En Eco-Benign Semi-Metal Tanning System to Cleaner Leather Production

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Abstract
In this study we developed a semi industrial-scale tanning process to replace chrome tanning in the production of high quality prosthetic leathers, based on a multi-step vegetable-aluminum tannage. Tara extract and mimosa extract were used as vegetable tanning agent in order to obtain a wet-white tanned leather; a pretannage with glutaraldeyde or preparation based on masked multi-functional phosphonium compound (THPS) were introduced to improve penetration. The treatment of pelt with THPS instead of chromium before vegetable-aluminium tanning allows one to reach a shrinkage temperature of up to 106 ^{o}C by using half as much tannin. The liquid of the phosphonium compounds and the tanning vegetable-aluminium solution are capable of biodegradation on the level of some proteins, which is evidenced by the ratio BOD: COD. Besides, the absence of chromium compounds in the liquid waste improves the biodegradation of the other substances. It was determined that leather treatment with both glutaraldehyde and phosphonium compounds positively influence on the leather ageing resistance. The leather tanned with tara have more stable properties. It is likely to be due to mechanism of tanning process. Peculiarities of interaction between vegetable tannages and collagen were studied by IR-spectroscopy. IR studies were carried out with universal Fourier IR-spectrometer TENSOR-37 (BRUKER, Germany). IR absorption spectra were investigated in the 400…4000 cm-1 region. The influence of pretreatment by different compounds before tanning on the thermal properties of derma collagen was studied by DTA.

Key words: wet-white leather, vegetable-aluminum tannage, pretreatment before tanning, non-pickling tanning technology, leather ageing resistance

1. Introduction
During last 20 year's new tanning methods, which allow refusing from the application of toxic chromium compounds, were developed (Senior 2000). Researchers throughout the world are looking for alternative tanning systems to overcome the problems of chromium tanning. Well-documented mineral tannages, like aluminium (Covington and Sykes 1984), silicon (D'Aquaino et al. 2004), titanium (Peng 2007), iron (Gaidau et al. 1998; Balasubraminian and Gayathri 1997) or zirconium salts (Sundarrajan 2003). The hydrothermal stability of the leather-tanned using these tanning materials is less than that of chrome-tanned leather. Pure vegetable tannages are thus not suitable as chrome replacements, whilst combination tannages employing vegetable tannins and metal salts are potential alternatives to chrome tanning, capable of producing hydrothermally stable leathers (Tang et al. 1992; Dasgupta 2002; Covington and Lampard 2005). Despite the fact that such tanning method enables to refuse from chromium compounds, on the other hand, it does not mean that obtained leather would be without inorganic salts. Due to the requirements, which continually become stricter for leather, especially medicine leather, and for recycling of leather wastes, the manufacture of inorganic salt free

leather becomes very important. The method of organic tanning using synthetic and vegetable tannins, aldehydes or phosphonium compounds (THPS) should be most alternative in such case. The use of glutaric aldehyde and it's derivatives combining with vegetable tannins could be as alternative instead chromium tanning (D'Aquino et al. 2004). It has been reported that THPS could be used as a chrome free tanning agent (Fatima et al. 2006; Musa 2012) and improved hydrothermal stability was observed when THPS was used in combination with other tanning agents (Plavan et al. 2009). This preparation has such advantages as fine tanning properties, low toxicity, high biodegradability and absence of metals (Fatima et al., 2005). A further environmental benefit is that THPS is rapidly oxidised, in the environment, to trihydroxymethylphosphine oxide which has a very low aquatic toxicity (Downward 1997).

2. Materials and methods

All materials used in leather processing were commercial grade. All materials used in leather processing were commercial grade: chromium compounds (commercial name Chromotel XGS) having basicity 33 % and 26% Cr_2O_3 (Russia); tara tannins (commercial name Chemitan TA) obtained from PP Chemipol Sp.Z.O.O (Poland); mimosa *Acasia Molisima* (commercial name Weibull) provided by Tanac S.A. (Brasil); $AlK(SO_4)\cdot 12H_2O$ used as tanning aluminium compound. THPS (commercial name Granofin FCC) were provided by Clariant. Other materials were conventionally using in leather industry materials which was obtained from Tannery enterprise "Joint-Stock Company Chinbar"(Kiev, Ukraine).

Physical testing of leather. The shrinkage temperature (Ts), which shows the hydrothermal stability of leather, was determined using a standard shrinkage meter. Qualitative indexes of leather (tensile strength, relative elongation), pH and amount of Cr_2O_3 in the solution were established using conventional methods.

IR-spectroscopy. IR-spectroscopy was employed to investigate the nature of interaction between the tannides and collagen. As a model of collagen, gelatin films with a thickness of 20 µm were used. To produce the films, tannide solutions with a concentration of 50 g/l were introduced into 4% acetic solution of gelatin at 35°C. The tannide consumption was 10% of the collagen mass. The obtained solution was poured onto a Teflon tray and dried until the film is formed at a temperature of 20-22 °C. IR absorption spectra were produced using the FT-IR spectrometer *TENSOR-37* (BRUKER, Germany).

Thermogravimetric, differential thermal analysis. TG and DTG were carried out by using the Paulig-Erdei derivatograph over the 22-760 °C temperature range in the air with simultaneous removal of destruction products. Temperature intervals of destruction of the samples under study were evaluated in terms of differentiation curves of mass loss. For the distruction the initial (T_{start}) and final (T_{fin}) temperatures were found as well as the maximum destruction rate temperature (DTG $_{maxima}$) and the change in the mass of samples at this rate.

Tanning processes. The method of combined tanning with THPS and other materials was developed using pelt (thickness – 2-2.2 mm), which was produced from sheep skin under conventional technology. The water consumption was 100 %. Duration of tanning was 2 hours at 20-22 °C. At the end of tanning sodium dicarbonate (1-1,5% of skin mass) was added to increase the pH. During the process the pH of the tanning solution and the shrinkage temperature (t_{sh}) of the semifinished item were determined. The final pH value was 5,2-5,5. Then the semifinished item was exposed to short-term neutralization, liquoring and drying.

The vegetable tanning was carried out after pelt treatment with phosphonium, where pyrocatechin (mimosa) and pyrogallol (tara) tannins were employed. The tannides extract (100 g/l) was added using 5 % tannins of pelt mass. The total amount of liquid (tannin extract and water) was 200 % on pelt mass. The semifinished item was left in the tanning solution for a night. After that, washing, fat-liquoring and drying were carried out. Qualitative indexes of leather are presented in Table 1. The control leather specimen

was produced according to the conventional technology of leather to prosthesis. This technology provides chroming with chromium compounds (0.5 % Cr_2O_3), treatment by emulsion of fat-liquoring materials and vegetable tanning (10 % tannins). Qualitative indexes of the leather are presented in Table 3 as well.

To evaluate the capability of the substances for biodegradation is possible by determining the BOD : COD ratio. In the application of traditional technologies ratio BOD: COD is 0.4-0.5. The BOD : COD ratio ≥ 0.6 evidences that the waste water can be purified by the natural way, that is by self-purification. The BOD : COD ratio is the higher, the greater the fraction of organic compounds in the total amount of the substances used.

In our research ageing resistance of leather was determined by oxidation in the copper ion – hydrogen peroxide system (Deasy Clara, 1967). The leather specimens were treated with 3% hydrogen peroxide solution containing $5 \cdot 10^{-4}$ M copper sulfate for 10 days. After each treatment the shrinkage temperature of the leather was determined.

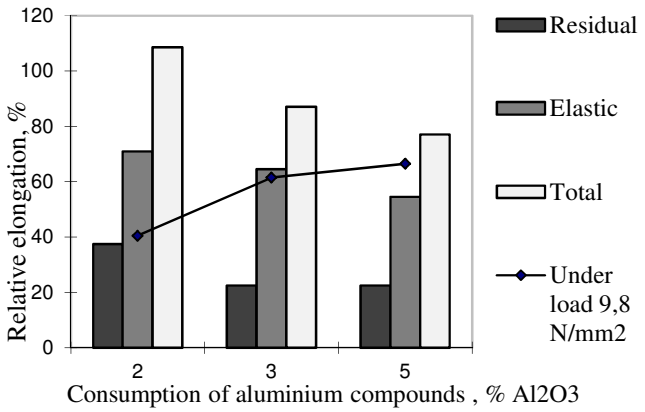

Fig.1. Changes in elastic properties of leather depending on the consumption of aluminium compounds for tanning

3. Results and discussion

The optimum and most practical quantities of vegetable tannin and aluminum were determined by varying the consumption of the former from 5 to 10% and the latter from 1 to 5% $A1_20_3$ (pickled weight basis). The THPS consumption was changed from 1 to 4 %. By determining the shrinkage temperature and physical-mechanical properties of the leather produced it was found out that a consumption of phosphonium of 2% provides optimum elastic and hydrothermal properties of the leather. Increasing the consumption of aluminium compounds up to 5%, leads to a decrease in the indexes of elastic and residual deformation (Fig. 1). Thus, a consumption of aluminium compounds of 2% Al_2O_3 is the most rational for producing strong leather with necessary elastic properties. To increase the shrinkage temperature of the leather, tanning with silicon compounds was used after pretreatment of the leather with glutaraldehyde. It was found out that the optimum consumption of sodium metasilicate is 1 % of the hide mass (for SiO_2), for producing leather with necessary elastic properties

The technology developed for producing prosthetic leather involves the use of 4% glutaraldehyde for the pretanning and sodium metasilicate, vegetable tannages, potassium alums for the main tanning, with their consumptions being 1 % for SiO_2, 10% for tannides, and 2% for Al_2O_3, correspondingly.

Results of determination of the physical and mechanical properties of the leather treated with THPS (Table 1) prove that there is an increase in the shrinkage temperature and, at the same time, a decrease in the tensile strength of the leather. On the one hand, it can give evidence that the tannages enhance leather structuring, but, on the other hand, it can result from calculations of the strength limit of leather depending on the thickness of specimens. In the case of tanning with THPS-vegetable tannins the thickness of leather increased due to full exhaustion of tannins and filling of derma.

The pH of the leather produced was higher (5.8–6.1) compared with the control specimen (4.2), which points to less acid amount in derma. Further, this property will have influence on durability of such leather when storing or wearing. The organoleptic analysis showed that the leather tanned with THPS had fine grain and was without break of leather. The treatment of pelt with THPS instead of chromium

before vegetable-aluminium tanning allows one to reach a shrinkage temperature of up to 106 °C. The exhaustion of tannins was practically complete.

The treatment of leather with both glutaraldehyde and phosphonium compounds promotes increasing its ageing resistance. An analysis of the results shows that during oxidation there occurs a decrease in the shrinkage temperature and tensile strength of leather, which points to its partial detanning. The shrinkage temperature of leather treated with phosphonium compounds decreased on the average by 43.5 %, which is lower than that for control sample (47.1 %), in contrast to leather treated with glutaraldehide, where the decrease in shrinkage temperature was 51.2 %.

Table 1. **Physical tests results of prosthetic leather**

Tanning agents	Consumption, %	Index					
		Tensile strength, N/mm^2	Relative elongation, %	t_{sh}, °C	pH of leather	Decrease of leather shrinkage temperature, %	
						After treatment of artificial sweat	After oxidation during 10 days
After glutaraldehyde pretanning							
Mimosa	5	16,1	80,0	100	5,8	19,6	54,2
Tara	5	14,7	100,0	96	5,5	16,6	47,1
After THPS pretanning							
Mimosa	5	13,2	75,0	105	6,1	7,4	46,2
Tara	5	12,7	86,0	106	5,8	5,5	39,3
Conventional method of tanning							
Cr_2O_3 Mimosa	0,5 10	12,8	65	94	4.2	10,1	47,7

It is the leather treated with both phosphonium compounds or glutaraldehyde tanned with tara tannides shows more stable properties in time, which is accounted for by the mechanism of tanning. The vegetable tannides mimosa and tara are different in their chemical structure. Unlike mimosa tannides, tara tannides have carboxyl groups in their structure (Faber 1990; Vitolo et al., 2003; Castell et al., 2011). As it is seen in the Figure 2, the differences in the spectra of the two films are observed in the low-frequency region (1500-600 cm^{-1}). In the spectrum of the gelatin film treated with tara tannides there appear two pronounced bands: 1) with a frequency of 1360 cm^{-1} (overtone at 1700 cm^{-1}), which is likely to correspond to the hydrogen bond between in-plane deformation vibrations of the –OH

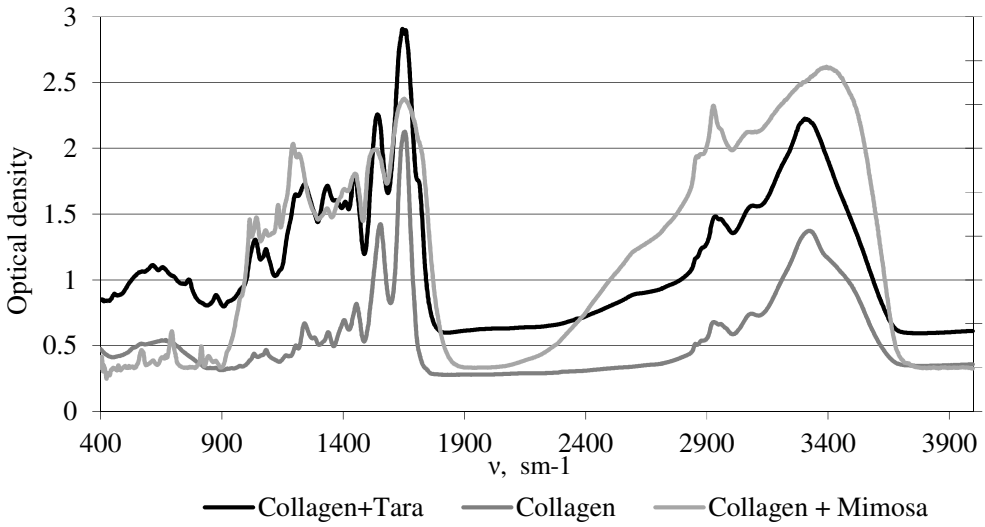

Fig. 2. IR spectrum of collagen before and after treatment of tannides

group and valence vibrations of the CO group (1300-1200 cm^{-1}), where the shift to the low-frequency region may be due to stronger hydrogen bonds, and 2) with a frequency of 1230-1200 cm^{-1}, which may correspond to asymmetric valence vibrations of =C–O– in aromatic compounds or to valence vibrations of the C–O(H) bond.

In the absorption spectrum of the gelatin film treated with tara tannides there appears a band at 770 cm^{-1}, which is characteristic of ring-puckering deformation vibrations of the C-H group of aromatic ring having 4 to 5 adjacent hydrogen atoms, and there disappears the band at 970 $см^{-1}$, which can be found in the spectrum of the gelatin film treated with mimosa tannides and is likely to correspond to in-plane deformation vibrations of the C-H bond of aromatic ring. Besides, in the spectrum of the gelatin film treated with tara tannides there is no absorption band at 1160 $см^{-1}$, in contrast to the spectrum of the gelatin film treated with mimosa tannides. Thus, interaction of such a vegetable pyrocatechin tannide as mimosa takes place by formation of hydrogen bonds between phenolic hydroxyl groups of tannides and amine groups of derma collagen. Interaction of tara tannides, which belong to the pyrogallol class, proceeds through both forming hydrogen bonds between phenolic hydroxyl groups of tannides and amine groups of derma collagen and forming co-ordination, ionic bonds between carboxyl groups of tannides and functional groups of derma collagen.

Thermooxidation destruction of leather after tanning has been studied for evaluation of structured transformation of derma collagen. For DTG and DSC studies were used samples of leather after vegetable-aluminium tanning with pre-treatment before tanning by 2% of phosphonium compounds (sample 1 – 5 % mimosa tannides, 1 % Al_2O_3 as potassium alums; sample 2 – 5 % tara tannides and 2 % Al_2O_3 as potassium alums); control sample – vegetable tanning (10 % mimosa tannides) after chroming of hide (0,5 % Cr_2O_3) and samples of leather with main tanning by vegetable tanning agents, potassium alums and sodium metasilicate with pretreatment before tanning by 4% of glutaric aldehyde (samples 3 – mimosa tannides - 5 %, SiO_2 -1 %, Al_2O_3 -1 %; 4 – tara tannides 5 %, SiO_2 - 1 %, Al_2O_3 - 2 %).

Our studies show that organic-mineral tanning provides the formation of a thermostable system of tanning agents in the structure of derma collagen as evidenced by a high temperature of maximum decomposition rate (Table 2).

Table 2. The results of thermooxidation destruction for samples of leather

Samples	T_{start}, °C	T_{fin}, °C	DTG_{maxima}, °C	$\Delta m_{T_{max}}$, %
1	58	680	313	38,1
2	55	719	306	34,4
3	70	730	316	34,8
4	55	655	321	38,7
Control	62	680	317	32,3

The relation between thermal characteristics of samples both quantity and composition of tannages has been found, which allows one to determine the degree of structuring for the tanning of derma collagen with the tanning materials and to evaluate the efficiency of the tanning process. The use of glutaric aldehyde and phosphonium compounds instead of chromium compounds in the preparation of raw hide for vegetable-aluminium tanning gives a more ordered structure of derma collagen due to formation of cross-linking, and foremost covalent, bonds in the interface space. A less heterogeneous, i.e. more homogeneous structure of derma collagen forms in tanning with mimosa tannins after pre-treatment of raw hide with glutaric aldehyde owing to spatial dimer, trimer and polymer structures produced in the interaction between glutaric aldehyde and derma collagen[4)]. As a result, hydrothermal resistance of the leather increases. A lower temperature and at the

Table 3. Thermodynamic features for melting process of collagen by DSC methods

Samples	T_{max}, °K	Cp_{max}, $кJ \cdot K^{-1} \cdot кg^{-1}$	ΔH, кJ/кg
1	393…403	7,14…7,28	352,8
2	393…398	10,83…10,75	508,8
3	403	8,27	469,8
4	398	11,26	583,1
Control	403	6,77	281,3

same time higher melting enthalpy ΔH of derma collagen (Table 3) point to the presence of flexible mobile bonds produced due to modification of collagen with organic compounds in tanning with tara tannins.

The pretanning of leather with both glutaric aldehyde and phosphonium compounds before vegetable tanning helps steady diffusion into derma, which gives microstructure with uniform, moderately dense arrangement of quite full bundles of collagen fibers with densely "sewed" papillary layer and the grain (Fig. 3). Due to this, the leather and the pelt gain improved qualities. The microstructure of derma in the control specimen reveals very dense arrangement of collagen fiber bundles, the bundles being thin and without distinct contour. There is also observed a distinct boundary between the layers of derma, which is characteristic of many types of sheepskin and can lead to exfoliation of leather when exploited. Such peculiarities of the derma microstructure in the investigated and control specimens fully correspond to their elastic properties and organoleptic evaluation.

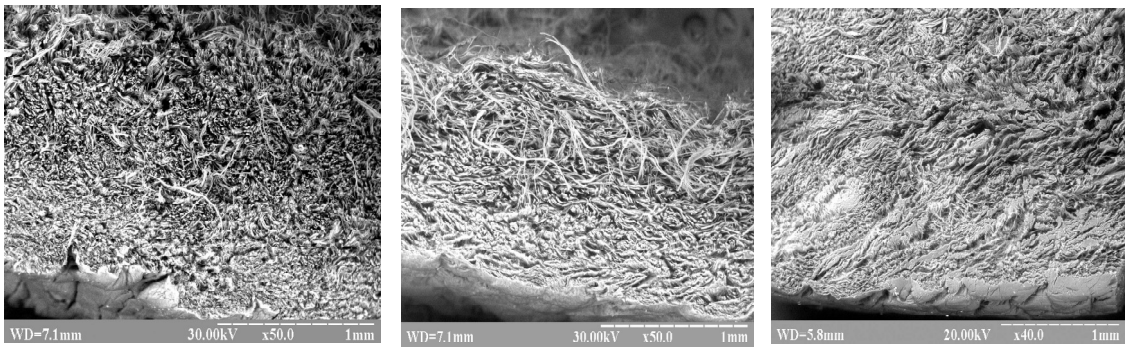

Fig. 3. Microstructure of leather after tanning by different methods: 1) glutaraldehyde –mimosa; 2) THPS–mimosa; 3) conventional method of vegetable tanning.

Table 4. Physical-chemical properties for leather of non-chromium method of tanning on pilot-scale

Qualitative indexes of leather	Developed technology	Conventional technology
Thickness of leather, mm	2,8-3,0	2,8-3,0
Shrinkage temperature, ^{o}C	98	98
Tensile strength, N/mm^2	18,2	20
Relative elongation at break, %	42	25
pH of tanned leather	5,0	4,5
Content in the leather, %:		
– substances which are extracted by organic solvents	8,5	9,8
– general water wash out substance	3,4	4,0
– chromium compounds	-	0,9

Hydrothermal stability, %	70,8	75,0

The best recipes developed were repeated on a semi industrial scale to confirm the hydrothermal stability obtained in the laboratory scale tests and to obtain the necessary leather samples for the physical and technical tests. After tanning on pilot-scale, a standard fatliquoring dyeing was applied in order to obtain the final product (crust leather) and to allow us to evaluate its main physical and technical properties. The results reported in Table 4, for these runs did not confirm the results obtained on the laboratory scale as regards the shrinkage temperature.

The liquid of the phosphonium compounds and the tanning vegetable-aluminium solution are capable of biodegradation on the level of some proteins, which is evidenced by the ratio BOD: COD = 0,49 and 0,58 mgO_2/l, correspondingly. Besides, the absence of chromium compounds in the liquid waste improves the biodegradation of the other substances.

4. Conclusions

The treatment of pelt with THPS instead of chromium before vegetable-aluminium tanning allows one to reach a shrinkage temperature of up to 106 ^oC by using half as much tannin. The technology developed can be used for producing prosthetic leather, which requires high hydrophobic and running stability as well as sweat resistance. Leather treatment with both glutaraldehyde and phosphonium compounds positively influence on the leather ageing resistance. The leather tanned with tara have more stable properties. The liquid of the phosphonium compounds and the tanning vegetable-aluminium solution are capable of biodegradation on the level of some proteins. Besides, the absence of chromium compounds in the liquid waste improves the biodegradation of the other substances.

5. Acknowledgments

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