirements for upper leather.

2. EXPERIMENTAL

The effectiveness of the BSMF resin as pre-tanning agent was tested within a novel process for the obtaining of upper leather from light and medium weight cattle hides. The framework technological process, which uses the BSMF product as pre-tanning agents in conjuction with a low-offer chrome tanning stage is given in Fig. 1. The conventional operations in the tanyard are also presented. The chromium offer is given as chromium oxide, Cr_2O_3 per 100 kg pre-tanned leather; the BSMF offer is given as liquid product, with 26% dry matter, per 100 kg delimed pelt.

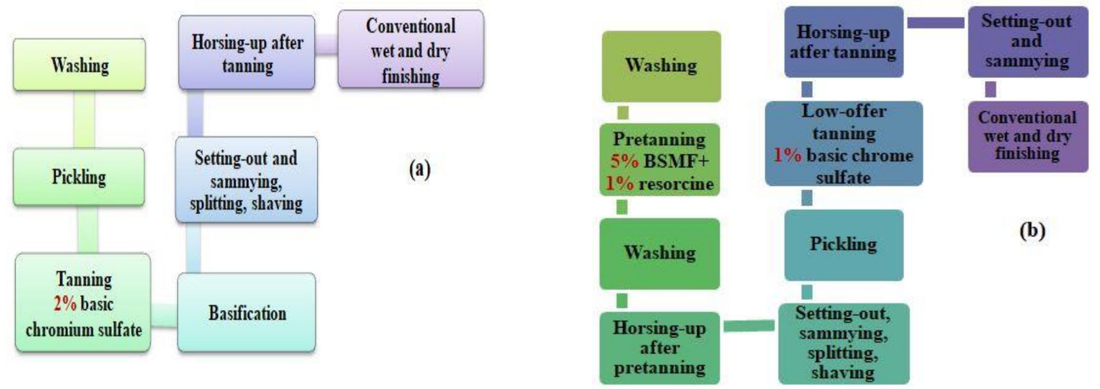


***Fig. 1**. Tanning process: (a) Conventional chrome tanning; (b) low-offer chrome tanning using a BSMF*

3. RESULTS AND DISCUSSIONS

3.1. Physico-mechanical and chemical characterization of the processed leather

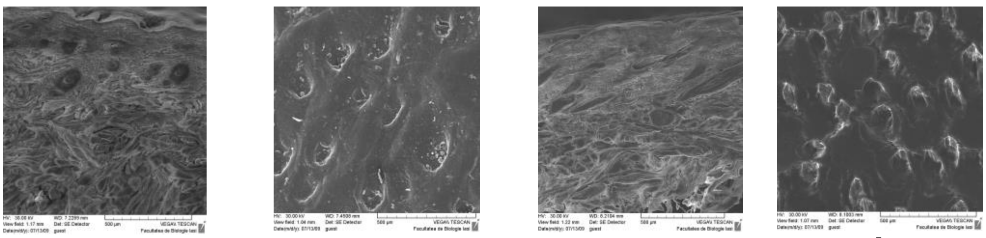
Physical and chemical tests of pretanned leather samples were performed in accordance with SR EN ISO 2418:2003, SR EN ISO 2419:2006 and SR EN ISO 4044:2002. From the test results, given in Table 1, it is obvious that the pretanning stage has a positive effect on the physico-mechanical behaviour of in-process leather. Improvement of firmness and compactness facilitates the execution of the mechanical operations such as splitting and shaving in the tanyard. Performing these operations before chrome tanning has the advantage of generating chrome-free collagenous wastes. Subsequent chrome tanning and vegetable retanning provides leather with characteristics similar to conventionally tanned leather, mainly as it regards the hydrothermal stability. The only noticeable discrepancy is related to the extractible matter content, which is much lower than that imposed by standards. Subsequent fatliquoring with carefully chosen fatliquoring products can make up for this shortcoming.

3.2. SEM Electron Microscopy

The performances of the novel tanning technology can be assessed by means of SEM images of leather surface and cross-section, in different processing stages. Comparative SEM images of finished leather obtained by the conventional chrome tanning process and by the novel technology, which includes an organic pre-tanning stage, are given in Figure 2. The cross-section of leather pre-tanned with the BSMF resin (Fig. 2 (c)) is less compact than the cross-section of the conventionally chrome tanned leather (Fig. 2 (a)), which proves that BSMF tannage alone cannot provide leather with the performances acquired by the chrome tannage. Physical deposition of the BSMF product in the interfibrillar voids, which is obvious in Fig. 2 (c), significantly contributes to the fibrilar matrix consolidation, which is the essential condition for splitting and shaving in the tanyard, before chrome tanning and vegetable retanning steps.

Table 1: *Characteristics properties of leather processed by the low-offer chrome technology*

No.	Characteristic / Property	UM	Assessment/Numerical value		Method of determination	Current values
			on wet-basis	on dry-basis		
1.	Water content, **U**	%	13,37	--	STAS 8574 / 1992	10 ÷ 15
2.	Total nitrogen (TKN), **N**	%	14,58	16,83	SR EN ISO 5397: 1996	--
3.	Dermal matter, **SD**	%	82,06	94,72	SR EN ISO5397:1996	--
4.	Mineral substances **SM**	%	1,87	2,15	SR EN ISO 4047:2002	min. 3,5 %
5.	Chromium oxide (Cr_2O_3), T	%	1,47	1,67	STAS 8602 - 90	max. 2,5 %
6.	Extractable fat matter, **SG**	%	2,70	3,11	SR EN ISO 4048:2002	max. 8 %
7.	Total dry matter	%	86,63	99,99	STAS 723 / 15 - 76	--
	Mass balance (U+SD +SM+SG)		**99,76**	--	Calculation	--
	Mass balance on a dry-basis (SD+SM+SG)			99,98	Calculation	--
8.	Grain appearance	--	not uptight	--	Organoleptically	--
9.	Feel	--	soft, warm	--	Organoleptically	--
10.	Firmness	--	semi rigid	--	Organoleptically	--
11.	Folding	--	large folds	--	Organoleptically	--
12.	Shrinkage temperature, $\mathbf{T_C}$	° C	97 ± 0,5	--	SR EN ISO3380 : 2003	100 ± 0,5 ºC
13.	Shrinkage coefficient , $\mathbf{I_C}$	%	3 ± 0,3	--	SR 5053 :1998	max. 5 %
14.	Tensile strength, $\boldsymbol{\sigma_R}$	N / mm ^{2}	39,8 ± 1,1	--	SR EN ISO 3376: 2003	min. 22
15.	Elongation at break, $\boldsymbol{\varepsilon_R}$	%	41 ± 3	--	SR EN ISO3376 : 2003	max. 80
16.	Tear strength, $\boldsymbol{\sigma_{R\ tear}}$	N / mm	46 ± 1,4	--	SR 5045 : 1999	min. 30
17.	Water vapor permeability	mg H_2O/24h	--	459		500 - 541



a b c d

Fig. 2: *SEM images of in-process leather*: a) *Cross-section of chrome-tanned leather; (b) Surface of chrome-tanned leather; (c) Cross-section of leather tanned with BSMF and chrome; (d) Surface of leather tanned with BSMF and chrome*

The cross-section images of the conventionally chrome-tanned leather (Fig. 2 2(a)) and of the leather processed according with the novel technology (BSMF pre-tannage + low-offer chrome tannage + vegetable retannage), given in Fig. 2 (c), are similar. Surface SEM image of the leather processed according with the novel technology (Fig. 2 (d)) is clearly different from the other two: pores are closed, the grain is tighter, and surface roughness is higher. This effects must be assigned to the vegetable tanning agent, which has an astringent action and modifies the cross-section distribution of the BSMF resin.

4. CONCLUSIONS

The proposed tanning process allows entire or partial replacement of chrome as tanning agent and provides the execution of splitting and shaving operations on the BSMF-pretanned leather, which avoids the generation of chrome-containing solid wastes. The BSMF tanning alone results in wet-white leather. The BSMF pretanning followed by a low-offer chrome tanning (1% chrome as chrome oxide) and a vegetable tanning step results in leather types that fully meet the requirements for upper leather. This is ascertained by the chemical and physicomechanical properties of finished leather and by the SEM images.

A tanning process that includes a BSMF resin pre-tanning and a low-offer chrome tanning provides leather with structural and compositional stability that meet the requirement for finished leather types.

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