INVESTIGATION OF THE PROPERTIES OF POLYMER-TITANIUM TANNED LEATHER

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In the present time, despite all the advantages, the use of chrome-based tanning components are reduced or excluded in leather production, primarily, because of its toxicity and ineffective use of the agents. The new chrome-free tanning method has been offered to replace ship skin pickling with polymeric treatment of rawhide and subsequent titanium tanning. Ammonium titanyl sulfate is used as a tanning agent while polymaleate – as a polymeric material. It has been established that the replacement of pickling with polymeric treatment improves diffusion and exhaustion of titanium tannins from the solution, which, in turn, ensures the formation of the Wet-White leather structure and its thermostability. Polymer-titanium tanning system not only increases the consumption of tanning agents, reduces treatment duration, but also improves physical and mechanical properties of finished leather: strength, elongation, volume yield, thickness yield, porosity, etc. This was confirmed by the results of scanning electronic microscopy, which prove that a tanning method affects morphological changes in leather structure and uniform distribution of tannin into the derma.

Keywords: polymer-titanium tanning, leather, structure, properties

INTRODUCTION

The need for more efficient use of raw materials and energy resources as well as greening of leather processing industry impose strict requirements to manufacturing processes and chemical materials used. In the tanning process it refers, first of all, to reducing treatment duration, restricting or even complete exclusion chromium compounds in the production cycle. The last requirement is explained by instability in time and oxidation potential of these compounds to bio-toxic chromium (IV) (Environmental Problems, 2003; Klimova, 1990).

Titanium tanning is one of the alternatives to chrome-based tanning and makes it possible to produce leather with performance properties close to chrome tanned leather, which are long-time resistant to environmental factors (Peng *et al*., 2007; Metelkin and Rusakova, 1980; Cherkashin and Chursin, 2012; Adiguzel Zengin *et al*., 202; Seggiani *et al*., 2014). The main drawbacks of titanium-tanned leather are stiffness and insufficient strength of the front layer due to uneven distribution of tanning compounds into the derma, which significantly reduces operational properties of leather goods. The existing methods of improving titanium tanning, which are based on a combination of titanium compounds with synthetic, organic (tannin, aldehydes) and mineral (zirconium, aluminum, silicon) tanning agents, improve leather structure and strength, but do not facilitate to strengthen certain important organoleptic, hygienic, elastic and dactylic properties of leather (Covington, 1988; Bandino and Plains, 1995; Halmetova *et al*., 2005; Madiev *et al*., 2009).

Therefore, it is important to further improve titanium-based tanning system using modern, non-toxic chemical materials that can ensure diffusion, uniform distribution and maximum fixation of tanning agents into the derma to make the leather structure and properties, as well as reduce the environmental impact (Nikonova and Andreyeva, 2015).

We have previously studied the process of tanning sheepskins using ammonium titanylsulfate in the presence of unsaturated polymaleate and polyacrylate polymeric compounds. The results of testing showed that this tanning system reduces processing time while ensuring relatively high hydrothermal stability and appropriate formation of Wet-White leather structure (Nikonova *et al*., 2015; Nikonova *et al*., 2016).

The objective of this study is to determine the effects of polymer-titanium tanning on the finished leather structure and its properties.

MATERIALS AND METHODS

Raw and Chemical Materials

Bated pelt of sheep skin obtained during leather garment manufacturing technology was used for the study (Balberova *et al*., 1986).

Polymaleate (product Kro) was applied as a polymeric material. It is a commercial technical material for leather production by Codyeco S.p.A. (Italy), which is non-toxic, water-soluble, and electrolyte resistant reagent of 21.5% active agent content (on dry residue).

Sodium chloride (95.0%), sulfuric acid (96.0%), and sodium hydrocarbonate (96.0%) were also applied in the study. The tanning was complete with ammonium titanyl sulfate of 40.4% basicity and 22.4% active agent content (on TiO_2).

All indicated materials for leather processing are technical products.

Experimental Conditions

The bated pelt from sheep skin was divided in two samples by the method of asymmetric trimming. One sample of the sheepskin (Experiment) was treated using polymer-titanium tanning, the replacement of traditional ship skin pickling with polymeric treatment. After polymeric treatment, the used solution was exhausted and the next processing was carried in the new solution with 5.0% sodium chloride pretreatment for 15 minutes to prevent acid swelling. Consumption of Kro was in amount 1.1%, temperature 36-38°C, process time − 90 minutes, and consumption of water − 1.0. The pH values after polymeric treatment was 6.5±0.1. The consumption of tanning agent in salt solution was 3.8% (expressed as TiO_2) at 36-38 °C. The pH values at the beginning of the tanning process range 1.1±0.1. Sodium hydrocarbonate was added in amount of 3.5% (1:20 w/v) to get pH values 3.9±0.2, which provided to improve the fixation of tanning agents during diffusion of titanium compounds in semi-finished cross-section.

Another part of the sheepskin (Control) was tanned with 5.0% titanium subsequent pickling with sodium chloride (5.0% in consumption) and sulfuric acid (0.6% in consumption) at 20-24°C (Metelkin and Rusakova, 1980; Balberova *et al*., 1986).

In all cases, the finish of the tanning process was determined by the stable boiling temperature. The duration of titanium-pickling tanning process was 9.0 hours, while polymer-titanium tanning lasted for 5.0 hours. Consumption of chemical materials was calculated based on limed pelt mass of samples.

All subsequent processes and operations were carried out using the known technology (Balberova *et al*., 1986).

The study was carried out in a laboratory setting with 10-liter shaking containers being used, thus ensuring the required temperature and constant mixing (frequency of shaking 8-12 min^{-1}). Physical and mechanical testing and chemical analysis was provided to determine how polymer-titanium tanning affects the finished leather properties.

Research Methods

Both traditional physical and chemical testing and modern methods of analysis were applied to ensure unbiased results of the study.

The pH control of solutions was determined by a pH meter PATECH PH-013M.

Tanned solutions were analyzed using a photocolorimeter AE-30F (ERMA Inc., Japan) for determination of TiO_2 content as per official method (Golovteeva *et al.*, 1971).

Physical and chemical testing and modern methods of leather analysis were conducted using official methods: moisture content ISO 4684:2005 (IULTCS/IUC 5), shrinkage temperature ISO 3380:2015 (IULTCS/IUP 16), hide substance ISO5397:1984 (IULTCS/IUC 10), strength of surface ISO 3379:2015 (IULTCS/IUP 9), strength and percentage extension ISO 3376:2011 (IULTCS/IUP 6), apparent density ISO 2420:2002 (IULTCS/IUP 5), мeasurement of thickness ISO 2589:2016 (IULTCS/IUP 4), мeasurement of area ISO 11646:2014 (IULTCS/IUP 32), content of substances extracted with organic solvents ISO 4048:2008 (IULTCS/IUC 4), water vapour absorption ISO 17229:2016 (IULTCS/IUP 42), water vapour permeability ISO 14268:2012 (IULTCS/IUP 15). Volume yield and porosity was calculated using the official method (Danilkovich, 2006).

The impact of leather processing on the formation of the porous structure of semi-finished Wet-White leather and uniformity of distribution of tanning agents was measured by electron microscopy. The testing was performed using a scanning electronic microscope (SEM JSM-6490-LV, JEOL, Japan) with integrated electron microprobe analyzer INCA Enerdy and energy dispersive spectroscopy (EDS+WDS, OXFORD, UK) with 50-20000 times magnification.

The diffusion of tanning agents into derma was measured (yellow colored sections after hydrogen peroxide treatment) every 30 minutes using an optical microscope Bresser Researcher Bino (Bresser, Germany) with 40-50 times magnification as per official testing method (Metelkin and Rusakova, 1980; Danilkovich, 2006).

RESULTS AND DISCUSSION

No complications were noticed during processing of leather samples; both tanned Wet-White samples and finished leather have a clean and silky grain smoothness and nice feel, were more filled and soft compared to control leather samples as per both sensory and visual assessment. Furthermore, it was discovered that the polymeric treatment prior to titanium tanning provide to reduce this process in 1.8 times and increase the exhaustion of titanium tanning agent from a solution in 1.6 times (table 1).

Table 1. Description of waste tanning waters

Index	Exhaustion of tanning agent (%)	Content of TiO_2 in waste solution (g/l)
Experiment	95.7	1.60
Control	94.8	2.56

The impact of tanning method on the morphological changes in collagen structure shown in SEM-micrographs of cross-sections of the tanned leather as presented in Figures 1 and 2.

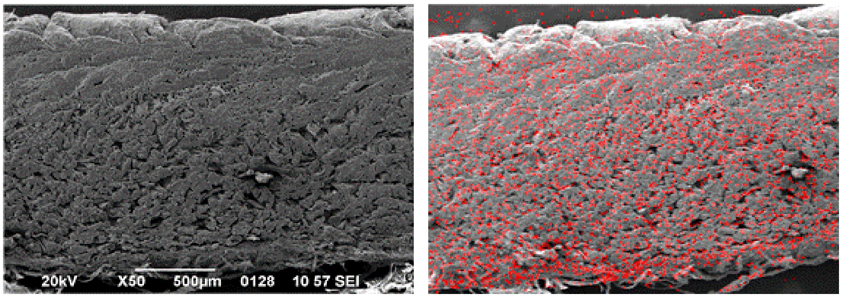

Figure 1. SEM-micrographs and EDS analysis of titanium-pickled tanned leather

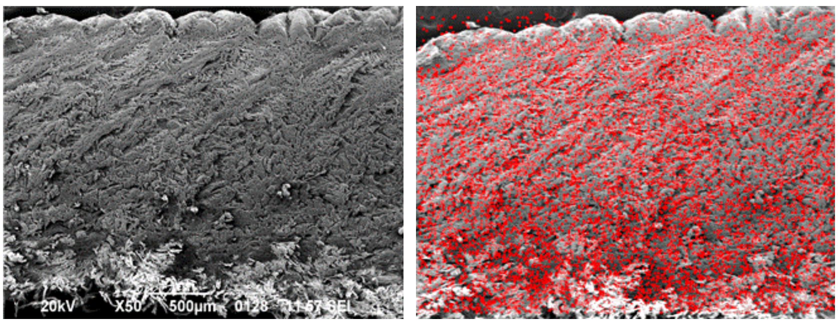

Figure 2. SEM-micrographs and EDS analysis of polymer-titanium tanned leather

As shown in figure 1, in cross-sections of titanium-pickling tanned leather samples the interlacing bundles of collagen are traced poorly, the spread of voids on the section area is unequal with a substantial increase in density in the direction of the grain surface. Since, of the insufficient structure loosening, the titanium-tanning agents are distributed unevenly into the derma.

SEM-micrographs of polymer-titanium semi-finished lather cross-sections (figure 2) show better interweaving of second-level fibers, uniform structure density throughout the cut area, increased distance both between individual fibers and their clusters, which will ensure proper diffusion and uniform distribution of titanium tanning agents into the derma and positively affect leather properties.

The results of physical and mechanical testing and chemical analysis (table 2) confirm that several leather parameters have been improved after applying a new tanning method, which involves the replacement of pickling with polymeric treatment (product Kro) and subsequent titanium tanning. Compared to the control leather sample the following indicators have been improved: strength in 1.3 times; strength of surface in 1.4 times; eextension at 10 MPa in 1.2 times; titanium oxide content in 1.2 times;

thickness yield by 8.8%; area yield by 10.1%; volume yield by 14.7%; shrinkage temperature by 12 °C, porosity by 10.4%.

Table 2. Influence of tanning method on the properties of leather

Index	Experi-ment	Control
Moisture content (%)	12.0	12.2
Content of TiO_2 (%)	6.4	5.2
Content of substances extracted with organic solvents (%)	9.5	11.0
Tensile strength (MPa)	12.4	10.0
Tear strength (N/mm)	28.0	20.0
Strength of surface (MPa)	12.4	8.7
Extension at tensile strength (%)	35.5	30.0
Volume yield (cm^3/100g)	139.6	119.1
Yield of thickness relative to bated pelt (%)	111.4	101.5
Yield of area relative to bated pelt (%)	89.0	80.0
Shrinkage temperature (°C)	92.0	80.0
Apparent density (g/cm^3)	0.38	0.42
Water vapour permeability ($mg/cm^2 \cdot h$)	2.48	2.47
Porosity, %	66.7	59.7

CONCLUSIONS

The study has investigated the impact of polymer-titanium tanning on garment sheepskin leather properties.

It was revealed that polymeric treatment before titanium tanning will improve performance and consumer leather properties. Polymer-titanium tanning system can increase the strength, elongation, volume yield, thickness and area yield, and porosity. These were also confirmed by the results of microscopic testing of semi-finished Wet-White leather, which show that titanium tanning agents are distributed more uniformity into the derma if a polymaleate (product Kro) is applied before tanning. The advantages of polymer-titanium tanning include the reduced processing cycle, chrome-free tanning system, better exploitation of titanium tanning agents and leather materials that will positively affect on the environment, energy and resources.

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