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Resource-saving technologies for the production of elastic leather materials: Collective monograph

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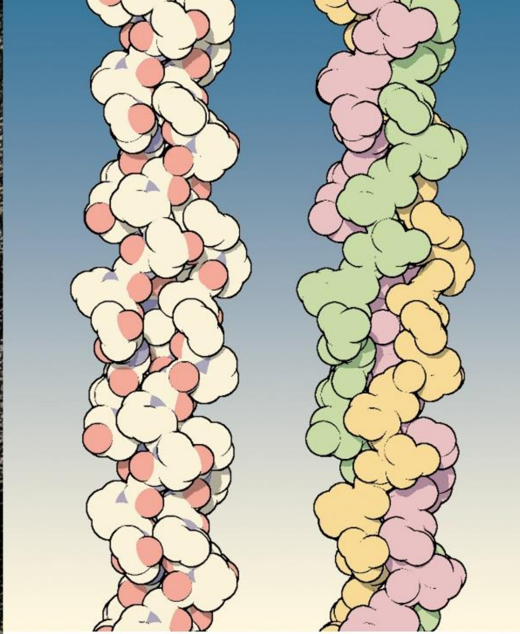
RESOURCE-SAVING TECHNOLOGIES FOR THE PRODUCTION OF ELASTIC LEATHER MATERIALS

COLLECTIVE MONOGRAPH



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Annotation:

This monograph contains a collection of recent research papers focusing on advancing existing technologies and developing new technologies to improve the environmentally friendliness and save resources during the production of elastic leather materials. The papers are organized based on the type of technological process used to preserve raw hides. A lot of attention is devoted to mathematical planning, simulations, and multicriteria optimization of the technological processes using newly developed chemical reagents. The monograph contains a complex study of physicochemical properties and characteristics of the resulting leather materials. The developed technologies were tested by the private joint-stock company Chinbar (Kyiv, Ukraine) and implemented at Ukrainian tanneries.
Total number of figures – 58, tables – 95, and references – 491.

Collagen image on the cover: David S. Goodsell, RCSB Protein Data Bank (doi:10.2210/rcsb_pdb/mom_2000_4).

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CONTENTS

INTRODUCTION

This monograph contains the results of the most recent studies on processing of raw leather and fur materials utilizing novel chemical reagents and examples of industrial implementation of the developed technologies. A wide variety of raw leather materials, namely cattle, porcine, rabbit, coypu, sheep, and equine hides, were used. The effect of new reagents, such as electrochemically activated water, modified montmorillonite, highly-dispersed SiO_2 nanoparticles, bacteria and enzymes, and modified azo dyes on the properties of elastic leather and fur materials has been investigated.

Most of the publications in this monograph are focused on studying a few related processes and their relationship with the subsequent processing of collagenous semi-finished leather products during multistage, mass- and energy-intensive technological cycle which usually involves applications of environmentally hazardous reagents. As a result of the presented studies, improved efficacy and environmental safety of leather and fur production was achieved.

The process of regeneration of water balance during the soaking of a variety of raw hides with different density and thickness and processed by methods involving application of electrochemically activated water has been studied in detail [1–3]. Particularly, the soaking of equine raw hides can be efficiently carried out using fractions of electrochemically activated water - a mixture of catholyte with anolyte at a ratio of 5 : 1 [2]. The environmentally harmful sodium sulfide and sodium carbonate and surfactant are excluded from this soaking solution. Authors of the work [3] studied the effect of the developed soaking method of differently preserved raw hides on the properties of the resulting leather materials. The dependence of water sorption on the type of electrochemically activated water and treatment duration was determined. Effect of composition of alkaline solution and its temperature on the structural transformation in raw hides during removing preservatives, globular proteins, and mucopolysaccharides from its structure has been studied [4].

In the work [5] the layer-by-layer concentration of gelatin hydrolyzed from a pickled hide from different topographical areas (cuts) upon varying the enzyme concentration and the duration of liming process was determined. A comprehensive study of the effects of tanning agents of different chemical nature on the process of dermal collagen structuring made it possible to establish the mechanism of interaction between chromium (III) compounds and alkyl carboxyethanolamines [6]. The aspects of application of vegetable tannins were also established. Structural transformations of dermal collagen during tanning were investigated by analyzing the isotherms of sorption-desorption of water vapor in the semi-finished product depending on the stage of its processing. At the same time, the authors performed thermogravimetric studies of the semi-finished product in the temperature range of 20–600 °C and determined the effect of acid-salt treatment and subsequent tanning with basic chromium compounds on its thermal and thermodynamic properties. Scanning electron microscopy study of the structure of semi-finished product, which was softened and tanned with basic chromium compounds and a syntantanide composition, was performed. The effect of montmorillonite modification on the chemocolloidal properties of tanning solutions containing chromium compounds and the physicochemical properties of semi-finished leather products were investigated [7]. X-ray diffraction study of the modified montmorillonite by chromium complexes depending on their ratio was carried out.

By using enzymes in the post-tanning processing of chrome-tanned semi-finished product, the authors [8, 9] established the dependence of the elastic-plastic properties of the material on the enzyme concentration, temperature, and process duration. It is shown that at the effective consumption of the biocatalytic modifier under optimal conditions, the stiffness of the semi-finished leather product is reduced twofold compared to the existing technology while maintaining its mechanical strength.

The interaction of anionic azo dyes, of different chemical composition, with titanium compounds was investigated in the work [10]. The effect of composition and concentration of azo dyes on the process of their sorption and diffusion in model systems – collagen fibers, gelatin, and semi-finished leather product of chrome tannage has been established. The colorimetric and exploitation properties of dyed elastic leather were reported.

The authors investigated the effect of highly-dispersed SiO_2 on the process of filling chrome-tanned semi-finished product from cattle hide and technological and physicochemical properties of resulting leather [11]. Dependences of the chemical content of the composition on the rate of its diffusion into the structure of chrome-tanned semi-finished products have been established [12], as well as on the physicochemical and elastic-plastic properties of leather filled with protein-tannides and protein-montmorillonite compositions. In the work [13], the effect of different fractions of electrochemically activated water in the filling composition on the chemical composition and physicochemical properties of macroporous semi-finished products from different areas was investigated.

In the process of forming hydrophobic materials - leather from raw cattle hides and fur velour from nutria, suitable for use in high humidity, the authors investigated the effect of chemical composition of the fatliquoring composition based on alkenyl maleic anhydride on water resistance and elastic-plastic properties of the material [14, 15]. The effect of alkenyl maleic anhydride composition on absorptivity and diffusivity, dynamic water wetting, and wetting of hydrophobized chrome-tanned hides was established in the work [16].

The performed complex research of step-by-step formation of leather and fur became the scientific basis for the development of innovative resource-saving technologies for manufacturing elastic materials. At the same time, the authors pay considerable attention to mathematical planning, modeling, and optimization of the developed technological processes.

To reduce the cost involved with the use of environmentally hazardous chrome tanning agent and industrial oil I-12A in the technology of tanning and fatliquoring of wool sheepskin, its multicriteria optimization was carried out [17]. To accomplish this, a modified gradient method of changing process parameters using a generalized objective function is used. The developed technology makes it possible to reduce the consumption of chrome tanning agent by 33 % and to replace the non-biodegradable plasticizer with sulfonated dipropylene glycol ester with a significant reduction in its consumption.

Optimization of the concentration of the filling composition ingredients used in the processing of the chrome-tanned semi-finished product is discussed [18, 19]. According to the McLean-Anderson method with considering the type of mathematical model "concentration of the ingredients of the filling composition – material properties" and the developed multithreaded program, an experiment plan was computed, a mathematical model was obtained, and optimal concentration of composition ingredients were established using the desirability function. The developed composition of the Aerosil-containing composition makes it possible to reduce the consumption of vegetable tanning agents. Semi-industrial testing of the developed technology for filling leather semi-finished product from cattle hides results in the formation of leather material with increased volume yield and elasticity compared to the current technology.

Highly-dispersed silica (IV) oxide has also been used to optimize the filling-fatliquoring process of leather semi-finished products [20]. Multicriteria process optimization was performed based on the central composite rotatable plan of the second-degree and the desirability function. According to the developed technology, which allows us to more efficiently use the raw material, the resulting light-colored leather produced in semi-industrial conditions are characterized by the increased elasticity and durability.

In the work [21] for multicriteria optimization of the filling-fatliquoring process of chrome-tanned semi-finished product, a mathematical model of the second-degree was used and a software module, which allows us to translate the problem into single-criteria optimization using minimax convolution of criteria and subsequent simplified optimization solution using Hooke-Jeeves method, was developed. The optimal values of the process parameters provide the formation of leather material with high area yield and increased elasticity compared to the current technology.

The application of an expert assessment of the quality of hydrophobized fur velour using the concordance coefficient confirmed by Pearson's criterion made it possible from 18 parameters provided to experts on functional, ergonomic, and aesthetic properties to establish parameter groups which affect the material quality [22]. Based on the essential quality parameters established by the expert method, a complex parameter which allows determining the efficiency of hydrophobization of velour by alkenyl maleic anhydride polymer with respect to its exploitation in high humidity was calculated [23].

The advantages of the developed resource-saving ecologically-oriented technologies of tanning pickled cattle hides compared to the current technologies for the production of the semi-finished product "wet blue" are given in the work [6]. Improving the technological conditions and application of novel reagents result in a substantial decrease in the consumption of mineral and vegetable tanning agents and the duration of the technological process. The developed technologies of tanning of leather semi-finished products are tested and implemented at private JSC Chinbar (Kyiv, Ukraine). A substantial decrease in the consumption of environmentally hazardous chromium tanning agent is achieved by using synthesized hydroxy sulfate-*Cr*-

montmorillonite complexes [7]. Industrial implementation of the developed technology made it possible to increase the yield of the elastic material.

The developed plasticizing process of tanned leather semi-finished product with hydrolytic enzymes made it possible to significantly reduce the duration of further mechanical processing [8, 9]. Compared to the previous technology used at PJSC Chinbar, the implemented technology provides a more efficient use of raw hides and results in an increased yield of the leather area. According to the technology [9], short-term enzymatic tanning of the semi-finished product at a higher temperature allows for the exclusion of the mechanical plasticizing process from the technological cycle. This results in an increase of the economic efficiency for the production of leather materials by reducing the raw hide and energy consumption.

At the final stage of production of elastic leathers, filling-plasticizing technologies using the protein hydrolysate of secondary products of leather production and modified montmorillonite were developed [12]. Such technologies made it possible to form leather materials with a more uniform structure and properties between topographic areas of the leather semi-finished product from cattle hides and sheepskins. The developed filling-plasticizing technologies allowed us to significantly reduce the cost of tanning agents and synthetic dispersants and was implemented at the companies of Ukraine: private JSC Chinbar (Kyiv), Vozko (Voznesensk, Mykolaiv region), and public JSC Svitanok (Lviv).

ABBREVIATIONS

ABBD	*acidic blue-black dye*
BKD	*black K dye*
AA	*aliphatic acid*
AAm	*acrylamide*
ACEA	*alkylcarboxylethanolamines*
AMA	*alkenyl maleic anhydride*
AMAC	*AMA composition*
AST	*ammonium sulfate titanylate*
B345D	*brown 345 due*
BCS	*basic chromium sulphate*
BET	*Brunauer–Emmett–Teller*
BNS	*β-naphthalene sulfonate*
BOT	*bound organic tannin*
BCM	*biocatalytic modifier*
CCRP	*central composite rotatable plan*
CF	*collagen fiber*
CH	*cattle hide*
CHS	*chromium hydroxyl sulfate*
CS	*code specification*
CSVT	*chromesyntanvegetable tanning*
CT	*current technology*
CTL	*chrome-tanned leather*
CTSFP	*chrome-tanned SFP*
CTSSFP	*chrome tannage of split SFP*
CTUSFP	*chrome tannage of unsplit SFP*
DADMAC	*diallyl dimethylammonium chloride*
DPGE	*dipropylene glycol ether*
DSTU	*ДСТУ (in Ukrainian), stands for "National Standard of Ukraine"*
ECA	*electrochemical activation*
ECAS	*electrochemically activated solution*
ECAW	*electrochemically activated water*
EDXS	*energy-dispersive x-ray spectroscopy*
EO	*electrolyzed oxidizing*
EP	*enzymatic plasticizing*
EPT	*EP treatment*
ET	*existing technology*
FA	*fine-dispersed aluminosilicate*
FE	*field emission*
FS	*fat substance*
GAG	*glycosaminoglycan*
GMA	*glycidyl methacrylate*
GOST	*ГОСТ (in Russian), stands for "National Russian Standard"*
HD	*hydrothermal denaturation*
HP	*hide powder*
HTS	*hydrothermal stability*
ISBN	*International Standard Book Number*

ISO	*International Organization for Standardization*
IUPAC	*International Union of Pure and Applied Chemistry*
JSC	*joint-stock company*
LC	*liquid coefficient*
LPH	*large pig hide*
LS	*lignosulfonate*
MDP	*mixture of dispersions of polymers*
MIOX	*mixed oxidant*
MM	*montmorillonite*
MMM	*modified MM*
NA	*naphthenic acid*
NFV	*nutria fur velour*
ORP	*oxidation-reduction potential*
OS	*organic solvent*
OST	*OCT (in Russian), stands for "Industrial Standard"*
OWS	*organic water-soluble substance*
PhEC	*Photoelectric Colorimeter*
PJSC	*private joint-stock company*
PS	*protein substance*
PTO	*potassium titanyl oxalate*
PVT	*polymer-vegetable filler*
QE	*quebracho extract*
rpm	*revolutions per minute*
SAM	*surface-active material*
SAT	*statistical acceptance test*
SEM	*scanning electron microscopy*
SFP	*semi-finished product*
SFPCT	*SFP of chrome tannage*
SFV	*sheepskin fur velour*
SL	*soaking-liming*
SVTSFP	*synthetic-vegetable tanning of SFP*
TOA	*titanyl oxalic acid*
TU	*ТУ (in Ukrainian), stands for technical specifications*
UAH	*Ukrainian Hryvnia (currency of Ukraine)*
UDC	*Universal Decimal Classification*
UV	*ultraviolet*
WA	*water absorption*
XGAAm	*xanthan gum – acrylamide*

1. USE OF ELECTROCHEMICALLY ACTIVATED AQUEOUS SOLUTIONS IN THE MANUFACTURE OF FUR MATERIALS

Danylkovych A., Lishchuk V., & Romaniuk O.

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Abstract: *The effect of electrochemically activated aqueous solutions on the preparatory processes of formation of corium structure during the treatment of fur skins with different contents of fatty substances was investigated. The use of electroactivated water, namely anolyte with antiseptic properties and catholyte with surface-active properties, helps to restore the hydration of fur skins and to remove soluble proteins, carbohydrates, and fatty substances. The activating effect of anolyte and catholyte can be explained by special physicochemical properties of electroactivated solutions, namely by the presence of free radicals, ions, and molecules which easily penetrate through cell membranes into the structure of non-collagenous components and microfiber structure of dermal collagen. The prolonged acid-salt treatment step is excluded from the process as a result of using electrochemically activated water with high oxidizing power. A low-cost technology of processing different kinds of fur skins utilizing electrochemically activated aqueous solutions provides a substantial economy of water and chemical reagents, a two- to threefold intensification of the soaking and tanning processes, and production of highly elastic fur materials with a specified set of physicochemical properties. At the same time the use of such toxic antiseptics as formalin and sodium silicofluoride are eliminated from the preparatory processes of the developed technology for fur treatment making the technological process ecologically safer.*

Keywords: *electroactivated aqueous solution; anolyte; catholyte; raw fur; soaking; degreasing; tanning.*

Introduction

The modern manufacturing processes must comply with stringent requirements with regard to the efficiency of the use of raw materials and chemical reagents, the decrease in energy consumption, intensification of technological processes, and improvement of sustainability. This is especially relevant for the chemical manufacturing industry which presupposes the use of large amounts of technological solutions with high concentration of chemical reagents, including toxic ones. This also directly concerns the manufacturing of fur and leather products. In view of this, effort is taken to reduce the costs and replace environmentally hazardous chemicals with new reagents, especially at the initial stages of processing raw materials.

For new technological procedures of effective physicochemical soaking of animal hides, the researchers obtained alkaline proteases and optimized their activity depending on pH and temperature. A substantial decrease in the oxygen consumption for treatment of spent technological solutions has been recorded. The researchers [1] studied the effect of 2–5 % protease on dehairing and the effect of 5–10 % lipase on degreasing of animal skins. The authors concluded that the application of these enzymes is environmentally safe, but their use over a prolonged time (8–12 h) should be restricted in view of the possibility of partially destroying skin collagen and decreasing the physicomechanical properties of skins.

The effectiveness of an ultrasonic field during soaking and degreasing of skins was highlighted previously [2, 3]. An increase of up to 23 % in water absorptivity of steerhide coupled with a 36 % decrease in the duration of soaking air-dried skins was revealed. By using ultrasound, the researchers [3] achieved a twofold decrease in the duration of degreasing under production-line conditions in comparison with control treatment, though, the developed technology requires complex manufacturing equipment [4].

The existing technologies of treating furs, depending on their structure, require three- to 20-fold higher consumption of water [5, 6] in comparison with leather production. Particularly, the consumption of water at the soaking stage per one ton of air-dried raw material is 9 m^3 for rabbit skins, 17 m^3 for sheepskins, 25 m^3 for fox skins, and at the stage of fox skin dyeing by oxidizing intermediates – 175 m^3 (including numerous washes).

One of the ways to improve sustainability of fur manufacturing and to reduce the consumption of water used for the preparation of technological solutions could be water activation by different methods, particularly, by magnetic field, ultrasound, agitation, heat treatment (heating, cooling, or freeze-thawing), or electrochemical activation (ECA) as a result of which water acquires anomalous properties [7, 8]. The physicochemical properties of ECA water and solutions of chemical reagents are largely accounted for by their declustered structure, high oxidation-reduction potential (ORP), and thermodynamic non-equilibrium state [9–11] which are preserved over an extended period of time. It was also discovered that ECA water intensifies biotechnological processes [12].

While studying the effect of ECA water on the structure and properties of biopolymers, it was established that one of its fractions, namely anolyte, has a bactericide effect on the flora of protein-based raw materials [13, 14] and its application allows excluding antiseptic reagents from the technological process. The bactericidal properties of ECA water were tested on plant and animal models, particularly, on hydra and *Ceriodaphnia dubia* [15].

The work [16] highlights the characteristics of anolyte and catholyte and their effect on the regulation of fermentation and genetic activity of distillers' yeast. At the same time, it is recommended to use ECA water for standardizing alcoholic beverages produced by different companies. A positive effect of activated water was observed in the synthesis of furfural [17] from vegetable waste with high content of pentosans. The use of ECA water with low pH as an active catalyst allows excluding acids from the technological process.

Since the preparatory stages of processing leathers and furs involve the use of sodium chloride in various concentrations, sodium carbonate, bicarbonate, and sulfate, the effect of ECA water on the physicochemical properties of these reagents is of great interest. The work [18] shows that ECA water with a negative ORP easily penetrates cells, whereas catholyte with high value of pH promotes effective release of lipids, glycosaminoglycans, and globular proteins from protein-based raw materials.

The use of ECA water in drying and moisturizing processes for manufacturing leather used for shoe uppers results in increasing the surface area of the final material due to the plasticization effect of ECA water on leather structure as opposed to industrial water. This is accounted for by increasing the deformation capacity of the leather material and reducing the stress during the drying. Particularly, application of catholyte enhances the deformation of samples by 1.5–5.0 % [19, 20] depending on the type of leather. At the same time, the pH and ORP stability of electroactivated water after boiling [21] allows its application in footwear manufacturing for production of shoe uppers. To increase the plasticity of fur skins and leather during their processing, it is recommended that the semi-finished product is treated with solutions of catholyte [22, 23] with low concentrations of benzyl alcohol, glycerin, and oxoaldehyde.

Thus, the analysis of literary sources testifies to the relevance of research on the use of ECA aqueous solutions for manufacturing leather and fur materials. The use of activated water in the treatment of raw protein-based materials can be effective, provided high stability of the properties of electroactivated aqueous solutions and their chemical activity towards non-collagen components of animal skins.

Problem Statement

When developing new and improving existing technologies for processing furs, especially at the preparatory stages which are characterized by long production cycles and usage of substantial volumes of aqueous solutions of chemical reagents, the problem of intensification of technological processes is especially relevant. One of the ways of solving this problem is to use electrochemically activated aqueous solutions and increase the efficiency of the preparatory stages of fur production.

Methods

The study is aimed to investigate the influence of electrochemically activated water on the efficiency of the main processes of fur production. Two fractions of electrochemically activated water will be used, namely anolyte and catholyte. The technology foresees implementation of a set of consecutive physicochemical procedures and mechanical operations during raw material processing. They include soaking of the raw materials for restoring the water content lost during curing, the removal of subcutaneous tissue, degreasing, acid and salt treatment, chemical structuring (i.e., tanning with chromium compounds), plasticization (i.e., fatliquoring and drying-moisturizing treatments).

To prepare technological solutions of chemical reagents we used distilled water supplemented with 0.2 g/L of sodium chloride for electric activation. Anolyte and catholyte were obtained with a pH range of 2.8–4.0 and 9.5–11.5 in the electric water activator of the research and production company “Ekovod” (technical specification TU U29.1-1285006876.001-2000) by using a silicon anode, steel cathode, and ion-exchange membrane made of cotton of special weaving [24, 25].

Enhanced chemical activity of declustered aqueous systems and technological solutions was explained by a number of electrochemical processes under the influence of electric current on water in the presence of an electrolyte. The water is ionized with the formation of a substantial number of highly active ionic radical elements, particularly [26]:

$$OH^-, H^+, H^\bullet, O^\bullet, OH^\bullet, HO_2^\bullet, HO_2^-, H_3O^\bullet, H_3O^+,$$
$$H_3O^-, Cl^\bullet, ClO^-, ClO_3^-, HCO_2^-, C_2O_4^{2-}.$$

The principal reactions that occur in the electric water activator are as follows:

on the anode

$$2H_2O - 4\bar{e} \rightarrow O_2 + 4H^+ \text{ and } 2Cl^- - 2\bar{e} \rightarrow Cl_2;$$

and on the cathode:

$$2H_2O + 2\bar{e} \rightarrow H_2 + 2OH^- \text{ and}$$
$$H_2O + 2Na^+ + 2\bar{e} \rightarrow 2NaOH + H_2.$$

The examination of physicochemical properties of the obtained anolyte (Fig. 1) shows a slight increase in its pH and a decrease in its ORP during its storage in a hermetically sealed container for 9 d.

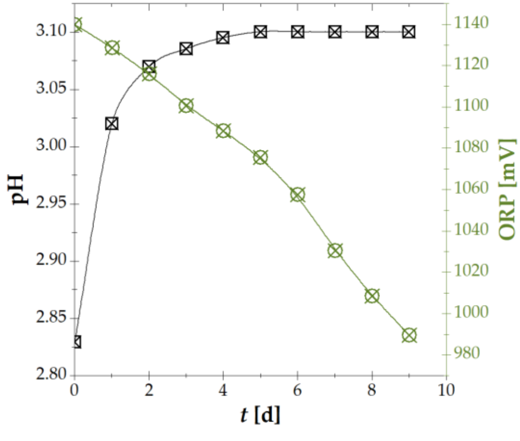

Fig. 1. Kinetics of pH change of anolyte and its ORP.

Similar effects were observed earlier [17]. It is necessary to note that the main changes in the pH of activated water occur in the first two days of storage, whereas its ORP decreases continuously. This can be explained by the neutralization of H^+ ions during their interaction with oxide compounds formed in electrochemical reactions. The results testify to the high stability of anolyte during storage. Water can be used in the technological process immediately after its activation by utilizing flow-through cylindrical electric activators [8].

Unprocessed air-dried nutria and rabbit skins were chosen for this study. Nutria skins had fat content 22.3 % and surface area 20–24 L (GOST standard 2916-84), whereas rabbit skins, which have higher density than those of nutrias, were 0.7–1.0 mm thick (GOST standard 2136-87).

The pH values of catholyte and anolyte were measured on the device pH-340. ORP was calculated by a potentiometric method using platinum and silver-chloride electrodes. The water content of the dermis of raw fur skins was assessed by a gravimetric method using AXIS Communications AB (Lund, Sweden) scale, model AD200.

Nutria skins were subjected to soaking using non-ionic surface-active materials (SAMs) according to the technical specification TU 2484-014-22284995-99. SN-23 and SPK-50 were dissolved in activated and distilled water at 19–21 °C and used at water-to-skins mass ratio equals to 9 : 1. The SAM concentration for soaking and degreasing was 0.5 and 2.0 g/L, respectively.

The tanning of rabbit and nutria skins from a control group was carried out using spent solution of anolyte supplemented with potassium alum $KAl(SO_4)_2{\cdot}12H_2O$ (GOST standard 4329-77) and basic chromium sulphate $Cr_2(SO_4)_n(OH)_{6-2n}$ with basicity of 39 % at 9 : 1 water-to-skins mass ratio. The amount of tanning agents was as follows: potassium alum – 10 g/L and chromium sulphate, expressed as Cr_2O_3, – 1.6 g/L for rabbit skins and 1.0 g/L for nutria skins. The basicity of the tanning agent was increased to pH 3.7–3.9 by adding a solution of sodium carbonate twice with an interval of 15 min.

The results were evaluated at the PJSC Chinbar (Kyiv, Ukraine) according to the methods of processing raw furs [27–29] presupposing the use of anolyte and catholyte. Nutria skins were soaked in anolyte and degreased in catholyte at 28–32 °C without the use of additional reagents. After degreasing, nutria skins were rinsed, pressed, and treated with anolyte twice to prepare them for the subsequent tanning. Rabbit skins were subjected to chrome tanning at 18–20 °C after soaking in the spent solution of anolyte and removal of subcutaneous tissue.

For comparative analysis we used fur skins obtained using existing technologies [31] which presupposed the treatment of raw fur at the following temperatures: soaking of nutria and rabbit skins – 30 and 38 °C, respectively; degreasing (for nutria skins) – 38 °C, pickling and tanning – 30 and 40 °C. The following amounts of chemical agents were used for processing of rabbit and nutria skins, respectively: sodium chloride – 140 and 130 g/L, SAMs – 3.5 and 5.0 g/L, 40 % formaldehyde – 1.0 and 0.5 g/L, sodium fluorosilicate – 0.8 and 1.5 g/L, sodium thiosulphate – 17.0 and 8.0 g/L, tanning agents – 16.4 and 14.0 g/L. The drying and humidifying technological processes and the operations involving the semi-finished product were carried out according to the existing requirements of treating rabbit and nutria skins.

The physicochemical properties were identified according to the previously described methodology [32]. The breaking strength was measured on a strength-testing machine RT-250M at extension rate of 80 mm/min. Hydrothermal stability (HTS) of the fur skins was measured as a temperature of the start of sample shrinkage during its heating in water at the rate of 2–3 °C/min.

Results and Discussion

The process of hydration of fur skins in an electroactivated solution of anolyte includes a reaction between hydrogen protons and negatively charged carboxyl groups of collagen macromolecules, and in case of catholyte – carboxyl groups with amine groups of collagen.

Under existing technology, the sources of H^+ and OH^-ions are dilute acids and bases. When anolyte is used, ionic links between the amino groups and carboxyl groups of polypeptide side chains are disrupted as a result of which amino groups of the biopolymer retain their positive charge, whereas ionized carboxyl groups are getting protonated. This leads to an increase in the degree of hydration of collagen due to an ion–dipole interactions and coulomb repulsion which lead to an increase in the water sorption by dermis. With the use of catholyte as opposed to anolyte the hydration of dermis of fur skins consists in the fact that the soaking process is accelerated due to neutralization of ionized amino groups of collagen.

The investigation of the effect of electroactivated aqueous solutions of catholyte, containing only 25 % of SAMs used in the existing technologies for processing of nutria skins to increase the hydration degree, suggests that the water lost during curing is getting restored at a considerable rate (Fig. 2) with most of the aqueous solution being absorbed in the first hour or two. Then this process slows down and the mass of skins is increased only by 10 % in the next 20 h. This may testify a redistribution of the absorbed aqueous solution in the fibers during which the solution passes from the large pores into the inter-fiber and microfiber spaces of the fine structure of the collagen of dermis. The use of catholyte, as compared to distilled water (control) accelerates the solution diffusion within the structure of skin tissue. The SAM SPK-50 solution in catholyte is the most effective, 18 % more than the control solution which presupposes the use of distilled water with 2 g/L SAM SN-23 (Fig. 2, curve 4).

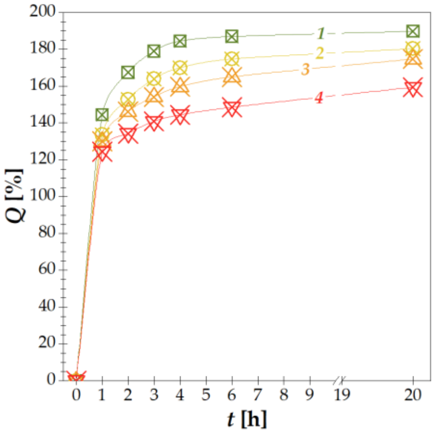

Fig. **2.** *Water absorption kinetics for nutria skin tissues in catholyte (1 and 2) and in distilled water (3 and 4) with SAM SN-23 (2 and 4) and SAM SPK-50 (1 and 3).*

The solution properties used for soaking and degreasing (Table I) indicates that pH of spent anolyte increases and pH of spent catholyte decreases by 1.3 and 1.5 times, respectively, whereas pH of the SAM solution in distilled water changes insignificantly. This testifies to enhanced chemical activity of electrochemically activated aqueous solutions and profound structural changes of the dermis and raw fur material. The substantial differences in the conductivity of SAM solutions in catholyte and anolyte compared to the solutions based on distilled water testify the enhanced chemical activity of electroactivated solutions, especially of catholyte. This is also confirmed by 3.9- and 1.8-times higher conductivity of the original anolyte and catholyte solutions as compared to the distilled water. The conductivity of the spent catholyte solution is increased 2.1-fold, and 2.4-fold as compared to distilled water.

The results of the process of degreasing nutria skins with a SAM solution in catholyte are listed in Table II.

The analysis of nutria skin tissues after treatment showed a higher effect of degreasing of skins with the use of catholyte and SAM SPK-50 as compared with distilled water. Moreover, 60 % of fatty substances were removed in the first soaking surpassing the control by 13.7 %. More effective degreasing of nutria skins is achieved by a higher hydration degree with the use of SAM solution based on catholyte.

Table I. *Physicochemical properties of aqueous solutions with SAM SPK-50 after degreasing of fur skins.*

Parameter	**Solution**		
	anolyte	**catholyte**	**distilled water**
pH	$\frac{2.8 \pm 0.1}{3.7 \pm 0.1}$	$\frac{10.7 \pm 0.2}{6.9 \pm 0.1}$	$\frac{6.7 \pm 0.1}{6.1 \pm 0.1}$
Specific conductivity [μS/cm]	$\frac{2800 \pm 90}{2640 \pm 80}$	$\frac{1270 \pm 40}{2760 \pm 90}$	$\frac{710 \pm 20}{1160 \pm 40}$

Note: *The numerator and the denominator correspond to the initial and final values of the solutions.*

Table II. *Content of fatty substances in dermis after fur skin soaking and degreasing.*

#	**Solution**	**SAM**	**Content of fatty substances [%] after**		
			soaking 1	**degreasing**	**soaking 2**
1	catholyte	SN-23	9.7 ± 0.2	3.32 ± 0.05	3.07 ± 0.05
2		SPK-50	9.0 ± 0.2	3.25 ± 0.05	3.12 ± 0.05
3	distilled water	SN-23	13.2 ± 0.3	4.09 ± 0.07	3.71 ± 0.06
4		SPK-50	10.1 ± 0.2	3.66 ± 0.06	3.25 ± 0.05

An increase in the chemical activity of electroactivated technological solutions is observed in the structuring of collagen of nutria skin tissue during their tanning with chromium compounds [30]. The results obtained in the subsequent processes of nutria skins treatment suggest that skin structuring is increased with the use of SAM solution in catholyte (Table III).

The HTS of dermis is increased as a result of more intensive removal of non-collagen components, including fatty substances, under the influence of active products of the electrochemical reaction that are present in the catholyte. This contributes to increased diffusion of tanning chromium compounds into the skin tissue and their subsequent efficient interaction with ionized carboxyl groups of polypeptide chains of collagen macromolecules. This effect is manifested to a greater extent in case of using non-ionic SAM SPK-50 as a part of a degreasing solution. It is necessary to note a certain decrease of HTS after acid-salt treatment as a result of the increase in the electrostatic repulsion between the amino groups of collagen macromolecules.

Table III. *Hydrothermal stability of nutria skins after consecutive treatments.*

#	Shrinkage temperature [°C] after		
	degreasing, soaking	**acid-salt treatment**	**structuring**
1	58 ± 1	56 ± 1	76 ± 1
2	58 ± 1	56 ± 1	79 ± 1
3	57 ± 1	54 ± 1	72 ± 1
4	57 ± 1	54 ± 1	73 ± 1

Thus, it was established that the use of technological solutions based on electroactivated water and lesser quantities of chemical reagents compared to the existing technology of processing fur provides an effective structuring of skin tissue with hydrothermal stability in accordance with the active standards. Such treatment of fur, even without the use of antiseptics, helps to preserve well-bond pillage with the dermis even after degreasing.

Approbation of Results of the Research

The results of the research on the effect of electroactivated aqueous solutions of anolyte and catholyte on the processes of nutria fur treatment were used for fur production at PJSC Chinbar (Kyiv, Ukraine). In view of the high chemical activity and specific physicochemical properties of anolyte and catholyte, they were used in the processing of furs without SAMs at different stages of the technological cycle.

At the stages of soaking, acid-salt treatment, tanning, and fatliquoring, we used anolyte solutions with pH of 2.8–4, while for degreasing we utilized catholyte solutions with pH of 9.5–11.5. After drying and moisturizing processes, the fur skins were refined.

The nutria skin samples obtained in the study testify to the fact that skin tissue with optimal physicochemical properties is formed with the use of anolyte with pH 2.8–3.0 and catholyte with pH 9.5–10.0 (Table IV).

Table IV. *Physicochemical properties of nutria skins.*

Parameter	**Treatment**			
	1	**2**	**3**	**4**
pH of anolyte	2.9 ± 0.1	3.4 ± 0.1	3.9 ± 0.1	—
pH of catholyte	9.7 ± 0.2	11.2 ± 0.3	10.7 ± 0.3	—
T_S [°C]	65.0 ± 1	69.0 ± 1	59.0 ± 1	63.0 ± 1
– FSAD [%]	3.62 ± 0.06	3.8 ± 0.06	3.3 ± 0.05	4.1 ± 0.07
– FSAF [%]	17.4 ± 0.4	18.3 ± 0.5	17.9 ± 0.4	16.2 ± 0.4
– Cr_2O_3 [%]	0.89 ± 0.02	0.83 ± 0.02	0.90 ± 0.02	0.93 ± 0.02
Strength ^{1} [N]	65.0 ± 3.3	64.0 ± 3.3	58.0 ± 3.0	62.0 ± 3.1
TE [%]	15.0 ± 1.4	13.2 ± 1.2	10.4 ± 0.9	12.7 ± 1.1
RE [%]	8.3 ± 0.6	9.7 ± 0.7	6.0 ± 0.4	6.2 ± 0.4

Note: *The volumes of fatty substances and chrome oxide are calculated on a dry basis. 2. T_S is the shrinkage temperature. FSAD and FSAF stands for fatty substances after degreasing and after fatliquoring, respectively; while TE and RE – for total and residual elongation. ^{1} denotes breaking strength for the entire skin.*

An increase in pH of anolyte (treatment 2) leads to decreasing the strength of the samples, which positively affects subsequent treatments, namely tanning and fatliquoring. Compared with the control samples, except for treatment 3, nutria skins treated with activated aqueous solution without SAMs have higher strength and hydrothermal stability and higher content of unconnected fatty substances after fatliquoring.

A decrease in shrinkage temperature and breaking stress given an over 3.5-fold increase in the pH of anolyte is caused by uneven distribution of chromium (III) compounds in the skin tissue as a result of their (mostly) superficial interaction with carboxyl groups of polypeptide chains of collagen.

To reveal the influence of fur skins density on the process and fur properties, we obtained samples of wool breed rabbit of average thickness. They were not subjected to degreasing due to substantially lower content of fatty substances in the skin tissue as compared to nutria skins. The test results for these skins are listed in Table V.

The fur skins had higher plasticity, twofold decrease in the shrinkage of dermis, and 10 % increase in volume yield as compared with the existing technology with the exception of treatment *3*. Moreover, we observed high chemical activity of anolyte for manufacturing of fur skins with elastic leather parts. The achieved swelling degree, namely 1.85–1.90 g/g, can be considered sufficient for further structure formation in subsequent treatments, taking into account that swelling degree required for the formation of high-quality fur material of sheepskin is 1.70–1.80 g/g even with the use of enzymes [31].

Thus, the use of activated water in preparatory processes of fur production allows excluding antiseptics, SAMs, and other soaking enhancers. It also allows merging the processes of soaking, degreasing, pickling, tanning, and fatliquoring and results in decreasing the duration of treatments twofold. The use of technological solutions with pH of 3.3–3.5 in acid-salt treatments enhances the effect of electroactivated water on the disruption of links between the macromolecules of collagen and other components due to the effect of oxygen-containing free radicals present in water as a result of electrochemical activation.

Table V. *Physicochemical properties of wool breed rabbits as treated by anolyte.*

Parameter	**Treatment**			
	1	**2**	***3***	***4***
pH of anolyte	2.9 ± 0.1	3.4 ± 0.1	3.9 ± 0.1	—
Hydration [g/g]	1.90 ± 0.02	1.85 ± 0.02	1.70 ± 0.02	1.80 ± 0.02
T_S [°C]	66 ± 1	65 ± 1	57 ± 1	64 ± 1
– FSAF [%]	14.2 ± 0.3	14.9 ± 0.3	15.7 ± 0.4	14.3 ± 0.3
– Cr_2O_3 [%]	1.27 ± 0.03	1.21 ± 0.03	1.14 ± 0.02	1.33 ± 0.03
Strength [1] [N]	74.0 ± 5.2	79.0 ± 6.6	68.0 ± 5.0	71.0 ± 5.2
Plasticity [%]	21.0 ± 2.1	19.0 ± 1.9	16.0 ± 1.6	17.0 ± 1.7
Shrinkage [%]	1.2 ± 0.1	1.4 ± 0.1	2.2 ± 0.2	2.8 ± 0.3
Volume yield [cm^3 per 100 g of PS]	240 ± 12	244 ± 13	200 ± 10	220 ± 11

Note: *see the notes to the Table IV; PS stands for protein substances.*

Conclusions

The effect of physicochemical properties of the electrochemically activated solutions on the processes of soaking, degreasing, pickling, tanning, plasticization, and on the structuring of tissue of fur skins with different contents of fatty substances was studied.

The effect of technological solution composition based on fractions of electroactivated water was established and their applications for effective processing of fur in the absence of antiseptics and surface-active materials are verified.

The use of electrochemically activated water at the stage of restoring the collagen structure of dermis and the degree of its hydration, accompanied by the release of globular proteins, carbohydrates, and lipids provides twofold acceleration of the process. The use of the fraction of electroactivated water with high oxidizing power makes the lengthy phase of acid-salt treatment unnecessary.

A low-cost technology of treating furs with different contents of fatty substances was developed and involves the use of solutions based on electrochemically activated water. The technology foresees substantial economy of water and chemical reagents, a two- to threefold acceleration of soaking and tanning processes, and the formation of fur materials with required physicochemical properties. The exclusion of such toxic reagents as formalin and sodium silicofluoride from treatment allows regarding this technology as ecologically safe compared to other technologies of fur production.

References

[1]. **Saran S., Mahajan R., Kaushik R., et al.** Enzyme mediated beam house operations of the leather industry: a needed step towards greener technology. *Journal of Cleaner Production* **54**, 1 (2013) 315–322; doi.org/10.1016/j.jclepro.2013.04.017.

[2]. **Morera J., Bartoli E., and Singla C.** Effect of ultrasound on bovine and ovine skins soaking. *Journal of Cleaner Production* **59**, 15 (2013) 79–85; doi.org/10.1016/j.jclepro.2013.06.060.

[3]. **Sivakumar V., Chandrasekaran F., Swaminathan G., et al.** Towards cleaner degreasing method in industries: ultrasound-assisted aqueous degreasing process in leather making. *Journal of Cleaner Production* **17**, 1 (2009) 101–104; doi.org/10.1016/j.jclepro.2008.02.012.

[4]. **Ma J., Hou X., Gao D., et al.** Greener approach to efficient leather soaking process: role of enzymes and their synergistic effect. *Journal of Cleaner Production* **78**, 1 (2014) 226–232; doi.org/10.1016/j.jclepro.2014.04.058.

[5]. **Danylkovych A.** Ecologically clean technologies for the garment industry based on the use of activated aqueous solutions (in Ukrainian). Fenix (Publisher «Фенікс») 2011, Kyiv.

[6]. **Danylkovych A., Mokrousova O., and Okhmat O.** Technology and materials of leather production: a study guide (in Ukrainian). Fenix (Publisher «Фенікс») 2005, Kyiv.

[7]. **Fidaleo M. and Moresi M.** Electrodialysis applications in the food industry. *Advances in Food and Nutrition Research* **51** (2006) 265–360; doi.org/10.1016/S1043-4526(06)51005-8.

[8]. **Aider Hsu S. and Kao H.** Effects of storage conditions on chemical and physical properties of electrolyzed oxidizing water. *Journal of Food Engineering* **65**, 3 (2004) 465–471; doi.org/10.1016/j.jfoodeng.2004.02.009.

[9]. **Kim C., Hung Y., and Brackett R.** Roles of oxidation–reduction potential in electrolyzed oxidizing and chemically modified water for the inactivation of food-related pathogens. *Journal of Food Protection* **63**, 1 (2000) 19–24.

[10]. **Shirahata S., Hamasaki T., and Teruya K.** Advanced research on the health benefit of reduced water. *Trends in Food Science & Technology* **23**, 2 (2012) 124–131; doi.org/10.1016/j.tifs.2011.10.009.

[11]. **Aider M., Gnatko E., Benali M., et al.** Electro-activated aqueous solutions: theory and application in the food industry and biotechnology. *Innovative Food Science & Emerging Technologies* **15** (2012) 38–49; doi.org/10.1016/j.ifset.2012.02.002.

[12]. **Cloete T., Thantsha M., Maluleke M., et al.** The antimicrobial mechanism of electrochemically activated water against *Pseudomonas aeruginosa* and *Escherichia coli* as determined by SDS-PAGE analysis. *Journal of Applied Microbiology* **107**, 2 (2009) 379–384; doi.org/10.1111/j.1365-2672.2009.04233.x.

[13]. **Robinson G., Lee S., Greenman J., et al.** Evaluation of the efficacy of electrochemically activated solutions against nosocomial pathogens and bacterial endospores. *Letters in Applied Microbiology* **50**, 3 (2010) 289–294; doi.org/10.1111/j.1472-765X.2009.02790.x

[14]. **Goncharuk V., Bagrii V., Arkhipchuk V., et al.** Biotesting of electrochemically activated water (in Russian). *Journal of Water Chemistry and Technology* **4** (2005) 399–411.

[15]. **Pankiv N., Palyanytsia L., Kosiv R., et al.** The influence of electrochemically activated water on the enzymatic action of distillers' yeast. *Eastern-European Journal of Enterprise Technologies* **6**, 63 (2013) 29–33.

[16]. **Kashkovskiy V. and Kamenskikh D.** The use of activated water in the acidic hydrolysis of vegetable waste with high content of pentosans. Conference proceedings "WasteEco Ukraine", Institute of Bioorganic and Oil Chemistry of National Academy of Sciences of Ukraine, Kyiv (2012) 47–49; http://waste.ua/eco/2012/biomass/hydrolysis/.

[17]. **Lee M., Kim Y., Ryoo K., et al.** Electrolyzed-reduced water protects against oxidative damage to DNA, RNA, and protein. *Applied Biochemistry and Biotechnology* **135**, 2 (2006) 133–144; doi.org/10.1385/ABAB:135:2:133.

[18]. **Lutsyk R., Matviyenko O., and Bovsunovskiy O.** The possibilities of using electroactivated water in technological processes of footwear manufacture. *Bulletin of the Kyiv National University of Technologies and Design* **2** (2005) 53–58.

[19]. **Zlotenko B., Danylkovych A., and Matviyenko O.** Ecologically clean technologies of the clothing and footwear industry with the use of activated

aqueous solutions (in Ukrainian). *Bulletin of the Kyiv National University of Technologies and Design* **5,** 2 (2008) 53–58.

[20]. **Bovsunovskyi O., Lutsyk R., and Melnyk M.** Research of the relaxation and physicomechanical properties of natural skins after plasticization with various aqueous solutions (in Ukrainian). *Bulletin of the Kyiv National University of Technologies and Design* **2** (2005) 88–91.

[21]. **Zorina E. and Zeleva G.** Dying of furs with various colorants (in Russian). *Omsk Scientific Bulletin* **19** (2002) 138–139.

[22]. **Zorina E., Zeleva G., and Nagornaya Z.** The impact of the nature of tanning agents and water on the plastic properties of skin tissue of furs and leather (in Russian). *Omsk Scientific Bulletin* **19** (2002) 140–141.

[23]. **Apukhovskiy A., Krutov V., and Kosinov B.** Process for producing drinking and medicinal water, UA patent 49551, September 16, 2002.

[24]. **Potapenko S., Kostiuk O., Kostiuk I., et al.** Mechanism for preparing silicon potable water, UA patent 19633, December 15, 2006.

[25]. **Prilutskiy V. and Bakhir V.** Electrically activated water: anomalous properties, mechanism of biological action. All-Russian Research and Testing Institute of Medical Equipment 1997, Moscow.

[26]. **Romaniuk A., Skidan V., and Tsymbalenko O.** Method for processing of fur raw material. UA patent 86367, December 25, 2013.

[27]. **Savchenko G., Zlotenko B., Tsymbalenko O., et al.** Method for soaking of fur raw material. UA patent 60836, June 25, 2011.

[28]. **Statsenko D., Romaniuk O., and Danylkovych A., et al.** Method for processing of fur raw material. UA patent 75108, November 26, 2012.

[29]. **Danylkovych A., Lishchuk V., and Strembulevich L.** Modern fur production. Fenix (Publisher «Фенікс») 2015, Kyiv.

[30]. **Danylkovych A. and Chursin V.** Analytical control in leather and fur production: a laboratory practicum (in Russian), Infra-M 2016, Moscow, 176 p.

[31]. **Simonov Y., Puchkova N., Grigoriev B., et al.** Fur coat and sheepskin processing (in Russian). Light and Food Industry 1983, Moscow.

2. REGENERATION OF RAW HIDE WATER BALANCE BY ELECTROCHEMICALLY ACTIVATED WATER [1]

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Abstract: *Improving the collagen structure which was impacted by curing process increases the efficiency of all subsequent structural transformations during leather production and results in the formation of a high-quality leather material. Herein, we studied the process of soaking green-salted horsehides in electrochemically activated aqueous solutions and the properties of resulting chrome-tanned leather. It was found that the process of soaking horsehides can be effectively carried out using an electrochemically activated solution (ECAS) – a mixture of catholyte and anolyte at a volume ratio of 5 : 1. Using this soaking solution, sodium sulfide (an environmentally harmful reagent), sodium carbonate, and detergent can be completely excluded from the technological solution. The use of ECAS at the soaking stage effectively regenerates the water balance of horsehides while maintaining a stable pH during the soaking process and increases the efficacy of liming and all subsequent processes. Considering the prominent structural differences (density and thickness) between the front and shell of horsehide, the developed method, which utilize ECAS for soaking, allows the entire process to be carried out on uncut horse hides instead of processing two parts separately, which is normally required. The chrome-tanned leather produced by the developed method in semi-industrial conditions has elastic-plastic properties which are superior compared to the leather produced by current technology. The developed method also results in increasing the area yield by 2.5 %. The resulting*

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elastic leather can be used for manufacturing a variety of articles, including clothing, accessories, and footwear.

Keywords: *collagen; horsehide; electrochemically activated water (ECAW); soaking; elastic-plastic properties; leather.*

Introduction

The development of innovative technologies to produce leather materials involves implementing effective ways to carry out a variety of chemocolloidal reactions during the processing of natural raw materials. Improving the structure of raw hides, particularly after the curing process during preparatory stages, increases the efficacy of all subsequent structural transformations and the formation of a high-quality final leather material. The use of aqueous solutions with novel chemical compositions can minimize the process length which is necessary to protect natural raw materials from biological damage by microorganisms, especially in the beginning of the hide processing [1]. These solutions should be also scalable and inexpensive considering the significant volumes which are used during multistage processing of raw hides.

Activated aqueous solutions can be used as new alternatives to technological solutions during the processing of raw hides. To produce the activated aqueous solutions, different methods, such as ultrasonic or electric fields, can be used [2, 3]. Treatment of animal hides and skins with activated solutions has a number of advantages over other varieties of water treatments which utilize traditional technological solutions [3–5]. Particularly, activated solutions maintain their properties, nonequilibrium thermodynamic state and high oxidation-reduction potentials (ORP), for a prolong time. These properties contribute to the intensification of biotechnological processes.

Among activated solutions, electrochemically activated (ECA) solutions have a potential role as disinfectants in medicine and industry due to their biocidal properties, *in situ* generation from inexpensive materials (water and salts such as $NaCl$), and environmental compatibility (refer to the review [6]). ECA solutions, also denoted as electrolyzed oxidizing (EO) water, mixed oxidant (MIOX) solutions, and electrochemically activated water (ECAW), are produced by electrolysis of dilute salt solutions in an electrolytic cell where the cathode and anode are separated by a membrane. Electrochemical activation of water yields two fractions, catholyte and anolyte, with highly specific physicochemical properties regarding pH, ORP, electroconductivity, and the presence of chemically active radicals and ions. The main reactions that occur during electroactivation of aqueous sodium chloride solutions can be summarized as

anode:	*cathode:*
$2H_2O - 4e^- \rightarrow O_2 \uparrow + 4H^+$ $2Cl^- - 2e^- \rightarrow Cl_2 \uparrow$	$2H_2O + 2e^- \rightarrow H_2 \uparrow + 2OH^-$

Depending on the operating parameters of electrolytic cell, the resulting anolyte solution will have a high ORP (oxidizing), a low pH (which can be neutralized by reconfiguring the electrolytic cell), and a variable concentration and type of chlorine-containing moieties. The catholyte will be characterized by low ORP (reducing) and a high pH. Catholyte and anolyte can be also combined in a specific proportion to achieve desirable properties of electroactivated solution. The relative volumes of catholyte and anolyte in a given solution will determine its final pH.

As an alternative to chlorine forms and other oxidants, ECA solutions also contain a mixture of reactive oxygen species and free radicals. Higher organisms possess antioxidant defense systems, whereas microorganisms generally do not. The presence of the free radicals, with their high oxidizing effects, in the solutions are considered of great importance to effectively destroy a wide variety of microorganisms. The active antimicrobial components of ECA solutions have been reported to include *HOCl*, hydroxyl radical, and other short-lived oxidative moieties like ClO_2.

Based on many reports, it has been shown that anolyte solutions have a broad spectrum of antimicrobial activity [6, 7, 16, 17, 8–15] while catholyte solutions are characterized by their cleaning properties, including biofilm removal [8, 10, 14, 15, 18, 19]. In addition to antibacterial and sporicidal activity, [6, 20, 21], ECA solutions have antiviral and fungicidal activities [6, 22] and inactivate toxins [6] while maintaining high biocompatibility [23] and antioxidative properties [24, 25].

ECA solutions have been used in many different areas [6], specifically for (*i*) the treatment and prevention of wound infection and periodontal diseases; (*ii*) medical device disinfection, including dental unit water lines [8], which if inadequately disinfected, may harbor polymicrobial biofilms containing potentially pathogenic organisms; and (*iii*) for disinfection of surfaces [10] and food products [26–28] which may help to control infection outbreaks.

Authors of the work [12] assessed the performance of sodium hypochlorite (*NaOCl*) and ECA water in terms of disinfection efficacy, disinfection by-products formation, and the stability of the disinfectant with respect to storage [12]. In the absence of or at low concentrations of dissolved organic carbon, ECA solution showed better disinfection efficacy in terms of *Escherichia coli* inactivation at both pH 5 and 7 while forming fewer by-products. Also, ECA solution was more stable during storage compared with *NaOCl* solution. Acidic ECA solution retains useful bactericidal activity for more than 12 months, which can significantly expand its potential applications [22]. During the recovery of ECA solution, the chemical components of the solution will shift spontaneously from their thermodynamically unequilibrated conditions to a stable non-active form. Thus, ECA solution will slowly revert to a dilute salt solution without presenting any environmental hazards. Moreover, ECA solutions can be effectively inactivated by organic matter and are considered as "green biocides" which can help to reduce the consumption of free chlorine and replace other toxic chemicals [22].

Many industrial processes can benefit from utilizing ECA solutions. For example, the high potential of catholyte as an environmentally friendly alternative to laundry detergents for sustainable consumption of cotton textiles have been described [18]. In addition to its cleaning properties, catholyte also exhibits a plasticization effect on the collagen structure of the dermis of leather materials which results in reduced stress at the final stage of product formation during footwear manufacturing [29]. As a result of the catholyte treatment of the leather part of fur and leather, the plasticity of the materials has been restored [30, 31].

Experimentally, the use of both catholyte and anolyte in the processing of raw fur materials was reported previously [32]. The anolyte was effectively used in the process of restoring the collagen structure of the raw material and releasing inter-fiber proteins, polysaccharides, and partially lipids [32]. Owing to anolyte bactericidal properties it was possible to carry out the process without adding antiseptic substances. At the second stage of soaking and degreasing the raw biomaterial, catholyte was used to remove the remaining lipids. The use of ECA solutions resulted in decreasing the time required to process fur materials without the application of toxic reagents [33].

Thus, the results of the aforementioned studies specify the particular physicochemical, cleaning, and antiseptic properties of the ECA solutions, especially, for processing plant and animal raw materials. This can indicate their promising application for the improvement and development of innovative methods for producing leather and fur. Utilizing solutions with a broad spectrum of antimicrobial activity at the preparatory stages becomes especially highly important after a new kind of bacterial defect on hides/skins and leather has been identified as a microbial biofilm which differs from the previously well-known bacteria-borne defects such as hair slip, red discoloration, and grain pilling [1].

Goal and tasks of the research

Thus, the goal of this work was to study the process of soaking green-salted horsehide using electrochemically activated solutions. To achieve this goal, the following tasks were defined:

– to determine the effect of various fractions of electrochemically activated water on the kinetics of water absorption by different areas (cuts) of horsehide;

– to establish the relationship between water sorption by horsehide and pH of the solutions used during the soaking;

– to determine the effect of the soaking process on the chemical composition and properties of the chrome-tanned leather which was produced by the developed method including soaking in electrochemically activated aqueous solutions in the semi-industrial conditions.

Materials and Methods

Leather, as a natural material, can differ significantly in properties not only between different types of hides and skins but also between its different regions [34]. The difference in properties between various regions is the most prominent for horsehides, yet the information on the tear strength variability and collagen fibril orientation together with other properties across horsehide are very scarce.

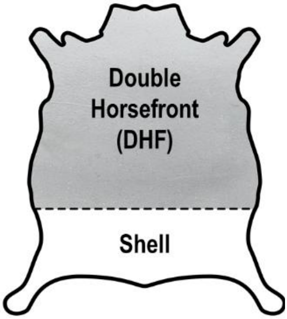

Fig. 1. *Standard horsehide leather cuts.*

In this study, the green-salted horse raw hide with the thickness and initial moisture content in the areas of the horsefront and shell (Fig. 1) equal to 2.2–2.7 mm and 47.8 % and 4.8–5.9 mm and 44.1 %, respectively, were used.

Laboratory testing. After raw hide fleshing and mechanical removal of its pelage, and before soaking, three samples (approx. 100 g each) were cut out from the horsehides and washed with water (50 % excess of the total sample mass) for an hour at 26–28 °C. Washing and soaking were carried out at a rotational speed of 15–17 rpm (in a vertical plane) using custom-made laboratory equipment shown in Fig. 2.

Fractions of ECA water – anolyte and catholyte with a pH 3.3 and 10.3, respectively, were produced by electrolysis of 5 mM *NaCl* solution in an electrolytic cell (Ekovod, technical specifications: TU У29.1-1285006876.001-2000) with a silicon anode, a steel cathode, and an ion-exchange cotton membrane [35,36]. For the regeneration of water balance which was affected during the curing process and transportation, horsehide soaking in solutions based on ECA water was studied. Particularly, catholyte, catholyte supplemented with Na_2S (2 g/L), and 5 : 1 catholyte-anolyte mixture was used to study the kinetics of water absorption. For controls, distilled water and industrial soaking solution [37] containing non-ionic surface-active substance SPK-50 (0.25 % of the sample mass, technical specifications: TU 2484-014-22284995-99), sodium

Fig. 2. *Photo of custom-made equipment used for washing and soaking of horse rawhide.*

carbonate (0.45 % of the sample mass), and sodium sulfide (0.30 % of the sample mass) were used.

The pH of the soaking solutions was measured with a pH meter (Gomel Plant of Measuring Devices, pH-340), while water content of the samples was determined gravimetrically.

For water absorption studies three samples per group were cut from the right and left half-skins of cured raw hides after their fleshing in the form of symmetrical strips close to the line separating front and shell. After removing the hair with a razor blade knife, the samples were weighted on scales (AXIS, AD200). After all the samples were washed simultaneously, they were carefully but thoroughly dried with filter paper to remove the excess surface water and weighed again. This procedure was repeated after 2, 4, 7, 17 h (Fig. 3) and 1, 3, 6, 16 h (Fig. 4). The water content in the samples was calculated according to the following formula:

$$WA = \frac{m_1 - m_2}{m_2}\ 100\ \%,$$

where WA – water absorbed by the sample [%]; m_1 and m_2 – the sample weight before and after drying [g]. To determine the dry weight after measurements the samples (2–2.5 g) were dried at 102 (± 2) °C for 4 h, equilibrated for 30 min in exicator at room temperature, and weighted.

Semi-industrial testing. After laboratory experiments, the horse hides were processed in semi-industrial conditions using the developed method and the current technology as a control. In the developed method a slightly alkaline ECA solution obtained by mixing catholyte and anolyte fractions at volume ratio 5 : 1 was used for soaking. In the developed method the soaking process was carried out using three halves (~1.2 m^2 each) of hides along the back bone line, while according to the current technology the horsefront and shell were processed separately yielding, respectively, elastic and boardy leather materials (Fig. 6).

For removal of the epidermis and hair from the horse pelts, the raw hide was further subjected to liming using a mixture of calcium hydroxide (4 % of the sample mass) and sodium sulfide (3 % of the sample mass). The processing of horse raw hides was carried out in a revolving drum (Doze, 0.39 m^3) at a private joint-stock company “Chinbar” (Kyiv, Ukraine). Further processing of the limed hides, including deliming, pickling, tanning, shaving, neutralizing, tanning with chromium salts and plant extracts, fat-liquoring, samming, setting out, and final drying, were performed according to the previously described technology [37]. Briefly, the horsehide after tanning with chromium (III) compounds (technical specifications: TU 2141-033-54138686-2003) was skiving to a uniform thickness of 1.4–1.5 mm; post-tanned with chromium (III) compounds in the amount of 2 % of the hide mass; neutralized with a mixture of sodium formate and sodium bicarbonate with a weight ratio of 4 : 1; filled with organic compounds: acrylic polymer Retanal RCN-40 (Cromogenia Units SA, 4 % of the hide mass) and quebracho (5 % of the hide mass); and fat-liquored with Trupol RA (Trumpler, 8 % of the hide weight mass). The filling-fat-liquoring process was completed after fixation of reagents in the structure of re-tanned hides with 10 % formic acid at pH 4.2. After the drying-moisturizing processes [38], the samples of the resulting semi-finished leather were set out.

Physicochemical characterization. The chemical composition and physicomechanical properties of the leather samples were determined by the methods described in our previous work [39] after their conditioning at 20 (± 2) °C and 65 (± 5) % relative humidity of the air (ASTM D1610–18). Briefly, the *total ash* was determined thermogravimetrically after oxidizing the sample (7.5 g) in air at 600 (± 25) °C until constant mass was reached

(ASTM D2617–17a and GOST 938.2-67). The weighed residual matter, termed "*ash*", was calculated as a percentage from the original sample. Liquid pycnometry was utilized to measure the *apparent density* of the samples (10 g) at 22 °C using kerosene as a solvent. Considering that collagen is the primary structural element in the extracellular matrix in animal hides/skins, the heat resistance of leather against shrinkage was characterized by the *hydrothermal denaturation* or *shrinkage temperature* (*Ts*) of collagen molecules [40] by gradually heating the sample in a mixture of glycerol and water with a 4 : 1 weight ratio at the heating rate of 2–3 °C/min (ASTM D6076–18 and DSTU 2726-94). Before the measurements, the samples were thoroughly soaked in water for 4 h at 20 (± 1) °C. *Chromium content* was determined by iodometric titration and expressed as the mass fraction of chromium (III) oxide. *Mechanical properties* (*tensile stress* and *elongation*) were measured using a tensile testing machine (PM-250M) at extension rate 90 mm/min. Initial length of 10 mm wide leather samples between clamps was 50 mm.

Content of the *bound organic tannins* (BOT) [%] in the leather samples was calculated using the following formula:

$$\omega_{BOT} = \omega_L - \omega_N,$$

where $\omega_L = 100 - (\omega_{TA} + \omega_{OS} + \omega_{OWS})$ – the mass fraction of leather substances on the dry weight [%]; ω_{TA} – the mass fraction of total ash (GOST 938.2-67) [%]; ω_{OS} – the mass fraction of organic substances (OS) extracted with organic solvents (OS) (GOST 938.5-68) [%]; ω_{OWS} – the mass fraction of organic water-soluble substances (OWS) (GOST 938.6-68) [%]; ω_N – the mass fraction of nitrogen-containing water extractable materials (determined according to the previously described methodology [38], ASTM D6016 – 17) [%].

The content of *substances extracted with organic solvents* was determined using a Zaichenko extraction apparatus. A crushed sample (5 g) within a paper shell was put into the extractor and solvent extraction with tetrachloromethane was carried out for 1.5 h. After solvent evaporation under vacuum, the fatty substances were dried in an oven at 128–130 °C for 1 h. After cooling the flask in the desiccator, the flask with unbound fatty acids was weighed and the mass fraction of OS was calculated.

To calculate the *yield*, the surface area of leather was determined using specialized electromechanical machinery (Svit, model 07484/P1).

Results and Discussion

Structure and composition of raw leather material. Collagen is the main and the most abundant structural protein in the extracellular matrix of various animal tissues, including skin, bone, and tendon. The fibrous collagen provides tensile strength, while glycosaminoglycans (GAGs), covalently linked to proteins to form proteoglycans, act as space-fillers and provide resistance to compression [41]. Skin components such as keratin, albumins, and globulins together with GAGs (e.g., hyaluronic acid), proteoglycans (e.g., dermatan sulfate), triglycerides, and lipids are usually removed during the earlier stages of hide and skin processing [42]. Removal of these non-collagenous proteins is a necessary step to produce soft leather material as it allows the collagen fiber structure to split apart. This "opening up" effect results in a successful implementation of all subsequent structural transformations.

Many varieties of collagen have been identified; for example, mammals have about 20 different genes which code various forms of collagen [41]. As a function of structure and supramolecular organization, collagen can be classified as fibril-forming (types I, II, III, V, and XI), fibril-associated (types IX, XII, and XIV), or network-forming (types IV, VII, VIII, and X) [43]. Tropocollagen, a collagen molecule, being a right-handed triple helix stabilized mostly by hydrogen bonding is the major structural element of collagen. Heterotrimers of two $\alpha1$(I) and one

$\alpha 2$(I) protein chains which only slightly differ in amino acid sequence are the dominant isoform of type I collagen. The polypeptide chains contain glycine at every third position and have a high proline and hydroxyproline content [41, 42]. All collagen molecules in a precursor form, called procollagen, are synthesized intracellularly by connective-tissue cells and then secreted by exocytosis. Additional peptide extensions at each end of procollagen hinder premature assembly of collagen molecules. Extracellular enzymes, procollagen proteinases, cut off these terminal extensions to allow collagen assembly only after the molecules have been extracted. At each end of the helical region of the procollagen molecule, there is a non-helical region known as telopeptide. Collagen, being a multi-hierarchical structure, is organized in four levels of macromolecular structure: first the collagen molecules pack together into collagen *fibrils*, then the fibrils are further organized into larger *fibril bundles*, then they are arranged into *fascicles*, and finally – into *fiber bundles*.

Water absorption by horse raw hide. The chemical treatments and mechanical processes used to produce leather from hides and skins result in structural changes in collagen fibrils and their supramolecular organization [44]. Even though the general chemistry used in hide and skin processing is well-known, the structural changes at the level of the collagen fibrils is just started to be revealed utilizing x-ray scattering techniques [45–47]. Herein we focused on the macroscopic effect of the composition of the soaking solutions on water sorption by horsehide and the correlations with the properties of corresponding final leather material.

Generally, the water sorption of collagen and other fibrous proteins in acidic and alkaline solutions is predominantly governed by the osmotic pressure difference arising between the protein phase and the external solution and by protein cohesion [48]. According to the literature data, the isoelectric point of collagen, which can be affected by the nature and ionic strength of the salts presented in the solution, is 4.7, although a second critical point in the collagen behavior has frequently been noted at pH 7.7 [49]. The maximum equilibrium swelling is usually observed at an external pH between 2–3 and 11–12, while the minimum – at the isoelectric point [50].

The kinetics of water absorption by green-salted horsehide was determined for technological solutions with different compositions (Fig. 3 and Fig. 4). It should be noted that the soaking process of the raw hide was carried out after washing the salt off the samples. To estimate the sorption of ECA solution by the dermis, the soaking process was also carried out using distilled water as an additional control (Fig. 4).

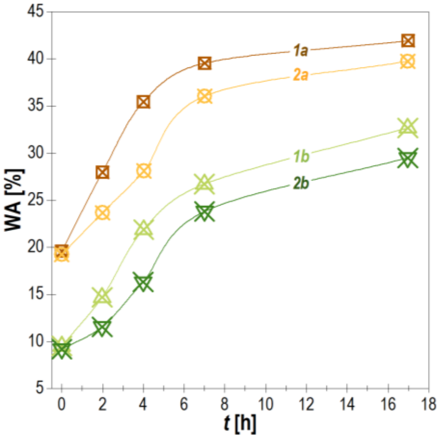

Fig. 3. *Kinetics of water absorption (WA) by the dermis of horse rawhide in a 5 : 1 mixture of catholyte and anolyte (1) and in a control soaking solution according to existing technology (2) for horsefront (a) and strip (b) areas.*

As it can be seen from the data, after rapid solution uptake within the first 3 h, a further increase in water content, which was not complete after 16–17 h, was observed. The results also indicate that solution composition significantly affects the kinetics of water absorption and the final water content in the samples. The most prominent effect was observed for the sample soaked in the mixture of catholyte and anolyte with a 5 : 1 volume ratio (Fig. 3) and catholyte (Fig. 4). This is manifested by faster

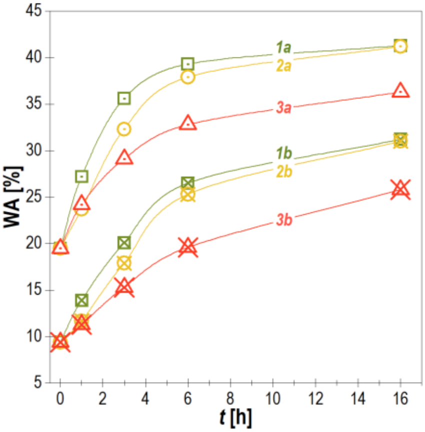

Fig. 4. Kinetics of water absorption (WA) by the dermis of horse rawhide in catholyte (1), catholyte and Na2S (2), and distilled water (3) for horse-front (a) and strip (b) areas.

water absorption, especially in the beginning of the soaking, and a higher water content after 17 h of soaking compared to the control group (existing technology). After the first hour of soaking, the horsefront absorbs twice as much water as the shell. Additionally, the pH of the solution is reduced to a greater extent for the control group (ΔpH = 3.4) and for catholyte group (ΔpH = 3.1) compared with the mixture of catholyte and anolyte for which the pH difference was 1.1 (Fig. 5).

The water sorption by horse raw hides is sensitive to the solution pH and its composition and increases with increasing pH until it reaches a maximum at 8.2 (Fig. 4 and Fig. 5). At pH lower than 8.2 the water content is decreased, while at higher pH it remains almost the same for horsefront or decreases for shell. The effect of solution composition can be seen comparing the kinetics of swelling horsehide in catholyte supplemented with Na_2S and in control soaking solution. Even though the initial pH of the solution is the same, the water sorption rate and the water content is lower for the samples swollen in the latter solution.

The water sorption by horsehides, in addition to hydration of hydrophilic groups of macromolecules, can be also explained by the local change in the protonation degree of carboxyl groups of collagen, GAGs/proteoglycans, and other macromolecules in the beginning of the soaking [51]. The observed decrease in pH within the first few hours (Fig. 5) can be explained by the neutralization of hydroxyl anions presented in the solutions by protons which were released during dissociation of carboxyl groups. The electrostatic repulsion between negatively charged carboxylate groups and an increased ion concentration inside the dermis due to ionization will result in an increase in osmotic pressure which can cause the observed increase in the water content. In addition to the increased osmotic pressure, the increased mobility of the collagen macromolecules due to the disruption of some of its physical and chemical crosslinks and removing (washing out) of non-collagenous components of the dermis can also contribute to the increased water content. Furthermore, negatively charged polysaccharide chains of GAGs even at low concentrations can form hydrophilic gels: their multiple negative charges at carboxyl groups attract cations, such as Na^+, that are osmotically active, causing large amounts of water to be absorbed by the sample. This gives rise to a swelling pressure, which is balanced by tension in the collagen fibers interwoven with the proteoglycans. [41].

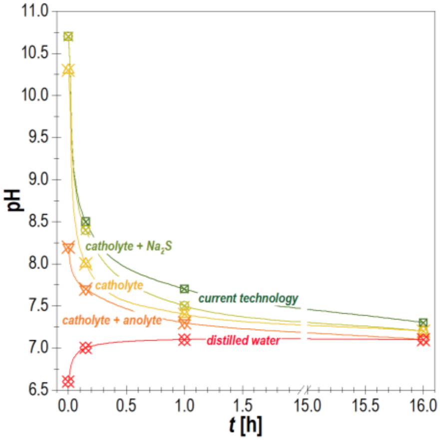

Fig. 5. *Change in the pH of technological solutions during soaking of horse rawhide.*

During the soaking process using an industrial soaking solution, uneven hydration (blistering), caused by the lower density of the outer layers and faster water absorption of alkaline solution (pH 10.7) which results almost in complete ionization of carboxyl groups, was observed. A similar effect of water absorption by the skin dermis was also found for the samples soaked in alkaline solutions of catholyte with and without sodium sulfide with pH 10.3 and 10.7, respectively. A uniform hydration, probably due to less rapid pH change, and more effective and homogeneous water absorption by the whole dermis using catholyte and anolyte mixture can indicate deeper changes in the structure of the dermis on the microfibrillar level.

Generally, faster kinetics of water absorption was observed for the horsehides soaked in electroactivated solutions (Fig. 3 and Fig. 4). This effect can be explained by the declasterization of the water structure after its activation and additional changes in the water structure and water/macromolecule interactions in the presence of ions and free radicals [32].

Among tested soaking solutions, the catholyte and anolyte mixture provides uniform swelling without blistering and more effective regeneration of water balance of raw leather material while maintaining a stable pH during the soaking process. Higher water content in the horsefront and shell samples soaked in a mixture of catholyte and anolyte and a smaller difference between them compared with the control group (Fig. 3) indicates the possibility of simultaneous processing of the whole hide rather than processing the two parts separately (*i.e.*, horsefront and shell).

Thus, in slightly alkaline solutions with moderate salt concentration (to avoid electrostatic screening and corresponding decrease in hydration) the water sorption will depend on solution solubilizing efficacy and its ability to decrease the collagen crosslinking degree.

The higher content of organic substances extracted from the raw material after soaking in ECA solution (Table I) compared with the control group (industrial soaking solution) also indicates more effective interaction of the activated water with the components of the dermis. This effect is more pronounced for the samples from shell which contains more soluble proteins and GAGs than the horsefront. Despite increased density of shell samples compared to the horsefront samples, 5.6 % more organic substances were extracted from the former samples. It should be noted that the process of soaking the shell samples in activated solutions is accompanied by significant foam formation indirectly indicating the extraction of GAGs along with other water-soluble proteins.

Table I. *Content of inorganic and organic substances in solutions after soaking of horsehide, apparent density, and hydrothermal stability.*

Area	**Solution**	**Mass fraction of substances [%]**		**Density [g/cm³]**	***Ts* [°C]**
		inorganic	**organic**		
Horse-front	**catholyte + anolyte**	14.4 ± 0.3	85.6 ± 1.7	1.18 ± 0.04	64.0 ± 0.6
	control	15.4 ± 0.3	84.6 ± 1.7	1.18 ± 0.04	63.0 ± 0.6
Shell	**catholyte + anolyte**	13.4 ± 0.3	86.6 ± 1.7	1.24 ± 0.04	62.0 ± 0.6
	control	18.2 ± 0.4	81.1 ± 1.6	1.21 ± 0.04	63.0 ± 0.6

Based on the results, soaking the horsehide in solutions of ECA water results in a higher efficacy of carrying out this process using a mixture of catholyte and anolyte at a volume ratio of 5 : 1 with pH 8.2. This eliminates the need to use the environmentally harmful sodium sulfide for soaking and facilitates the process with a smaller change in pH at the initial soaking stage. Higher water content and less variation in water content between the horsefront and the shell after soaking using a mixture of catholyte and anolyte compared with the control indicate the possibility of carrying out the entire technological cycle of manufacturing leather from green-salted raw hide using the whole horsehide.

Properties of the horse leather produced in semi-industrial conditions. To test the developed method in the semi-industrial conditions, the three half-skins from green-salted horse hides were used. The differences between developed method and current technology are summarized in Fig. 6.

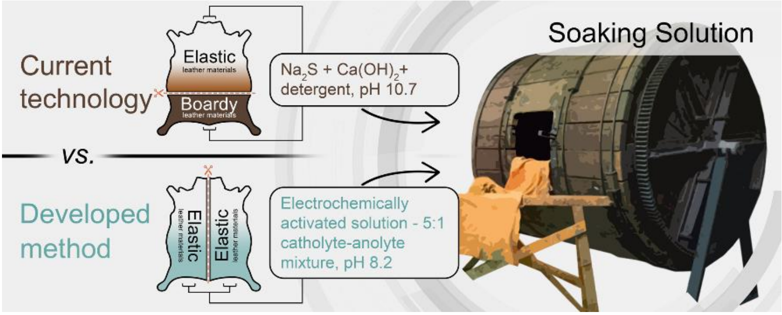

Fig. 6. *The differences in soaking stage between developed method and current technology during semi-industrial processing of horse raw hides.*

Table II. *The content of inorganic substances in the pickled horsehides processed using developed method and existing technologies.*

Technology / Method	Leather cut	Ash [%]
Developed	**horsefront**	0.92 ± 0.02
	shell	1.18 ± 0.02
Existing	**horsefront**	0.85 ± 0.02
	shell	1.05 ± 0.02

The results of the liming process are shown in Table II and Table III. As it can be seen from the data, the pickled horsehide produced by the developed method contains 8.2 and 12.4 % more inorganic substances for horsefront and shell areas compared with the existing technology. This indicates the profound structural changes in the soaked hides using ECA water, especially within the denser parts of raw hides – shell.

The properties of leather material are closely related to organization and supramolecular structure of collagen and results from the interplay of electrostatic, hydrophobic, and van der Waals interactions in addition to hydrogen and covalent bonds [43]. During liming in a strongly alkaline environment further disruption of intra- and intermolecular bonds within fibrous collagen structure and the formation of weakly dissociated salts of calcium hydroxide with carboxyl groups were observed [52]. The hydrothermal stability of a leather material will reflect the stability of collagen structures at the molecular level and at several levels of supramolecular structure [43]. The shrinkage temperature of leather is affected by many different factors, most of which appear to alter the number and nature of crosslinks between adjacent polypeptide chains of the collagen protein macromolecules [53–56]. The value of the shrinkage temperature of leather is commonly used as an indicator of the type and degree of tannage, or both. For both the developed and current method, this is testified by a decrease in the density after liming with a corresponding decrease in hydrothermal stability (Table III and Table IV). Based on shrinkage temperature, the pickled horse half-skins processed according to the developed method are structurally more "opened up" and prepared for the effective tanning-fatliquoring.

Table III. *Properties of pickled horsehides limed in semi-industrial conditions according to the existing technology.*

Technology / Method	**Density [g/cm³]**		**T_S [°C]**	
	horsefront	**shell**	**horsefront**	**shell**
Developed	1.03 ± 0.03	1.12 ± 0.03	51.0 ± 0.5	57.5± 0.6
Existing	1.03 ± 0.03	1.12 ± 0.03	52.0 ±0.5	59.0 ± 0.6

The half-skins processed by the developed method and current technology in semi-industrial conditions after drying-moisturizing treatments were analyzed based on their chemical composition and physicomechanical properties (Table IV). Comparative analysis of leather samples obtained according to the developed method indicates a higher content of tanning compounds of chromium and organic matter than those obtained by existing technology. At the same time, the amount of unbound fatty substances is 6 and 12 % higher for areas of horsefront and shell processed using the developed method. These data correlate with the heat resistance of leather samples. The filled leather obtained according to the developed method is 2–3 °C more hydrothermally stable.

The increased content of fatty substances and uniform distribution within the structure of the leather obtained by the developed method will promote the mobility of the collagen fibrils under deformation. This statement is confirmed by the observed decrease in the density and increase in elastic-plastic properties of the leather material. This is especially true for the tensile strength and deformation of leather from the horsefront and shell areas. Both characteristics increase by 9–11 % (tensile strength) and 8–9 % (elongation before fracture).

Overall, the developed method utilizing ECA solution for soaking provides an efficient regeneration of water balance of horse raw hide and its further processing. This is also evidenced by an increase in the area to 0.4 m^2 per 100 kg of raw hides. Based on the studied properties, the resulting leather can be used for manufacturing of clothing, accessories, and footwear.

Summary

It was established that the process of soaking of horse raw hides can be effectively carried out using the ECA solution – a mixture of catholyte and anolyte at a volume ratio of 5 : 1. The environmentally harmful reagent which is commonly used for leather soaking, such as sodium sulfide, together with sodium carbonate and surface-active substance(s) have been completely excluded from the composition of the soaking solution.

Table IV. *Characteristics of the filled leather.*

Parameter	**Technology / Method**	
	developed	**existing**
Mass fraction † [%]		
– Cr_2O_3	$\frac{4.1 \pm 0.08}{3.6 \pm 0.08}$	$\frac{3.8 \pm 0.08}{3.3 \pm 0.08}$
– substances extracted with OS	$\frac{8.7 \pm 0.2}{6.6 \pm 0.1}$	$\frac{8.2 \pm 0.2}{5.9 \pm 0.1}$
– bound organic tannings	$\frac{12.9 \pm 0.3}{8.7 \pm 0.2}$	$\frac{12.2 \pm 0.2}{7.9 \pm 0.2}$
Shrinkage temperature T_S **[°C]**	$\frac{115 \pm 1}{111 \pm 1}$	$\frac{113 \pm 1}{108 \pm 1}$
Density [g/cm³]	$\frac{0.63 \pm 0.02}{0.66 \pm 0.02}$	$\frac{0.65 \pm 0.02}{0.70 \pm 0.02}$
Tensile strength [MPa]	$\frac{19.7 \pm 1.2}{22.6 \pm 1.4}$	$\frac{17.7 \pm 1.1}{20.8 \pm 1.2}$
Elongation at 10 MPa [%]	$\frac{36 \pm 2}{25 \pm 3}$	$\frac{34 \pm 2}{24 \pm 1}$
Elongation before break [%]	$\frac{67 \pm 4}{49 \pm 3}$	$\frac{62 \pm 4}{45 \pm 3}$
Yield [m²/(100 kg of raw hides)]	15.1 ± 0.3	14.7 ± 0.3

Note: *The numerator and denominator correspond to the values for horsefront and shell, respectively, while † denotes that the mass fraction was recalculated on the dry basis.*

Taking into account the peculiarities of the structure of horsehide, particularly, drastic difference in the thickness and the density of the horsefront and shell, an effective regeneration of water balance of the dermis takes place when a mixture of catholyte and anolyte is used to provide a stable pH environment during entire soaking process. The higher water content for the horsefront and shell samples during soaking and smaller difference between them compared to the samples processed using existing technology provide (1) the effective process of liming and (2) the basis for the processing of the whole horse raw hide at once into elastic leather. Soaking of green-salted horse raw hides in a mixture of catholyte and anolyte results in the formation of leather with the increased elastic-plastic properties and increase area yield by 2.5 % compared with the existing technology which involves separate processing of the horsefront and shell. The leather made from the horse raw hides processed using the developed method meets the requirements of DSTU 3115-95 “Leather for garments. General specifications” and the international standard ISO 9001:2008 for “Quality management systems – requirements”, and can be used for manufacturing of clothing, accessories, and footwear.

References

[1]. **B. Cadirci, H. Ozgunay, C. Vural, et al.** A new defect on leather: microbial bio-film, *J. Am. Leather Chem. Assoc.* **105** (2010) 129–134.

[2]. **G. Plutakhin, M. Aider, A. Koshchaev, et al.** Theoretical bases of electrochemical treatment of aqueous solutions (in Russian), *Sci. J. Kuban State Agrar. Univ.* **92** (2013) 1–25.

[3]. **M. Fidaleo and M. Moresi.** Electrodialysis applications in the food industry, *Adv. Food Nutr. Res.* **51** (2006) 265–360; doi.org/10.1016/S1043-4526(06)51005-8.

[4]. **S.-Y. Hsu and H.-Y. Kao.** Effects of storage conditions on chemical and physical properties of electrolyzed oxidizing water, *J. Food Eng.* **65** (2004) 465–471; doi.org/10.1016/j.jfoodeng.2004.02.009.

[5]. **S. Shirahata, T. Hamasaki, and K. Teruya.** Advanced research on the health benefit of reduced water, *Trends Food Sci. Technol.* **23** (2012) 124–131; doi.org/10.1016/j.tifs.2011.10.009.

[6]. **R. Thorn, S. Lee, G. Robinson, et al.** Electrochemically activated solutions: evidence for antimicrobial efficacy and applications in healthcare environments, *Eur. J. Clin. Microbiol. Infect. Dis.* **31** (2012) 641–653; doi.org/10.1007/s10096-011-1369-9.

[7]. **T. Cloete, M. Thantsha, M. Maluleke, et al.** The antimicrobial mechanism of electrochemically activated water against *Pseudomonas aeruginosa* and

Escherichia coli as determined by SDS-PAGE analysis, *J. Appl. Microbiol*. **107** (2009) 379–384; doi.org/10.1111/j.1365-2672.2009.04233.x.

[8]. **D. E. Wilsmann, D. Carvalho, G. Z. Chitolina et al.** Electrochemically-activated water presents bactericidal effect against salmonella heidelberg isolated from poultry origin. *Foodborne Pathog. Dis*. 2019, **1–6**. https://doi.org/10.1089/fpd.2019.2682.

[9]. **V. V. Goncharuk, V. A. Bahryi, V. A., V.V. Arkhypchuk, and R. D. Chebotarov.** Biotesting of electrochemically activated water (in Russian). *J. Water Chem. Technol.* 2005, **4**, 399–411.

[10]. **J. Marais and V. Brözel.** Electro-chemically activated water in dental unit water line, *Br. Dent. J.* **187** (1999) 154–158; doi.org/10.1038/sj.bdj.4800228.

[11]. **R. Thorn, G. Robinson, and D. Reynolds.** Comparative antimicrobial activities of Aerosilized sodium hypochlorite, chlorine dioxide, and electrochemically activated solutions evaluated using a novel standardized assay, *Antimicrob. Agents Chemother*. **57** (2013) 2216–2225; doi.org/10.1128/AAC.02589-12.

[12]. **J. Swan, E. Deasy, M. Boyle, et al.** Elimination of biofilm and microbial contamination reservoirs in hospital washbasin U-bends by automated cleaning and disinfection with electrochemically activated solutions, *J. Hosp. Infect*. **94** (2016) 169–174; doi.org/10.1016/j.jhin.2016.07.007.

[13]. **M. Akbulut and A. Ünverdi Eldeniz.** *In vitro* antimicrobial activity of different electrochemicallyactivated solutions on *Enterococcus faecalis*, *Eur. Oral Res*. **53** (2019) 44–50; doi.org/10.26650/eor.20194564125648.

[14]. **K. Ghebremichael, E. Muchelemba, B. Petrusevski, et al.** Electrochemically activated water as an alternative to chlorine for decentralized disinfection, *J. Water Supply Res. Technol. - AQUA* 60 (2011) 210–218; doi.org/10.2166/aqua.2011.034.

[15]. **K. Gulabivala, C. Stock, J. Lewsey, et al.** Effectiveness of electrochemically activated water as an irrigant in an infected tooth model, *Int. Endod. J.* **37** (2004) 624–631; doi.org/10.1111/j.1365-2591.2004.00867.x.

[16]. **A. Pogorelov, O. Suvorov, A. Kuznetsov, et al.** Disintegration of bacterial film by electrochemically activated water solution, *Bull. Exp. Biol. Med.* **165** (2018) 493–496; doi.org/10.1007/s10517-018-4202-y.

[17]. **A. Solovyeva and P. Dummer.** Cleaning effectiveness of root canal irrigation with electrochemically activated anolyte and catholyte solutions: a pilot study, *Int. Endod. J.* **33** (2000) 494–504; doi.org/10.1046/j.1365-2591.2000.00342.x.

[18]. **N. Cronjé, H. Steyn, and R. Schall.** Catholyte as an environmentally friendly detergent: effect on the colourfastness of black dyed textiles, *J. Text. Inst*. (2019) 1–8; doi.org/10.1080/00405000.2019.1703489.

[19]. **M. Pogorelova, A. Kuznetsov, and O. Suvorov.** Does electrochemically reduced water remove bacterial film?, *Int. J. Pharm. Res. Allied Sci*. **7** (2018)

139–142.

[20]. **J. Rogers, G. Ducatte, Y. Choi, et al.** A preliminary assessment of *Bacillus anthracis* spore inactivation using an electrochemically activated solution (ECASOL™), *Lett. Appl. Microbiol.* **43** (2006) 482–488; doi.org/10.1111/j.1472-765X.2006.02002.x.

[21]. **G. Robinson, S. Lee, J. Greenman, et al.** Evaluation of the efficacy of electrochemically activated solutions against nosocomial pathogens and bacterial endospores, *Lett. Appl. Microbiol.* **50** (2010) 289–294; doi.org/10.1111/j.1472-765X.2009.02790.x.

[22]. **G. Robinson, R. Thorn, and D. Reynolds.** The effect of long-term storage on the physiochemical and bactericidal properties of electrochemically activated solutions, *Int. J. Mol. Sci.* **14** (2013) 457–469; doi.org/10.3390/ijms14010457.

[23]. **N. Michel, J. Paletta, M. Kerwart, et al.** Role of electrochemically activated solution in asepsis in osteoblasts and chondrocytes *in vitro*, *J. Investig. Surg.* **29** (2016) 157–166; doi.org/10.3109/08941939.2015.1098757.

[24]. **M. Lee, Y. Kim, K. Ryoo, et al.** Electrolyzed-reduced water protects against oxidative damage to DNA, RNA, and protein, *Appl. Biochem. Biotechnol.* **135** (2006) 133–144; doi.org/10.1385/ABAB:135:2:133.

[25]. **T. Kinjo, J. Ye, H. Yan, et al.** Suppressive effects of electrochemically reduced water on matrix metalloproteinase-2 activities and *in vitro* invasion of human fibrosarcoma HT1080 cells, in: Cytotechnology, Springer Netherlands, 2012: pp. 357–371; doi.org/10.1007/s10616-012-9469-7.

[26]. **Z. Yang, Y. Li, and M. F. Slavik.** Antibacterial efficacy of electrochemically activated solution for poultry spraying and chilling, *J. Food Sci.* **64** (1999) 469–472; doi.org/10.1111/j.1365-2621.1999.tb15065.x.

[27]. **R. Thorn, J. Pendred, and D. Reynolds.** Assessing the antimicrobial potential of Aerosilised electrochemically activated solutions (ECAS) for reducing the microbial bio-burden on fresh food produce held under cooled or cold storage conditions, *Food Microbiol.* **68** (2017) 41–50; doi.org/10.1016/j.fm.2017.06.018.

[28]. **I. Surdu, D. Vătuiu, Ş. Jurcoane, et al.** The antimicrobial activity of neutral electrolyzed water against germs and fungi from feedstuffs, eggshells and laying hen house, *Rom. Biotechnol. Lett.* **23** (2018) 13607–13614.

[29]. **R. Lutsyk, O. Matvienko, and O. Bovsunovskyi.** Possibilities of using electroactivated water in technological processes for shoe production (in Ukrainian), *Bull. Kyiv Natl. Univ. Technol. Des.* **2** (2005) 53–58.

[30]. **E. Zorina, G. Zeleva, and Z. Nagornaia.** The effect of the nature of tanning agents and water on the plastic properties of the skin tissues of fur and leather (in Russian), *Omsk Sci. Bull.* **19** (2002) 140–141.

[31]. **E. Zorina and G. Zeleva.** Dyeing of fur with various dyes (in Russian), *Omsk Sci. Bull.* **19** (2002) 138–139.

[32]. **A. Danylkovych, V. Lishchuk, and O. Romaniuk.** Use of electrochemically activated aqueous solutions in the manufacture of fur materials, *Springerplus* **5** (2016) 1–11; doi.org/10.1186/s40064-016-1784-6.

[33]. **A. Danylkovych, O. Mokrynska, and O. Okhmat.** Technology and materials for leather production (in Ukrainian), Fenix (Publisher «Фенікс») 2009, Kyiv.

[34]. **M. M. Basil-Jones, R. L. Edmonds; S. M. Cooper, et al.** Collagen fibril orientation and tear strength across ovine skins. *J. Agric. Food Chem.* 2013, 61 (50), 12327–12332. https://doi.org/10.1021/jf4038375.

[35]. **A. Apukhovskyi, V. Krutov, and B. Kosinov.** Process for producing drinking and medicinal water, UA patent 49551, September 16, 2002.

[36]. **S. Potapenko, O. Kostiuk, I. Kostiuk, et al.** Mechanism for preparing silicon potable water, UA patent 19633, December 15, 2006.

[37]. **A. Danylkovych and B. Chursyn.** Technological methodology for production of variety of leather materials for upper shoe parts and shoe lining, leather haberdashery from cattle and horse hides (in Ukrainian), PJSC Chinbar, Kyiv, 2003.

[38]. **A. Danylkovych and O. Korotych.** Optimization of leather filling composition containing SiO_2 nanoparticles, *J. Am. Leather Chem. Assoc*. **114** (2019) 333–343.

[39]. **A. Danylkovych and V. Chursyn.** Analytical control in leather and fur production: a laboratory practicum (in Russian), Infra-M, Moscow, 2016, 176 p.

[40]. **Y. Zhang, B. Mansel, R. Naffa, et al.** Revealing molecular level indicators of collagen stability: minimizing chrome usage in leather processing, *ACS Sustain. Chem. Eng.* **6** (2018) 7096–7104; doi.org/10.1021/acssuschemeng.8b00954.

[41]. **B. Alberts, D. Bray, K. Hopkin, et al.** Essential cell biology, fourth ed., Garland Science (Taylor & Francis Group), New York, 2013.

[42]. **A. Covington.** Modern tanning chemistry, *Chem. Soc. Rev.* **26** (1997) 111–126; doi.org/10.1039/cs9972600111.

[43]. **E. Brown.** Collagen - a natural scaffold for biology and engineering, *J. Am. Leather Chem. Assoc.* **104** (2009) 275–285.

[44]. **K. Sizeland, R. Edmonds, M. Basil-Jones, et al.** Changes to collagen structure during leather processing, *J. Agric. Food Chem*. **63** (2015) 2499–2505; doi.org/10.1021/jf506357j.

[45]. **J.K Buchanan, Y. Zhang, G. Holmes, et al.** Role of x-ray scattering techniques in understanding the collagen structure of leather. *ChemistrySelect* 2019, **4** (48), 14091–14102. https://doi.org/10.1002/slct.201902908.

[46]. **R. Naffa, C. Maidment, M. Ahn, et al.** Molecular and structural insights into skin collagen reveals several factors that influence its architecture. *Int. J.*

Biol. Macromol. 2019, **128**, 509–520. https://doi.org/10.1016/j.ijbiomac.2019.01.151.

[47]. **Y. Zhang, B. Ingham, S. Cheong, et al**. Real-time synchrotron small-angle x-ray scattering studies of collagen structure during leather processing. *Ind. Eng. Chem. Res.* 2018, **57** (1), 63–69. https://doi.org/10.1021/acs.iecr.7b03860.

[48]. **J. H. Bowes and R. H. Kenten.** The swelling of collagen in alkaline solutions. 1. Swelling in solutions of sodium hydroxide. *Biochem. J.* 1950, **46** (1), 1–8. https://doi.org/10.1042/bj0460001.

[49]. **J. H. Highberger**. The isoelectric point of collagen. *J. Am. Chem. Soc.* 1939, **61** (9), 2302–2303. https://doi.org/10.1021/ja01878a010.

[50]. **J. Knaggs**. Studies on collagen. The changes which collagen undergoes when treated with solutions of hydrochloric acid and sodium hydroxide. *Biochem. J.* 1929, **23** (6), 1308–1327. https://doi.org/10.1042/bj0231308.

[51]. **Yu. Samchenko, Z, Ulberg, and O. Korotych**. Multipurpose smart hydrogel systems. *Adv. Colloid Interface Sci.* 2011, **168** (1–2), 247–262. https://doi.org/10.1016/j.cis.2011.06.005.

[52]. **J. Basford**. The soaking, unhairing and liming process: part 1 of 3. The practicalities of the soaking process. *World Leather* 2006, **19** (7), 23–26.

[53]. **P. Fratzl**. Collagen: structure and mechanics, an introduction. In *Collagen: Structure and Mechanics*; Springer US, 2008; pp 1–13. https://doi.org/10.1007/978-0-387-73906-9_1.

[54]. **C. A. Miles, N. C. Avery, V. V. Rodin, and A. J. Bailey**. The increase in denaturation temperature following cross-linking of collagen is caused by dehydration of the fibres. *J. Mol. Biol.* 2005, **346** (2), 551–556. https://doi.org/10.1016/j.jmb.2004.12.001.

[55]. **L. P. Witnauer and J. G. Fee.** Effect of diluents on fusion temperature of the crystalline regions in plain and tanned cowhide. *J. Polym. Sci.* 1957, **26** (113), 141–150. https://doi.org/10.1002/pol.1957.1202611302.

[56]. **P. J. Flory and R. R. Garrett.** Phase transitions in collagen and gelatin systems. *J. Am. Chem. Soc.* 1958, **80** (18), 4836–4845. https://doi.org/10.1021/ja01551a020.

3. THE INFLUENCE OF ELECTROCHEMICALLY ACTIVATED WATER ON RAW HIDE SOAKING AND PHYSICOMECHANICAL PROPERTIES OF LEATHER [2]

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Goal. *To investigate the influence of raw hide soaking in electrochemically activated water on physicomechanical properties of leather.*
Methodology. *The efficacy of soaking of hides, preserved by different methods, in electrochemically activated water – catholyte with different pH values, was examined with regard to moisture content and plasticity, while physicomechanical properties of leather were evaluated by tensile strength, elongation, and stiffness.*
Findings. *The advantages of using electrochemically activated water (catholyte with pH 8.5, 10.0, and 11.5) for soaking of green-salted and air-dried hides with moisture content of 56.2 and 12.3 %, respectively, consist in restoring moisture content close to the native state of green hide, increasing plasticity, and achieving physicomechanical properties of the leather that meet the standard requirements.*
Originality. *The effect of hides soaking in electrochemically activated water on dermis plasticity and physicomechanical properties of the leather was studied.*
Practical value. *Application of electrochemically activated water instead of chemicals used in the soaking solutions for the existing technology results in producing leather with higher quality, reduces the*

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[2] *The title has been modified; the original title is "The influence of electrochemically activated water on raw hide soaking and physico-mechanical properties of leather". The original paper was published in Ukrainian.*

soaking process by 1.6-2.0 times, and increases environmental friendliness of the leather processing technology.

Keywords: *green-salted hides; air-dried hides; soaking; activated water.*

Introduction

High-quality leather material can be formed by the implementation of technologies based on science using highly effective chemical reagents and raw materials of proper quality without damages which could be caused by curing. Predominantly the type of raw materials determines the method of preservation – green-salting, dry-salting, etc. At the same time, larger hides are mainly preserved by green-salting or brining, while smaller hides (skins) – by dry-salting or air-drying [1].

In multistage processing of raw leather materials, the special role belongs to the soaking process during which the structure and moisture content are getting restored and all subsequent physicochemical processes of the corresponding technology – effectively implemented. Among the above curing methods, the air-dried raw leather materials lose the highest amount of water, the content of which varies widely depending on the species, age, and living conditions of animals. Therefore, for the soaking process, which requires significant volumes of aqueous solutions [2], a particularly urgent problem is the exploration and development of new efficient chemical reagents with high diffusion capacity to ensure (1) the distribution of technological solutions of chemical reagents within the leather structure, and (2) the diffusion, first of all, of preservatives and globular proteins from a semi-finished product. At the same time the technological solution must have bactericidal properties to prevent the development of microorganisms and defects in raw leather materials. To prepare this solution, electrochemically activated (ECA) water can be used, whose chemical activity is a result of the presence of highly active ions and radicals [3, 4] and the absence of a water clustered structure [5].

Soaking of the raw leather material [6] using electrochemically activated water fraction – catholyte, intensifies the process twice as compared to the existing technology, while significantly reduces the costs of chemicals and water in the tanning processes of the formation of leather material and excludes from the process such toxic reagents as formalin and sodium hexafluoro silicate.

A solution based on catholyte with the addition of benzyl alcohol or glycerin can be used to treat fur before dyeing [7]. To improve the plastic properties of the dermis of fur and leather, a solution containing catholyte, sodium chloride, glycerol, and glyoxal can be utilized [8].

Thus, the use of electrochemically activated water for preparation of the technological solution of chemical reagents for soaking leather materials can be promising, since it helps to shorten the duration of the process, consumables, and improve the physicomechanical properties of the semi-finished leather product.

Problem Statement

Investigation of the efficiency of electrochemically activated water fraction – catholyte, for soaking raw cattle hides cured by various methods and comparative analysis of the plasticity of pickled hides and physicomechanical properties of the finished leather manufactured according to the developed and existing technology will be carried out.

Methods and Materials

In the study, we used green-salted and air-dried cattle raw leather materials from the bend area with a thickness of 2.6 mm and a moisture content of 56.2 and 12.3 %, respectively. The 5×15 cm samples were assembled into batches using the previously described [9].

To prepare the technological solution, electrochemically activated water fractions – catholyte with a pH of 8.5, 10.0, and 11.5 were used at 25–27 °C. Catholyte was obtained using the electroactivator of the scientific and production company "Ekovod" (technical specification TU U29.1-1285006876.001-2000) with the addition of 0.2–0.5 g/L sodium chloride [10].

Soaking of green-salted raw materials was carried out in catholyte with a liquid coefficient (LC) of 1.3–1.5 L/kg for 4 and 6 h. Air-dried samples were pre-soaked in catholyte for 10 and 12 h with LC 2.0 L/kg of the weight of green hide. After that, the samples of raw materials were kneaded in a mobile apparatus with a LC of 1.5 L/kg at a rotation rate of 8–12 rpm for 1.5 and 2 h and soaked at a LC of 1.3–1.5 L/kg for 5, 7, and 8 h.

For the control samples the processing time of green-salted raw materials was up to 8 h using 0.5 % sodium carbonate [2], while for samples from air-dried raw materials the processing time was up to 30 h including preliminary soaking stage which lasted for 19 h. The presoaking solution contained sodium sulfite – 0.8 %, surfactant – 0.3 %, and sodium hexafluoro silicate – 1.5 % of the weight of the raw material. At the same time, for the soaking of air-dried samples sodium carbonate in an amount of 1.5 % of the weight of the raw material was used [11].

All subsequent processes and operations with tested and control samples were carried out using the existing technology.

The efficiency of soaking of raw leather materials in electrochemically activated water was investigated by determining the moisture content in the dermis [9] and skin plasticity, which was determined by the magnitude of the relative deformation under the force equals 25 % of the breaking load (load mode) and after being in a free state (discharge mode). The duration of each mode was 5 min [12].

Physicomechanical characteristics of leather materials – strength and deformation, were determined after drying-moisturizing processes according to the previously described procedure [9]. The samples were deformed using a tensile testing machine RT-250M at an extension rate of 80 mm/min. The stiffness was measured using the device for testing the stiffness and elasticity PZhU-12M (State-owned enterprise "Scientific Research Institute "Elastik", Ukraine). The results of treatments of green-salted raw materials under three different conditions are listed in Table I.

Results and Discussions

As it can be seen from the results (Table I), the moisture content of the raw leather material depends on the pH of the catholyte and increases with increasing pH reaching a maximal value for treatment *3*. The final pH of the technological solutions is reduced by 1.5 units in comparison with the initial pH under all experimental conditions. In comparison with the existing technology, for treatment *1* and *3* a corresponding decrease and an increase in moisture content are observed, whereas for treatment *2*, when the processing time is reduced by half, the moisture content in the dermis is almost the same. It should be noted that in the existing technology, alkaline and surface-active reagents are used to achieve the required moisture content (67.1 %).

Table I. *Technological aspects of soaking green-salted raw materials in activated water.*

Indicator	**Soaking treatment**			
	1	**2**	***3***	***4***
pH of catholyte				
– initial	8.5	10.0	11.5	9.5
– after soaking	7.0	8.5	10.0	9.0
Liquid ratio [L/kg]	1.5	1.4	1.3	1.4
Processing time [h]	6	4	4	8
Moisture content [%]	64.9	67.5	69.0	67.1

A denser structure of air-dried bend samples accounts for a significant loss of moisture, thus the sample pre-soaking and subsequent kneading, which increases the overall process duration, is required. The nature of the pH dependence of the water absorption of raw materials of this type of preservation is similar to that for green-salted raw materials (Table I), but with slightly lower moisture content (Table II).

Table II. *Technological aspects of soaking air-dried raw materials in activated water.*

Indicator	**Soaking treatment**			
	1	***2***	***3***	***4***
pH of catholyte				
– initial	8.5	10.0	11.5	9.5
– after soaking	7.0	8.5	10.0	9.0
Liquid ratio [L/kg]				
– pre-soaking	2.0	2.0	2.0	2.0
– kneading	1.5	1.5	1.5	1.5
– soaking	1.5	1.4	1.3	1.4
Processing time [h]				
– pre-soaking	12	10	10	19
– kneading	2.0	1.5	2.0	1.5
– soaking	8.0	5.0	7.0	8.5
Moisture content [%]	61.1	66.2	68.3	65.8

Since the hydration degree of the dermal collagen of the raw leather material is defined by the collagen structure, the approximation of the moisture content in samples to its value in the native state of raw materials (at least 65 %) indicates that the soaking process is effective for treatment 2. This can be explained by (1) the interactions of the stratified structure of the collagenous raw material with activated water and a different effect of the pH of the catholyte on the diffusion kinetics predominantly from the subcutaneous tissue side and (2) the effective interactions of free radicals and water ions with interfibrillar glycosaminoglycans, fat inclusions, and collagen polypeptide chains. Soaking in catholyte with the initial pH 8.5 completed with insufficient hydration of the raw leather material due to the reduced water content in the dermis. With an increase in the initial pH up to 11.5, the increased concentration of ionized molecules of water and its free radicals facilitate enhanced water diffusion into the dermis from the subcutaneous tissue side, which resulted in a slight swelling.

After the soaking stage, the moisture content and elasticity of the semi-finished product is controlled, usually organoleptically. The method used to determine the plasticity [12] allows studying all the samples simultaneously, and based on the elongation values, obtained in unloading mode, calculations were performed, the results of which are shown in the Fig. 1.

Samples of green-salted and air-dried raw leather materials after soaking in catholyte according to treatment *2* were soft to touch across the entire area and had greater plasticity. This confirms the theory [13], according to which the untanned collagen has a loose spatial mesh which allows depending on the moisture content under tensile stretching to get an oriented alignment of polypeptide chain segments and also longitudinal sliding of the chains relative to each other.

Therefore, the value of the total deformation in the case of tensile stretching of the sample (load mode) increases, which is the reciprocal to elastic deformation (unloading mode), in addition, with increasing moisture content the deformation relaxation time increases.

The leather samples were obtained by the implementation of all subsequent technological processes and operations by applying the existing technology to the samples of green-salted and air-dried raw leather materials soaked using the above four treatments. The physicomechanical properties of the leather samples are listed in Table III.

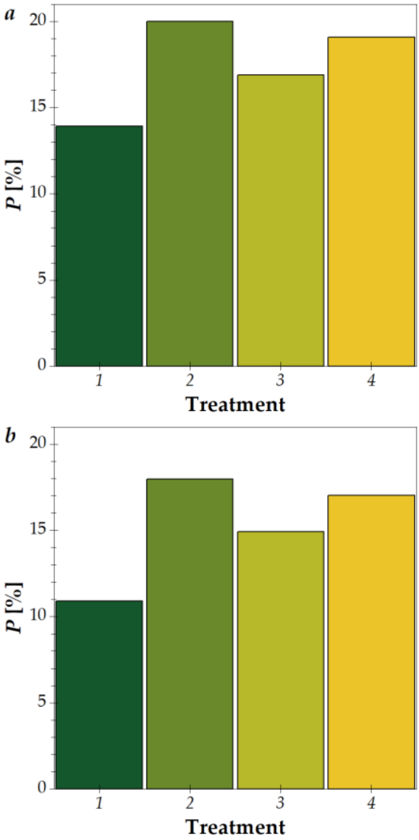

Fig. 1. *Plasticity of dermis leather of bend samples after soaking under four different treatments the green-sated (a) or air-dried (b) raw leather materials using catholyte.*

According to the results (Table III), the highest value of the elongation at 10 MPa of the leather samples from treatment *2* corresponds to the maximal plasticity index, while the lowest value of elongation for leather samples from treatment *1* corresponds to the minimal value (Fig. 1). Thus, it can be assumed that the degree of leather elongation at 10 MPa or under tensile stretching is consistent with the plasticity magnitude of raw leather material after soaking. As it is known, tanning increases the density of spatial collagen mesh resulting in increased stiffness and reduced orientation of the elements of its structure under force application. Therefore, for leather samples (treatments *1* and *3*) with lower elongation values at 10 MPa, greater stiffness values are observed, and for the leather sample from treatment *2* – the stiffness value is the smallest. In addition, for leather samples from treatment 2, made from both green-salted and air-dried raw materials, the tensile strength at fracture onset on a grain is greater than in the samples from other treatments.

Table III. *Physicomechanical properties of leather obtained from green-salted and air-dried raw materials.*

Indicator	**Soaking treatment**			
	1	2	*3*	*4*
Tensile strength [MPa]	$\frac{22.4}{21.0}$	$\frac{20.0}{19.2}$	$\frac{18.2}{17.3}$	$\frac{19.5}{18.7}$
Tensile strength at fracture onset on the grain side [MPa]	$\frac{16.5}{14.8}$	$\frac{19.0}{18.5}$	$\frac{17.8}{16.5}$	$\frac{18.2}{17.0}$
Elongation [%]				
– at 10 MPa	$\frac{21.7}{24.0}$	$\frac{31.0}{33.0}$	$\frac{24.0}{26.0}$	$\frac{29.0}{32.0}$
– at break	$\frac{51.0}{57.0}$	$\frac{67.0}{71.0}$	$\frac{56.0}{59.0}$	$\frac{64.0}{69.0}$
Stiffness [cN]	$\frac{46.0}{41.7}$	$\frac{31.0}{30.0}$	$\frac{42.0}{39.0}$	$\frac{32.0}{34.4}$

Note: *The numerator and denominator correspond to the leather obtained from green-salted and air-dried hides.*

Thus, the physicomechanical properties of leather samples from all treatments, that have been studied using fracture tensile strength and elongation at 10 MPa, corresponds to the requirements of DSTU 3115-95.

Conclusions

A significant influence of the developed soaking method of natural raw materials of various preservation methods on the formation of a complex of physicomechanical properties of the obtained leather material is established.

The advantages of using electrochemically activated water for soaking green-salted and air-dried raw leather materials consist in restoring a moisture content close to the native state of raw materials, in reducing the duration of the process by 2 and 1.9 times, respectively, and in excluding such environmentally harmful reagents as hexafluoro silicate and sodium sulfite.

The leather material obtained by the developed technology is characterized by increased plasticity, and according to the complex of physicomechanical properties it corresponds to the requirements of DSTU 3115-95 "Leather for garments. General specifications".

References

[1]. **Danylkovych A. and Lishchuk V.** Technology and equipment for leather and fur production] (in Ukrainian). Fenix (Publisher «Фенікс») 2007, Kyiv.

[2]. **Danylkovych A., Mokrousova O., and Okhmat O.** Technology and materials for leather production (in Ukrainian). Fenix (Publisher «Фенікс») 2009, Kyiv.

[3]. **Fidaleo M. and Moresi M.** Electrodialysis applications in the food industry, *Advances in Food and Nutrition Research* **51** (2006) 265–360; doi.org/10.1016/S1043-4526(06)51005-8.

[4]. **Shirahata S., Hamasaki T., and Teruya K.** Advanced research on the health benefit of reduced water, *Trends in Food Science & Technology* **23**, 2 (2012) 124–131; doi.org/10.1016/j.tifs.2011.10.009.

[5]. **Lishchuk V. and Danylkovych A.** Physicochemical aspects of structure formation in pickled hides (in Ukrainian), *Bulletin of the Kyiv National University of Technologies and Design* 2, 22 (2005) 59–68.

[6]. **Danylkovych A., Lishchuk V., and Romaniuk O.** Use of electrochemically activated aqueous solutions in the manufacture of fur materials, *SpringerPlus* **5**, 214 (2016); doi.org/10.1186/s40064-016-1784-6

[7]. **Zorina E. and Zeleva G.** Dying of fur with various dyes (in Russian), *Omsk Scientific Bulletin* **19** (2002) *138–139*.

[8]. **Zorina E., Zeleva G., and Nagornaya Z.** The effect of the nature of tanning agents and water on the plastic properties of the skin tissues of fur and leather (in Russian), *Omsk Sci. Bull.* **19** (2002) 140–141.

[9]. **Danylkovych A. and Chursin V.** Analytical control in leather and fur production: a laboratory practicum (in Russian), Infra-M, Moscow, 2016, 176 p.

[10]. **Potapenko S., Kostiuk O., Kostiuk I., et al.** Mechanism for preparing silicon potable water, UA patent 19633, December 15, 2006.
[11]. **Balberovoy N.** Handbook of the tanner (technology) (in Russian). Legprombytizdat 1986, Moscow.
[12]. **Tsymbalenko O., Statsenko D., Matviienko O., et al.** Method for determination of pickled hide plasticity, UA patent 77317, February 11, 2013.
[13]. **Kutyanin G.** Investigation of physicomechanical properties of leather (in Russian). Gizlegprom 1956, Moscow.

4. STRUCTURAL TRANSFORMATIONS OF COLLAGEN-CONTAINING RAW MATERIALS UNDER ALKALINE TREATMENT [3]

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Chemistry & Chemical Technology **10**, 3 (2016) 379–385
http://science2016.lp.edu.ua/chcht/structural-transformations-collagen-containing-raw-materials-under-alkaline-treatment

Abstract: *As a result of studies of structural transformations of raw leather materials during chemocolloidal processes under alkaline dispersion treatment, collagen of the dermis releases preservative agents and globular proteins. The conditions of rawhide alkaline treatment under which the structure of a semi-finished product with preserved amino acid composition of collagen of the dermis is formed, have been outlined. A comparative analysis of the developed technology of a leather semi-finished product formation from cattle rawhide has been carried out.*

Keywords: *rawhide; collagen of the dermis; structure; semi-finished product.*

Introduction

Because of the variety of collagen-containing raw materials, a wide range of reagents with varying nature used in a multistage technological process, and high requirements for a set of properties for finished leather materials, there is a need to develop innovative technologies based on the results of systematic chemocolloidal and structural research. It is caused by the fact that at each stage of a technological cycle, a structure of a semi-finished leather product is formed which significantly

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[3] *The title has been modified; the original title is "Structural transformations of collagen containing raw materials under alkaline treatment".*

affects the efficiency of all subsequent stages and the properties of final leather materials.

Well-known works in the field of rawhide soaking and liming (SL) generally refer to technological aspects of this problem. Moreover, much attention is paid to the process of hide dehairing. Particularly, the soaking of fresh-slaughtered and preserved cattle hides in the presence of sodium carbonate, non-ionic surfactants, and proteolytic enzymes was studied [1, 2]. As a result of these studies, it was found that the duration of the soaking process of preserved rawhide should be at least 4–6 h [1] or 8 h [2], and for fresh-slaughtered hides – twice less at 296 K. Furthermore, the completeness of the technological process was monitored according to the increase in weight if cattle hides and change in properties of technological solutions.

The authors of the work [3] used lipolytic enzymes along with non-ionic surfactants during rawhide soaking and dehairing. By doing so, the use of non-ionic surfactants was reduced and wastewater ecological properties were increased. The application of calcium peroxide, amines, enzymes, and hydrogen peroxide [4] during hide dehairing gave an opportunity to discard sodium sulfide from the technological process. In addition, the use of oxidizing mixture with sodium hydroxide and percarbonate for hide dehairing [5] in the presence of alkaline protease at the second stage of liming contributed to the formation of leather material with high performance properties upon the completion of the entire technological cycle. The work [6] is dedicated to studying the composition of the interfibrillar components extracted from rawhide. The authors have shown that the amount of proteoglycans extracted from the dermis depends upon the duration of soaking and liming processes.

Considering multistage processes and duration of soaking and liming, there is an objective necessity to conduct a set of chemocolloidal and structural studies during the process of soaking and liming which determine a hide structure formation at all following stages of the technological cycle of rawhide transformation into polyfunctional leather materials.

The current work presents the research findings on the process of rawhide alkaline treatment, diffusion of alkaline dispersion into the structure of hide dermis and release of non-fibrous components into a solution, and evolutionary changes of dermis structure properties for a scientific explanation of a technology of primary formation of a semi-finished product structure and an efficient conducting of all subsequent technological processes of polyfunctional material production.

Materials and Methods

The green-salted cattle rawhide was used for the investigation, which was collected into batches by taking into account the weight of the hide. Sodium carbonate, sodium hydrosulfide, sodium sulfide, and calcium hydroxide, produced according to the standards, were used for liming of collagen-containing raw materials. The concentration of alkaline reagents was varied in the range of 4–35 g/L.

Alkaline solution sorption by the dermis was determined gravimetrically [7]; the degree of structuring of the semi-finished leather product was determined by heating the sample at 2–3 K/min and measuring temperature at onset of shrinkage; the thermal resistance of enzyme(s) was determined as the time required for a complete destruction of a sample section in the presence of pancreatin. Diffusion depth of $Ca(OH)_2$ into the dermis structure was determined using an optical microscope MBI-3 for sections stained with phenolphthalein. Gelatin hydrolysate fraction from a semi-finished product was measured using a photoelectric colorimeter PhEC-56M according to the calibration curve “absorbance-dry residue content for pickles hide” at a wavelength of 520 nm. Distilled water was used as a reference standard.

The amino acid composition of collagen of the dermis dried with alcohol-ether mixture was determined by ion exchange chromatography [8] using an automatic T-339 acid analyzer "Mikrotechna" (the Czech Republic) and Ostin LGANB sodium polystyrene sulfonate ion exchange resin in a lithium citrate buffer utilizing a single-column. Porosity of semi-finished product was calculated from picnometrical volume measurements in kerosene using the actual and apparent densities of samples dried with alcohol-ether mixture. The structural changes of semi-finished product after soaking and liming were determined using a scanning electron microscope REMMA-102 (Ukraine) [9]. The samples for the structural studies were prepared in the form of cross sections (about 1 mm thick) from a semi-finished product dehydrated in alcohol-ether mixture and sputter-coated with a 3–5 nm silver layer. The further technological processes of polyfunctional leather formation after liming were carried out according to the industrial technology of PJSC Chinbar (Kyiv, Ukraine).

Results and Discussion

Physicochemical properties of rawhide during structural transformations

Profound rawhide structural transformations are caused by a set of chemocolloidal processes which begin at the stages of soaking and liming. During these processes, disruption of amide intermolecular bonds facilitates the active interaction of chemical reagents with collagen of the dermis. At the same time, a critical influence on the rawhide structural transformations is made by both the solution composition and the conditions of their interaction with collagen of the dermis. The results of the study of the effect of temperature and concentration of Na_2CO_3 on the process of diffusion and desorption of $NaCl$ and globular proteins at 1.5 : 1.0 weight ratio of reagent dispersion-to-rawhides are shown in Table I.

Table I. *Change in moisture content of dermis and its components under reverse diffusion.*

Soaking duration [h]	Moisture content [%]		$NaCl$ [g/L]	Globular proteins [g/L]	
	301 K [1]	293 K [2]		301 K	293 K
0	47.5	47.5	0	0	0
2.5	57.0 / 59.0	56.0 / 58.0	78.0	2.73	2.16
5.0	62.5 / 64.5	60.5 / 63.0	107.0	3.64	2.62
6.0	63.5 / 65.5	61.0 / 64.3	126.0	4.26	2.87
8.0	65.3 / 66.5	62.3 / 65.0	138.0	4.94	3.93
9.0	65.7 / 67.0	62.5 / 65.0	141.0	5.21	4.31

Notes: *The numerator and denominator correspond to the values without the use of sodium carbonate and with its concentration of 4 g/L (1) or 12 g/L (2).*

As one can see from Table I, with the increase in temperature, Na_2CO_3 concentration, and duration of the liming process, the moisture content increases. The temperature increase by 8 K allows reducing a Na_2CO_3 concentration threefold and the time of its interaction with rawhides to 5–5.5 h by 37–39 %. Therefore, carrying out the soaking process of rawhide at 301 K provides a maximal similarity of a semi-finished product by its moisture content to the native state (70 % [10]). Also, a maximal mobility of collagen of dermis is achieved which will facilitate an effective diffusion of chemical reagents into its structure. At the same time, a release of globular proteins and 69.0 % of $NaCl$, a preserving agent, occurs at the studied temperatures. In the subsequent alkaline treatment of a semi-finished product, which includes rinsing, there is practically a complete release of these components from the structure.

A further interaction between the dermis of animal hides and more active chemical alkaline reagent $Ca(OH)_2$, the destruction of chemisorbed and chemical bonds between albumins, globulins, mucopolysaccharides, lipids, and components of collagen fibrous structure is occurred [11]. Further removal of these components from the pickled hides into the technological dispersion takes place during mechanical deformation of a semi-finished product in the mobile device. It is worth noting that elastin and reticulin remain in the structure of hide dermis under alkaline treatment due to their high chemical resistance.

The study of $Ca(OH)_2$ diffusion processes into the dermis (Fig. 1) are characterized by a high initial rate with its subsequent gradual decrease. At the same time, the process intensity is increasing with the increase of reagent concentration, while the duration of the reagent penetration at the depth of 70 % of the dermis thickness is decreasing twofold with its concentration equals to 35 g/L in comparison with a minimal concentration in the technological dispersion. It can be caused by an efficient interaction of $Ca(OH)_2$ dispersion with collagen of the dermis, as a result of which its structure is getting more homogeneous. At the same time, amide bonds between the side polypeptide chains of collagen break up and free carboxy groups form complex compounds with $Ca(OH)_2$ [12]. Along with this, a part of a diffused alkaline reagent is located in macropores of a semi-finished product in a free state.

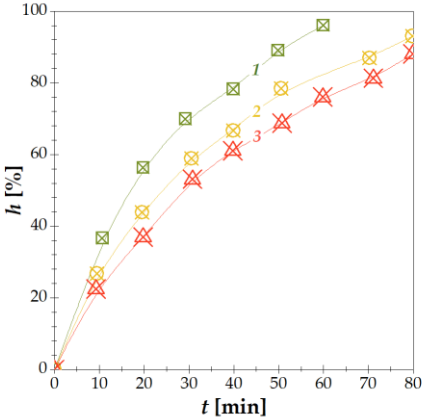

***Fig. 1**. Kinetics of $Ca(OH)_2$ diffusion into dermis at 301 K: 35 g/dm^3 (1); 15 g/dm^3 (2), and 5 g/dm^3 (3).*

As a result of chemical interaction of alkaline dispersion with collagen of the dermis, further changes happen within the next 12 h. During prolonged interaction of a semi-finished product with $Ca(OH)_2$ dispersion, water absorption of hydrophilic samples increases significantly (Table II).

The results of the research show that after alkaline treatment of the semi-finished product by $Ca(OH)_2$ and Na_2S dispersion, the moisture content depends on the ratio of the technological dispersion to semi-finished product reaching the maximal value at the highest ratio (treatment *3*). The reason for this can be an increased dispersity of alkaline reagent particles at a lower concentration and the corresponding value of particle diffusion in the semi-finished product which promotes water absorption. It should be noted that the minimal water absorption is observed for the samples without previous moisturizing before alkaline treatment (treatment *4*) containing preservative agents, or at the minimal ratio (treatment *1*).

Table II. *Properties of a semi-finished product after alkaline treatment.*

Parameter	**Treatment**				
	1	**2**	***3***	***4*** [1]	***5***
LC [L/kg]	0.5	1.0	1.5	1.5	3.0
$Ca(OH)_2$ [g/L]	30.0	15.0	10.0	10.0	5.0
Na_2S [g/L]	36.0	18.0	12.0	12.0	6.0
Moisture content [%]	78.0	81.0	81.5	77.7	84.5
T_S [2] [K]	331	317	327	333	330
Area yield [%]	89.0	92.0	93.0	88.0	89.0

Note*: 1) without rawhide soaking; 2) shrinkage temperature of pickled hide. LC stands for liquid coefficient – the ratio of dispersion volume to rawhide mass.*

From the results of the research on properties of semi-finished product after alkaline treatment, it can be seen that the moisture content correlates with hydrothermal stability of the samples. This may indicate a simultaneous impact on the structure of the semi-finished product interaction of alkaline reagents with dermal collagen and the formation of internal strains which contributes to decrease of hydrothermal stability due to excessive water absorption by dermal collagen as a result of high hydrophilicity of the sorbed alkaline reagents. The minimal values of shrinkage temperature indicate the largest degree of fibrillar structure separation and its potential availability to further effective technological treatments.

Summing up the above-said, the most significant changes in corium collagen take place at the concentration of $Ca(OH)_2$ 10–15 g/L and the ratio of technological dispersion volume to raw material weight from 1.0–1.5 to 1.0. Certain increase of shrinkage temperature of the pickled hides is caused by its excessive absorption which results in increase of elastic properties of dermis. Under these conditions of alkaline treatment of semi-finished product, the maximal area yield of the semi-finished leather product is achieved indicating deeper structural changes of dermal collagen.

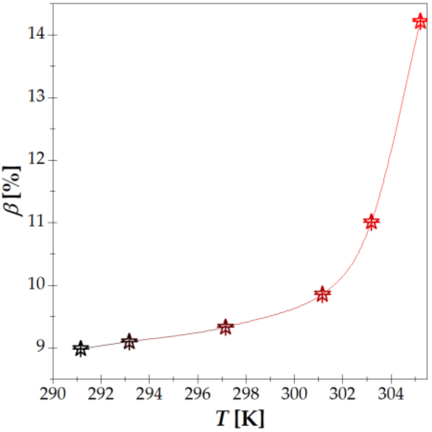

***Fig. 2.** Dependence of the amount of the hydrolyzed gelatin (β) from the pickled hides on the temperature during liming.*

At the same time the amount of the hydrolyzed collagen – gelatin after alkaline treatment of semi-finished product at different temperatures, can indicate the integrity of the semi-finished product structure (Fig. 2). The considerable increase of the amount of the hydrolyzed gelatin starting from the temperature 301 K confirms the beginning of destructive processes in the inter- and intramolecular bonds of the collagen macromolecules. Thus, as the results of the conducted investigations demonstrate, it is reasonable to carry out the soaking-liming processes of the rawhide material at the temperatures below 301 K.

The study of the amino acid composition of the semi-finished product limed at 301 K confirms the previous results (Table III).

Table III. *The amino acid compositions of the corium collagen hydrolysate before and after liming.*

Amino acid	**Molar fraction of amino acids [%]**		
	Before liming	**After liming at**	
		293 K	**301 K**
Alanine	11.92	11.76	11.88
Arginine	5.24	5.18	5.13
Aspartate	4.77	4.82	4.92
Glutamate	9.16	9.12	9.21
Glycine	28.43	28.64	28.81
Histidine	0.63	0.61	0.57
Hydroxylysine	0.69	0.72	0.63
Hydroxyproline	6.96	7.17	7.29
Isoleucine	1.37	1.34	1.38
Leucine	2.94	2.97	2.86
Lysine	2.98	2.96	2.93
Methionine	0.51	0.53	0.58
Phenylalanine	1.52	1.48	1.44
Proline	13.79	13.82	13.68
Serine	3.92	3.59	3.62
Threonine	1.96	2.03	1.91
Tyrosine	0.54	0.56	0.57
Valine	2.67	2.70	2.59

The analysis of the corium hydrolysates has shown that the content of amino acids in the samples limed at 293 and 301 K practically does not differ. Certain differences between the determined glycine amount and the theoretically calculated value 33.3 % [13] can be explained by the presence of non-collagen proteins in the collagen of the dermis.

The results of the electron microscopy are the direct evidence of the substantial structural transformations in the corium during leather material formation during soaking and liming processes (Fig. 3). The raw skin after soaking has consolidated fibrous structure (Fig. 3a), certain fibrils and elementary fibers of which are combined into bundles between which there are empty spaces which are filled after soaking with the dispersion of alkaline reagents. During the next liming the structure of corium becomes more homogeneous (Fig. 3b) as a result of the further absorption of the alkaline dispersion. At the same time, corium collagen is temporarily structured by Ca^{2+} ions.

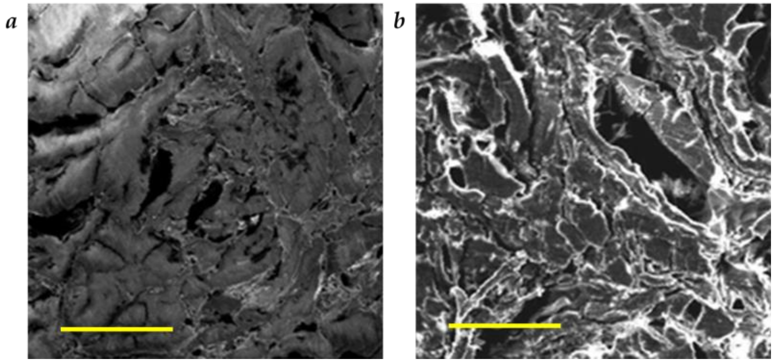

Fig. 3. *Scanning electron microscopy micrographs (400×) of the hide cross section after soaking (a) and after liming (b). Scale bar – 100 μm.*

The conducted research on the microstructure transformation during formation of the picked hide provide the opportunity to notice the peculiarities of releasing soluble proteins – globulins and albumins, mucopolysaccharides, and partially lipids form the corium collagen structure and their substitution by clustered aqueous solutions of chemical reagents.

This allows forming the pickled hide with preserved structure of initial corium of rawhide. This is due to the presence of the technological dispersion within the formed fibrous porous structure of the pickled hide which fills interfibrillar and interfibrous spaces created during liming and prevents significant convergence of the structural elements and the consolidation of the entire structure. Later, at a certain technological stage of leather material formation, the clustered water is displaced by the relevant chemical reagents. As a result of this mechanism of the formation of pickled hide and finished leather material, a considerable diffusion rate of the reagents during soaking and liming processes is being achieved.

Thus, the investigation of the changes of the chemocolloidal characteristics and the structure of the corium collagen under alkaline agent treatment gives reasons to conclude that the increasing of temperature up to 301 K will facilitate the effective formation of the semi-finished leather material during further stages of its processing.

Technologies of rawhide soaking and liming

As a result of integrated studies on soaking and liming processes of hides, the technologies were developed and later applied for manufacturing polyfunctional leather materials. The area of application of pickled semi-finished product largely depends on the type of rawhide and technological details of its further processing. While the area of applicability is limited for small rawhide leather materials, in the case of large rawhides due to the application of developed technological processing, the leather material assortment and its polyfunctionality significantly increase. The effectiveness of the use of raw materials in the second case can be significantly raised by increasing the area of semi-finished products in multiple doubling and its convenience of cutting out received material.

The developed technologies for soaking and liming of cattle hide differ significantly from the previously existing technologies based on the cost of chemicals and water, treatment duration of raw materials, energy savings, and environmental efficiency (Table IV).

***Table IV**. Characteristics of soaking and liming technologies of green-salted rawhide processing.*

Characteristics	**Technology**			
	1	2	*3*	4
Consumption				
Material [kg/t]	58.5	62.5	78.0	129.3
– Na_2S	20.0	20.0	12.0 [†]	29.5
– $Ca(OH)_2$	24.0	30.0	33.0	80.8
Water [m^3/t]	5.0	4.2	4.8	11.5
Energy [kW/t]	22.7	18.6	20.6	38.3
Process duration [h]	19.0	20.0	19.0	44.5
– soaking	6.0	5.0	5.0	8.5
– liming	12.0	14.0	13.0	34.0
– washing	1.0	1.0	1.0	2.0
Content [‡] [g/L]				
– sodium sulfide	4.3	4.8	4.6	8.0
– calcium hydroxide	3.6	4.0	4.2	16.0
keratin	19.0	0.8	0.5	19.0

Note: *[†] + 9.0 kg/t sodium hydrosulfide (NaSH); [‡] in spent solution.*

All developed technologies are implemented at an elevated temperature – 8–10 K higher. The technology *1* [10] provides processing of hides in one stage and results in decreasing of the cost of reagents and water by 2.2–2.3 times, electricity – by 1.7, duration of treatment – by 2.3, and the content of sulfides and calcium hydroxide – by 1.9 and 4.4 times, respectively.

In contrast to technology *1* and technologies *2* and *3* [12, 13] are carried out at two stages and are fundamentally different in recycling hair keratin. These technologies provide cost reduction in chemicals by 1.7–2.0 times. Therewith the keratin content in spent solutions is reduced by 24–38 times compared with the technology of one-stage liming.

Analysis of the properties of pickled hide (Table V) illustrates that after liming the semi-finished product formed by the developed technology is characterized by parameters, the values of which do not differ from the previously existing technologies. However, slightly less gelatin hydrolysis from pickled hide may indicate a higher thermal stability of dermal collagen obtained by the developed technology.

Table V. *Physicochemical characteristics of pickled hide.*

Characteristics	**Technology**			
	1	***2***	***3***	***4***
T_S **[K]**	328	329	327	327
Enzymatic and thermal stability [min]	58	57	53	51
Hydrolyzed gelatin, 330 K [%]	9.8	10.7	10.3	12.5
Deformation [%] at				
– 1 kPa	11.0	13.0	12.0	6.0
– 5 kPa	33.0	30.0	32.0	25.0
– elastic	32.0	34.0	29.0	41.0
– plastic	34.0	37.0	39.0	27.0

At the same time the elastic-plastic properties of the pickled semi-finished product obtained by the developed technology is characterized by increased deformability of less dense peripheral areas of hides and lower values of elastic deformation. This will facilitate the leather material formation with increased area yield.

Thus, the obtained research results of the soaking and liming process and efficiency analysis of developed technologies, including properties of pickled semi-finished products, indicate the possibility of their efficient application depending on specific conditions of industrial production.

Conclusions

As a result of the research on the structural transformations of rawhide during chemocolloidal processes in the presence of alkaline dispersion, collagen of the dermis releases preservative agents and globular proteins, thus facilitating the accessibility of hydrophilic functional groups for interacting with chemical reagents. The conditions of green-salted rawhide alkaline treatment under which the chemocolloidal state of the rawhide approaches the moisture content specific for fresh-slaughtered hides, have been outlined. It occurs with increase in the temperature of the process to 301 K and threefold decrease of sodium carbonate concentration in the technological solution. During further alkaline treatment of rawhide by calcium hydroxide, an evolutional separation of fibrillar collagen structure of the dermis with its active participation in forming coordination complexes and increasing the dermis water absorptivity takes place.

We determined the conditions of rawhide alkaline treatment under which the amino acid composition of the dermal collagen is preserved and the optimal moisture content provide the efficient carrying out of the further processes and operations of leather materials formation. The technologies of cattle rawhide soaking and liming which were developed and implemented into the industrial production refer to material-saving, energy-saving, and ecologically efficient ones. The technology *3* of two-stage soaking and liming, which is the basis for the follow-up studies of the polyfunctional leather materials formation, can be considered to be the most advanced.

References

[1]. **Stockman G., Didato D., Steele S., et al.** *World Leather* **23** (2010) 31.

[2]. **Stockman G., Didato D., Steele S., et al.** *Journal of the American Leather Chemists Association* **103** (2008) 76.

[3]. **Pelckmans J., Fennen J., and Christner J.** *World Leather* **21** (2008) 31.

[4]. **Lampard G.** *Leather International* **212** (2010) 24.

[5]. **Aldema-Ramos M. and Liu C.** *Journal of the American Leather Chemists Association* **105** (2010) 222.

[6]. **Madhan B., Rao J., and Nair B.** *Journal of the American Leather Chemists Association* **105** (2010) 145.

[7]. **Danylkovych A.** Practicum in chemistry and technology of leather and fur (in Ukrainian). Fenix (Publisher «Фенікс») 2006, Kyiv.

[8]. **Kaplan N. and Colowick N.** (ed.). Preparation and assay of substrates, volume 3. Academic Press 1957: New York – London; in: Methods in enzymology, edited by Moore S. and Stein W.

[9]. **Gouldstein Dzh., Nyubery D., Echlyn P., et al.** Scanning electron microscopy and microanalysis (in Russian). Mir (Publisher «Мир») 1984, Moscow.

[10]. **Danylkovych A.** Physicochemical principles of alkaline treatment of dermis (in Ukrainian) in: Ecologically oriented technologies for production of leather and fur materials for manufacturing of competitive goods (in Ukrainian). Fenix (Publisher «Фенікс») 2011, Kyiv, 39–133.

[11]. **Michaylov A.** Leather collagen and principles of its processing (in Russian). Light Industry (in Russian) 1971, Moscow.

[12]. **Lishchuk V. and Danylkovych A.** *Bulletin of the Kyiv National University of Technologies and Design* **2** (2005) 59.

[13]. **Lishchuk V., Danylkovych A. and Zhyhotsky O.** *Light Industry (in Russian)* **2** (2011) 27.

[14]. **Lishchuk V., Bekharskyi V., Tsemenko G., et al.** A method for hides unhairing and liming, UA patent 68772, August 16, 2004.

[15]. Lishchuk V. and Danylkovych A. A method for unhairing-liming the leather raw stock, UA patent 11907, January 16, 2006.

5. ENZYMATIC TREATMENT OF LEATHER SEMI-FINISHED PRODUCT IN THE PROCESS OF SOFTENING [4]

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Abstract: *Enzyme application in animal hide treatment technologies is caused by their strong and specific catalytic action in various chemical transformations. Effect of concentration of proteolytic enzymes – pancreatin and Chemizym BH, and treatment duration on the softening of green-salted bullhide after dehairing-liming, washing, splitting, and deliming was studied. The effectiveness of the enzymes was estimated by determining the amount of the hydrolyzed gelatin in pickled and softened hides and physicochemical properties of semi-finished products. At the enzyme concentration of 2.2 g/L, temperature of 35–37 °C, and long-term hide softening, the amount of gelatin hydrolyzed from the dermis reaches 45.0 %, and for the papillary layer this indicator is getting close to 100 %. The results were used in manufacturing the semi-finished product "crust". The investigation of physicomechanical properties of the semi-finished product have allowed determining the duration of the softening process that provides an optimal range of performance properties. The results can be used for softening process optimization in the manufacturing technology of the semi-finished product "crust" to ensure the required material quality at the consumption of enzyme Chemizym BH of 0.3 % and water of 100 % of the pickled hide mass. Twelve-hour dehairing - rawhide liming and one-hour hide softening at the optimal activity of enzyme Chemizym BH can be considered effective in the manufacturing technology of bullhide materials for footwear, clothes, and fancy goods.*

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[4] *The title has been modified; the original title is "Enzymic treatment of leather intermediate product in the process of softening".*

Keywords: *enzyme; proteolytic activity; semi-finished product; hide; liming; softening; physicochemical properties.*

Introduction

Leather and fur production are marked by many stages, complexity, and environmental pollution during chemical transformations of raw materials into finished materials. In this regard, at different stages of processing of protein raw materials, biologically active substances, to which the enzymes belong, have found application. Their wide use in the processing of animal hides/skins is due to an enzyme strong specific and catalytic effect in various chemical transformations. Of the known six classes of enzymes [1, 2], the enzymes of the third class – hydrolases, which include subclasses of esterase, glycosyl-hydrolases, peptidases, and amidases, significantly accelerate bond-cleavage reactions (peptide, amide, and ester) and they are the most often used in leather and fur production in which the carboxyl groups of biopolymer belong to the basic amino acids lysine and arginine. Therefore, owing to the enzymatic treatment of raw leather and fur materials, it is possible to achieve different effects, particularly, degreasing, dehairing, and increasing the elastic properties of the semi-finished product. However, the study of the softening process whose duration determines the physicochemical properties of the material produced from natural rawhides, remains relevant.

Problem Statement

Enzymes of a specific action can be used to effectively influence the inter-fiber elements of a semi-finished product to release non-collagen components from dermis. Therefore, the choice of the type of enzyme, its concentration, and the duration of the process, will allow optimizing the technological procedure for processing of raw leather and fur materials, decrease the amount of harmful chemicals used, and improve the environmental friendliness of the production overall.

Literature Review

Enzymes of proteolytic, glycosidic, and lipolytic actions can be used during soaking and liming processes [3], whereas the deliming process can be carried out with Lithudac L and Novo Bate WB enzymes which are active in acidic medium [4]. Alkaline lipases or a combination of alkaline proteases and lipases can be used to carry out the degreasing process and increase its effectiveness [5]. Enzyme protosubtiline G10× is promising for the dehairing process of rabbit skins [6, 7]. Proteolytic enzymes and trypsin can be used to process chrome waste [8].

When choosing enzymes to accelerate the physicochemical processes of soaking, degreasing, dehairing, and softening, the conditions of preserving raw materials and their intended use are essential. Particularly, the technology for processing air-dried rabbit skins at the soaking stage involves the use of enzymes such as maltavamorine G10×, pectofoetidine P10×, and amylosubtiline G3× [9], which allows not only shortening soaking time but also reducing the defectiveness of pelts during their mechanical processing due to increased plasticity of dermis.

The use of enzymes protosubtiline G3×, pectofoetidine P10×, and maltavamorine G10× for soaking [10] and pectoavamorin P10× and pectofoetidine P10× for processing sheepskins with denser corium and size more than 90 dm^2 in the presence of surfactant [11] accelerates the removal of lipids and impurities of protein and carbohydrate nature from the hair and dermis. Such components can be attributed to polyfunctional, since along with enzymes which catalyze the hydrolysis of fats (lipids) they also contain other enzymes, particularly proteases and glycosidases. With preliminary degreasing of sheepskins by protosubtiline G3× in the presence of surfactant, the enzyme promotes destruction of fat cell membranes and fat emulsification.

The enzyme activity is significantly dependent on the pH of the medium. Particularly, lipavamorine G3× [12] exhibits lipolytic activity in the pH range 5.5–8, protosubtiline G3× has maximal proteolytic activity at pH 7.5–8 and another 80 % of its activity can be retained at the pH range 6.5–9, while protosubtiline G10× shows maximal proteolytic activity at pH 10.7. Increasing the alkalinity of the medium to pH 12.5 leads to a decrease in activity by 60–70 %. The enzyme Tannerzyme retains more than 90 % of the proteolytic activity in the pH range of 9–12, which can be used in the dehairing and liming of raw leather materials.

In addition to pH, the optimal activity of enzymes depends on the temperature of the process. It is established [12] that the maximal proteolytic activity of protosubtiline G3× is observed at a temperature range of 40–50 °C, while at 30 and 65 °C the activity decreases to 50 %. The optimal activity of lipavamorine G3× is observed at 35–37 °C, and at 20 °C its activity is reduced by 30 %. At 55 °C, the enzyme is completely inactivated. The temperature optimum for the activity of protosubtiline G3× is 60–65 °C, at 35–37 °C its activity is reduced by 44 %.

It should be noted that chemical reagents, such as sodium chloride and sodium sulfide, calcium hydroxide, ammonium sulfate, etc. have a significant effect on the activity of the enzymes. In this case both the increase and decrease in their proteolytic activity can occur. The proteolytic activity of protosubtiline G10× decreases by 10–15 % in the presence of sodium chloride or ammonium sulfate, and by 5 % in the presence of calcium hydroxide [3]. Sodium carbonate has a positive effect on the proteolytic activity of alkaline proteinases. Activity of technical enzyme actinomycetes III, which has two maximums of proteolytic activity, is on average decreased by 10–15 % in the presence of ammonium chloride; sodium chloride, sulfate, and sulfite; or sodium hydrosulfite. Sodium sulfide almost completely reduces the proteolytic activity of investigated enzymes.

Thus, the analysis of the use of enzymes in the processes of leather and fur production has shown that there is no straightforward relationship between the activity and the effect that is achieved in a particular technological process. In this regard, when developing new technologies or improving existing ones which utilize enzymes, it is necessary to take into account the entire assortment and concentration of chemical reagents that can be used at a certain stage of processing of raw leather and fur materials.

The Goal and Objectives of Research

In the paper, the process of softening of pickled semi-finished leather product and its transformation into “crust” utilizing polyfunctional enzymes – pancreatin and Chemizym BH (Chemipol, Poland), was studied.

The goal of research is to determine the efficacy of pancreatin activity on pickled pelt, the optimal water consumption during softening, and the duration of the process in the presence the enzyme Chemizym BH.

For research, cattle rawhides are used, particularly, a green-salted bullhide after liming for 12 h at 27–28 °C, the following washing for 5 and 12 d at 18–22 °C and splitting for a thickness of 2.1 ± 0.1 mm, and deliming and softening at 35–37 °C for 1–3 h. The process of softening of pickled pelt was carried out in the presence of (1) polyfunctional enzyme product – technical pancreatin (OST 49-167-81), which contains a number of proteolytic enzymes [3] – proteinases and peptidases, the main of which is trypsin, and lipase, amylase and elastase, and (2) Chemizym BH with an activity of 10 units/mg at pH 7.8–8.5 and temperature 32–37 °C [13]. For the preparation of the "crust" semi-finished product, the pickled pelt was softened utilizing Chemizym BH and tanned for 5–7 h at 20–22 °C with chromium compounds (OST 6-18-219-82). The consumption of chromium compounds and water was 5 % and 40 %, respectively, of the pickled pelt weight after acid-salt treatment. The basicity of the chromium tanning compounds was increased by adding magnesium oxide.

The efficacy of pancreatin enzyme product was determined from the amount of gelatin hydrolyzed from pickled and pickled-softened pelts [14]. Preliminary preparation of samples from a semi-finished product for water sorption-diffusion studies is carried out by sample dehydration in alcohol-ether mixture. For diffusion and physicomechanical testing, the samples were standardized under normal conditions: relative humidity 65 ± 5 % and temperature 20 ± 2 °C. Methods for determining hydrolyzed gelatin, sorption-diffusion and physicomechanical properties of a semi-finished product are described previously in the work [14]. The physicomechanical properties of "crust" semi-finished product was determined using a RT-250M machine at an extension rate of 90 mm/min.

Enzyme Effect on Softening a Semi-finished Product

Previous studies of the process of softening of a semi-finished product made from a half-skin of long-term liming for 1.5 years [15] showed (Table I) that with an increase in the duration of alkaline treatment, a significant increase in the acid capacity of the dermis and, correspondingly, a decrease in its shrinkage temperature. As a result of softening, a slight decrease in acid capacity is observed. This can be due to the blocking of the functional groups of collagen by the adsorbed enzyme. The decrease in the shrinkage temperature of pickled and softened pickled pelts at 13–14 °C indicates a decrease in the interaction between the macromolecules of the dermal collagen. Liming for 1.5 years led to the destruction of the biopolymer.

The increase in the liming duration from 5 to 12 d is accompanied by an increase in the amount of gelatin hydrolyzed from the pickled pelt in 2.8 and 3.4 times, respectively, for the butt and the belly (Table II).

Table I. *Physicochemical properties of softened pickled pelts.*

Liming duration [d]	**Acidic capacity [meq/g]** [†]			**Shrinkage temperature [°C] of pelt**		
	pickled	**softened for**		**pickled**	**softened for**	
		1 h	**4 h**		**1 h**	**4 h**
7	1.08	1.05	0.97	64.0	63.0	63.0
14	1.05	0.96	0.97	62.0	61.0	60.0
30	1.15	0.91	1.05	57.0	56.0	56.0
60	1.77	1.57	1.44	50.0	50.0	49.0

Note: *[†] of dried pickled pelt mass.*

Table II. *Kinetics of gelatin hydrolyzation from different areas of softened pickled pelts.*

Area	**Liming duration [d]**	**Hydrolyzed gelatin [%]** [†]			
		pickled	**softened for**		
			1 h	**2 h**	**3 h**
Butt	5	$\frac{3.0}{3.0}$	$\frac{8.7}{14.9}$	$\frac{7.1}{14.5}$	$\frac{5.7}{14.2}$
	12	$\frac{8.3}{8.3}$	$\frac{12.4}{27.4}$	$\frac{12.7}{28.4}$	$\frac{12.4}{28.8}$
Belly	5	$\frac{4.0}{4.0}$	$\frac{12.1}{23.8}$	$\frac{11.7}{23.1}$	$\frac{11.4}{18.7}$
	12	$\frac{13.5}{13.5}$	$\frac{34.0}{41.2}$	$\frac{29.9}{37.5}$	$\frac{29.8}{36.7}$

Note: *pancreatin consumption in the numerator and denominator is 0.6 and 2.2 g/L, respectively; [†] of dried pelt mass.*

This effect is enhanced by increasing the concentration of the enzyme product of pancreatin from 0.6 g/L to 2.2 g/L and the amount of hydrolyzed gelatin increases by 18.7 and 27.4 %, respectively, for the butt and the belly. This indicates the destruction of not only intermolecular bonds, but also the partial destruction of polypeptide chains of the dermal collagen.

With a significant decrease in the concentration of the enzyme product of pancreatin in the technological solution, with its consumption of 0.05 % of the weight of the dried pickled pelt, and a corresponding decrease in its activity upon dilution (Table III), an insufficient degree of softening is observed at the ratio of the pelt weight to the technological solution of 1 : 3. At the same time the gelatin hydrolysis decreases sharply. The desired degree of softening of the pickled pelt is achieved at water consumption of 100–200 % of the weight of the dried pickled pelt and the amount of hydrolyzed gelatin of 8.9–12.1 %.

Table III. *Efficacy of softening pickled pelts.*

Water consumption [%] †	Hydrolyzed gelatin [%] †	Organoleptic evaluation
100	12.1	good
200	8.9	satisfactory
300	7.7	inadequate
400	7.4	unsatisfactory

Note: *† of dried pickled pelt mass.*

Investigation of layer-by-layer gelatin hydrolysis from the pickled pelts after liming for 3 d at a concentration of the enzyme product 2.2 g/L and a temperature of 35–37 °C (Table IV) shows that the gelatin hydrolysis from delimed pickled pelts of the papillary layer is 3.6 times higher than from the reticular dermis.

As it can be seen from Table IV, after softening for an hour gelatin hydrolysis significantly increases, while after 3 h of pancreatin treatment gelatin hydrolysis for the papillary region approaches 100 %, whereas for the reticular dermis the effect is expressed 2.7 times weaker. Thus, after liming for 5 d, almost all the collagen of the papillary layer of the dermis turns into gelatin, with the exception of basal membranes.

Table IV. *Layer-by-layer gelatin hydrolysis from softened pickled pelt in the presence of pancreatin.*

Pickled pelt	Gelatin hydrolysis from layer [%] †	
	papillary region	reticular dermis
Delimed	16.9	4.7
Softened for 1 h	93.6	34.8
Softened for 3 h	99.5	36.1

Note: † of dried pickled pelt mass.

Interpretation of Research Results

The use of the enzyme product Chemizym BH at a consumption of 0.3 % of the weight of the pelt after liming and at water consumption of 100 % (Table V) allows obtaining after softening pickled pelt, which in comparison with the sample after liming has increased porosity, particularly, a specific surface area reaches 22 %.

This can be explained by the destruction of all types of interstructural bonds of the non-collagen components of the dermis with polypeptide chains of the biopolymer, even such strong ones as ionic and covalent. Along with this, air and vapor permeability increase, moreover, for the former one the growth is greater.

However, the diffusion of water vapor is complicated by the fact that sorption and desorption processes occur simultaneously. A significant difference between the processes of diffusion of the components of the air and the water vapor from the flesh and grain sides is explained by the presence of large open pores on the flesh layer of the semi-finished product, which is formed by splitting into two layers the pickled semi-finished product. An increase in the porosity of the semi-finished product after its softening is accompanied by an increase in hygroscopicity and sorption of water vapors, which is important for the comfortable usage of leather products.

Table V. *Sorption-diffuse properties of softened pickled pelts.*

Parameter	Semi-finished product	
	pickled	pickled-softened
Porosity [%]	57.0	66.0
Maximal sorption of water vapor [%]	48.0	57.0
Hygroscopicity [%]	54.0	63.0
Specific surface [m²/g]	112.0	137.0
Capillary moisture [%]	89.0	106.0
Water vapor permeability [mL/(cm²·h)] at the		
– flesh side	12.0	15.0
– grain side	3.5	6.0
Air permeability [mL/(cm²·h)] at the		
– flesh side	690.0	910.0
– grain side	570.0	690.0

The efficacy of the softening process can also be observed in the specificity of the kinetics of changes in the complex of physicomechanical parameters (Table VI). Particularly, after an hour of softening of the pickled pelt, the strength of both the leather semi-finished product at rupture and its grain layer increases by 21 % compared to the pickled samples. An increase in the duration of softening to 3 h results in approximation of strength value to a value for the pickled semi-finished product, which indicates the weakening of inter-fiber bonds due to the longer duration of the enzymatic treatment. At the same time, the deformation parameters of the samples of the “crust” semi-finished product are increasing. The same effect yields an increase in the residual deformation, which will worsen the ability to form a leather material during the manufacturing process.

Thus, softening for 1 h provides an optimal set of exploitational properties and increased elasticity of the grain layer of the «crust» semi-finished product, which is manifested in the same values of the appearance of a crack on the grain side and the tensile strength of the samples at break.

Table VI. *Physicomechanical properties of the semi-finished product "crust".*

Parameter	Semi-finished pickled product			
	pickled for	softened for		
		1 h	2 h	3 h
Tensile strength [MPa]	12.0	14.5	13.7	12.4
Crack appearance on the grain side [MPa]	10.2	14.5	13.7	12.4
Elongation at 10 MPa [%]	23.0	31.0	35.0	42.0
Elongation at break [%]	36.0	47.0	52.0	64.0
Residual elongation [%]	6.0	11.0	14.0	23.0

Conclusions

For effective formation of the structure and properties of the semi-finished leather product, it is necessary to maintain an optimal ratio between the duration of liming and softening processes under a certain fixed technological regime of raw material processing.

In the production of chrome-tanned elastic leathers for shoe, clothing, and haberdashery products, the duration of the dehairing-liming can be considered sufficient for 12 h and softening for 1 h under standard conditions using the enzyme product Chemizym BH at a consumption of 100 % of the weight of the pickled semi-finished product.

The examined results of the study suggest a wide use of enzyme products in the soaking and liming processes of processing of raw leather materials, which significantly reduce the application of harmful chemical reagents and ensure an increase in the ecological compatibility of production.

References

[1]. **Severina E.** Biochemistry. Textbook (in Russian). GEOTAR-Media 2004, Moscow.

[2]. **Gonskiy I. and Maksimchuk P.** Human biochemistry (in Ukrainian). Ukrmedknyga 2001, Ternopil.

[3]. **Shestakova I.** Enzymes used for leather and fur production (in Russian). Legprombytizdat 1990, Moscow.

[4]. **Širvaitytė J., Valeika V., Beleška K., et al.** Bating of pelts after deliming with peracetic acid. *Proceedings of the Estonian Academy of Sciences* **55** (2006) 93–100.

[5]. **Afsar A. and Cetinkaya F**. Studies on the degreasing of skin by using enzyme in liming process. *Indian Journal of Chemical Technology* **15** (2008) 507–510.

[6]. **Sukhoverkova A., Antipova L., Kosenko I., et al.** Modern methods of manufacturing of dehaired hides from rabbit skins (in Russian). *Modern Problems of Science and Education (in Russian)* **3**, 2 (2009) 74–75.

[7]. **Antipova L., Vasilenko O., Kosenko I., et al.** Enzymic technology of dehairing rabbit skins (in Russian). *Announcer of the Voronezh State Technological Academy* **3**, 37 (2008) 61–65.

[8]. **Choundhary R., Jana A., and Jha M.** Enzyme technology applications in leather processing. *Indian Journal of Chemical Technology* **11** (2004) 659–671.

[9]. **Gricenko I.** Single technology of treatment of rabbit skins (in Russian). Central Scientific Research Institute of Information and Technical and Economic Research of Light Industry (in Russian) 1990, Moscow, pp. 13, 29, and 45.

[10]. **Biriukov A.** Technology of fur sheepskin processing (in Russian). Central Scientific Research Institute of Information and Technical and Economic Research of Light Industry (in Russian) 1990, Moscow, pp. 85, 167, 169, and 197.

[11]. **Biriukov A.** Technology of woolskin processing (in Russian). Central Scientific Research Institute of Information and Technical and Economic Research of Light Industry 1982, Moscow, pp. 22 and 82.

[12]. **Taylor M.** Enzymes assist recovery of chrome and high-value protein from shavings. *World Leather* (1994).

[13]. **Danylkovych A., Romaniuk O., and Statsenko D.** Formation of porous structure of leather under the influence of electroactivated proteolytic enzyme solutions (in Russian). XIX International Scientific and Practical Conference "Leather and fur in the XXI century: technology, quality, ecology, education". Publishing House of the East-Siberian State University of Technology and Management 2013, Ulan-Ude, 42–48.

[14]. **Danylkovych A.** Practicum in chemistry and technology of leather and fur (in Ukrainian). Fenix (Publisher «Фенікс») 2006, Kyiv.

[15]. **Babakina V.** Application of enzymes in leather production (in Russian). Rostekhizdat (in Russian) 1962, Moscow.

6. STRUCTURING OF COLLAGEN OF THE DERMIS DURING RAWHIDE FORMATION

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Abstract: *The research on chemocolloidal characteristics of the stepwise formation of a structured semi-finished leather product has been carried out. It is established that the activity of basic chromium sulfate complexes increases significantly upon transition from anionic to cationic form. During plasticizing of dermis structure by alkylcarboxyethanolamine tannins, diffusion of basic chromium sulfate complexes into dermis accelerates and provides a high level of chemical structuring of collagen of the dermis. Environmentally-effective chrome-tanning technologies for production of leather rawhide "wet blue" and non-chrome-tanning technologies for producing semi-finished leather products of polyfunctional application were designed.*

Keywords: *rawhide; collagen of the dermis; structuring; tanning.*

Introduction

In the multistage process of manufacturing polyfunctional leather materials along with alkaline treatments of collagen-containing rawhide, irreversible, mainly chemical structuring of dermal collagen, plays a special role. Produced semi-finished product is characterized by increased resistance to moisture, chemicals, microorganisms, and mechanical influences. Dynamic porous structure of the semi-finished product is capable of evolutionary change in subsequent operations and processes of technological cycle, where the replacement of tanning solution with reagents that largely determine the functional properties of leather material takes place. The efficacy of the structuring process of the collagen of the dermis significantly depends both on its colloidal and chemical state and on the chemical composition, structure, and tanning conditions of semi-finished product.

A wide range of chemicals are used for structuring of collagen of the dermis. On the one hand, the chemicals are supposed to provide a necessary complex of physicochemical properties of leather material while the developed technologies – to have a minimal negative effect on the environment, on the other hand. Particularly, this applies to chromium tannin compounds which are used in large volumes and for which relatively low efficiency of application is observed (70–80 %) [1]. The need for its use is caused by the necessity to form leather material with improved elastic-plastic properties. This causes a large number of research studies in search of new effective reagents and conditions for their use in tanning technology. Along with chromium compounds for structuring the collagen of the dermis inorganic tanning compounds of aluminum (III), zirconium (IV), titanium (IV), and iron (II) [1, 2] and organic tannins – tannids, aldehydes, and derivatives of the naphthalene, polyphenols, and others are used [3, 4].

For providing a leather material with complex exploitational properties, considerable interest is focused on alternative tanning methods [2, 5, 6] which utilize the tannins of different composition. Thus, the use of alginic acid aldehyde with glutaraldehyde, oxazolidine, and tetrakis(hydroxymethyl)phosphonium sulfate [5] provides improved physicochemical properties of semi-finished product with shrinkage temperature of 97 °C while reducing the content of hazardous substances in waste solutions. The work mentions that to obtain a material with high hydrothermal stability it is necessary to use at least two different types of reagents.

Significant increase of efficiency of chromium (III) compounds in structuring leather semi-finished product may occur when chemical compounds with active imino- and carboxyl groups are applied [7]. Particularly, this can be applied to microemulsion of butyl acrylate copolymer and polymer based on amino acids with the molecular weight of 6×10^5 Da and particle size of 40 nm. This semi-finished product is characterized by shrinkage temperature higher by 16 °C compared to that of chrome tanning. Significant reduction of the content of chromium (III) compounds in tanning solution is achieved through vegetable tanning by pretreating semi-finished product with oxazolidinium with final treatment by chromium tanning agent.

The research papers [9, 10], in which the positive influence of the collagenase enzymes on the effectiveness of tanning of the leather semi-finished material has been observed, arouse interest. Thereby the tanning effectiveness increases by 60 %, the hydrothermal stability of the semi-finished product increases, and the duration of tanning process decreases. It happens due to disruption of interfibrillar bonds that intensifies the diffusion of tannins into the corium. The environmentally-safe tanning process of the semi-finished product is achieved owing to the use of nano-SiO_2 and enzymes. The stage of liming is excluded from the process [11]. It should be noted that the final semi-finished product with the shrinkage temperature of 371 K without liming has a high density but insufficient elasticity. Despite the fact that the tanning composition synthesized based on methacryloxypropyl silica, maleic anhydride, and styrene in the toluene medium at 358 K in the presence of benzoyl peroxide with its following neutralization increases the shrinkage temperature and the thickness of the semi-finished material by 17 K and 70 %, respectively [12], it does not contribute to the increase of the elastic leather material area, which limits its practical usage. Under the total excluding of chrome (III) compounds from the tanning process [13] it is impossible to obtain leather material with the complex of necessary elastic-plastic properties.

The influence of external fields, namely the supersonic one [14, 15], and pressure [16] can contribute to the increase of the structuring process intensity. The comparative study of the semi-finished material tanning in static and dynamic conditions under the effect of supersonic energy has discovered considerably higher (almost 4 times) effectiveness in the former case. Carrying out the tanning process of the semi-finished material using chrome (III) compounds under the pressure up to 10 MPa using CO_2, as in the previous case, requires using of special equipment and implies additional expenses.

Taking into account the important role of the tanning process in technologies of leather materials production, a large number of works, mainly of empirical character, uses a large variety of chemical agents for structuring collagen of the dermis. It is important to note rather small number of articles, in which chemocolloidal regularities and structural transformations of the semi-finished product at this stage of the technological cycle are being observed. The variety of chemical composition and structure of the used agents stipulates the specific mechanism of their action in the process of obtaining the structured material that requires carrying out of systematic scientific research in this area, which can be used as the basis for development of scientifically-based technologies of chrome-tanned semi-finished material production – wet blue, combined methods, and leather materials of polyfunctional application.

This article presents the investigation results of the mechanism of action of the base chrome (III) sulphate, derivatives of ethanolamine, and tannins of the pyrocatechine class (condensed) at the structuring of the corium collagen and developed technologies for the production of the tanned semi-finished product.

Methods and Materials

For experiments the samples of the limed semi-finished product have been used. The product was obtained by using previously developed and introduced at PJSC Chinbar (Kyiv, Ukraine) technology of liming-soaking with the usage of the enzyme during the soaking stage and sodium hydrosulfide and amine at 300–302 K during liming process. After washing and fleshing the halves of the semi-finished product with the thickness of 6.3–6.7 mm decreased to 2.4–3.0 and 3.0–4.2 mm depending on the peculiarities of its structuring. Before tanning the half-skins, the semi-finished product underwent deliming-softening treatment at 307–309 K for the conversion of structured calcium into a soluble state using ammonium sulphate and further disruption of mucopolysaccharides bonds with collagen macromolecules in the presence of the enzyme protosubtilin G3× and anionic surfactant.

Hide powder (HP) from cattle hides have been used as a collagen specimen.

For the tanning of rawhide, the following agents have been used:

– basic chromium sulphate (BCS), $Cr_2(SO_4)_n(OH)_{6-2n}$ (technical specification, TU 2141-033-54138686-2003);

– tannins of mimosa and willow (GOST 17-121-71);

– synthetic tanning agent β-naphthalene sulfonate (BNS) – a synthesis product of 2-naphtholesulfonic acid with dioxidiphenylsulfone (technical specification, TU 17-06-165-89).

Alkylcarboxylethanolamines (ACEA; technical specification, TU 3480224-79) have been used as a regulating reagent of BCS interaction with collagen:

$$HO(CH_2)_2NH_3^+ \cdot {}^- O(O)CR,$$

where R is the radical of aliphatic acids of fraction C_7–C_9 (ACEA AA) (GOST 23239-89) or the radical of naphthenic acid of gas-oil fraction (ACEA NA) (GOST 13302-77) containing 25–30 % of polycyclic acids and with average molecular weight of 244 Da.

The investigation of interaction of corium collagen with ACEA and BCS were carried out on model systems using HP which was modified in 0.8 % solution of ACEA with the 1:10 weight ratio of HP to the solution of the chemical agent with the following addition after 30 min of the same quantity of BCS with basicity 38 % at 293 K. For HP samples after the acid–saline processing the solution of $NaCl$ and H_2SO_4 at 5.5 and 0.6 % of the mass of the hydrated HP, respectively, was used. After 2 h from the beginning of the process 10 % of 0.3 % Na_2CO_3 solution relative to the HP weight was added. The duration of the BCS processing was 5 h.

In the tanning process of semi-finished product also $NaCl$ (technical specifications, TU 9192-069-00200009527-98), $HCOOH$ (GOST 1706-78), and H_2SO_4 (GOST 2184-77) have been used.

The pH testing of BCS aqueous solutions and other tanning substances was conducted on pH-340 apparatus. The sorption of ACEA and BCS by corium collagen was analyzed by gravimetrical and chemical methods, respectively [17]. The hydrothermal stability of the semi-finished product was evaluated by the temperature (T_{HS}) of the onset shrinkage during sample heating in water-glycerin mixture. The dependence of sorption of water vapors (W) by the semi-finished product on their relative elasticity (φ) was analyzed at 293 K according to the previously described methods [18]. The dependence of the relative diffusion depth (h) of the structuring agent on the duration of processing was analyzed on sample cross section using MBI-3 microscope.

The thermal and thermodynamic characteristics of the modified HP were analyzed thermogravimetrically on the derivatograph OD-102 of F. Paulik – J. Paulik – L. Erdey system (MOM, Budapest, Hungary) within the temperature range of 293–

873 K at the heating rate of 10 K/min [19] in the helium atmosphere. The ordering effect of the HP collagen structure was evaluated as an enthalpy of melting (ΔH), relative to the thermal effect of the standard – benzoic acid, and the total activation energy of destruction (E_a), which characterizes the defects in the supramolecular collagen structure, was calculated using Frieman-Carrol method [20]. The thermostability of HP was evaluated according to the weight lost upon heating to 573K (Δm_{573}). The temperatures of the onset and the maximum of melting, T_{om} and T_{mm}, respectively, the temperature of the onset of destruction T_{od}, and the temperature T_{md} at which the maximum destruction rate is reached testify the interaction intensity between macromolecules of HP collagen.

The electron microscopy study of the rawhide structure was carried out using scanning electronic microscope REMMA-102 (Selmi, Ukraine) [21]. The optimization of the tanning process with identification of the optimal parameters for its control and the condition of the semi-finished product have been carried out using compositional rotatable Box-Hunter design of the second-degree and the Harrington's function [22].

Results and Discussion

The mechanism of interaction of hydroxyl-chromium sulphate complexes with dermal collagen

For carrying out the semi-finished product structuring process effectively, it is necessary to implement availability and chemical activity of certain functional groups of the dermal collagen and the base chromium sulphate or other tanning agent. Depending on the chemical composition of the structuring agent it is necessary to activate acidic and basic groups using chrome compounds or vegetable tanning agents. The fragment of the microfibril [23] (Table I) can give evidence about the peculiarities of the chemical composition of collagen of the dermis.

According to Table I, collagen of the dermis on the nanostructured level is characterized by the presence in the polypeptide chains of macromolecule of amino acids with different chemical activity, which varies depending on the external pH. The charges of the microfibril triads are located in its structural weaknesses unevenly, along which the links with structuring agent are formed. The centers of interaction are located in the lateral polypeptide chains at different distances from it, due to their length, and form more accessible amorphous areas of microfibrils.

Table I. *The microfibril fragment.*

Triad number	**Macromolecule fragment number**					**Charge**
	1	**2**	**3**	**4**	**5**	
8	GGG FFF QQQ	GGG **EEE** P′P′P′	GGG AAL P′P′P′	GGG *KKK* **EEE**	GGG PPP AAA	– 3, + 3 – 3
9	GGG PPP P′P′P′	GGG AAP P′P′A	GGG PPP SSA	GGG SST *KKK*	GGG PPP *RRR*	+ 6
10	GGG **EEE** P′P′P′	GGG NNS *KKK′*	GGG AAA *RRR*	GGG PPP *RRR*	GGG PPP P′P′A	+ 9
11	GGG **EEE** P′P′P′	GGG **DDE** TTS	GGG **EEE** *RRR*	GGG **EED** TTQ	GGG SSP AAS	– 12 + 3

Note: *The notation of amino acids according to IUPAC: glycine – G, phenylalanine – F, glutamic acid – E, alanine – A, leucine – L, lysine – K, proline – P, glutamine – Q, hydroxyproline – P′, serine – S, arginine – R, asparagine – N, hydroxylysine – K′, aspartic acid – D, threonine – T; the lines on the left indicate stable areas of triads.*

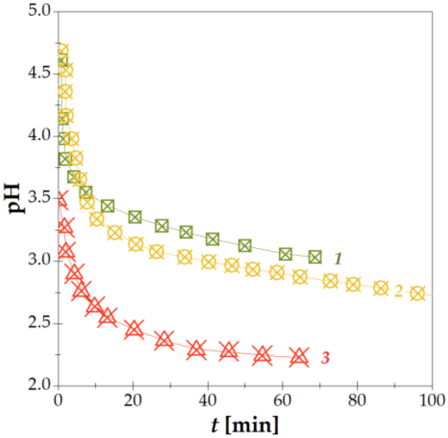
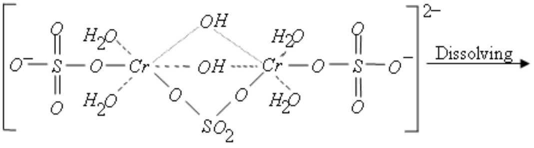


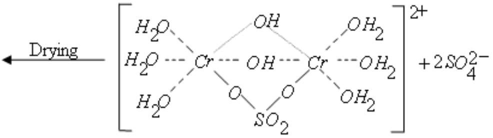
Fig. 1. *Kinetics of pH change during dissolving BCS with different concentration: 40 g/dm³ (1) and 10 g/dm³ (2, 3) at 293 K (1, 2) and 310 K.*

In the hydrated state the intermolecular distances increase to 0.6–0.8 nm [23] and between the microfibrils – to 2.7 nm [23]. Considering the size of chromium hydroxyl sulfate (CHS) complexes after the transition in cationic form – 0.7 nm, we can assume that the structure of collagen of the dermis will be available to interact with BCS after the appropriate preparation. For larger particles of the structuring agents, their interaction with collagen of the dermis occurs on the microfibrillar and fibrillar levels.

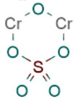
Considering the characteristics of the complex structure of BCS it is possible to regulate its interaction with collagen of the dermis. The results of BCS dissolution in water showed a significant decrease in pH solution, which is especially intense during the first 10 min (Fig. 1). Moreover, this effect is more clearly seen at a higher temperature.

The process of dissolving BCS may occur according to the following reaction:





Thus, there is a transition of sulphate groups from the inner sphere of the anionic form complexes to the outer one, as a result of their displacement with water molecules. As a result, a cation form of CHS complexes with a decreased activity at lower pH is formed. At higher pH the nuclearity of CHS complexes increases as a result of combining chrome complexes through interaction of hydroxyl groups with their following condensation [25] and formation of bonds with participation of sulphate groups:



Considering the location of the carboxyl groups and the distance between them in the collagen microfibril with the volume 1D, that corresponds to a displacement of one macromolecule toward another by 67 nm [26], the possible types of bonds that form CHS complexes with neighboring macromolecules of single-level or adjacent triads – type 1, through one or two triads – type 2, and through the macromolecule and one or two triads – type 3, were examined (Fig. 2).

GGG	GGG	GGG	GGG	GGG
FFF	***$3RCOO^-$***	AAL	KKK	PPP
QQQ	P′P′P′	P′P′P′	***$3RCOO^-$***	AAA
GGG	GGG	GGG	GGG	GGG
PPP	AAP	PPR	SST	PPP
P′P′P	P′P′A	SSA	KKK	RRR
GGG	GGG	GGG	GGG	GGG
$3RCOO^-$	NNS	AAA	PPP	PPP
P′P′P′	KKK′	RRR	RRR	P′P′A
GGG	GGG	GGG	GGG	GGG
$3RCOO^-$	***$3RCOO^-$***	***$3RCOO^-$***	***$3RCOO^-$***	SSP
P′P′P′	TTS	RRR	TTQ	AAS

Fig. 2. *Possible interactions of CHS complexes in collagen microfibril.*

If two carboxyl groups interact with one molecule of binuclear CHS complex or the one of higher nuclearity, then bonds of type 1 and 3 in collagen dermis can be formed according to distance between ionized carboxyl groups. At the beginning of collagen interacting with binuclear CHS complexes, bonds of type 1 are formed. If pH increases, the size of chrome complexes increases due to hydrolysis of BCS which promotes formation of bonds of type 2 and 3. The possible number of formed outer- and intermicrofibrillar bonds is given in Table II.

Table II. *The number of possible bonds of CHS complexes in 1D volume of collagen microfibril.*

Bond type	Distance [nm]	Number of bonds	
		inner	outer
1	0.6–0.8	27	42
2	0.8–1.4	29	54
3	> 1.4	27	45

While calculating the number of possible bonds of CHS complexes with collagen it was taken into account that the number of carboxyl groups in volume 1D of microfibril that can interact is 226. The number of possible bonds of type 1 is 61 % and of type 2 – 73 %, which is due to more advantageous geometrical position of carboxyl groups to form the bonds of this type. Actually, there will be less carboxyl groups in comparison to number of bonds of type 1, as the bonds of types 2 and 3 are formed after gradual increase of technologic solution pH to 4.2–4.4 at an increase of basicity of CHS complexes and accelerated structuring of dermal collagen. Upon 100 % participation in interaction of carboxyl groups of collagen with CHS complexes, if one carboxyl group bonds one atom of chrome, 5.5 g of binuclear complexes are required on 100 g of collagen. In practice, the number of chrome complexes that effectively take part in chemical structuring of collagen of the dermis corresponds to 60–65 % of the total number of carboxyl groups in collagen.

The increase of basicity and number of CHS complexes that interact with dermal collagen helps to increase its hydrothermal stability which changes symbatically with the effectiveness of interaction and degree of structuring (Table III).

Table III. *Hydrothermal stability of dermal collagen under the effect of CHS complexes.*

CHS complexes		**Cr_2O_3 [%] in semi-finished product**	**T_S collagen [K]**	
Cr_2O_3 [%] relative to limed semi-finished product weight	**Basicity [%]**		**after stabilization**	**after 12 h**
1.1	34.0	3.47	374	378
1.2	42.0	3.78	377	380
1.3	34.0	4.12	380	384
1.3	26.0	4.89	379	386

The effect of basicity on hydrothermal stability is observed while interacting during the first stage of binuclear CHS complexes structuring. It should be noted that shrinkage temperature of semi-finished product has the maximal value when the nuclearity of CHS complexes is increased in (during) 12 h, and so it depends on the kinetics of their interaction with dermal collagen.

The sorption results by semi-finished product and its structure change show the effective interaction of CHS complexes with dermal collagen (Fig. 3). The sorption isotherm of water vapor can indicate a wide distribution of pore sizes in the samples and its sorption increase in the area of capillary condensation. At the beginning of sorption, the isotherms are characterized by linear dependency of moisture content (W) in the samples on relative pressure up to 0.1–0.2.

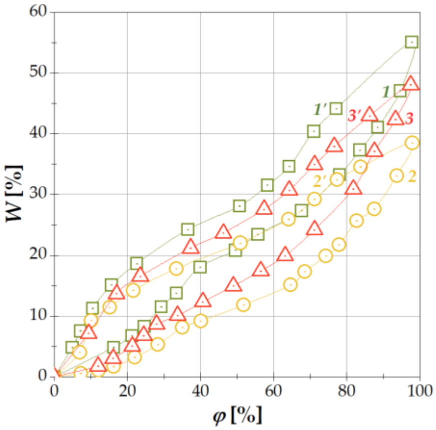


Fig. 3. Isotherms of water vapor sorption (1–3) and desorption (1′–3′) by samples after enzymatic treatment (1 and 1′), treatment with CHS complexes (2 and 2′), and alkaline treatment (3 and 3′).

Hysteresis on the sorption–desorption curves corresponds to the higher value of residual moisture during desorption and it indicates high hygroscopicity of dermal collagen at different processing stages. The maximal value of water vapor sorption by dermal collagen of structured CHS complexes reaches 17 % compared with the samples of enzymatic treatment. It shows the decrease of concentration of collagen hydrophilic groups as a result of their active interaction with CHS complexes and intermolecular bonds formation. It should be noted that the hydrophilicity of structured dermal collagen is high and moisture content in it will decrease during further technological processing.

To provide the effective diffusion of CHS complexes into dermal structure it is necessary to decrease the activity of carboxyl groups of collagen macromolecules by decreasing pH or their temporary blocking. The results of thermogravimetric study (Fig. 4 and Table IV) show that derivatograms are characterized by the presence of two endothermic effects that are overlapped in a considerable temperature interval. The first endothermic effect corresponds to the melting of crystalline collagen while the second

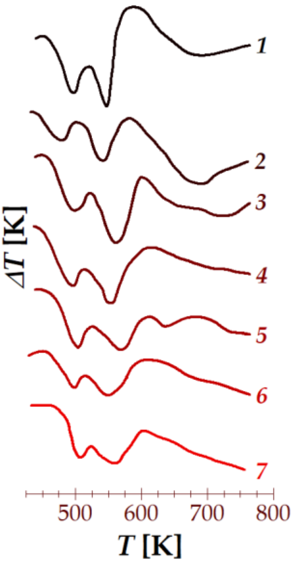


Fig. 4. *Thermograph of HP: without treatment (1), acid-salt treatment (2), acid-salt treatment + BCS (3), ACEA NA (4), ACEA NA + BCS (5), ACEA AA (6), and ACEA AA + BCS (7).*

Table IV. Thermodynamic and thermal characteristics of HP modified with ACEA.

HP treatment	Melting temperature [K]		ΔH [kJ/kg]	Temperature of destruction [K]		Δm_{300} [%]	E_a [kJ/mol]
	T_{bm}	T_{mm}		T_{bd}	T_{md}		
without treatment	454	497	25.8	514	551	20.8	109
acid–salt	448	485	46.6	502	546	22.1	85
acid–salt + BCS	458	503	46.5	522	557	19.2	118
ACEA NA	452	492	50.7	512	553	21.1	107
ACEA NA+ BCS	463	506	43.2	525	565	14.8	127
ACEA AA	453	494	51.5	513	551	21.4	104
ACEA AA + BCS	476	508	44.8	523	561	16.7	122

one – to its thermal destruction. Thermodynamic and thermal characteristics determined from the curves indicate that after acid-salt treatment the samples become more stable and less likely to be destroyed. After acid-salt treatment the thermodynamic and thermal characteristics decrease and significant increase in weight loss and destruction rate of the samples increase compared to the original HP. It indicates the lower thermal stability of collagen towards destruction. This effect can be caused by partial dehydration of structural elements of dermal collagen as a result of osmotic effect of transition of free water molecules of collagen into salt solution that fill the inter structural space starting from inter macromolecular ones. During this process inter structural space in collagen is increased.

Unlike acid-salt treatment after modification of HP with ACEA, temporary blocking of carboxyl groups of collagen by basic ACEA groups and its structural plasticizing effect on inter macromolecular interactions in collagen takes place. It can be seen in the increase of ΔH of modified HP. The next processing of HP powder with BCS, both after acid-salt and ACEA treatments, is accompanied by increase of thermal and thermodynamic characteristics of structured samples as a result of interaction of CHS complexes with ACEA and collagen forming chemical special chemical bonds between carboxyl groups of neighboring polypeptide chains of biopolymer.

The treatment with BCS of HP, previously modified with ACEA, is accompanied by an increase of thermodynamic characteristics compared with HP from previous treatment. It can indicate an active effect of ACEA on the increase of structuring activity of CHS complexes. More uniform diffusion of CHS complexes into the dermal collagen microfibrils is possible as a result of additional interaction of ACEA molecules with dermal collagen.

The dependence of rawhide hydrothermal stability on ACEA concentration in the technological solution indicates the plasticizing effect of ACEA on the structure of collagen of the dermis during its structuring (Table V). As it can be seen from the data, T_{HS} and BCS sorption by semi-finished product after treatment with ACEA and CHS complexes reach the extreme value depending on the ACEA concentration in technological solution while these

Table V. The properties of rawhide structured with BCS in the presence of ACEA.

Hide treatment	ACEA [g/L]	BCS sorption [%]	Cr_2O_3 [%]	α	T_S of collagen after processing [K]	
					ACEA	BCS
ACEA AA	13.0	82.0	4.5	0.68	63.0	98.0
	24.0	88.0	4.8	0.85	62.0	112.0
	35.0	94.0	5.1	0.89	61.0	117.0
	46.0	87.0	4.6	0.83	60.0	109.0
ACEA NA	13.0	86.0	4.7	0.71	63.0	102.0
	24.0	92.0	5.0	0.92	62.0	118.0
	35.0	89.0	4.8	0.87	61.0	109.0
	46.0	83.0	4.4	0.81	59.0	106.0
acid–salt treatment	—	43.0	2.4	0.59	48.0 [1]	77.0
without treatment	—	74.0	4.0	0.43	64.0	87.0

Note: *1) T_S of semi-finished product after acid-salt treatment.*

values for acid-salt treatment are significantly lower. Moreover, distribution coefficient (α) of chrome compounds in dermal layers is lower than in semi-finished product after ACEA treatment. It can indicate that the previous ACEA treatment of semi-finished product before its structuring provides a high uniformity of the process of collagen interacting with ACEA and BCS complexes.

When the amount of ACEA is small, slight decrease in T_{HS} of the dermis is detected. Thus, one can observe plasticizing effect caused by partial destruction and corresponding weakening of interchain hydrogen bonds with slight destabilization of the collagen structure facilitating diffusion of CHS complexes in the volume of the dermis and the formation of higher number of chemical bonds of type 1–3. With increasing concentration of ACEA, plasticizing effect is enhanced resulting in stronger destabilization of the collagen structure, which manifests itself in further reduction of its T_{HS} and BCS sorption after reaching the extreme value.

A significant increase of collagen T_S observed in the ternary system is caused by the interaction of the carboxyl groups of the collagen with ACEA at the beginning of its treatment by the solution and BCS stabilized by ACEA, which contributes to reduction of the activity of CHS complexes on the first stage of collagen structure stabilization and facilitates the diffusion of ACEA-BCS complexes into its microfibrillar structure. On the second stage monoethanolamine ACEA interacts with chromium (III) cation in its first coordination sphere. There is a domination of the interactions between chromium cations located nearby, and ionized carboxyl groups of collagen over the interactions between these groups and free ACEA. As a result of competitive interaction, collagen carboxyl groups enter the near sphere of chromium (III) complex, thus pushing ligands placed in trans configuration relative to the cycle formed by monoethanolamine cation ACEA.

Trans-effect of monoethanolamine ACEA contributes to entering ionized carboxyl groups of collagen in the near sphere of chromium complexes and formation of coordination bonds between them. In excess of ACEA, compared to the optimal number, significant decrease appears in BCS activity due to increased complexation of its particles with this reagent and transition of stabilized chromium complexes into neutral complexes with the decrease of their chemical activity accompanied by a decrease of semi-finished product T_{HS}.

Thus, the use of ACEA in prestabilizing treatment of semi-finished product allows carrying out the stabilization of collagen structure of the dermis and its formation using BCS complexes with reduced basicity. The use of complexes with low basicity provides a required pH value of environment for effective structuring and stabilization of semi-finished product.

Interaction of Tannins and Rawhide

Environmental requirements for modern technologies lead to hazardous chemicals and materials usage reduction in manufacturing processes. In this regard, promising technologies of rawhide processing is the use of structuring agents of plant origin – vegetable tannins, which can form a large number of hydrogen bonds with the amino groups of collagen macromolecules and effectively fill the microscopic pores in the structure of the dermis and act as active filler. Since the size of the tannin particles is much larger compared to CHS complexes [27], we can expect a low rate of their diffusion in rawhide structure (Fig. 5). To a large extent this explains the need to fix the structure of the dermal collagen by low-molecular weight agents, including BCS, formaldehyde, sodium polyphosphate, and others [28].

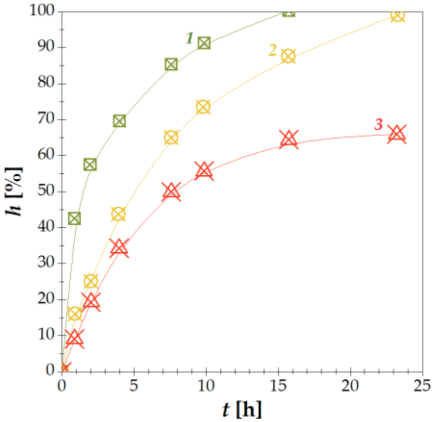


Fig. 5. *Diffusion kinetics of tannins into semi-finished product structured by CHS: 4 : 1 mimosa-BNS mixture (1), mimosa (2), and willow (3).*

According to the results of the study of vegetable tannins diffusion in the semi-finished product (3.0 mm in thickness) pre-structured with CHS complexes (1.0 % Cr_2O_3 of the weight of semi-finished product) (Fig. 5), the minimal rate of particles diffusion is observed in the case of willow tannins, while the maximal rate – for a mixture of mimosa tannins and syntan BNS. In the first case tannins penetrate at the depth of only 66 % of the semi-finished product thickness during 24 h, while tannins mixture diffuses throughout the semi-finished product during 16 h. Intermediate value takes mimosa tannins that penetrate the semi-finished product during 24 h.

The data indicate the smaller particle size of mimosa tannins compared to willow tannins. A significant increase in the rate of tannin diffusion and possible structuring acceleration of the semi-finished products with the use of synthetic tanning BNS is caused by its disaggregation effect on particles of vegetable tannins and corresponding decrease in their size.

The study of influence of vegetable tannin type on structuring of the semi-finished product (Fig. 6) shows that pre-stabilized structure of semi-finished product with CHS complexes has T_{HS} equal to 357 K which further increases due to the interaction with plant tannins of a polyphenolic type.

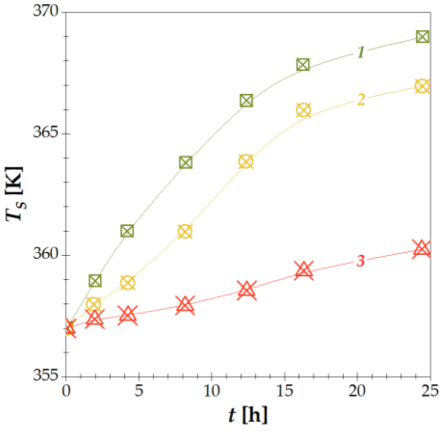


Fig. 6. Dependence of T_{HS} of semi-finished product structured by CHS complexes on duration of its interaction with tannins: 4 : 1 mimosa-BNS mixture(1), mimosa (2), and willow (3).

The dependence of T_{HS} on structuring duration is adequate to diffusion kinetics of vegetable tannins into the structure of semi-finished product. The maximal effect of structuring is observed using a tanning mixture of mimosa and synthetic BNS. It is important to note that reduced diffusion depth and smaller effect of their interaction with dermal collagen is accompanied with a slight increase in T_{HS} due to interactions of tannins with microfibrils in the surface layers of the semi-finished product.

The evolution of structure of dermal collagen in the presence of CHS complexes and vegetable tannins is shown on cross section microimages of the semi-finished product at various stages of treatment (Fig. 7). As it can be seen from Fig. 7a, bundles of collagen fibers of the dermis after enzymatic treatment of pickled semi-finished product are connected in structural elements of larger sizes; the pores being evident between them.

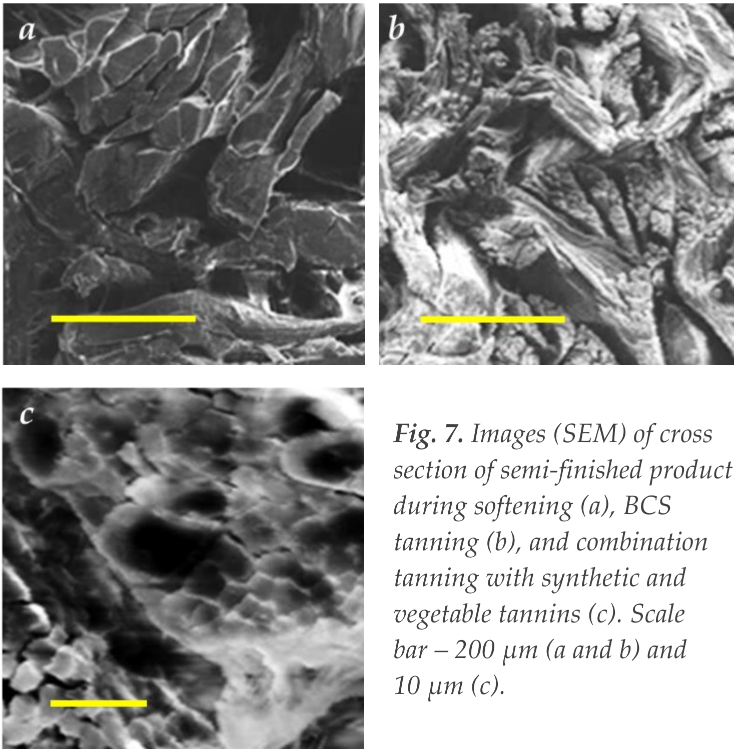


Fig. 7. *Images (SEM) of cross section of semi-finished product during softening (a), BCS tanning (b), and combination tanning with synthetic and vegetable tannins (c). Scale bar – 200 μm (a and b) and 10 μm (c).*

During acid-salt treatment followed by dermal collagen structuring by CHS complexes, the division of fiber bundles into elementary fibers begins to appear (Fig. 7*b*) with an increase in number of pores and a decrease of their size. After synthetic structuring of the dermal collagen due to precipitation of tannin particles on the surface of fiber bundles, the properties of the studied structure of samples have not appeared clearly, even at 2500× magnification (Fig. 7*c*). At the same time large pores remain visible.

Thus, the results on the diffusion kinetics of 4 : 1 tannin mixture of mimosa and synthetic BNS, relatively high hydrothermal stability of structured dermal collagen, and microscopy study give reason for the application of synthetic and vegetable tannins in leather treatment technologies of the semi-finished products.

Tanning technologies of leather semi-finished product

Taking into account the peculiarities of structuring process of dehaired semi-finished product using tanning compounds of different chemical composition in the implementation of appropriate technologies will determine the effectiveness of the following treatments taking into account the specifics of the previous treatment and formation of leather materials for different functional purposes. The rational use of chemicals must be associated with the structure of semi-finished leather product and depend on the innovation level of used technology.

Based on the previous set of scientific and technological research, a number of optimized technologies for chrome tanning of the dermal collagen yielding a semi-finished leather product "wet blue" [29] and using compounds of synthetic nature and vegetable tannins was developed. The effectiveness of the developed technologies is testified by the results of their comparison with the previously existing industrial technologies at JSC Chinbar (Kyiv, Ukraine) for chrome [30] and chromesyntanvegitable tanning (CSVT) [31]. Comparative characteristics of developed technologies are given in Table VI. In the developed tanning technologies, the CHS complexes of anionic form were used [32, 33], while cationic form of tannins was used as a control. Technology of chrome tanning of split semi-finished product (CTSSFP) involves the use of anionic forms of basic chromium sulphate during tanning of semi-finished product with 3.0 mm in thickness after liming, softening with enzyme agent, and treatment with alkyl carboxyethanolamine emulsion for 0.5 h followed by the addition of $NaCl$ at 291–293 K at drum rotation 8–9 rpm. Tanning is performed on the spent technological solution.

Technology of chrome tanning of unsplit semi-finished product (CTUSFP) unlike CTSSFP technology implies the use of rawhide of over 3.0 mm in thickness after softening and salting of semi-finished product by $NaCl$ concentration of 250 g/L and followed by acid-salt treatment. For this purpose, formic (85 %) and sulfuric (100 %) acids are used (0.25 and 0.50 of the weight of limed semi-finished product, respectively). After a technological solution is drained out, ACEA is added and drum rotation is prolonged for 5 h.

Technology of synthetic tanning of semi-finished product (STSFP) requires twice longer alkaline treatment for deeper loosening of its fibrous structure of the semi-finished product caused by the use of tanning agents with larger particle sizes. To ensure effective tannin diffusion into the structure of semi-finished product with 2.4 mm in thickness, after its acid-salt treatment the product is structured by BCS with significantly less consumption, compared to chrome tanning technologies. Before synthetic tanning the semi-finished product has been processed using a fresh solution containing synthetic BNS (consumption 2.5 % of tannins of the weight of semi-finished product) for 1 h with addition of ACEA emulsion and its subsequent structuring by vegetable tanning agent.

Table VI. *Characteristics of tanning technologies of leather semi-finished product.*

Parameter	Tanning technology				
	CTSSFP	CTUSFP	SVTSFP	Control	
				chrome	CSVT
BCS [%] [1]	4.4	5.2	1.6	8.8	2.4
ACEA	0.6	0.7	3.0	–	–
sodium chloride	2.5	4.0	4.5	6.0	6.0
water	20	40	50/120	70	100/120
mimosa extract	–	–	10	–	12
BCS basicity [%]	33.0	34.0	40.0	38–42	38–42
Total duration [h]	6.0	11.0	24.0	18.0	10 [4] / 42
BCS absorption [%] of the original mass	96.5	93.2	98.0	75.6	89.3
Hydrothermal stability [K]	107.0	106.0	85.0	104.0	87.0
Cr_2O_3 [%] [2]	3.9	4.1	–	4.6	–
Area yield [%] [3]	93.0	94.0	97.0	87.0	95.0
Consumption of energy [kW]	42.0	66.0	144.0	108.0	196.0

Note: *1) of the mass of limed semi-finished product; 2) on a dry basis; 3) of pickled hide area; 4) the duration of preparation for tanning with synthetic and vegetable tannins; CTSSFP, CTUSFP, and SVTSFP stands for the technology of chrome tanning of split semi-finished product, chrome tanning of unsplit semi-finished product, and synthetic and vegetable tanning of semi-finished product.*

Comparative analysis of chrome tanning and previously existing technologies shows significant reduction of BCS, sodium chloride, and water consumption. Moreover, these technologies provide a considerable decrease in the treatment duration with corresponding savings in electricity. Environmentally safer SVTSFP technology provides significantly lower costs of chromium compounds. This is owing to lower T_s of tanned rawhide compared to chromevegetable tanning technologies. However, this technology provides the highest area yield of hide that is used to make a certain range of footwear products. Due to efficient use of chromium compounds in chrome and synthetic tanning these technologies belong to environmentally friendly and energy-saving.

Conclusions

Comprehensive study of the effect of tanning compounds of different chemical nature on the process of structuring collagen of the dermis made it possible to establish the mechanism of interaction of chromium compounds and alkylcarboxyethanolamine, and specifics of the use of tannins. It was established that the activity of basic chromium sulfate systems is increased significantly during transition from anionic to cationic form. These binuclear complexes of chromium (III) due to their nanosize diffuse into the structure of the dermis reaching polypeptide chains of collagen microfibrils to form coordination bonds between ionized carboxyl groups of side chains of its macromolecules. While plastifying structure of the dermis by alkylcarboxyethanolamine due to the temporary blocking of active functional collagen groups, diffusion of basic chromium sulfate complexes into the dermis increases, that ensures their effective participation in the structuring process.

It has been shown that efficient use of tannins in rawhide tanning is ensured after previous interaction of dermal collagen with basic chromium sulfate complexes and disaggregation of particles of tanning agents while using synthetic tanning agent. Investigation of hydrophilicity of the semi-finished product in the processes of its physicochemical treatments indicates a significant decrease in the content of technological solution in the semi-finished product during chemical structuring, which is going to be reduced dynamically during further treatments connected with substitution of technological solutions of reagents.

The developed technologies for tanning semi-finished product from cattle rawhides, as compared to previously existing technologies at PJSC Chinbar (Kyiv Ukraine), are characterized by 1.7–2.2- and 4.0-time reduced consumption of chromium (III) compounds for chrome and synthetic tanning of leather materials, respectively. At the same time the duration of the process cycle of chrome tanning is reduced by 1.6 and 3.0 times with corresponding decrease in power consumption. Effectiveness of each technology for producing “wet blue” semi-finished product significantly depends on the kind of rawhide, primarily on its surface area and thickness. Significant decrease of chromium compounds in waste solutions after tanning gives grounds to include the developed technology to an ecologically efficient one. Particularly, it concerns the technology of synthetic tanning. With that, this technology provides the highest saving of scarce raw hides by maximizing the area yield of the material. The technology for producing “wet blue” semi-finished product obtained from different kinds of rawhide at PJSC Chinbar have been implemented. The semi-finished product corresponds to the international standard ISO 9001:2008 “Quality Management System. Requirements”, while the developed technologies expand the assortment of leather materials of polyfunctional application.

References

[1]. **Surkova A., Abdullin I., Zhuravlev B., et al.** *Bulletin of Kazan Technological University* (Publisher «*Вестник Казанского технологического университета*») **6** (2009) 91.

[2]. **Hui C., Jun G., and Zhihua S.** *Journal of the American Leather Chemists Association* **106** (2011) 18.

[3]. **Covington D., Song L., Suparno O., et al.** *World Leather* **23** (2010) 35.

[4]. **Pustylnik J.** *Shoe Leather Industry* (Publisher «*Кожевенно-обувная промышленность*») **3** (2008) 22.

[5]. **Jayakumar G., Bala L., Kanth I., et al.** *Journal of the American Leather Chemists Association* **106** (2011) 50.

[6]. **Covington A.** *Journal of the American Leather Chemists Association* **103** (2008) 7.

[7]. **Kanagaraj J., Gupta S., Baskar G., et al.** *Journal of the American Leather Chemists Association* **103** (2008) 36.

[8]. **Gupta S.** *Journal of the American Leather Chemists Association* **104** (2009) 92.

[9]. **Kanth S., Kannan P., Usharani N., et al.** *Journal of the American Leather Chemists Association* **105** (2010) 16.

[10]. **Kanth S., Kannan P., Usharani N., et al.** *Journal of the American Leather Chemists Association* **104** (2009) 405.

[11]. **Liu Y., Chen Y., Yao J., et al.** *Journal of the American Leather Chemists Association* **105** (2010) 84.

[12]. **Pan H., Qi M., and Zhang Z.** *Chinese Chemical Letters* **19** (2008) 435.

[13]. **Krishnaraj K., Thanikaivelan P., and Chandrasekaran B.** *Journal of the American Leather Chemists Association* **105** (2010) 71.

[14]. **Morera J., Bartoli E., Serrano M., et al.** *Journal of the American Leather Chemists Association* **105** (2010) 150.

[15]. **Morera J., Bartoli E., Combalia F., et al.** *Journal of the American Leather Chemists Association* **105** (2010) 369.

[16]. **Renner M., Weidner E., and Brandin G.** *Chemical Engineering Research and Design* **87** (2009) 987.

[17]. **Danylkovych A.** Practicum in chemistry and technology of leather and fur. Fenix (Publisher «Фенікс») 2006, Kyiv.

[18]. **Greg S. and Syng K.** Adsorption, specific area, and porosity (in Russian). Mir 1984, Moscow.

[19]. **Paulik F., Paulik J., and Erdey L.** *Zeitschrift fur analytische Chemie*. **160** (1958) 241.

[20]. **Rabek Ya.** Experimental methods in chemistry of polymer (in Russian). Mir (Publisher «Мир») 1983, Moscow, 340 p.

[21]. **Gouldstein Dzh., Nyubery D., Echlyn P., et al.** Scanning electron microscopy and microanalysis (in Russian). Mir (Publisher «Мир») 1984, Moscow.

[22]. **Akhnazarova S. and Kafarov V.** Optimization methods of experiments in chemical technology (in Russian). Vysshaia Schkola 1985, Moscow.

[23]. **Lishchuk V., Danylkovych A., and Zhyhotsky O.** *Light Industry* (in Russian) **2** (2011) 27.

[24]. **Heidemann E.** *Das Leder.* **46** (1995) 149.

[25]. **Mikhailov A.** Leather collagen and basics of its processing (in Russian). *Light Industry* (1971), Moscow.

[26]. **Nikitin V., Persky E., and Utevskaia L.** Age-related and evolutionary biochemistry of collagen structure (in Russian) Naukova dumka 1977, Kyiv.

[27]. **Mikhailov A.** Chemistry of tanning agents and tanning processes (in Russian. Gizlegprom 1953, Moscow.

[28]. **Danylkovych A.** *Scientific Bulletin of Poltava University of Consumer Cooperation of Ukraine* 1 (2009) 52.

[29]. **Danylkovych A.** (ed.). Formation and stabilization of dermis structure (in Ukrainian) in: Danylkovych A. (ed.) in: Ecologically oriented technologies for production of leather and fur materials for manufacturing of competitive goods (in Ukrainian). Fenix (Publisher «Фенікс») 2011, Kyiv, 134–265.

[30]. **Lishchuk V.** Manual on "Technology of production of chrome-tanned leather of different thickness and assortment for upper and inner parts of footwear and haberdashery products from animal hides" (in Ukrainian). PJSC Chinbar 1992, Kyiv.

[31]. **Lishchuk V.** Manual "Technique for the production of shoe yuft from chromesyntanvegetable-tanned cattle hides" PJSC Chinbar1992, Kyiv.

[32]. **Danylkovych A. and Sidliar Yu.** The method for tanning of fur leathers. UA patent 36805, April 16, 2001.

[33]. **Danylkovych A. and Sidliar Yu.** The method for treatment of fur leathers. UA patent 36806, April. 16, 2001.

7. RESOURCE-SAVING CHROME TANNAGE OF LEATHER WITH MODIFIED MONTMORILLONITE [5]

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Abstract: *As it is described in the paper, the twofold decrease in consumption of chromium tanning agent can be achieved by combined use of montmorillonite modified with hydroxy chromium solutions and basic chromium sulphate at the 1 : 2 ratio of chromium oxide (III) to montmorillonite. The semi-finished product obtained by the developed method exceeds control samples by its physicomechanical properties. The developed method can be characterized as being more environmentally efficient and resource-saving owing to 3.2–4.6 times lower chromium oxide (III) content in the spent solution.*

Keywords: *hydroxy chromium solution; montmorillonite; modification; tanning; collagen; semi-finished product.*

Introduction

Chromium compounds of various chemical composition are widely used in the existing technology of leather manufacture [1–3], with around 90 % [4] of the globally produced leather. Taking considerable toxicity of chromium compounds [5] into account, systematic scientific and technological studies are being conducted to select less harmful agents to replace mentioned above substances. Despite the considerable number of works in this field, due to the wide variety of leather materials, such studies still remain relevant. In this view, the development and application of materials that combine properties of both fillers

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[5] *The title has been modified; the original title is "Resources-saving chromium tanning of leather with the use of modified montmorillonite".*

and structure-forming agents [6–8] may be promising. That is specifically true for the materials that are based on highly hydrophilic aluminosilicates distinguished by their high dispersibility in water. The use of such bi-functional materials may be efficient for hide and skin processing technologies.

Experimental Part

The goal of this study is to investigate the tanning process of leather semi-finished product with the use of modified montmorillonite (MMM). The bentonite of Dashukivske deposit (Ukraine) was used in the study, with the content of main mineral – montmorillonite. The montmorillonite modification includes the following stages:

– obtaining sodium montmorillonite (*Na*-MMM) dispersion by treating bentonite dispersion with sodium carbonate (6.0 % of the dry mineral weight) [9],

– obtaining hydroxychromium-montmorillonite (hydroxy-*Cr*-MMM) by treating *Na*-MMM with the solution of basic chromium sulfate (BCS) – $Cr_2(SO_4)_n(OH)_{6-2n}$ (technical specification: TU 2141-033-541386-2003) with consumption 10.0 % of Cr_2O_3 [10].

The adsorption of hydroxychromium complexes by MMM was quantified from absorption spectra of initial and equilibrated solutions in the wavelength range of 570–585 nm using UV-vis spectrometer Specord (Germany).

The structural changes in MMM after modification with hydroxychromium complexes were studied using x-ray diffraction techniques (DRON-3 with filtered Co Kα radiation). Specific surface area of hydroxy-*Cr*-MMM were determined by Brunauer–Emmett–Teller (BET) method from nitrogen adsorption at –196 °C using a gravimetric procedure.

Hydroxy-*Cr*-MMM was used for chrome tanning of pickled hide obtained by the previously described technology [2] under 4 different treatment conditions (Table I) with liquid coefficient (LC, the ratio of water volume to weight of raw hide) for water equals to 0.8. Pelt was tanned with BCS in the presence of hydroxy-*Cr*-MMM. Before tanning the pickled hide was treated for 10 min with the solution containing sodium chloride and formic acid, respectively, 6 and 0.2 % of the weight of pickled hide. Treatment 4 was set as a control one with the use of 2.0 % chromium (III) oxide [2]. The basicity of the BCS solution was gradually increased with sodium carbonate in two steps at 50% consumption each time in 40 min and 2 h. Two samples were taken from each group, and their shrinkage temperature was measured. The technological solutions were analyzed after tanning for residual chromium (III) oxide concentration and pH.

After 24 h of keeping the tanned samples under a polyethylene film, they were neutralized by sodium bicarbonate and sodium formate, at 0.8 and 0.5 %, respectively. Then, fat-liquoring was performed with the use of "Provol BA" (6.0 % of the weight of chrome-tanned product) recalculated for technological product of company "Zimmer & Schwarz" (Germany). The experimental samples were slimy and plastic, while the control sample was darker and rougher at the grain side.

After washing and samming, the samples were dried by hanging of laid on filter paper at 20–23°C and relative humidity of 55–60 %. After wetting the samples back to 30–32 %, softening/stretching, and final drying by hanging to 14–16 %, the samples were ironed at 70–80 °C. The experimental samples were smoother, more light-colored at the grain side, and stretchable. The control samples were harder to iron and smooth, and were characterized by higher shrinkage as compared to the experimental samples.

The chemical composition and physicochemical properties of obtained samples and chromium (III) oxide content in spent solutions were evaluated [11].

Table I. *Characteristics of tanning process.*

#	Cr_2O_3 [%]		Hydroxy-*Cr*-MMT [%]	pH after 12 h of tanning	Increase in basicity		
	BCS	MMT			Na_2CO_3 [%]	pH after	
						40 min	2 h
1	0.9	0.1	1	3.6	0.4	3.9	4.2
2	0.8	0.2	2	3.6	0.4	4.0	4.2
3	0.7	0.3	3	3.8	0.4	4.1	4.2
4	2.0	0	0	2.8	0.6	3.8	4.2

Results and Discussions

Modification of montmorillonite by hydroxychromium complexes may result in new applications, for example, it can be used as a new reagent for tanning.

The adsorption (*A*) of polymeric hydroxychromium cations (Fig. 1, curve *1*) depends on the basicity of chromium solution and it is able to exceed the exchange inorganic capacity by 2–5 times. Fig. 1 shows, that if the ratio of *OH*/*Cr* = 0, then the adsorption of hydroxychromium cations only slightly exceed the capacity of *Na*-MMM exchange (0.72 meq/g). With the increase in basicity of chromium solution from 0 to 0.1, chrome adsorption by *Na*-MMM abruptly increase. It is

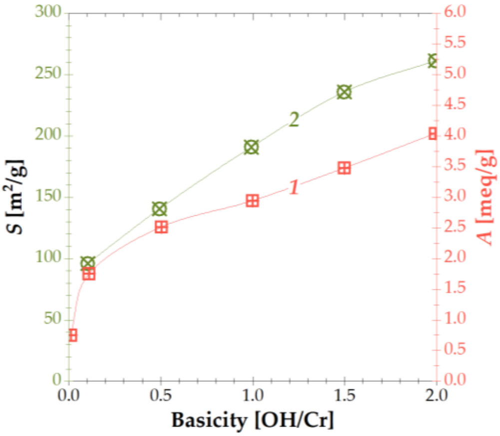

Fig. 1. *Chemocolloidal properties of hydroxy-Cr-MMM.*

connected with the appearance of polymeric forms of chrome in solution (dimers, tetramers, etc.) [12]. As it is seen from Fig. 1 (curve 2), hydroxy-*Cr*-MMM has a highly-developed specific surface area (*S*).

The analysis of diffractograms of hydroxy-*Cr*-MMM (Fig. 2) suggest that hydroxychromium cations of various degrees of polymerization and sizes are intercalated into the interlayer space of MMM crystals increasing d (001) to 1.68 nm. The variations in the basal spacings (Fig. 2) can be attributed to differences both in the nature and the orientations of the interlayer species [13, 14].

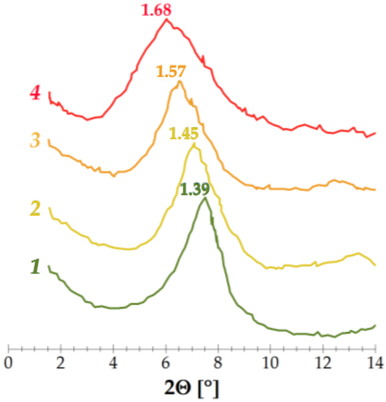

Fig. 2. *X-ray diffractograms of Na-MMM modified with 0.1 M solutions of hydroxychromium complexes with different basicity OH/Cr: 0.1 (1); 0.5 (2); 1.5 (3); and 2.0 (4).*

Apparently, in the process of drying beveling of silicate layers occurs mainly at different places along the edges because of non-homogeneous splitting of layered structure by hydroxychromium cations of various sizes. Hydroxy-*Cr*-MMM acquires highly developed micro- and mesoporous turbostratic structure. This is confirmed not only by the width of diffraction maxima but also by the abrupt increase of accessible specific surface area of hydroxy-*Cr*-MMM, which ranges from 95 to 260 m^2/g (Fig. 1).

As a result, hydroxy-*Cr*-MMM expand its surface area and absorptivity towards collagen of dermis during tanning.

The stabilization and formation of dermal collagen structure at tanning stage is determined by chemical composition of the functional system used [15]. With this, both chemical composition and physicochemical properties of leather semi-finished product changes considerably. Particularly it is confirmed by combined use of hydroxy-*Cr*-MMM and BCS.

As it can be seen from the results (Table II), the increase in the hydroxy-*Cr*-MMM content in leather semi-finished product is accompanied by an extreme dependence of the chromium (III) oxide content in its structure, which indicates the effective impact of MMM on the interaction of chromium complexes with active groups of collagen macromolecules.

Table II. *Chemical composition of chrome-montmorillonite-tanned samples.*

Parameter	Treatment			
	1	*2*	*3*	*4*
Moisture content [%]	13.7	12.7	12.4	12.9
Cr_2O_3 [%] †	2.1	2.5	2.4	4.3
Ash [%] †	5.6	6.7	7.8	5.7
Substances extracted with OS [%] †	6.6	6.5	6.3	6.8
Protein substances [%]	73.9	73.9	72.7	74.3
Cr_2O_3 in spent solution [g/L]	2.1	1.4	1.5	6.5

Note: *The parameters marked with † are calculated on a dry basis.*

This effect can be explained by structure-forming and plasticizing effect of hydrophilic aluminosilicate on the availability of ionized carboxyl collagen groups for interactions with hydroxychromium complexes, the contents of which are being reduced in the tanning system. Thereby, hydroxyl groups of montmorillonite, located in the inner sphere of hydroxychromium complexes, are getting replaced by more active ionized carboxyl groups of collagen. After reaching 1 : 2 ratio of Cr_2O_3 to MMM, hydroxychromium complexes efficiency in the system drops dramatically. With this, as inorganic substance content increases in the structure of semi-finished product, a simultaneous decrease in protein substances is being observed. The advantage of the developed technology over the control one is a considerable decrease of chromium (III) oxide content in spent solutions.

It is worth mentioning the effective combined use of hydroxy-*Cr*-MMM and BCS in structure-forming and stabilizing of dermal collagen in comparison with the standard use of chromium compounds. Even with twofold decrease in tanning substance consumption in the first case, for the semi-finished product relatively high values of shrinkage temperature were observed, the former increases up to 94 °C in the tanning system of the second type for semi-finished product treatment (Table III).

Table III. *Physicochemical properties of hydroxy-Cr-montmorillonite tanning samples.*

Parameter	**Treatments**			
	1	***2***	***3***	***4***
T_S [°C]	92.0	94.0	88.0	100.0
Tensile strength [MPa]	24.0	29.0	27.0	25.0
Tensile strength for grain layer [MPa]	16.0	21.0	19.0	16.0
Elongation at 9.8 MPa [%]	18.0	24.0	26.0	29.0
Elongation at break [%]	44.0	52.0	54.0	58.0
Residual elongation [%]	11.5	12.0	11.0	14.0
Plastic elongation [%]	32.5	41.0	43.0	44.0
Apparent density [g/cm^3]	0.638	0.627	0.610	0.685
Volume yield [cm^3 per 100 g proteins]	215.0	218.0	226.0	194.0
Area yield [%]	102.0	105.2	103.1	100.0

Investigation of physicomechanical properties of semi-finished product produced by the developed technologies indicates that tensile strength of semi-finished product and strength for grain side reach extremum values, which are being 16 and 31 % higher, as compared to the control treatment, while the deformation parameters of studied samples have smaller values, and they increase with increasing content of modified montmorillonite. It can be explained by lower shrinkage due to plasticizing effect of hydroxy-*Cr*-MMM.

The diffusion depth of modified montmorillonite microparticles into intermicrofibrillar gaps promotes effective separation of collagen structure and its protection after removing the moisture, providing an increase in volume yield of semi-finished product and the extreme value in the yield of leather area. This effect can be explained by structural specifics of dermal collagen related to the tilt angle of fiber bundles to the leather surface.

Conclusions

The effect of montmorillonite modification with hydroxychromium complexes on the structural properties of inorganic dispersions was investigated. It is shown that with increasing the basicity of chromium compounds the adsorption of polynuclear complexes of chromium by montmorillonite increases and the cation exchange capacity exceeds by 2–5 times. Modification of montmorillonite is accompanied by expansion of the crystal lattice d(001) to 1.68 nm.

The high sorption ability and specific surface of hydroxy-*Cr*-MMM has a positive effect on the collagen structure formation during chrome tanning.

Combined application of hydroxy-*Cr*-MMM and BCS results in production of chrome-tanned semi-finished product containing 1.7–2.0 times less amount of chromium (III) oxide while reducing the amount of chromium tanning agent twice. The use of hydroxy-*Cr*-MMM solutions enables efficient control over reactions between chromium compounds and functional collagen groups due to its reactive-plasticizing effect. Resulted semi-finished product exceeded control samples by its physicomechanical properties. The developed technology may be classified as environmentally-efficient by reducing 3.2–4.6 times of chromium (III) oxide content in spent solution.

References

[1]. **Danylkovych A., Hryshchenko I., and Lishchuk V.** The innovative technology of leather and fur materials and products: Monograph (in Ukrainian). Fenix (Publisher «Фенікс») 2012, Kyiv.

[2]. **Danylkovych A., Mokrousova O., and Okhmat O.** Technology and materials for leather production (in Ukrainian). Fenix (Publisher «Фенікс») 2009, Kyiv.

[3]. **Danylkovych A and Nahornyi P.** Transformation of hydroxy sulfate-chromium complexes during tanning process (in Ukrainian). *Ukrainian Chemistry Journal* **68**, 8 (2002) 78–80.

[4]. **Slaats H.** The tanning processes. *World Leather* **12,** 7 (1999) 37.

[5]. **Danylkovych A. and Zhyhotsky A.** Ecological aspects of modern technologies of leather and fur production (in Ukrainian) *Proceeding of SIET 12—02 "Modern information and energy-saving technologies of human life support* (in Ukrainian)" **12** (2002) 51–53.

[6]. **Mokrousova O.** The organomineral composition for retanning-filling of leather semi-finished product. *Proceedings of the 3rd International Conference on Advanced Materials and Systems*; Bucharest, Romania, September 16–18, 2010; 85.

[7]. **Mokrousova O. and Danylkovych A.** Formation of collagen structure of derma by mineral dispersions. *Scientific Proceedings of Riga Technical University. Material science and applied chemistry* **1** 14 (2006) 83.

[8]. **Mokrousova O.** Technological ways for use of the mineral dispersion in leather manufacturing. Monograph: Innovative materials and technologies in made-up textile articles and footwear. Publisher "Politechnika Łódzka" 2008, Łodzi 146.

[9]. **Mokrousova O. and Moraru V.** Effect of inorganic alkaline reagents on the dispersity and deflocculation of clay minerals dispersions applied as leather fillers. *Proceedings of XIV International Clay Conference "Micro et Nano Scientiale Mare Magnum"*, Castellaneta-Marina, Italy; June 14–20, 2009; 80.

[10]. **Mokrousova O. and Moraru V.** The effect of montmorillonite modification by Cr (III) compounds on its microcrystalline structure and electrosurface properties. *Proceedings of the XIX Congress of the Carpathian-Balkan Geological*

Association, Aristotle University of Thessaloniki, Thessaloniki, Greece; September 23–26, 2010; 99.

[11]. **Danylkovych A.** Practicum in chemistry and technology of leather and Fur. Fenix (Publisher «Фенікс») 2006, Kyiv.

[12]. **Laswick J. and Plane R.** Hydrolytic polymerization in boiled chromic solutions. *J. Amer. Chem. Soc.* **81** (1959) 3564–3567.

[13]. **Brindley G. and Yamanaka S.** A study of hydroxy-chromium montmorillonites and the form of the hydroxy-chromium polymers. *American Mineralogist* **64** (1979) 830–835.

[14]. **Melville Carr R.** Hydration states of interlamellar chromium ions in montmorillonite. *Clays and Clay Minerals* **33**, 4 (1985) 357–361.

[15]. **Plavan V., Valeika V., Kovtunenko O., et al.** THPS pretreatment before tanning (chrome or non-chrome). *Journal of the Society of Leather Technologists and Chemists* **93**, 5 (2009) 186.

8. AN IMPROVEMENT OF THE TECHNOLOGY OF MANUFACTURING SUPPLE LEATHER THROUGH ENZYMATIC PLASTICIZING OF A STRUCTURED SEMI-FINISHED PRODUCT

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Abstract: *We have developed a technology of enzymatic plasticizing of chrome-tanned semi-finished leather by using protosubtilin G3× for the leather production. To develop the enzymatic plasticizing technology, we utilized a chrome-tanned semi-finished product, after it was neutralized, which was derived from large pig hides with an average area of 180 dm^2 (a weight of 6.8 kg) and cattle (heavy heifer) hides with an average weight of 24.3 kg. The average area of the finished leather material was 133.0 dm^2 and 316.0 dm^2, respectively. Enzymatic plasticizing was produced by applying protosubtilin G3× at 54 °C. Enzymatic plasticizing of semi-finished leather compared with the control technology ensures the formation of the material structure with deformation and plastic properties increased by 28.0–44.0 % and 26.0–43.0 %, respectively, for pig and heavy heifer hides.*

The process of enzymatic plasticizing of chrome-tanned semi-finished leather is enabled by the disruption of hydrogen and natural links between the lateral chains of collagen macromolecules as a result of forming temporary enzyme-collagen complexes, followed by blocking released functional groups with fat emulsion. This reduces the duration of mechanical plasticizing by half after drying and moisturizing.

The current technology used by the PJSC Chinbar (Kyiv, Ukraine), which includes enzymatic plasticizing by enzymaz 10TD, provides an increased area yield of the leather material from semi-finished hides of pigs and heavy heifers compared with the control technology, *respectively, by 3.5 and 4.0 %, and an opportunity to get an economic benefit of 1200 and 3300 UAH per 100 m² of the finished material. The use of protosubtilin G3× in the developed technology of enzymatic plasticizing under optimal conditions helps reduce the duration of mechanical plasticizing two times and increase the area yield by 6.3 and 5.4 %, respectively, for leather obtained from hides of pigs and cattle. This can provide an economic benefit of 1860 UAH and 4450 UAH per 100 m² of the finished material compared with the control technology. The developed energy-efficient and cost-effective technology of enzymatic plasticizing of chrome-tanned semi-finished leather from cattle and large pig hides can be considered promising for introduction into the manufacturing of supple leather materials.*

Keywords: *enzymatic plasticizing; chrome-tanned semi-finished product; leather material; area yield.*

Introduction

Transformation of natural leather materials is characterized by a multistage technological processing with a substantial use of various chemical reagents which significantly extends the duration of manufacturing. Herewith, an efficient use of raw hides, decreased processing time using technological equipment, and energy-savings [1] stipulate the development of innovative technological aspects. To increase the economic efficiency of industrial enterprises [2–4], it is necessary to develop and implement new environmentally friendly technologies that will decrease mass and energy consumption, thus increasing efficiency and reducing production costs. Therefore, the economic efficiency of enterprises and leather production technologies should be defined in view of the significant methodological difficulties associated with the multifactor nature of the problem [5]. Given the ecological aspects of producing leather and fur materials, it is essential to improve the existing technologies by using environmentally friendly reagents and materials that are especially valuable in resource-intensive technologies.

Important work in this direction consists in developing, first of all, energy-saving technologies through the use of effective bioreagents.

Analysis of Previously Published Studies and Statement of the Problem

Among the eco-efficient materials that are widely applied in various fields of industrial production, a special place is occupied by bioactive protein reagents of plant, microbial, or animal origin due to their high reactivity in biochemical processes [6, 7]. Enzymes are known to be used at various stages of manufacturing leather and fur materials. The work [8] describes the use of protosubtilin G3×, pectofoetidin P10×, and maltavamorin G10× to accelerate hydration of air-dried hides. Enzymes of pectoavamorin P10× and pectofoetidin P10× together with non-ionic surfactants accelerates removal of lipids and hydrocarbons from the dermis and contaminants, including those of protein nature, from the pelage when processing sheepskin larger than 90 dm^2 with a dense skin tissue [9]. These multifunctional enzymes besides interacting with lipids exhibit also proteolytic and glycosidic effects.

Enzymes accelerate the physicochemical processes of converting animal hides and skins into leather materials through soaking, degreasing, liming, and softening. These processes significantly depend on the methods of preserving the natural material and the leather application. The length of technological processing at the stage of soaking the flint-dried hides is reduced by the use of amilosubtilin G3×, maltavamorin G10×, and pectofoetidin P10× [10]. Moreover, by increasing the plasticity of the dermis, the defects of raw hides are reduced during their mechanical processing.

While soaking hides in limewater, it is recommended to use enzymes with proteolytic, glycosidic, and lipolytic effects [11]. Herewith, the lime can be removed by enzymes Lithudac L and Novo Bate WB which are active in an acidic environment [12]. The efficiency of degreasing can be increased by using alkaline lipases or their combination with alkaline proteases [13]. Rawhides can be effectively dehaired with the enzyme called protosubtilin G10× [14, 15]. Proteolytic enzymes and trypsin can be used even in the recycling of secondary resources of production of chrome-tanned hides [16].

The effectiveness of using enzymes also greatly depends on the pH and temperature of the environment which requires careful monitoring of the technological processes. According to the work [17], the proteolytic activity of protosubtilin G3× at the optimal pH is maximized at 45–55 °C, and its activity is reduced by 50 % at 30 °C and 65 °C. While the enzyme of lipavamorin G3× exhibits optimal performance at 35–37 °C, it is completely inactivated at 55 °C. The optimal temperature for protomesenterin G3× is within a range of 60–65 °C.

Thus, enzyme type greatly accelerates the biochemical liming-soaking and pre-tanning processes in transforming leather and raw fur materials, and it is rather prospective to use them in post-tanning technologies. Moreover, their effective impact on the structured semi-finished product can be achieved with the help of enzymes with increased thermal stability. Due to this, one can expect a shortening in the duration of the technological process, a lower consumption of raw materials per unit area, and formation of supple leather materials.

The Goal and Tasks of the Study

The goal of the study is to improve the technology of producing supple leather through developing the process of enzymatic plasticizing of a chrome-tanned semi-finished product.

To achieve this goal, the following tasks were identified:

– to study the deformation and plastic properties of semi-finished leather derived after its enzymatic plasticizing from raw cattle hides and large pig hides (LPHs);

– to carry out a comparative analysis of the technologies of enzymatic plasticizing of structured semi-finished leather;

– to determine the effectiveness of the developed technologies of enzymatic plasticizing of semi-finished leather.

Materials and Methods of Studying Enzymatic Plasticizing of Semi-finished Leather

In developing the technologies of enzymatic plasticizing, we used a semi-finished product of chrome-tanning after the neutralizing process. The material was derived from large raw hides of cattle (heifer) of an average weight of 24.3 kg and LPHs of an average area of 180 dm^2 (6.8 kg) at the cost of 42.0 UAH and 28.0 UAH per kg and 1 m^2, respectively. The average area of the finished leather material was 316.0 dm^2 and 133.0 dm^2. Enzymatic plasticizing was carried out using protosubtilin G3× (EP-1) produced by the company "Enzyme" (Ukraine) which is typically obtained by the liquid culturing of *Bacillus subtilis* 103. One gram of the enzyme preparation has the following composition (in enzyme units): neutral protease – 70, β-glucanase – 196, xylanase – 147, α-amylase – 298, and alkaline protease – 10, 960.

Enzymatic plasticizing of semi-finished leather was carried out in a Dose steel drum, Dozemat DD-7.5 produced by Ring Maschinenbau GmbH (Germany) with a drive capacity of 13.5 kW at a rate of 1 m^3 of water use per 1 ton of the semi-finished product. Further mechanical plasticizing was held in a sliding drum Dose 4648MI (Ring Maschinenbau GmbH, Germany) with the energy consumption of 9 kW per hour. With the developed technology, the process was carried out at 53–55 °C in the presence of fatliquor (0.4–0.8 % of the weight of the semi-finished product) for 1 and 3 h for semi-finished cattle hides and LPHs, respectively. According to the technology of the PJSC Chinbar

(Kyiv, Ukraine), enzymatic plasticizing was carried out while using the preparation enzymaz 10TD (EP-2), produced by Cromogenie (Spain), at 38–42 °C for 2–4 h and 12–14 h, respectively, for the semi-finished products from cattle hides and LPHs. Under the previously existing technology of producing supple leather in the absence of enzymatic plasticizing of structured semi-finished hides of cattle and LPHs for show uppers [18], the duration of the mechanical plasticizing process increased significantly.

The technological efficiency of enzymatic plasticizing of semi-finished leather is estimated based on the area and physicomechanical properties determined by previously described methods [19] for finished leather for shoe uppers. The economic effect of the considered technologies was evaluated by the difference between the cost of increasing the area, weight, and energy consumption in producing leather by the developed technology and the one practiced by the PJSC Chinbar versus the control technology, taking into account the cost of enzymes:

$$E^{EP} = \frac{100(\Delta AP_h - m_{en}P_{en} - EP_e)}{A_l},$$

where E^{EP} is the economic effect of enzymatic plasticizing per 100 m^2 of leather [UAH]; ΔA is the increase of the area of leather material produced by the control technology [m^2]; P_h is the price per 1 m^2 of hides [UAH]; m_{en} is the mass of the enzyme spent to process one ton of semi-finished leather [kg]; P_{en} is the price of 1 kg of enzyme [UAH]; E is the energy consumption for enzymatic and mechanical plasticizing of one ton of semi-finished leather [kW/h]; P_e is the price of 1 kW/h of energy [UAH]; A_l is the area yield of leather from one ton of the chrome-tanned semi-finished product by the control technology [m^2].

Thus, our study includes a comparative analysis of technological and economic characteristics of enzymatic plasticizing technologies for manufacturing supple leather materials for shoe uppers.

A Comparative Analysis of Technologies of Enzymatic Plasticizing

The use of enzymes in the technologies of physicochemical treatments of hides in manufacturing supple leather materials (Fig. 1) can have significant effect on preparation the fibrous structure of a chrome-tanned semi-finished product for further effective technological processing and primarily for filling with vegetable tannins.

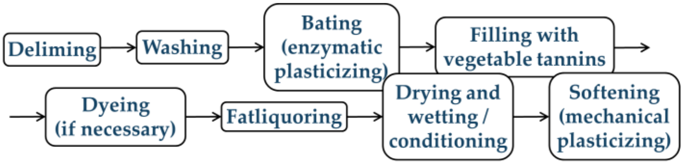

Fig. 1. *A technological flowchart of producing leather by enzymatic plasticizing of a chrome-tanned semi-finished product.*

The properties of the chrome-tanned semi-finished leather after an enzymatic plasticizing treatment (EPT) with protosubtilin G3× and enzymaz 10TD are shown in Table I. The results indicate that with an increase in the processing temperature to 54 °C for both semi-finished cattle hides and LPHs the duration of EPT is reduced three to four times compared with the technology used by the PJSC Chinbar, whereas the physicomechanical properties remain rather high. Besides, an elongation at 10 MPa and elongation at break have maximal values for the samples obtained by the developed technology. Meanwhile, the strength of the semi-finished leather after enzymatic plasticizing is slightly higher compared with samples obtained by the control technology.

Evaluation of the semi-finished leather elasticity alongside its stiffness varies according to the deformation parameters obtained under uniaxial tension (Fig. 2).

Fig. 2 shows that the semi-finished product of cattle hides is characterized by lower stiffness and, consequently, higher elasticity compared with the semi-finished LPHs.

Table I. *The technology of an enzymatic plasticizing treatment of chrome-tanned semi-finished leather and its physicomechanical properties.*

Indicator	**EPT technology**				**Control technology**
	Developed technology			**PJSC Chinbar**	
	1	**2**	***3***		
Enzyme consumption at [mL of 0.1 N *NaOH*]	1.1	0.9	0.9	1.0	—
Fatliquor [%]	0.4	0.6	0.8	—	—
Temperature [°C]	37	54	58	40	—
Processing time [h]:					
– for cattle hides	1.5	1	1	4	—
– for LPHs	4	3	3	13	—
Fatliquoring [%]	6.6	6.4	6.2	7.0	7.0
Tensile strength [MPa]	$\frac{19.4}{17.3}$	$\frac{19.5}{18.4}$	$\frac{18.5}{17.7}$	$\frac{18.1}{17.9}$	$\frac{18.3}{17.5}$
Elongation at 10 MPa [%]	$\frac{28.3}{30.2}$	$\frac{33.9}{38.0}$	$\frac{35.0}{29.0}$	$\frac{33.5}{37.3}$	$\frac{27.8}{29.6}$
Elongation at break [%]	$\frac{59.0}{51.0}$	$\frac{76.0}{58.0}$	$\frac{69.0}{53.0}$	$\frac{72.0}{57.0}$	$\frac{58.0}{49.0}$

Note: *The numerator and the denominator are the indicators of the finished leather obtained from cattle and pig hides.*

This effect is achieved with an active technological solution of enzymes such as protosubtilin G3× and enzymaz 10TD in the amounts of 0.9 mL and 1.0 mL, respectively, in a 0.1 N sodium hydroxide solution but at a shorter duration of the enzymatic plasticizing process, which is four times shorter compared with the technology of the PJSC Chinbar. It should be noted that the semi-finished product obtained by the control technology has significantly higher stiffness and lower values of other physicomechanical properties.

The technological and economic advantages of the developed technology and the one industrially practiced by the PJSC Chinbar over the control technology are shown in Table II. According to the results, the technologies that have been developed and industrially practiced by the PJSC Chinbar provide a significantly larger area yield of the finished leather material. The technology of the PJSC Chinbar and the developed technology can increase the area yield of the leather material by 3.5–3.8 % and 5.1–5.9 %, respectively. Thus, the output of

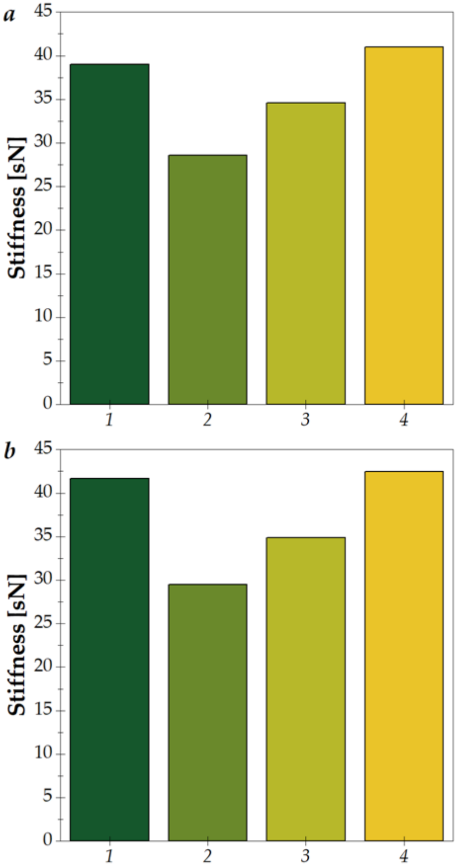

Fig. 2. *A dependence of the stiffness of the semi-finished leather from cattle hides (a) and large pig hides (b) on the temperature of its enzymatic plasticizing: 1 – 37 °C; 2 – 54 °C; 3 – 58 °C; and 4 – without processing with an enzyme*

leather from rawhides according to the developed technology over the technology of the PJSC Chinbar increases by 1.8–2.2 %.

Table II. *The technological and economic efficiency of enzymatic plasticizing of one ton of chrome-tanned semi-finished leather.*

Indicator	**Technology**		**Efficiency**	
	EPT	**Control**	**technological (+, –)**	**economic [UAH] (+, –)**
The leather output area [m²]				
– after EP-1	$\frac{346.0}{412.1}$	$\frac{325.5}{391.0}$	$\frac{20.5}{21.1}$	$\frac{14477}{7293}$
– after EP-2	$\frac{338.4}{404.7}$	$\frac{325.5}{391.0}$	$\frac{12.9}{13.7}$	$\frac{10\,898}{4671}$
Enzyme consumption [kg]				
– during EP-1	$\frac{9}{10}$	—	$\frac{-9}{-10}$	$\frac{-1148}{-1275}$
– during EP-2	$\frac{10}{10}$	—	$\frac{-10}{-10}$	$\frac{-850}{-850}$
Enzymatic plasticizing [h]:				
– EP-1	$\frac{1}{3}$	—	$\frac{-1}{-3}$	$\frac{-12.7}{-77.0}$
– EP-2	$\frac{4}{13}$	—	$\frac{-4}{-13}$	$\frac{-50.6}{-164.3}$
Mechanical plasticizing				
– EP-1 & EP-2	$\frac{9}{12}$	$\frac{20}{24}$	$\frac{11}{12}$	$\frac{188.1}{205.2}$
EPT efficiency [UAH per 100 m2]				
– during EP-1				$\frac{4448}{1865}$
– during EP-2				$\frac{3348}{1195}$

Notes: *1) EP-1 and EP-2, respectively, correspond to the technologies that have been developed and industrially practiced by the PJSC Chinbar. 2) The numerator and the denominator refer to the finished leather from cattle hides and LPHs.*

The energy costs for processing semi-finished products by the technologies that have been developed and industrially practiced by the PJSC Chinbar concern the operating duration of mobile equipment and its capacity at the stages of enzymatic and mechanical plasticizing. Moreover, the decrease in the duration of mechanical plasticizing reduces energy costs 2.0–2.2 times. Total energy consumption for processing semi-finished cattle hides by the developed technology compared with the control technology is reduced by 1.9 times, and for processing LPHs it is reduced by 1.5 times. The technology practiced by the PJSC Chinbar can provide energy savings only in the processing of semi-finished cattle hides: total energy consumption is reduced by 1.3 times.

Taking into account the cost of increasing the area of the leather material, the consumption of enzymes and the energy spent for enzymatic and mechanical plasticizing, the economic benefit from the technology of the PJSC Chinbar over the control technology is 1200–3300 UAH per 100 m^2 of supple leather for shoe uppers; in terms of the developed technology versus the control one – it increases by 33–56 %.Thus, we can assume that the technology of processing raw cattle hides and large pig hides into supple leather materials by using enzymatic plasticizing of a chrome-tanned semi-finished product is more promising compared with the previously used technologies.

The Peculiarities of Enzymatic Plasticizing of Structured Semi-finished Leather

The use of enzymes at various stages of producing leather and fur materials is justified by their specific effect on both collagen and other components of the dermis of animal hides, depending on the characteristics of the physicochemical processes of converting them into materials. The biocatalytic effect of enzymes, when converting raw hides and fur into an appropriate material, is predetermined by the similarities between their chemical nature and the dermal collagen. It should be noted that at the stages of soaking, alkaline treatment (liming and dehairing), deliming, and softening, the use of enzymes is predetermined by profound disruptive changes in the semi-finished leather, which is connected with the disruption of covalent, ionic, and hydrogen bonds between both macromolecules of the dermal collagen and with its components. Particularly, the presence of enzymes at the stage of liming significantly accelerates the process of cleavage of amide bonds in the lateral chains of collagen.

The effect of an enzyme at the stage of the dermis plasticizing after its chemical structuring with a basic chromium sulphate to form spatial intermolecular relationships involving ionized carboxyl groups of collagen [20] is manifested primarily by the disruption of hydrogen and ionic bonds. The effectiveness of the active center of the enzymes of protosubtilin G3× and enzymaz 10TD is predetermined by the participation of their amino acid residues of aspartic and glutamic acids, tyrosine, serine, arginine, lysine, oxylysine, and histidine in the formation of intermediate complexes with lateral chains of collagen macromolecules. Given the isoelectric point of proteins and the pH environment of 5.6–5.8, the polypeptide chains exist in a deprotonated form and exhibit basic properties.

After the disruption of the intermediate enzyme-collagen complexes, the released functional groups of lateral chains in collagen interact with particles of a fat emulsion, thereby increasing the mobility of the macromolecules of a structural protein. This helps utilize the plasticizing and biocatalytic activities of an enzyme. The resulting plasticizing effect of an enzyme ensures an even distribution of the organic filler throughout the volume of the semi-finished leather due to some reduction in the activity of its interaction with the collagen of the structured dermis. Further plasticizing of the structure of the filled semi-finished leather is facilitated by its fattening. It should be noted that it is the process of enzymatic plasticizing of the semi-finished product structure that twice reduces the duration of the subsequent mechanical plasticizing after drying and moisturizing.

Thus, the enzymatic plasticizing process in the technology of manufacturing supple leather from semi-finished cattle hides and large pig hides improves the deformation and plastic properties of the obtained material and thus significantly increases their area yield, which testifies to an increase in the technological and economic efficiency of the technologies that we have studied.

Conclusions

We have developed a technology of enzymatic plasticizing of chrome-tanned semi-finished leather based on using protosubtilin G3× in the production of supple leather. Enzymatic plasticizing of chrome-tanned semi-finished leather from raw cattle hides and large pig hides forms the structure of a leather material with mechanical and plastic properties increased by 26.0–43.0 % and 28.0–44.0 %, respectively.

The technology of enzymatic plasticizing by the PJSC Chinbar, which involves the use of enzymaz 10TD, provides an increase in the area yield of leather from semi-finished cattle hides and large pig hides by 4.0 % and 3.5 %, respectively, compared with the control technology; it allows obtaining an economic benefit of 3300 and 1200 UAH per 100 m^2 of the finished material.

The developed technology of enzymatic plasticizing compared with the control technology helps increase the area yield of the leather material by 6.3 % and 5.4 %, reduce the duration of mechanical plasticizing twice, and achieve the economic benefit of 4450 and 1860 UAH per 100 m^2 of the finished material from raw materials of cattle and pigs, respectively. The developed energy-efficient and more cost-effective technology of enzymatic plasticizing of chrome-tanned semi-finished leather from cattle hides and large pig hides can be considered promising for incorporation into the manufacturing of supple leather materials.

References

[1]. **Lishchuk V.** Management of competitive leather production (in Ukrainian). Fenix (Publisher «Фенікс») 2005, Kyiv.

[2]. **Paseka D. and Hrynko T.** Factors of increasing company efficiency (in Ukrainian), *Economics and Management – 2013: prospects for integration and innovative development (in Russian)* **4** 2013; http://confcontact.com/2014_04_25_ekonomika_i_menedgment/tom4/48_Paseka.htm

[3]. **Bohdanovych O.** Analysis of company performance efficacy based on reconciling the interests of groups of economic influence (in Ukrainian). *Marketing and management (in Ukrainian)* **1** (2012) 45–58.

[4]. **Vashchenko A.** Efficiency of manufacturing activity in the management of industrial companies (in Ukrainian). *Economics Bulletin (in Ukrainian)* **1** (2014) 80–87.

[5]. **Hryshchenko I., Danylkovych A., and Voloshenko E.** Economic and environmental aspects of the development of modern leather production. *News of higher-educational institutions* (in Russian). *Technology of Light Industry (in Russian)* **3** (2013) 78–82.

[6]. **Dekhtiarenko N.** Production of enzymes in Ukraine (in Ukrainian), *Research Bulletin of the National Technical University of Ukraine "Kyiv Polytechnic Institute"* **3** (2013) 48–58.

[7]. **Novikov V., Sydorov O., and Shvedov O.** Trends in the development of commercial biotechnology (in Ukrainian), *Visnyk of the National Academy of Sciences of Ukraine* **2** (2008) 25–39.

[8]. **Biriukov A.** Technology of fur sheepskin processing (in Russian). Central Scientific Research Institute of Information and Technical and Economic Research of Light Industry (in Russian) 1990, Moscow, pp. 85, 167, 169, and 197.

[9]. **Biriukov A.** Technology of woolskin processing (in Russian). Central Scientific Research Institute of Information and Technical and Economic Research of Light Industry (in Russian) 1982, Moscow, pp. 22 and 82.

[10]. **Gricenko I.** Single technology of treatment of hides of rabbit (in Russian). Moscow: Central Scientific Research Institute of Information and Technical and Economic Research of Light Industry (in Russian) 1990, Moscow, pp. 13, 29, and 45.

[11]. **Shestakova I.** Enzymes in leather and fur production (in Russian). Legprombytizdat 1990, Moscow, p. 128.

[12]. **Širvaitytė J., Valeika V., Beleška K., et al.** Bating of pelts after deliming with peracetic acid, *Proceedings of the Estonian Academy of Sciences* **55** (2006) 93–100.

[13]. **Altan A. and Fatma C.** Studies on the degreasing of skin by using enzyme in liming process, *Indian Journal of Chemical Technology* **15** (2008) 507–510.

[14]. **Sukhoverkova A., Antipova L., Kosenko I., et al.** Modern production methods of depilated rabbit hides (in Russian). *Modern Problems of Science and Education* **3**, 2 (2009) 74–75.

[15]. **Antipova L., Vasilenko O., Kosenko I., et al.** Enzymic technology of dehydration of rabbit skins (in Russian). *Announcer of the Voronezh State Technological Academy* **3**, 37 (2008) 61–65.

[16]. **Choundhary R., Jana A., and Jha M.** Enzyme technology applications in leather processing. *Indian Journal of Chemical Technology* **11** (2004) 659–671.

[17]. **Taylor M.** Enzymes assist recovery of chrome and high-value protein from shavings. *World Leather* (1994) 38.

[18]. **Danylkovych A., Mokrousova O., and Okhmat O.** Technology and materials for leather production (in Ukrainian). Fenix (Publisher «Фенікс») 2009, Kyiv.

[19]. **Danylkovych A.** Practicum in chemistry and technology of leather and fur. Fenix (Publisher «Фенікс») 2006, Kyiv.

[20]. **Heidemann E.** Eine erweiterte Theorie der kochfesten Gerbung, Lokalisation im Kollagen, *Das Leder* **1** (1994) 2–12.

9. PLASTICIZATION OF SEMI-FINISHED LEATHER OF CHROME TANNAGE USING BIOCATALYTIC MODIFIER [6]

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Abstract: *The goal of the work is to study the plasticizing process of chrome-tanned cattle hides for the production of elastic leather materials. The effect of biocatalytic modifiers on the elastic properties of chrome-tanned semi-finished leather product is investigated. The technological parameters of the process of plasticizing-filling of semi-finished leather products are determined. The developed plasticizing process of semi-finished leather products using biocatalytic modifier 3 and Aerosil A-300 provides the formation of leather materials with improved elastic-plastic properties while saving chemical reagents by 20–25 %. The resulting filled leather material according to the complex of properties meets the requirements for elastic leather materials for garments according to DSTU 3115-95, the interstate standard for leather for the shoe uppers GOST 939-88, and the requirements of the international standard of quality management systems ISO 9001:2008. Thus, The developed technology of plasticizing-filling of semi-finished leather product allows increasing the yield of leather material for 6.7 % compared with the existing technology.*

Keywords: *semi-finished product of chrome tannage; plasticization of semi-finished product; biocatalytic modifier; leather properties.*

Introduction

Modern technologies for the processing of raw hides into highly elastic leather materials must meet the requirements for

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[6] *The title has been modified; the original title is "Plasticification of leather semi-finished chrome tanning using biocatalitic modifier".*

material and energy consumption and reduce the cost and improve environmental safety of leather production. In this respect, the improvement of existing technologies and the development of new ones facilitate to use scarce natural raw materials more efficiently and to replace imported high-priced reagents with scientifically sound and environmentally friendly domestic ones. In this regard, the improvement of the elastic properties of leather materials allows expanding their variety and polyfunctional use in various fields.

For the formation of highly elastic leather materials, a wide range of chemically and biologically active reagents of various compositions are used. It is foreseen that those reagents result in increased mobility of elements of the fiber structure of leather materials to maintain a complex of important exploitational properties of the finished material. Palm oil with a modified silicone compound containing end hydroxyl groups followed by esterification with maleic anhydride and sodium bisulfite [1] was used for plasticizing leather for garment. For the production of various soft leather materials, a plasticizing anionic composition Coripol ALF based on lecithin which includes natural and synthetic components has been developed by TFL company [2]. The developed composition has low viscosity, provides high stability, and increases light- and heat-resistance of leather material. The work [3] shows the advantages of using polyamide carboxyl acid over a traditional fatliquor. Specialists from Lanxess company recommend this reagent as a universal plasticizer for garment, shoe, and upholstery leather. In this case, the resistance of natural material to light and heat, high intensity of colors after dyeing, and biodegradation of the developed plasticizer is illustrated.

Plasticization of the structure of air-dried raw hides occurs due to the use of biologically active reagents [4]. At the same time, the leather defects are reduced during mechanical processing. For this purpose, bioactive composition Lithudac LI Novo Bate WB are used during deliming [5], and at the stage of removal of natural fatty acids, alkaline lipases or their combination with alkaline proteases are used.

The effect of copolymers based on ethyl- and butyl acrylate on the physicomechanical properties of semi-finished leather product was investigated [6]. Improvement of elastic-plastic properties of leather material have been reported. In the work [7], the plasticizing effect is shown when using compositions based on poly(butyl acrylate) and polyethylene glycol in the manufacturing leather and parchment. The authors explain this effect by blocking the functional groups of the dermal collagen and the weakening of the intermolecular interactions of the elements of its supramolecular structure. In contrast to acrylic polymer emulsions, amil furazan formaldehyde resin, modified with isopropyl alcohol, also improves leather thermal properties and makes the leather shrink less during drying [8]. The use of a composition based on montmorillonite and polyacrylic acid [9, 10] allows the formation of leather with increased orientation of the material fibrous structure during deformation.

Thus, due to the complex hierarchical structure of raw hides [11], for the plasticization of natural materials appropriate chemical reagents, including biologically active modifiers of collagen structure, should be used. It should be noted that little attention is paid to the aspects of efficacy of application of raw leather materials in the referenced works.

Problem Statement

The goal of this work is to study the plasticizing process of chrome-tanned cattle hides for the production of elastic leather materials which will ensure the formation of elastic leather with improved elastic-plastic properties. In this work the following tasks have been defined:

- to choose biocatalytic modifiers (BCMs) of collagen structure;

- to investigate the effect of BCM consumption on elastic-plastic properties of semi-finished leather product;
- to determine optimal temperature of BCM application on the structural and mechanical properties of semi-finished leather product;
- to implement plasticization with BCMs in the manufacture of leather material in semi-industrial conditions.

Materials and Methods

For experiments under laboratory conditions, we used a chrome-tanned semi-finished product shaved to uniform thickness of 1.4 mm and with a shrinkage temperature of 109 °C. The semi-finished product was obtained from bend area of cattle hide – green-salted bullhide. Batches containing eight 10×18 cm samples were selected by the method described previously [12]. In semi-industrial conditions, calfskins were used after shaving to thickness of 1.3 mm and selected into batches by the method of alternating halves.

As a biocatalytic modifiers, hydrolytic plasticizing agents obtained from *Bacillus subtilis* and *Aspergillus awamori* cultures were used [13]. In this case, BCM-3 is a mixture of two modifiers at 1 : 1 ratio.

Before plasticization, the semi-finished product of chrome tannage was neutralized to a pH 5.4 by sodium formate and sodium bicarbonate at 1 : 1 ratio and washed with warm water for 10–15 min. Depending on the plasticizing conditions the temperature of water was increased to 65–85 °C with a water-to-semi-finished product ratio of 1 : 1.5. Plasticization of the semi-finished product was performed for 20 min. Then, the temperature of the technological solution was reduced to 53–55 °C by the addition of water with a temperature of 19–21 °C for further plasticizing with fatliquor Trupon DL (Trumpler) at a consumption of 7 and 6 % of the mass of the semi-finished product for treatment *1* and *2*, respectively, for 30–40 minutes

(Table I). At the same time with Trupon DL addition, the composition based on the phenolic compounds of the Trupon G (Trumpler, Germany) and the quebracho extract (China) was applied. For treatment *2* semi-finished product 5 min before adding the fatliquor was treated with a suspension of highly-dispersed silicon oxide, Aerosil A-300, which was produced by pilot plant (Kalush, Ukraine) of the Chuiko Institute of Surface Chemistry. The existing technology uses a composition based on lightfast resin (hexamethylenetetramine polymer) tanning agent Relugan D (BASF, Germany), syntan Trupotan G (Trumpler, Germany), and vegetable tannins of quebracho (China). Processing of the samples was completed by fixation of the plasticizer in the structure of the semi-finished product by decreasing pH of the technological solution with potassium alum to 4.0–4.2, followed by washing for 10 min. The control samples were plasticized only with fatliquor.

Table I. *Composition of the plasticizing-filling composition.*

Parameter	**Parameter values [% of the weight of semi-finished product after sammying]**		
	Treatment		**existing technology**
	1	***2***	
BCM-3	0.2	0.2	0
Aerosil A-300	0	1	0
Trupon DL	7	6	7
Relugan D	0	0	2
Trupotan G	2	2	3
Quebracho	5	5	6

The batches of semi-finished products were processed in a glass flask for 10 L with built-in shelves for the mixing at a continuous rotation at 18–20 rpm using a ball-bearing two-valve mill M-188-01. The plasticized semi-finished product was subsequently subjected to drying-moisturizing treatments with decreasing its moisture content to 13–15 %.

In semi-industrial conditions, the water consumption for plasticizing semi-finished product was reduced to a ratio of 1 : 1. The process was carried out in a Doze steel drum (Ring Maschinenbau GmbH, Germany) with a volume of 0.39 m^3 (Fig. 1) at 71–75 °C. The semi-finished product after plasticizing with BCM-3 using the experimental technology *2* was filled with 1.0 % of highly-dispersed silicon oxide, Aerosil A-300, with the size of primary particles of 4–50 nm and a specific surface area of 50–380 m^2/g [14, 15]; 2 % of the replacement synthetic tanning agent Trupotan G (Trumpler, Germany); and 5 % of quebracho extract recalculating per active substance. To complete the filling process, formic acid was used after its dilution with water 1/10.

Fig. 1. *Doze steel drum at public joint-stock company Chinbar.*

The chemical composition of the filled semi-finished product and its physicomechanical parameters were determined using the previously published methods [12]. At the same time, the mechanical characteristics of the resulting semi-finished product were measured using a device for testing the stiffness and elasticity PZhU-12M (State-owned enterprise "Scientific Research Institute "Elastik", Ukraine) and a tensile testing machine RT-250M at an extension rate of 90 mm/min. The area of the semi-finished product was determined using specialized electromechanical equipment (Svit, Czech Republic; model 07484/P1).

Results and Discussion

Taking into account the complex of physicochemical and biological characteristics of biocatalytic modifiers of the dermal collagen structure, the effect of their consumption on the physicomechanical properties of semi-finished leather product of chrome tannage have been carried out (Table II). As it can be seen from the data, with the increase in the content of BCM-1 and BCM-2 in the technological solution at 75 °C, the stiffness of the material decreases at a consumption of 0.1 % of the weight of the semi-finished product. This effect is more pronounced for BCM-1. At the same time, the tensile strength is practically unchanged. In the case of BCM-3, the effect of reducing stiffness and, accordingly, increasing the elasticity of leather material is more pronounced compared to each of the collagen modifiers used separately.

Table II. *Physicomechanical properties of plasticized semi-finished products.*

Modifier	**BCM consumption [% of the semi-finished product weight]**				
	0	**0.1**	**0.2**	**0.3**	**0.5**
BCM-1	$\frac{41.0}{19.4}$	$\frac{30.0}{19.0}$	$\frac{28.0}{21.0}$	$\frac{27.0}{20.3}$	$\frac{27.0}{17.5}$
BCM-2	$\frac{40.0}{19.0}$	$\frac{33.0}{18.8}$	$\frac{32.0}{20.0}$	$\frac{32.0}{19.8}$	$\frac{31.0}{18.0}$
BCM-3	$\frac{40.0}{19.2}$	$\frac{23.0}{19.7}$	$\frac{19.0}{21.5}$	$\frac{18.0}{19.6}$	$\frac{18.0}{17.2}$

Note: *Numerator and denominator correspond to stiffness [cN] and tensile strength [MPa].*

It should be noted that the absolute value of the rigidity of the material plasticized with BCM-3 at a consumption of 0.1 and 0.2 %, respectively, decreases in 1.7 and 2.1 times compared with the control samples.

The effect of the temperature of the plasticizing process of semi-finished leather products with various biocatalytic modifiers at consumption of 0.2 % on its elastic-plastic properties is given in Table III. In the studied temperature range, there is a decrease in stiffness and increase in elasticity of samples for all three modifiers, especially for BCM-3. In this case, at 81–85 °C, the stiffness decreases by 2.35 times, and the elongation at 10 MPa increases by 35 % compared with the control sample. It should be noted that when processing leather material at a temperature above 75 °C, the elastic-plastic characteristics remain practically unchanged.

Table III. *Physicomechanical properties of plasticized semi-finished products at different temperatures.*

Temperature [°C]	**Modifier**			
	without BCM	**BCM-1**	**BCM-2**	**BCM-3**
61–65	$\frac{40.0}{26.6}$	$\frac{29.7}{30.1}$	$\frac{34.7}{28.3}$	$\frac{24.3}{32.0}$
66–70	$\frac{39.0}{26.2}$	$\frac{28.5}{30.6}$	$\frac{33.2}{28.9}$	$\frac{23.0}{33.5}$
71–75	$\frac{39.0}{27.4}$	$\frac{27.9}{31.5}$	$\frac{31.7}{29.8}$	$\frac{20.0}{34.3}$
76–80	$\frac{40.3}{27.0}$	$\frac{27.0}{32.3}$	$\frac{30.1}{30.3}$	$\frac{19.0}{34.0}$
81–85	$\frac{41.0}{26.0}$	$\frac{27.0}{32.0}$	$\frac{29.8}{30.7}$	$\frac{17.0}{35.0}$

Note: *Numerator and denominator correspond to stiffness [cN] and elongation at 10 MPa [%].*

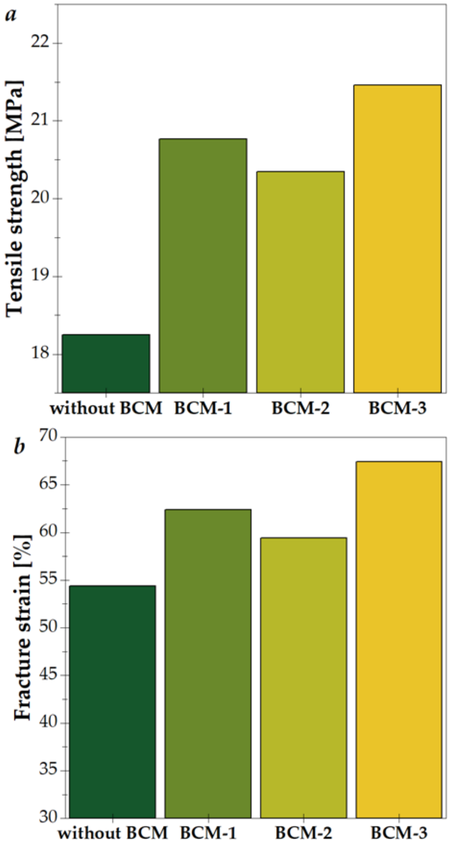

Fig. 2. *The dependence of the tensile strength (a) and elongation at break (b) of the semi-finished leather product on the type of biocatalytic modifier.*

The tensile strength of the semi-finished product plasticized with BCM slightly increases compared to the control sample, especially this is noticeable for BCM-3 resulting in 17.0 % increase (Fig. 2*a*). This also applies to the elongation at break of the plasticized semi-finished product (Fig. 2*b*).

Approbation of biocatalytic technology was carried out at PJSC Chinbar (Kyiv, Ukraine). For plasticizing-filling semi-finished leather products the compositions listed in Table I were used.

Analysis of the constitution of used compositions suggests that the developed technologies are characterized by a reduced consumption of filling reagents by 27.0 % compared with the current technology and the minimal use of Aerosil A-300 compared with the previously developed Aerosil-filling technology [16].

Investigation of the complex of elastic-plastic properties of semi-finished leather product of chrome tannage using a modifier of collagen structure can testify to their plasticizing effect on the structure of the tanned semi-finished product. A disruption of not only physical interfibrillar bonds, but also chemical bonds between collagen and mucopolysaccharides components of the dermis is taking place, which in the absence of biocatalytic modifiers consolidate the structure of the tanned semi-finished product and contributes to its stiffness.

The results of the study of mechanostructural and technological properties of semi-finished product of chrome tannage plasticized with BCM-3 and filled with reagents used in similar control technology, are given in Table. IV. According to the data, the leather semi-finished product produced by the developed technology using a complex biocatalytic modifier has lower stiffness and higher elongation at 10 MPa for 33–47 and 38–74 %, respectively, compared with the existing technology. This results in increased volumetric yield and surface area of the material. At the same time, according to strength and elongation at break, the formed material corresponds to that obtained by the existing technology. Incorporation of Aerosil into the structure of the semi-finished leather product preliminary plasticized with BCM-3 increases the yield of the material area by 1.6 %, and compared with the current technology – by 6.7 %. This effect may be due to the higher degree of orientation of the elements of the fibrous structure of the semi-finished leather product as a result of its fixation during thermomechanical processing on a scintillating machine (Svit, Czech Republic; model 07716P1).

Thus, the technology of plasticizing-filling semi-finished leather product of chrome tannage with the use of biocatalytic modifier and highly-dispersed Aerosil A-300 results in the formation of highly elastic leather material. Bioplasticizing technology for the production of elastic natural materials can be used for filling semi-finished products of chromeless tannage at lower temperatures of plasticization. This technology was implemented in the semi-industrial conditions at the private PJSC Chinbar.

Table IV. *Physicochemical properties of semi-finished leather products.*

Parameter	**Parameter values**		
	ET *1*	**ET 2**	**CT**
Mass fraction [%] of			
– moisture	13.7	14.1	13.9
– proteins †	68.9	68.1	67.7
– ash	6.5	7.6	6.7
– Cr_2O_3	4.1	4.0	4.3
– substances extracted with OS	6.4	6.7	7.4
– bond organic tannins	13.8	13.9	14.7
T_S **[°C]**	113.0	113.0	111.0
Volume yield [cm³ per100 g proteins †]	234.0	239.0	227
Porosity [%]	57.0	55.0	49.0
Air permeability $[cm^3/(cm^2 \cdot h)]$	253.0	249.0	237.0
Tensile strength [MPa]	21.7	22.5	21.3
Elongation at 10 MPa [%]	39.0	37.3	21.0
Elongation at break [%]	61.0	60.0	57.0
Stiffness [cN]	19.0	21.0	28.0
Yield of leather material [%]	105.1	106.7	100.0

Note: *† denotes that nitrogen content was quantified using Kjeldahl method and recalculated for protein content; ET, CT, and OS stand for experimental technology, current technology, and organic solvents, respectively.*

Conclusions

Considerable effect of a biocatalytic modifier on the elastic-plastic properties of the leather semi-finished product is established at 71–75 °C with its consumption of 0.2 % of the mass of the semi-finished product.

It is shown that when the biocatalytic modifier is effectively used, the stiffness of the semi-finished leather is reduced twice compared to the existing technology while maintaining its mechanical strength.

It was established that the optimal temperature of the plasticizing process using biocatalytic modifiers should be carried out at 25–30 °C below the shrinkage temperature of the semi-finished leather product. At the same time, the initial plasticization of semi-finished leather products is possible in the temperature range of 66–80 °C, however, with the temperature decrease, the duration of the process increases.

The developed plasticizing process of the semi-finished leather product utilizing biocatalytic modifier 3 provides the formation of leather materials with improved elastic-plastic properties and results in saving of chemical materials by 27.0 % and raw materials up to 6.7 % compared to the existing technology. The resulting filled leather material according to the complex of properties corresponds to the elastic leather materials for garments according to DSTU 3115-95, the interstate standard on leather for shoe uppers GOST 939-88, and the requirements of the international standard of quality management systems ISO 9001:2008. The authors continue to investigate the inhibitory and activating effects of chemical reagents on the composition activity, its effectiveness for processing the semi-finished product, the ingredient content of the plasticizing-filling composition in the presence of new biocatalytic modifiers of the collagen structure, and their effective modification of the semi-finished product of chrome tannage.

References

[1]. **Wang C., Feng S., and Wu J**. Preparation of organosilicon modified palm oil fatliquor. *The Journal of the American Leather Chemists Association* 106 (2011) 161–169.

[2]. New fatliquor for soft articles from TFL. *World Leather* **24**, 2 (2011) 6.

[3]. Leather softening technology. *Leder und Häute Markt* 1 (2009) 38.

[4]. **Shestakova I., Moiseeva L., and Miriniva T.** Enzymes in leather and fur production (in Russian). Legpromizdat 1990, Moscow.

[5]. **Afsar A. and Cetinkaya F.** Studies on the degreasing of skin by using enzyme in liming process. *Indian Journal of Chemical Technology* **15** (2008) 507–510.

[6]. **Ma J. and Lu H.** Elasticity studies on leather retanned with various types of acrylic polymers. *Journal of the American Leather Chemists Association* **103**, 11 (2008) 363–369.

[7]. **Nikitin M., Melnikov E., Suchshkov A., et al**. Plasticization of leather and parchment (in Russian). *TPS* **19** (1998) 172–174.

[8]. **Mariliz G., Silva D., and Vigannico I.** Leather retanning with hydrolyzed protein. *Journal of the American Leather Chemists Association* **105** (2010) 195–202.

[9]. **Chen Y. and Shi B.** Nanotechnologies for leather manufacturing: a review. *Journal of the American Leather Chemists Association* **106**, 8 (2011) 261–273.

[10]. **Zhang X., Liu Q., and Zhang W.** Nanocomposites of acrylate-organosilicon resin/layered silicate for leather finishing. *Journal of the Society of Leather Technologists and Chemists* **90**, 6 (2006) 250–254.

[11]. **Lishchuk V., Plavan V., and Danylkovych A**. Transformation of the collagen structure during beam-house processes and combined tanning. *Proceedings of the Estonian Academy of Sciences* **12**, 3–1 (2006) 188–198.

[12]. **Danylkovych A. and Chursin V.** Analytical control in leather and fur production: a laboratory practicum (in Russian), Infra-M 2016, Moscow, 176 p.

[13]. **Varbanets L., Avdiiuk K., and Borzova N.** Producing, properties, and practical applications (in Ukrainian). *StattiOnline: Agricultural Sciences, Biotechnology* **7** (2017); http://www.stattionline.org.ua/agro/biotehnolog/575-vidilennya-vlastivosti-praktichne-zastosuvannya.html

[14]. **Iler R.** The chemistry of silica: solubility, polymerization, colloid and surface properties and biochemistry of silica. Part I. Mir (Publisher «Мир») 1982, Moscow.

[15]. Aerosil (fumed silica dioxide) – web article; http://www.silica.su/ru/perechen-produkczii/834-aerosil.html

[16]. **Danylkovych A., Bilinskyi S., and Kudzieva A.** Utilization of highly-dispersed silica oxide in the technology for production of semi-finished leather (in Ukrainian) *Herald of Khmelnytskyi National University. Technical Sciences* **6**, 243 (2016) 112–116.

10. IMPROVING THE PROCESS OF DYEING A LEATHER SEMI-FINISHED PRODUCT BY TITANIUM COMPOUNDS

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Abstract: *We developed technology of dyeing semi-finished leather product of chrome tannage investigating the processes of interaction in the system "dermal collagen – azo dye – titanium compounds". Physicochemical properties of the technological solutions of azo dyes, modified by titanium compounds of different chemical composition, were explored. A more energetic interaction was established between the brown azo dye 345, the molecules of which contain phenolic group, and titanium compounds with possible formation of chelate compounds.*

A study of sorption kinetics of azo dyes by collagen fibers, structured by chromium compounds, revealed a significant dependence of sorption of the dye, the molecules of which contain less auxochrome $-SO_3Na$ *groups, on temperature in the presence of titanyl oxalate. In this case, absolute values of the sorption of the dye at 20 °C are twice lower compared to the brown dye 345. With increasing concentration of the dye with a lower molecular weight, acidic blue-black, modified by ammonium sulfate titanylate, its diffusion into the gel of gelatin is reduced twice with an increase in the concentration up to 80 g/L. An increase in the concentration of the dye in the system is symbatic to an increase in the activity of its interaction with collagen, accompanied by reduced diffusion into the gel of gelatin. It was found that filling a semi-finished product of chrome tannage with acrylic polymers contributes to the increase in chemisorption of azo dye when using ammonium sulfate titanylate by 1.5 times.*

The effect of the composition of dyestuff solution on the coloristic properties of a filled semi-finished product was demonstrated after *fixating the dye on its surface by ammonium sulfate titanylate. We determined optimal ratio of ammonium sulfate titanylate and a dye, which ensures the formation of leather material with a higher color saturation of the surface of a semi-finished product by 2.1–2.9 %, maximal resistance to wear and lightfastness in comparison with the control technology. The developed technology of comprehensive filling-dyeing-fatliquoring enables reduction in the consumption of azo dye, exclude at the final stage of coloration additional consumption of a dye and environmentally harmful compounds of chromium by the use of ammonium sulfate tytanilate as a fixative of dye with a fivefold saving of reagent.*

Keywords: *dyeing a leather semi-finished product; azo dye; titanium compound; coloristic indicators; mechanical properties.*

Introduction

Increasing demands for greener chemical technologies and to products quality necessitate improvement and development of new technological processes. This is especially important for multistage and material-intensive physicochemical processes that require the use of a wide range of chemical reagents. In this regard, special attention should be paid to the production of leather materials, which uses significant amounts of water [1, 2]. In this case, the processes of dyeing a semi-finished leather product require consideration of its condition and essentially depend on the chemical composition of dyes and supplementary reagents. The latter provide diffusivity of dyes, the coloration of a semi-finished product, homogeneity and color saturation of the surface. It enables reduction in thickness of the coating film and manufacturing high-quality leather with aniline coating [3]. It should be noted that to achieve a uniform and intense coloration, modern technologies after a combined process of dyeing-fatliquoring may include additional coloring with the fixation of the dye by environmentally harmful chromium compounds. In this regard, it is relevant to design new dyeing compositions and conditions of their use for the development of resource-saving environmentally friendly technologies.

Literature Review and Problem Statement

Natural leather materials are distinguished by its structure, difference in density for particular areas, and the peculiarity of previously performed technological treatments. Thus, for the effective process of dyeing, the essential conditions are, first of all, research and development of relevant dyeing compositions that include dyes of natural and synthetic origin. Paper [4] explored the process of dyeing leather with henna extract, the major component of which was 2-hydroxy-1,4-naphthoquinone with the use of mordents of various chemical composition, particularly, sulphates of aluminum, iron, and zinc. The process was carried out at the concentration of dye 2.5–25 % and pH of the technological solution 4–7. Under optimal conditions: 20 % concentration of dye, pH 4, and 60 °C, the leathers were characterized by high resistance to wear and sweat, however they have only satisfactory lightfastness.

High lightfastness of dyed leathers was achieved as a result of the conducted research on the dyes of plant origin [5]. It was found that preliminary use of mordant salts of aluminum, copper (II), tin (II), and natural dyes (rhine, indus, pacific, caspian, henna, and hemine) made it possible to obtain quality leathers with a wide range of color shades. The authors explained the results by the effective diffusion of dyes into the structure of leather and their interaction with mordant salts.

The process of dyeing leather of wool sheepskin by the hypericum extract was examined [6, 7]. The formation of high-quality colored material of yellow, green, and yellow-brown colors is explained by the formation of coordination complexes of dye with mordents.

To increase the efficiency of the process of dyeing leather, authors of the paper [8] recommend modifying acidic dyes with plasma, which facilitate increasing the stability of coloration towards dry and wet rubbing and reduce the concentration and duration of dyeing a leather semi-finished product. Surface and inner modification of chrome-tanned leather for shoe uppers by the method of treatment with high-frequency low-temperature reduced-pressure plasma [9] allows for the intensification of technological process of dyeing raw cattle hides. Additional treatment of leather with plasma after drum dyeing [10] results in an increased depth of dye diffusion into the volume of a semi-finished product and improvement of physicochemical properties. It should be noted that this leads to a longer duration of treatment and to labor intensity of the technological process that negatively affects the cost of products.

The process of dyeing the suede of wool sheepskin tanned using the compounds of titanium and low-temperature plasma was explored [11]. The use of ammonium sulfate titanylate provides for the possibility to increase the absorption of acidic dyes when dyeing a semi-finished product and the saturation of the dyed surface in comparison with the samples of chrome-tanned leather. According to the results, structure of a semi-finished product is significantly affected by the method of treatment with low-temperature plasma. Unfortunately, the authors did not examine the peculiarities of influence of low-temperature plasma and ammonium sulfate titanylate on the structure of a semi-finished product.

To intensify the process of dyeing a semi-finished product with anionic colorants at its filling with acrylic polymers of combining dyeing and fatliquoring processes, it is recommended to use alkyl-aryl sulphates in production technology for their stabilization [12]. In this case, the efficiency of coloration significantly increases.

Therefore, the efficiency of dyeing a semi-finished leather product is to a large extent determined by the properties and structure of the material that are achieved at the preceding stage of its treatment. In this case, when compared with the environmentally friendly natural colorants that require additional treatment of a semi–finished product by mordant reagents and do not yield lightfast coloring, the use of synthetic dyes that have a defined chemical composition and which allow the intensification of the process of dyeing looks promising. Thus, the search for technologically and environmentally effective dyes fixatives which provide color saturation and uniformity of materials coloration remains relevant.

The Goal and Tasks of the Study

The goal of this work is to study the process of dyeing a semi-finished leather product, structured by chromium compounds, with anionic colorants in the presence of titanium compounds.

To achieve this goal, the following tasks were set:

– to determine the peculiarities of interactions between titanium compounds and azo dyes;

– to explore the sorption of azo dyes by collagen fibers and their diffusion capacity;

– to determine optimal conditions for dyeing with modified azo dyes of a leather semi-finished product in the comprehensive process of filling-dyeing-fatliquoring.

Materials and Methods

In accordance with the set goal, in the work we used a semi-finished product of chrome tannage (SFPCT) for the production of leather materials with 1.1–1.6 mm thickness for shoe and garment leathers (technical specification: TU U 00302391-03-98) obtained from green-salted cattle hides (CHs) according to the technology [1]. Before dyeing, a leather semi-finished product, structured by tanning with chromium (III) compounds, was exposed to mechanical processing to remove excess moisture (samming) and even the thickness throughout the area with subsequent restoration of hydrophilic state of the structure of dermis.

To examine the interaction between the components in the system “dye – titanium compounds – collagen”, we used the gelatin T-7 (technical specification: TU U 24.6-00418030-002:2007) at pH 5.7 and the hide powder (HP; technical specification: TU 8670-020-05431555-95). Gelatin as 4 % gel was used in the experiments. A model system for a leather semi-finished product was HP obtained at the leather factory named after Radishchev (St. Petersburg, Russia) by breaking down the structure of middle layer of bullhide (35–40 kg) into fibers under alkaline treatment. From a structural perspective, HP is a set of polypeptide fibrils composed of macromolecules of collagen fibers (CFs). To block the carboxyl groups, HP was structured with basic chromium sulphate (BCS) $Cr_2(SO_4)_n(OH)_{6-2n}$ (technical specification: TU 2141-033-54138686-2003) using the previously published method [13].

A study of the sorption of acidic blue-black dye (ABBD) was performed on CFs, modified by a mixture of dispersions of polymers (MDP) containing the emulsion MBM-3 (technical specification: TU 6-01-186-89) and the dispersion MX-30 (technical specification: TU 6-01-289-82) in the ratio of 1 : 1.

In the work we used anionic dyes [14, 15] with chemical structure depicted in Fig. 1.

ABBD belongs to the *bis*-, while brown 345 (B345) and black K (BKD) – to the *tris*-azo compounds with molecular weights 614, 867 and 795 Da, respectively. They differ the location and number of sulphate- and other functional groups and the length of hydrophobic region, which predetermines their technological properties. The studied azo dyes are characterized by stability of coloration at pH 2–7.

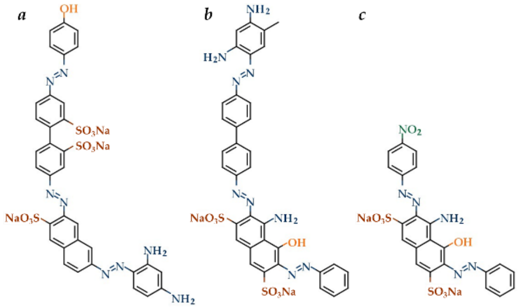
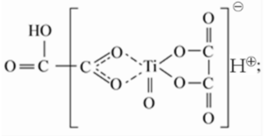


Fig. 1. Chemical structure of anionic azo dyes: brown 345 (a), black K (b), and acidic blue-black (c).

Titanium compounds were used as the dye fixatives:

– ammonium sulfate titanylate $(NH_4)_2SO_4 \cdot TiO_4 \cdot H_2O$ (AST) (technical specification: TU 95.290-79) contained 19.6 % of titanium (IV) oxide at a Schorlemer basicity of 44.8 %;

– 1.05 M of titanyl oxalic acid (TOA) synthesized by the method [16] with the following structural formula:



– potassium titanyl oxalate (PTO).

Ammonium sulfate titanylate was used in the form of a solution with the concentration of 0.66 M at pH=0.75. The concentrations of technological solutions of TOA and PTO are 0.2 M at pH 0.85 and 2.1, respectively. Titanium compounds were combined with dyes at 20 °C at weight ratio of TOA/PTO-to-dye in a range of 0.5–2.0 to 1.0.

Sorption of dyes on CFs was carried out in a hermetically closed glass container at 18–22 °C and by stirring at 43–47 rpm with subsequent washing at 58–62 °C for 60 and 80 min, respectively. The dye consumption was 8 % of the weight of CFs for TOA and PTO and 75 % of the weight of CFs for the dye, while water-to-CFs ratio (liquid coefficient, LC) was 16. Unbound dye was quantified from the difference after sorption and after washing dyed CFs with distilled water at LC of 32 at 63–67 °C on the device "water bath shaker" (Elpan, Poland, model 357) at 150 rpm. The amount of chemisorbed dye by the structure of CFs was defined by its absence in the washing solution.

The dye absorption by CFs [mg/g] was examined colorimetrically using photoelectric colorimeter KFK-2M at 670 nm and 5 mm pathlength. The calibration curve for a dye in the concentration range of 0.05–2.5 g/L was used for quantification. The change in pH of the technological solution during dying was determined by the potentiometric method using the universal ionometer EB-74 (Ukraine).

Physicochemical properties of the dyed leather material were determined by the previously described techniques [13]. Particularly, the tensile strength and elongation of material, σ_b and ε_b were measured at the tensile machine RM-50M at the extension rate of 90 mm/min, its elasticity was calculated from material stiffness (R) using a device PZhU-12M (Russia) for determination of stiffness and elasticity. Colorimetric parameters of a semi-finished product were measured on the device PT-4 (Russia) for determining the color fastness to dry and wet rubbing by the gray scale standard. Hydrothermal stability of HP was determined as a shrinkage or hydrothermal denaturation temperature (T_{HD}) of collagen fibers upon heating in water.

Thus, we used a complex of research methods to determine effectiveness of using titanium compounds in the technology of dyeing elastic leather material.

Interaction of Titanium Compounds with Anionic Dyes and Their Sorption by HP

A study of the interaction of anionic dyes with titanium (IV) compounds was carried out by examining the kinetics of change in pH of the technological solutions and absorptivity (Fig. 2). As it is demonstrated by the results in Fig. 2*a*, in all cases of interaction between the dyes and titanium compounds, the increase in the content of titanium modifier results in decreasing pH of the system. After reaching pH 2.9–3.9, the intensity of this effect decreases.

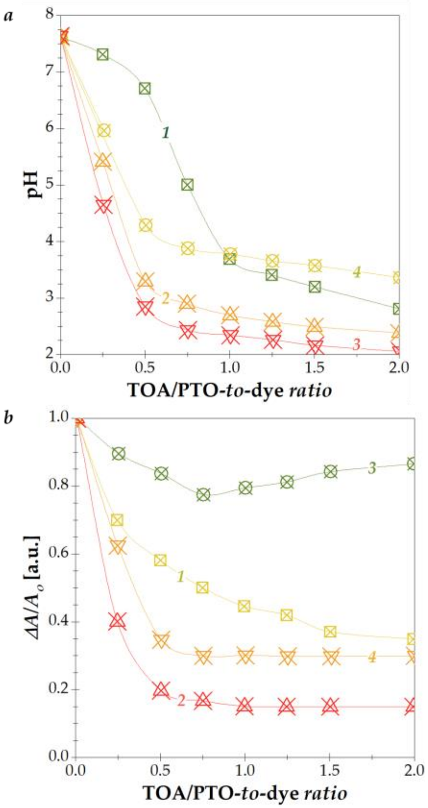


Fig. 2. *Dependence of pH (a) and relative absorptivity (b) of the solutions of dyes B345 (1 and 2) and BKD (3 and 4) on the weight ratio of TOA/dye (1 and 3) or PTO/dye (2 and 4).*

It should be noted that when we combine 0.2 M solutions of TOA and PTO with pH 0.85 and 2.1, respectively, with the dye, pH decreases to a lesser extent in the case of B345D when interacting with TOA, especially at pH up to 4.0. At the same time, pH of the solution of BKD is more sensitive to TOA. An intermediate position is taken by the curve of dependence of pH of B345D (Fig.2*a*, curve 2) on the PTO content in the system. When further increasing the content of chromium compounds in the system, the nature of change in pH may indicate less effective interaction between the BKD and PTO.

The interaction between azo dye and titanium compounds is revealed by the results of observation of absorptivity change under varying composition of their solutions after combining the components (Fig. 2*b*). With an increase in concentration of titanium compounds in the solution of dye to the ratio 0.50–0.75, the decrease in relative absorptivity of the technological solution is observed. In this case, this effect is expressed to a larger degree for the system "PTO – azo dye B345". After a sharp change in absorptivity, the intensity of this effect is significantly reduced except for the solution TOA/BKD. Inflection point on the curves of dependence of absorbance on the composition of the system "TAO/PTO-dye" and type of the dependence may indicate the interaction between their components defined by their chemical structure.

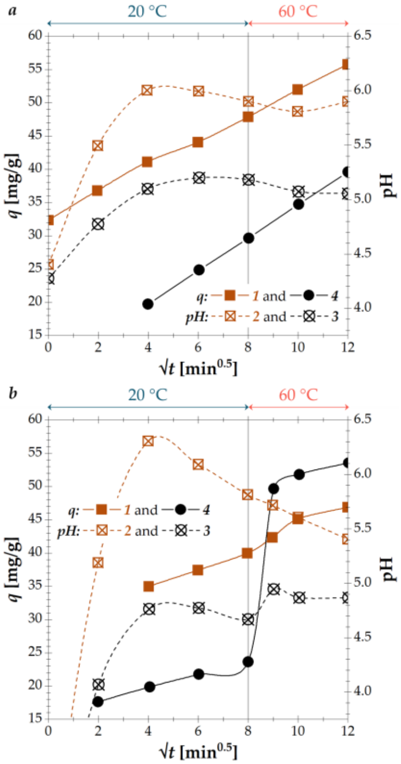


Fig. 3. *Kinetics of sorption (1 and 4) of the dyes B345 (1 and 2) and BKD (3 and 4) by CFs and change in pH of their solutions (2 and 3) upon component interaction: without TOA (a) and in the presence of TOA (b).*

Chemical activity of the anionic dyes and their products of interaction with titanium compounds is also reflected upon interaction with a hydrophilic adsorbent of protein nature – structured collagen fibers with the available for interaction groups of basic character. Results of the sorption of anionic dyes on CFs are demonstrated in Fig. 3. In accordance with the Fick's law [17], the kinetic dependences agree with the curves for sorption kinetics of the type III and indicate the absence of induction period during sorption of anionic dyes on CFs. As it is demonstrated by the data in Fig. 3*a*, the B345D is absorbed more effectively on the surface of particles of CFs compared with the BKD, and practically does not depend on the temperature of the process.

During sorption of dyes on CFs, the pH at the beginning of the process increases to a larger extent for the B345D during first 30 min with its consequent stabilization. The absence of induction period and temperature dependence of sorption for the studied dyes on CFs may indicate an insignificant role of the diffusion mechanism and the availability of surface functional groups of its particles for the interaction with molecules of the dye.

The results of the sorption of anionic dyes in the system "dye – titanium compounds – CFs" (Fig. 3*b*) indicate that the modified dye is sorbed less effectively compared with the original dye at 20 °C. When the temperature increases to 60 °C, there is a sharp increase in the sorption of BKD that exceeds the sorption of B345D. It should be noted that pH of the solutions of both dyes during first 30 min of interaction significantly increases and reaches pH 5–6 with its subsequent stabilization.

Thus, titanium compounds significantly affect the sorption of anionic dyes by HP, especially when the temperature of the process is increased up to 60 °C.

Technology of Dyeing a Leather Semi-finished Product Using Ammonium Sulfate Titanylate

Given an active interaction of azo dyes with titanium compounds and collagen fibers and the effect of pH and temperature, to further develop the technology of dyeing a leather semi-finished product of chrome tannage, we used the industrial product ammonium sulfate titanylate and ABBD which differs from the BKD by its lower molecular weight and decreased number of azo- and amino groups (Fig. 1).

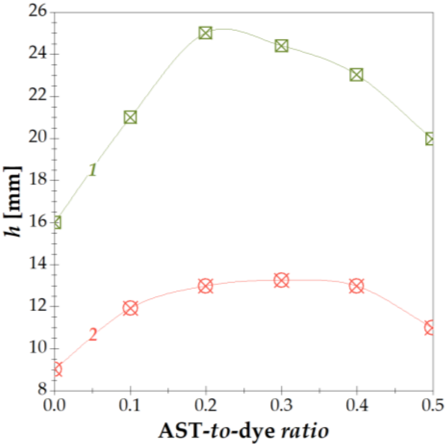


***Fig. 4.** Dependence of diffusion depth of dye into the gel of gelatin on the ratio of AST/ABBD and concentration of the dye: 16 g/L (1) and 80 g/L (2).*

To determine the optimal AST-to-dye ratio in the process of dyeing a semi-finished product, we studied the effect of the ratio on the depth of diffusion (*h*) into gel of gelatin. As it can be seen from the results (Fig. 4), the depth of diffusion decreases with the increasing concentration of the dye. Moreover, if, at the concentration of the dye 80 g/L, maximal value is reached in the range of AST/ABBD ratios from 0.1 to 0.4 (Fig. 4, curve 2), with a decrease in concentration of the dye to 16 g/L, a maximum is observed at the AST/ABBD ratio of 0.2 (Fig. 4, curve *1*).

For the simulation of technological process of dyeing a leather semi-finished product, we studied the sorption of ABBD modified with a mixture of dispersions of polymers depending by CFs on the stage of addition of AST into the sorption system (Table I).

As it is demonstrated by the results (Table I), the sorption of dye significantly increases in the presence of AST. In this case, chemisorption of an azo dye considerably increases when AST is added after the modification of collagen with MDP. If, AST is added before the modification of collagen, the chemisorption of the dye by CFs increases by 44 %, but if it is added after its modification – by 120 %, which indicates a fixative role of AST in the process of sorption the azo dye by the structure of collagen. This is confirmed by the increase in shrinkage temperature of CFs by 5 °C compared with the treatment without using AST. In this case, pH of the system is reduced by 1.5 units. Thus, the effectiveness of sorption interaction between a dye and collagen significantly increases after its modification with MDP.

Table I. *Sorption of ABBD on CFs at the 1 : 5 AST-to-dye ratio and concentration of structured protein in the system at 6 %.*

#	**Stage of AST addition**	**Dye sorption [%]**	**Chemisorbed dye [%]**	**pH**	**T_s [°C]**
1	**without AST**	81.0	36.0	5.1	78.0
2	**modified with MDP – before**	97.0	52.0	3.8	81.0
3	**– after**	99.0	79.0	3.6	83.0

A study of the process of dyeing a leather semi-finished product with ABBD using AST was carried out according to the technology for coloring and fatliquoring processes at JSC Vozko (Ukraine). With this purpose, at constant rotation the semi-finished product was neutralized by sodium formate and bicarbonate, washed, filled with acrylic polymers, and dyed at the ABBD consumption of 4 % of the weight of the semi-finished product. LC was 0.5 and the process was carried out at 18–22 °C. After that, LC was increased to 1.5 and, at 60 °C, the fatliquor was added. In 40 min the solution of AST (0.4–1.6 % of the weight of the semi-finished product) was added and the mixture was stirred for 30 min. The resulting samples of the semi-finished product after washing at 18–20 °C were dried and exposed to mechanical processing in a stretching-vibration machine.

According to the control technology, a semi-finished product after the filling-dyeing-fatliquoring process was subjected to final dyeing with the consumption of the dye at 1 % and chrome tanning agent at 4 % of the weight of the semi-finished product. LC was 1.5 and the process was carried out at 38–42 °C. Total duration of treatment was 60 min.

Results of the investigation of the process of dyeing a semi-finished product of chrome tannage using ABBD and the fixative AST, obtained in laboratory and industrial conditions at the JSC Vozko (Ukraine), are listed in Table II. High saturation of surface coloration of both grain and flesh side of the semi-finished product is achieved at the consumption of 0.6 % AST of the weight of the semi-finished product. In this case, the values of color saturation of the semi-finished product surface exceeded control samples by 2.1–2.9 %. Compared with the control sample, we saved 1 % of azo dye and achieved fivefold consumption decrease of AST as a dye fixative which was used as a replacement of chromium compounds.

To determine optimal conditions for performing a combined process of filling-dyeing-fatliquoring of a chrome-tanned semi-finished product, we performed study in semi-industrial conditions at the JSC Chinbar (Kyiv, Ukraine). It should be noted that the experiments were carried out taking into account previous studies with the use of AST at the stage of fixation of the anionic dye after fatliquoring a semi-finished product according to the technology of JSC Vozko (Ukraine) by reducing the consumption of azo dye and excluding the chromium compounds which are used in the control technology as a dye fixative. As it is demonstrated by the results given in Table III, the efficacy of dyeing a semi-finished product, based on its coloristic characteristics, increases with an increase in the content of AST in the technological solution and reaches maximal value at the AST-to-dye ratio of 0.2–0.4. At the same time, the resulting material displays a tendency towards certain enhancement of mechanical properties.

Table II. *Color saturation of the surface of a leather semi-finished product stabilized by AST.*

Side	**Consumption of AST [% of the mass of semi-finished product after samming]**				**Control technology at JSC Vozko**
	0.4	**0.6**	**1.0**	**1.6**	
papillary region	$\frac{96.5}{-}$	$\frac{97.2}{97.7}$	$\frac{96.9}{96.3}$	$\frac{96.2}{-}$	$\frac{96.0}{94.8}$
reticular dermis	$\frac{96.1}{-}$	$\frac{97.8}{97.2}$	$\frac{96.8}{96.9}$	$\frac{95.8}{-}$	$\frac{95.5}{95.1}$

Note: *numerator and denominator correspond to the data measured under laboratory and industrial conditions, respectively.*

Thus, by the set of physicochemical properties, the resulting dyed leather produced by the developed technology with the use of AST meets the requirements of DSTU 3115-95 for elastic leather materials for garments. Therefore, the developed technology of combined filling-dyeing-fatliquoring of a chrome-tanned semi-finished leather product in the manufacture of elastic leather materials utilizes ammonium sulfate titanylate for fixating azo dyes with different molecular weight in the structure of a semi-finished product. In this case, ecologically harmful chromium compounds are excluded and the consumption of dye is significantly decreased compared to the industrial technology.

The quality of leather material produced by the developed technology meets the Ukrainian standard on elastic leather materials processed from cattle hides.

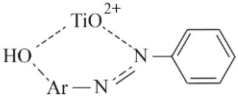
Table III. *Coloristic and mechanical properties of the dyed leather.*

AST consumption [%] [1]	AST/ABBD molar ratio	Colorfastness [points] against			σ_b [MPa]	ε_b [%]	R [cN]
		rubbing		light			
		dry	wet				
0	0	3	2	3	18.9	59.0	24.0
5	0.1	4	3	3	19.1	59.0	24.0
10	0.2	5	4–5	4	19.3	58.0	25.0
20	0.4	5	5	5	19.7	57.0	26.0
25	0.5	5	5	5	20.0	55.0	28.0

Note: *[1] on a dry basis.*

Peculiarities of Interaction in the System of "Azo Dye - Titanium Compounds - Dermal Collagen"

Analysis of results on the interaction between azo dyes and titanium compounds may indicate the formation of molecular and heteromolecular associates of TOA/PTO-dye involving the ionized auxochrome groups of the basic and acidic nature of the dye. A stronger interaction between the azo dye B345 and TOA and PTO may be caused by the participation of phenolic hydroxyl group of this dye and the ionized azo group in the pH range of 3.9–2.2 in the formation of chelate compounds with TiO^{2+} ions similarly to Ti^{4+} [18] according to scheme:



Decreased activity of interaction between the BKD and PTO is largely due to the presence in its molecule a hydrophobic part and decreased activity of hydroxy group of naphthenic ring. In this case, minimal values of absorptivity in the system "titanium compound – azo dye" predetermines, at the ratio of 0.5, a decrease in electron density of the conjugated bonds of azo groups of molecules of the dye.

Results of the sorption of azo dyes on the structured CFs by chromium (III) compounds indicate the formation of bonds between the ionized sulphate groups of azo dyes and amino and imino groups of protein fibers. In this case, carboxy groups of CFs are coordinated in the complex compounds of chromium (III).

In the process of sorption of dyes by CFs, substantial role is belonging to the process of aggregation of their molecules. Less active interaction of azo dyes in the presence of TOA might be due to the greater degree of aggregation of molecules of BKD and, accordingly, its decreased participation in the sorption interaction between its molecules and CFs. With an increase in the temperature of medium up to 60 °C, the degree of aggregation of BKD abruptly decreases compared with B345D and its sorption substantially increases. As a result of this, a product of the interaction between a dye and TOA in the structured CFs is sorbed more intensively.

A study of diffusion process of ABBD modified with AST by the gel of gelatin that models the structure of dermal collagen of a semi-finished product indicates the possibility to regulate the process of dyeing. Kinetics of the coloration process of gelatin with a dye of lower molecular weight can be explained by the existence in the system of two processes associated with the interaction of AST and azo dye and reduction in chemical activity of auxochrome groups of the dye that helps its diffusion into the gel of gelatin. After the deactivation of these groups, the interaction between gelatin and AST increases, leading to its additional structuring as a result of which the diffusion of the modified azo dye slows down. This effect is more pronounced when a dyestuff solution of higher concentration is used.

The use of the model system of dermal collagen in the form of CFs in the sorption of the modified ABBD made it possible to reveal their participation in the interaction with CFs. An increased sorption of the dye by CFs after its modification with AST and CFs treatment by acrylic polymers may indicate active collagen participation in the dye sorption, especially in the presence of AST. A role of the interaction of modified dye during its sorption by CFs in the presence of dispersions of acrylic polymers is particularly clear by the magnitude of chemisorption, which reaches maximal value in the case of treatment of CFs with polymer dispersion. An increase in the chemical activity of the modified dye can be explained by the formation of complex compounds [19] with active collagen groups at pH 3.6–3.8. This is evidenced by an increase in hydrothermal stability of the dyed collagen of dermis. An increase in the concentration of groups, interacting with the dye, in the system "dermal collagen – acrylic polymers – modified dye" predetermines further increase in chemisorption of ABBD. The use of the dye in the technological process of dyeing a leather semi-finished product results in high color saturation of its surface and fastness to rubbing and light.

Thus, for the bulk interactions between a collagen material, structured by chromium (III) compounds, and azo dyes, fixed with titanium complexes, during the interaction of components, it is necessary to perform the process of dyeing after filling a semi-finished product. In this case, AST should be introduced into the system after the treatment of a leather semi-finished product and increase the temperature up to 60 °C.

Discussion of Results on Dyeing Leather Semi-Finished Product

As a result of a comprehensive study on the interactions between azo dyes with different chemical structure and titanium compounds in the process of their sorption by CFs, we established a dependence of this process on the chemical composition. In this case, the sorption capacity of azo dyes increases during their interaction with titanium compounds. A study of the interaction between AST and an azo dye during its diffusion into the model system of dermal collagen, the gel of gelatin, revealed a special role of titanium compounds, which manifests itself in its additional structuring. It should be noted that chemisorption of azo dye after interaction with AST is intensified after treating CFs with a mixture of acrylic polymers, which provided the basis for a more efficient conducting of the process of dyeing leather semi-finished product after its filling. It presents the possibility to utilize AST as a fixative agent for azo dyes at the final stage of a combined process of filling-dyeing-fatliquoring leather semi-finished product.

Under optimal conditions of the technological process, when using azo dye of acidic type, one achieves a bulk dyeing of dermis with high surface color saturation of grain side, fastness to rubbing and light upon the interaction with AST. Compared with the control technology, which implies a final dyeing with the use of chromium compounds, the developed technology excludes this harmful reagent and azo dye. The developed technology facilitates achieving uniform coloring of the surface of a semi–finished product. This enables the formation of leather with a thin polymer coating of aniline finish that highlights natural pattern of the grain side, characteristic for certain types of raw hides.

Conclusions

We studied physicochemical properties of the technological solutions of azo dyes modified by titanium compounds of different chemical composition. A more energetic interaction was observed between the brown azo dye 345, the molecules of which contain phenolic group, and titanium compounds with possible formation of chelate compounds.

A study of kinetics of the sorption of azo dyes by collagen fibers, structured by chromium compounds, revealed a significant dependence of sorption of the dye, the molecules of which contain less auxochrome –SO_3Na groups, on temperature in the presence of titanyl oxalic acid. In this case, absolute values of the sorption of a dye at 20 °C are twice lower compared to brown 345 dye. With increasing concentration of the dye with a lower molecular weight, acidic blue-black, modified by ammonium sulfate titanylate, its diffusion capacity into the gel of gelatin is reduced twofold with an increase in AST/ABBD ratio at the concentration of the dye 80 g/L. An increase in the concentration of dye in the system is symbatic to an increase in the activity of its interaction with collagen, accompanied by reduced diffusion capacity into the gel of gelatin. It was found that filling semi-finished product of chrome tannage with acrylic polymers contributes to the increase in chemisorption of azo dye by 1.5 times when using ammonium sulfate titanylate.

The effect of the composition of dyeing solution on the coloristic properties of filled semi-finished product was demonstrated when fixing the dye on its surface by ammonium sulfate titanylate. We determined optimal ratio of ammonium sulfate titanylate and a dye, which ensures the formation of leather material with a higher color saturation of the surface of a semi–finished product by 2.1–2.9 %, maximal fastness to rubbing and light compared with the control technology. The designed technology of combined filling-dyeing-fatliquoring facilitate decrease in the consumption of azo dye, exclude at the final stage of dyeing additional consumption of a dye and application of environmentally harmful chromium compounds by substituting them with ammonium sulfate titanylate as a fixative agent of dye. This results in fivefold decrease in reagent consumption. Elastic leather material formed by the developed technology complies with the interstate standard on leather for the show uppers (GOST 939-88) and meets requirements of the ISO 9001:2008 for international standard of quality management systems.

References

[1]. **Danylkovych A., Mokrousova O., and Okhmat O.** Technology and materials for leather production (in Ukrainian). Fenix (Publisher «Фенікс») 2009, Kyiv.

[2]. **Smekhovski K.** The problem of wastewater from leather industry in Poland (in Russian). *Shoe Leather Industry* (Publisher «*Кожевенно-обувная промышленность*») **3** (1996) 30–31.

[3]. **Kasian E. and Smila A.** Aniline leather finishing with dispersions of colored polyurethanes (in Ukrainian). *Bulletin of the Kyiv National University of Technologies and Design* **1** (2007) 57–64.

[4]. **Musa A. E., Modhan B., Madhulatha W., et al.** Coloring of leather using henna – natural alternative material for dyeing. *Journal of the American Leather Chemists Association* **5**, 104 (2009) 183–190.

[5]. **Raghava Rao J., Prakash A., Thangaraj E., et al.** Natural dyeing of leathers using natural materials. *Journal of the American Leather Chemists Association* **2**, 103 (2008) 68–75.

[6]. **Shagina N. and Azimova F.** Technology of dyeing wool sheepskins with vegetable dyes from *Hypericum perforatum* using aluminum mordents (in Russian). *Natural and applied sciences* (Publisher «*Естественные и прикладные науки*») **5** (2010) 143–144.

[7]. **Azimova F. and Shagina N.** Dyeing method of wool sheepskins with Hypericum perforatum vegetable dye using aluminum mordents (in Russian). *Shoe Leather Industry* (Publisher «*Кожевенно-обувная промышленность*») **2** (2012) 43–44.

[8]. **Gainutdinov R., Sharifullin F., Abdullin I., et al.** Preparation of modified dyes by plasma treatment (in Russian). *Shoe Leather Industry* (Publisher «*Кожевенно-обувная промышленность*») **1** (2015) 21–23.

[9]. **Tikhonova N., Abdullin I., and Makhotkina L.** High-frequency plasma of reduced pressure in the manufacture of shoes (in Russian). *Bulletin of Kazan Technological University* (Publisher «*Вестник Казанского технологического университета*») **4** (2009) 131–135.

[10]. **Abdullin I., Makhotkina L., Tikhonova N., et al.** A method of manufacturing a natural leather (in Russian). RU patent 2378386, October 1, 2010.

[11]. **Surkova A., Abdullin I., and Parsanov A.** The effect of ammonium sulfate titanylate on semi-finished wool sheepskins (in Russian). *Shoe Leather Industry* (Publisher «*Кожевенно-обувная промышленность*») **1** (2010) 32–34.

[12]. **Baiandin V., Klenovskaia N., Zhivova Z., et al.** Intensification of dyeing and fatliquoring processes by the combined method (in Russian). *Shoe Leather Industry* (Publisher «*Кожевенно-обувная промышленность*») **4** (2003) 25–26.

[13]. **Danylkovych A.** Practicum in chemistry and technology of leather and fur. Fenix (Publisher «Фенікс») 2006, Kyiv.
[14]. **Laptev N. and Bogoslovskii B.** Chemistry of dyes. Chemistry (Publisher «Химия») 1970, Moscow.
[15]. **Stepanov B.** Introduction to chemistry and technology of organic dyes (in Russian). Chemistry (Publisher «Химия») 1984, Moscow.
[16]. **Fild R.** Organic chemistry of titanium (in Russian). Mir (Publisher «Мир») 1964, Moscow.
[17]. **Bokhtein B.** Atoms wander in the crystal (in Russian). Science (Publisher «Наука») 1984, Moscow.
[18]. **Venkatamaran K.** (ed.) Chemistry of synthetic dyes. Vol. III. Gostekhizdat (Publisher «Гостехиздат») 1974, Leningrad, pp. 1665–2113.
[19]. **Metelkin A. and Rusakova N.** Titanium tannage (in Russian). Light Industry (Publisher «Легкая индустрия») 1990, Moscow.

11. HIGHLY-DISPERSED SILICON DIOXIDE IN THE TECHNOLOGY OF MANUFACTURING LEATHER SEMI-FINISHED PRODUCT [7]

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Herald of Khmelnytskyi National University. Engineering Sciences **6** (2016) 112–116; *http://er.knutd.edu.ua/handle/123456789/6011*

Abstract: *The goal of the work is to determine the effect of highly-dispersed silicon dioxide on the properties and filling of wet blue leather during the production of elastic leather materials. The process of filling wet blue leather with the highly-dispersed silicon dioxide in the production of leather material for garments and shoe uppers was studied. In the paper we determined the effect of filling composition on complex of physicomechanical properties and hygienic quality of elastic leather materials. Particularly, strength and water vapor permeability of filled leather exceed a control sample by 10.5–12.0 and 25.0–30.0 %. The resulting filled leather according to its properties meets the reequipments of National standard of Ukraine (DSTU 3115-95) for leather material for garment, the international standard for shoe uppers (GOST 939-88), and international standard on quality management system (ISO 9001:2008). Therefore, the optimal concentration of highly-disperse* SiO_2 *in filling composition, which yield elastic leather materials with required complex of physicochemical, sanitary, and hygienic properties, was determined.*

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[7] *The title has been modified; the original title is "Use of highly disperse silicon oxide in manufacturing technology of leather semis". The original paper was published in Ukrainian.*

Keywords: *semi-finished leather; filling composition; dermal structure; leather property.*

Introduction

Modern production of polyfunctional leather materials requires significant improvement of the existing and development of innovative technologies using new reagents and materials. Along with this, due to the multistage technology of processing of natural raw materials, there is a need to increase the efficiency of individual processes related to the preliminary and subsequent processing in the technological cycle of the production of leather material. Considering a certain technogenicity and a significant consumption of the materials during leather production, an essential aspect of this problem is to efficiently use technological materials based on scientifically justified conditions of their use. Given the fact that existing technologies utilize a significant number of reagents and materials from foreign providers, which extremely increases the cost of leather products, it is important to develop new domestic materials and research the conditions for their effective use, particularly, in post-tanning processes.

Technology for production of leather materials involves various chemocolloidal processes and utilizes synthetic and natural reagents and mechanical processing with qualities of resulting leather materials being considerably dependent on their intended purpose [1, 2]. In the technologies of manufacturing elastic leather semi-finished products, compositions of hydrophilic polymers of polyacrylic series with other reagents were used at the stage of filling [3, 4]. This results in the material to be more compacted, thick, strong, and elastic with simultaneous decrease in the surface unevenness. The authors [5] have shown that the use of the aqueous emulsion of copolymer of butyl acrylate and styrene results in the formation of leather materials with increased thermal stability, strength, and elasticity.

Effective formation of complex hierarchical structure of dermal collagen in semi-finished leather products at the tanning-filling stage requires the usage of a number of reagents of a certain chemical composition. Herewith, each of the ingredients performs a certain chemocolloidal function, particularly, the diffusion of the components of the technological solution is insured up to the microfibrillar level and will contribute to maintaining the leather structure in a dispersed state during removal of moisture upon drying. The use of a composition including nitrogen-containing hydrophilic polymers and acrylic emulsion A [6] provides an increased resistance to friction, improved mechanical properties (strength and elasticity), and minimizes the shrinkage of the semi-finished product during finishing. The composition of protein hydrolysate, glutaraldehyde, and vegetable tanning agents provides the formation of high-quality material [7] with a reduction of technogenic impact on the environment. For the production of leather material with enhanced elastic-plastic characteristics, filling compositions which contain vegetable tannins are used [8, 9]. At the same time, the filling process is combined with fatliquoring.

In recent years, during the production of leather materials in the filling compositions, mineral reagents of natural origin are used [1, 10, 11]. The expediency of use for filling of leather semi-finished product of chrome tannage with modified bentonite containing 85 % montmorillonite has been shown. In this case, an increase in the bulk structuring of the dermis was observed together with the area increase of the leather and improvement of physicomechanical and deformation properties. The use of modified bentonite composition with sodium polyphosphate (2–4 % of the weight of the fleshed semi-finished product) [12, 13] can considerably increase the thickness and volume yield of leather material and increase its surface area to 104.8–105.7 % compared to the leather processed without bentonite. A composition including Na-montmorillonite, acrylic acid copolymer, aldehyde, and chromium sulfate, when used during tanning-filling process [14–17], allows increasing the thickness of the material, its strength, including tensile strength and biaxial stretching under ball punch deformation. The addition of sodium lignosulphonate into the bentonite dispersion [18] evens out the thickness of the semi-finished product, minimizes its shrinkage, and increases the yield of the surface area of the final material.

The use of the composition for tanning-filling semi-finished product of chrome tannage [19–21], which includes montmorillonite and polyacrylic acid, allows forming leather with a smooth grain side and a pleasant feel. Analysis of physicomechanical properties of leather indicates an increase in the orientation of structural collagen fibers in the material during deformation.

The effects of using a zeolite mineral in a composition for filling a leather semi-finished product have been previously studied [22–24]. In this case, macroporous structure of the dermis is getting condensed, the filling of peripheral sections of semi-finished product is increasing, and, accordingly, the thickness of the final leather, but the yield of surface area is decreased.

So, during the tanning-filling processes of leather semi-finished products, a wide range of natural mineral reagents of different chemical composition with the corresponding complex of chemocolloidal properties can be used. In this case, the surface of their particles is either pre-modified or modified during the preparation of the technological composition. The effectiveness of compositions is mainly determined by their chemical content. In this regard, the development of new filling and tanning compositions utilizing a highly-dispersed synthetic oxide ingredients can have a significant scientific and practical value.

Thus, goal of this work was to determine the effect of highly-dispersed silicon dioxide on the filling process and the properties of semi-finished leather of chrome tannage for the production of elastic leather materials.

Materials and Methods

To determine the effect of highly-dispersed silicon dioxide on the formation of leather material from green-salted cattle hide, we used chrome-tanned leather (CTL) with thickness of 1.5–1.6 mm in the form of symmetric strips (10×75 cm), divided into three batches and numbered from backbone line. The studied semi-finished product was obtained at the PJSC Chinbar (Kyiv, Ukraine) by the method used for production of shoe uppers. Samples of semi-finished products were used after samming and shaving.

The process of filling semi-finished product was performed after washing and neutralizing samples up to pH 5.4 using bromocresol green indicator in polyethylene containers with a volume of 1 L using 1.2 : 1.0 ratio of volume of technological solution to the weight of semi-finished product (liquid coefficient, LC), at a consumption of the filling composition 11 % of the weight of the semi-finished product. The process was carried out at 28–30 °C and constant rotation in a vertical plane at 18–20 rpm in a custom-build equipment (Fig. 1).

Fig. 1. *Custom-build equipment for technological processing of leather semi-finished product.*

The composition of the filling composition included the following chemical reagents:

- Trupon DL (Trumpler, Germany) – an electrolyte resistant fatliquoring reagent;
- Relugan D (BASF, Germany) – lightfast resin tanning agent or producing soft leathers with a dry residue of 96 %;
- Trupotan G (Trumpler, Germany) – a replacement syntan for the retanning of shoe upper leather and suede with an active substance content of 93 %, based on phenolic compounds and has a negative charge;
- quebracho (China) – a tanning agent extracted from the wood of a South American tree with 85 % content of vegetable tannins and 5–6 % of ash (calculated on a dry basis).
- highly-dispersed silicon dioxide A-300 produced by pilot plant (Kalush, Ukraine) of the Chuiko Institute of Surface Chemistry with the size of its protoparticles 1–2 nm, primary particle size of 4–50 nm, and a specific surface area of 50–380 m^2/g [25].

Aerosil A-300 was used in a mixture with fatliquor Trupon DL. After 10 minutes of processing semi-finished product, Relugan D was added to the technological solution, and after 10 more minutes a dispersant of vegetable tannins, Trupotan G, and quebracho were added. The total duration of the filling-tanning process was 150 min. Samples of filled semi-finished products were further subjected to fatliquoring with Trupon DL (7 % of the mass of the semi-finished product). The filling process of semi-finished leather was completed at pH 4.0–4.2. The following technological processes and operations of filling-tanning of leather semi-finished products were performed according to the technology of PJSC Chinbar.

The investigation of the chemical composition of the filled semi-finished product and its physicomechanical properties were carried out according to the previously described methodology [26]. The mechanical properties of the leather materials were determined on a tensile testing machine RT-250M at a sample extension rate of 90 mm/min and a device PZhU-12M (Russia) for determination of stiffness and elasticity. Sanitary and hygienic properties – air and vapor permeability, were evaluated, respectively, on the device for the determination of air permeability and using a desiccator method at 20–21 °C. Volume yield [cm^3 per 100 g of proteins] of leather semi-finished product was determined as the ratio of volume of air-dried sample to volume which was calculated as a product of sample mass and specific volume [cm^3 per 100 g of proteins]. Porosity [%] was calculated as a ratio of pore volume to sample volume.

Results and Discussion

The prospects of the usage of synthetic silicon dioxide at the filling-tanning stage are provided, first of all, by its high dispersity and the presence of hydroxyl groups on particle surface. Because of this, this hydrophilic filler, Aerosil A-300, was used in the technology of transformation of raw leather materials in post-tanning processes. The consumption of ingredients of the filling-tanning composition containing Aerosil A-300 is given in Table I. The functional purpose of each ingredient was taken into account at constant consumption of condensed polyphenols of quebracho and fatliquor. The consumption of Aerosil A-300, the dispersibility of which was facilitated by the use of the sulphited fatty substances Trupon DL, was changed in the direction of reducing the amount of Relugan D and Trupotan G compared to the control. At the maximal consumption of Aerosil A-300 the amount of these ingredients was reduced twofold.

The effect of the filling-tanning composition on physicochemical properties is given in Table II. Compared with the control sample, the content of the proteins decreases with the increase of the content of highly-dispersed silicon dioxide. At the same time the amount of tannins increases in the semi-finished product.

At a minimal consumption of Aerosil A-300, there is an increase in the porosity of the chrome-tanned leather with a shrinkage temperature of 113–115 °C. In this case, the absolute values of porosity in the loose topographic areas (cuts) increase by 8–11 % compared with the control. Along with this there is an increase in the thickness of leather material and its volume yield, respectively, by 9–10 % and 11.0–12.6 %.

Table I. *Ingredient consumption for the composition used for filling-tanning of leather semi-finished product.*

Ingredient	**Consumption [% of the weight of semi-finished product] for treatment**			
	control	***1***	***2***	***3***
Aerosil A-300	0	1	2	3
Trupon DL	1	1	1	1
Relugan D	2	2	1	1
Trupotan G	3	2	2	1
Quebracho	6	6	6	6

The character of the dependence of the physicomechanical characteristics of the final leather material, in general, correlates with changes in its physical characteristics with increasing the content of the Aerosil A-300 in the semi-finished product. An increase in the strength and elongation of the leather at 1.0 % consumption of Aerosil A-300 compared to the control sample can be explained by deep inter-microfibrillar diffusion of silicon dioxide nanoparticles. After removing moisture during drying-moisturizing processes, the elements of the fibrous structure of the leather semi-finished product remain in a dispersed mobile state with a possible orientation during deformation. However, at a maximal consumption of Aerosil A-300 there is a slight decrease in the deformation characteristics of the leather. In this case, compared with the control sample, the stiffness of the filled leather decreases by 24.0–30.0 %.

Table II. *Chemical composition and physical properties of leather semi-finished product.*

Parameter	**Parameter value**			
	treatment			
	control	***1***	***2***	***3***
Mass fraction [%] of				
– moisture	13.3	14.1	14.4	14.7
– proteins †	68.3	66.8	66.1	65.7
– ash	5.4	6.3	7.1	7.7
– Cr_2O_3	4.2	4.0	3.8	3.5
– substances extracted with OS	8.3	8.5	8.6	8.9
– bound organic substances	14.7	15.6	15.9	15.8
T_S **[°C]**	113.0	114.0	115.0	114.0
Thickness [mm]	1.30	1.39	1.43	1.40
Volume yield [cm^3 **per 100 g of proteins †]**	213	237	240	235
Porosity [%]	48.0	56.0	58.0	59.0
Tensile strength [MPa]	21.0	23.5	23.0	23.5
Elongation at 10 MPa [%]	25.0	31.0	32.0	33.0
Elongation at break [%]	59.0	64.5	64.5	63.0
Stiffness [cN]	38.0	29.0	27.0	28.0

Note: *† denotes that nitrogen content was quantified using Kjeldahl method and recalculated for protein content.*

The character of the dependence of the sanitary and hygienic properties of the dehydrated leather semi-finished product with increase of the amount of Aerosil A-300 (Fig. 2) correlates with the change in its porosity. In this case, the vapor and air penetration reach the maximal values in the topographic areas (cuts) of bend and belly, respectively, at the 1.0 and 2.0 % consumption of Aerosil A-300.

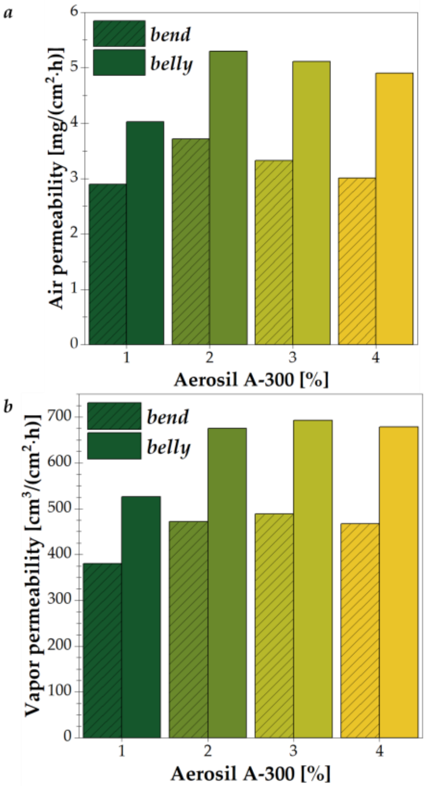

Fig. 2. *Dependence of air (a) and vapor (b) permeability of leather semi-finished product on the concentration of Aerosil A-300 and topographic area (cut).*

Such a character of the dependence of vapor and air permeability on the amounts of Aerosil A-300 can be due to the chemocolloidal properties of silicon dioxide and the mechanism of water vapor and air diffusion through the structure of leather material. If water vapor penetration through the natural material causes the adsorption of water molecules on the surface of the modified structure of dermal collagen by its functional groups, followed by their desorption, then in the case of air permeability, the mechanism is determined, mainly, by porous structure of the material. With an increase of Aerosil A-300 amount to over 2.0 % there is an uneven distribution of the filling-tanning composition in the structure of the dermis – to a greater extent in the superficial papillary layer of the dermis, which complicates the further diffusion of the ingredients of the filling composition into the structure of the material.

Thus, a highly-dispersed silicon dioxide can be used in the composition for filling-tanning of leather semi-finished products as a partial substitute for imported ingredients to improve physical, chemical, and sanitary characteristics of elastic leather materials. Application of the developed method in the production of leather materials requires further research for the optimization of its composition.

Conclusions

Investigation of the process of filling-tanning of chrome-tanned leather semi-finished product using highly-dispersed silicon dioxide showed the effectiveness of the partial replacement of imported dispersing reagents.

Incorporation of highly-dispersed silicon dioxide into the leather material results in an increase in the physicomechanical properties of the final leather material. The optimal consumption of a highly-dispersed silicon dioxide component is found to be within 1–2 % of the weight of the semi-finished product in regard to physicochemical and sanitary-hygienic characteristics of leather material. In this case, compared with the control sample, the leather strength increases by 10.5─12.0 % and the vapor permeability – by 25.0–30.0 %.

The character of the dependence of the properties of the leather semi-finished product on the concentration of highly-dispersed silicon dioxide is caused by the peculiarities of the concentration-based diffusion of its particles into the structure of the dermal collagen. At a minimal concentration of fatliquor in the filling composition and an increase in the ratio of silicon dioxide nanoparticles-to-fatliquor up to 3 : 1, there is a significant increase in the concentration of the filler in the papillary layer of the dermis.

The positive effect of highly-dispersed silicon dioxide on the sanitary and hygienic properties of leather material in its peripheral topographic areas (cuts) is established. The resulting filled leather material according to the complex of properties meets the standards of elastic leather materials for garments according to DSTU 3115-95, the interstate standard on leather for the shoe uppers GOST 939-88, and the requirements of the international standard of quality management systems ISO 9001:2008.

References

[1]. **Hryshchenko I., Danylkovych A. (ed.), and Mokrousova O.** Polyfunctional leather materials: monograph (in Ukrainian). Fenix (Publisher «Фенікс») 2013, Kyiv.

[2]. **Danylkovych A.** (ed.) Innovative technologies of production of leather and fur materials and products: monograph (in Ukrainian). Fenix (Publisher «Фенікс») 2012, Kyiv.

[3]. **Ma J. and Lu H.** Elasticity studies on leather retanned with various types of acrylic polymers. *Journal of the American Leather Chemists Association* **103**,11 (2008) 363–369.

[4]. **Danilin D., Studenikin S., Zykova N., et al.** Effect of distribution of filling polymers in the layers of the split (in Russian). *Shoe Leather Industry* (Publisher «*Коженно-обувная промышленность*») **6** (2009) 46-48.

[5]. **Nashy E., Hussein A., and Essa M.** Novel retanning agents for chrome-tanned leather based on emulsion-nano particles of styrene/butyl acrylate copolymers. *Journal of the American Leather Chemists Association* **106**, 9 (2011) 241–248.

[6]. **Ramazonov B., Kadirov T., Toshev A., et al.** Filling of skins with nitrogen-containing polymers (in Russian). *Reports of the Academy of Sciences of the Republic of Uzbekistan* (Uzbek publisher «*Доклады Академии наук Республики Узбекистан*») **2** (2008) 64–67.

[7]. **Mariliz, G., Silva D., and Vigannico I.** Leather retanning with hydrolyzed protein. *Journal of the American Leather Chemists Association* **105** (2010) 195–202.

[8]. **Chursin V., Bordunova E., and Osipov A.** Effect of biopolymer compositions on the elastic-plastic and strength properties of leathers (in Russian). *Leather and shoe* (Publisher «*Кожа и обувь*») **2**. 29 (2008) 16–18.

[9]. **Wang C., Feng S., and Wu J.** Preparation of organosilicon modified palm oil fatliquor. *Journal of the American Leather Chemists Association* **106** (20011) 161–169.

[10]. **Mokrousova O.** Highly-dispersed mineral fillers for the skin (in Ukrainian). *Bulletin of the Kyiv National University of Technologies and Design* **1**, 38 (2008) 354–358.

[11]. **Mokrousova O., Kachan R., and Kozar O.** Modern aspects of post-tanning processes of leather production (in Ukrainian). *Bulletin of the Kherson National Technical University* **1**, 48 (2014) 128–136.

[12]. **Mokrousova O., Danylkovych A., Martsin I.** Filling capacity of highly-dispersed minerals of different crystalline structures (in Ukrainian). *Bulletin of the Kyiv National University of Technologies and Design* **2** (2008) 34–43.

[13]. **Mokrousova O. and Danylkovych A.** Filling of leather semi-finished product. Modification and use of bentonite dispersions (in Ukrainian). *Bulletin of the Khmelnytskyi National University* **3**, 1 (2008) 239–244.

[14]. **Ma J., Chen X., Chu Y., et al.** The preparation and application of a montmorillonite-based nanocomposite in leather making. *Journal of the Society of Leather Technologists and Chemists* **87**, 4 (2003) 131–134.

[15]. **Mishra J., Kim I., and Ha C.** New millable polyurethane/organoclay nanocomposite: preparation, characterization and properties. *Macromolecular Rapid Communications* **24** (2003) 671–675; doi.org/10.1002/marc.200350008.

[16]. **Ma J., Hu Z., and Liu L.** The acrylic resin leather coating agent modified by nano-SiO_2. *Journal of Composite Materials* **40** (2006) 2189–2193.

[17]. **Mokrousova O. and Danylkovych A.** Formation of collagen structure of derma by mineral dispersions. *Scientific proceedings of Riga Technical University* **1**, 14 (2007) 83–91.

[18]. **Mokrousova O. and Danylkovych A.** Adsorption of sodium lignosulphonate on hydroxychromium montmorillonite (in Ukrainian). *Bulletin of the Kyiv National University of Technologies and Design* 2 (2011) 133–139.

[19]. **Chen Y., Fan H., and Shi B.** Nanotechnologies for leather manufacturing: a review. *Journal of the American Leather Chemists Association* **106**, 8 (2011) 261–273.

[20]. **Bao Y., Ma J., and Wang, Y.-L.** Preparation of acrylic resin/montmorillonite nanocomposite for leather tanning agent. *Journal of the American Leather Chemists Association* **104**, 10 (2009) 352–358.

[21]. **Zhang X., Liu Q., and Zhang W.** Nanocomposites of acrylate-organosilicon resin/layered silicate for leather finishing. *Journal of the Society of Leather Technologists and Chemists* **90**, 6 (2006) 250–254.

[22]. **Kozar O., Mokrousova O., and Konoval V.** Assessment of relaxation and deformation characteristics of leather for shoe uppers filled with natural minerals (in Ukrainian). *Bulletin of the Kyiv National University of Technologies and Design* **4** (2013) 107–115.

[23]. **Kozar O., Mokrousova O., and Konoval V.** Deformation characteristics of genuine leather, manufactured using natural minerals. *Proceedings of the XIII International Conference "Baltic Polymer Symposium"*, Vilnius University, Trakai, Lithuania; September 18–21, 2013; p. 141.

[24]. **Kozar O., Mokrousova O., and Victor T. M.** (2013). Evaluation of parameters of shape stability of the hides modified with organomineral compositions (in Ukrainian). *Intercollegiate collection "Scientific notes" of Lutsk National Technical University* (Ukrainian journal «Міжвузівський збірник «Наукові нотатки») **41** (2013) 135–137.

[25]. **Iler R.** The chemistry of silica: solubility, polymerization, colloid and surface properties and biochemistry of silica. Part I. Mir (Publisher «Мир») 1982, Moscow.

[26]. Aerosil (pyrogenic silicon dioxide); www.silica.su/ru/perechen-produkczii/834-aerosil.pdf.

[27]. **Danylkovych A. and Chursin V.** Analytical control in leather and fur production: a laboratory practicum (in Russian), Infra-M, Moscow, 2016. 176 p.

12. IMPROVEMENT OF THE FILLING-PLASTICIZING PROCESSES OF FORMING MULTIFUNCTIONAL LEATHER MATERIALS [8]

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Abstract: *The paper is focused on the filling-plasticizing processes at the final stages of forming multifunctional leathers from various types of raw hides using new compositions. The content of a tannin-based composition was found to affect the process of its diffusion throughout the structure of the semi-finished chrome-tanned product. Particularly, we have determined that the depth of diffusion of the filling composition in loose areas (cuts) was close to 100 % with a composition consumption of 5 % of the mass of the semi-finished product; in dense areas (cuts) even at an increased consumption, the diffusion was only 80 % of the thickness of the semi-finished product. The structure of the filling-plasticizing composition was developed to form various leathers from cattle and sheep hides. A protein hydrolysate and a highly dispersive modified aluminosilicate have been shown to affect the process and physicochemical properties of semi-finished leathers. If the filling-plasticizing composition contains optimal amounts of montmorillonite and protein hydrolysate at 4–2 % of the semi-finished leather mass, the obtained leather materials are characterized by tensile strengths of 15–16 and 20–22 MPa, respectively for sheepskin and bovine hides, and corresponding stiffness of 15–16 and 21–22 cN. The use of montmorillonite in the filling-plasticizing compositions during processing semi-finished chrome-tanned products provides stability of the dispersed structure during further processing and its mobility in the*

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[8] *The title has been modified; the original title is "Improvement of the filling and plasticization processes of forming multifunctional leather materials".*

cyclic deformation of the products. The complex study of the process of filling-plasticizing semi-finished chrome-tanned products was used for developing effective technologies to produce elastic materials for shoe uppers and garment leather with the necessary physicomechanical properties and increased volume and area yields by 270–310 and 5–6 % cm^3 per 100 g of proteins, respectively, in comparison with the yields of the existing industrial technology.

Keywords: *semi-finished leather product; filling-plasticizing process; tannin; montmorillonite; technology; physicochemical property; microstructure.*

Introduction

Improvement of the existing and development of new technologies of forming multifunctional leather materials especially focuses on the final physicochemical processes – filling and plasticizing of the semi-finished product (SFP). This is basically caused by finalizing the chemical composition changes, compacting the structure, reducing the moisture content by replacing water with filler particles and plasticizing reagents, and making even physicomechanical, sanitary, and other exploitational properties throughout the area of the formed material. The efficiency of these processes is greatly affected by the conditions of their implementation, the chemical composition of the used reagents, chemocolloidal properties of the latter, and the structural state of the semi-finished product that was achieved at the previous stages of treatment.

A scientifically-based choice of fillers and plasticizers for further formation of the already structured semi-finished products considers that some fillers impregnate, first of all, in relatively large pores, whereas plasticizing requires the incorporation of reagents of significantly smaller sizes into intermicrofibrous and intermolecular openings that are 2.74 and 0.6–0.8 nm, respectively, in size [1, 2]. Formation of multifunctional leather materials predetermines, to a large extent, significantly different content of fillers and plasticizers [1, 3]. Hence, there has been intensive research on developing novel chemical reagents to improve the filling and plasticizing technologies of producing leather materials.

Analysis of the Previous Findings and Problem Statement

At the final stages, leather materials with complex hierarchical structures of the dermis collagen are formed utilizing a wide range of natural and synthetic reagents. Particularly, new technologies of leather manufacturing sometimes apply acrylic polymers and compositions based on them [3–5]. Filling and retanning a semi-finished leather product are combined with its plasticizing, which is called fatliquoring in the relevant technological literature. The use of aqueous dispersions of hydrophilic polyacrylates allows increasing the density, strength, and elasticity of leather material as a result of additional structuring of semi-finished products. An optimal chemical composition of the copolymer with a consumption of 2–4 % significantly increases the split leather thickness and significantly reduces its unevenness throughout topographic areas [4]. The previous findings [5] show how copolymers that are synthesized from acrylic acid and monomers of various chemical compositions affect the elastic-plastic properties of the filled leather material. It has been found that the use of copolymers, such as ethyl acrylate and butyl acrylate, increases the elasticity of the resulting leather materials. Water emulsions of copolymers of butyl acrylate and styrene of various particle sizes form leather materials with increased thermal stability and with improved strength and elasticity [6]. At the same time, the waste water contamination is reduced.

The process of filling-retanning chrome-tanned products with Polynex acrylic copolymers of various chemical compositions [7] at a consumption of 4.0–5.0 % allow obtaining elastic leather with a dense structure of its final elements, which facilitates the processing of a grain side of a semi-finished product when it is polished. The authors recommend using a specific copolymer composition at the stage of filling semi-finished leather for shoes and garments with various thickness of leather materials. Acrylic polymer emulsions based on the synthesized amino furazan formaldehyde resin, as a filling-retanning reagent, modified with isopropyl alcohol allows obtaining leather materials with a decreased shrinkage by 1.5–4.0 % during drying [8]. In addition to filling-retanning capacities, the reagent increases the hydrophobicity of semi-finished leathers [9]. This effect is observed clearly in vegetable and synthetic tanning of hides used for production of saddlery leather. It is necessary to note that dimethylformamide resin used as a solvent reduces the hydrothermal stability of chrome-tanned semi-finished products and bleaches them. Unlike the modified amino furazan formaldehyde resin, sulfonated melamine formaldehyde oligomers [10] that are used in finishing the chrome-tanned semi-finished products enhance their fullness and elasticity and color intensify. However, after the finishing, the hides contain up to 10 mg/kg of free formaldehyde.

Studies [11–14] raise an important problem of forming leather material from low-grade raw hides. The authors synthesized sulfoaromatic polymers by polycondensation of sulfonated resorcinol with a phenol-urea-formaldehyde resin aqueous dispersion with particle size of 0.7–1.4 μm at pH 6.0–6.7, which ensures its high diffusivity in the structure of the chrome-tanned semi-finished product obtained from hides of medium-size heifers. Despite the increase in the size of copolymer particles in the structure of semi-finished leathers to 3.0–3.4 μm, the formed leather material has higher density and elasticity in comparison with the leather produced with the use of the Ecofix industrial composition. Application of the designed copolymer can increase the degree of filling and improve elastic-plastic characteristics of the material.

Filling semi-finished leather product can be efficient with the use of a set of materials the chemical composition of which has optimal chemocolloidal properties. Particularly, one study [15] showed that finished leather materials have an improved fastness to rubbing, improved strength and flexibility, and lower shrinkage during finishing utilizing compositions based on nitrogen-containing hydrophilic polymers and acrylic emulsion A.

Considerable scientific and technological interest have works which study the effect of polymer-vegetable fillers (PVFs) on the formation and properties of leather materials. In another study [16] tanning agents based on acrylamide (AAm) and glycidyl methacrylate (GMA) were synthesized and used in conjunction with lignosulfonates (LS), a quebracho extract (QE), and chitosan. Based on elasticity, the resulting leather materials allow arranging the PVFs (at 5 % consumption) in the following sequence: QE > AAm-chitosan > GMA–LS > AAm–LS > AAm–QE. By increasing the thickness, the synthesized tanning agents follow the series: QE > QE–AAm > AAm–LS. This effect is less pronounced in the case of VPF tanning agents AAm–QE and AAm–LS, which is caused by blocking a part of active groups in their molecules and higher molecular weight and an increased particle size in comparison with QE. However, since VPF GMA–LS have reactive functional groups in their molecules, they ensure high physicomechanical properties in leather materials due to additional structuring of the dermal collagen. Compatibility of aqueous styrene-acrylic dispersions and hydroxyethyl cellulose allowed developing the filling compositions containing vegetable tannins [17]. With a consumption of 8 % of composition, the resulting leather materials have increased elastic-plastic and strength characteristics.

Filling a semi-finished leather with a hydrolyzed protein, glutaraldehyde, and vegetable tannins allows producing high-quality leather [18] and reducing the waste production and its impact on the environment. Whey containing 2.5–5.0 % of proteins with gelatin at a ratio of 10 : 1 [19] can be used in filling semi-finished leather for shoe uppers and upholstery where it improves the physicomechanical properties of the final material having an enhanced colorability.

In hide processing technologies it is desirable to combine individual technological processes, such as filling-fatliquoring-dyeing, by gradually introducing certain chemicals or their compositions. Technical studies describe fatliquor as compositions containing natural and synthetic reagents for producing leather with improved elastic characteristics [20]. Particularly, specialists of the TFL company have developed a lecithin-based anionic composition that is characterized by high stability, lightfastness, and heat resistance. The researchers have also synthesized a plasticizing composition based on palm oil. The latter was amidated by diethanolamine in the presence of sodium methoxide and further modified with silicone oil containing terminal hydroxyl groups. It was followed by esterification with maleic anhydride and further sodium bisulfite treatment. The derived plasticizer was used to form a highly elastic leather material.

The combined process of filling-fatliquoring of the semi-finished material utilize the following composition: stabilized acrylic copolymers – 5 %, QE – 3 %, a fatliquor based on natural and synthetic fats and oils – 8 %, with addition of a complex-forming emulsifier [21, 22]. Leather obtained under optimized conditions is characterized by high degree of structure filling, greater thickness uniformity, and the necessary range of exploitation properties. This decreases the “loose grain” defect up to 50 % and reduces the consumption of vegetable and synthetic tanning agents.

The researchers [23, 24] recommend using a phospholipid-based liposome composition with added hydrophobic and hydrophilic reagents in filling leather materials. Researchers have showed a significant impact of additives – petroleum jelly, castor, linseed, and hemp oils – both on the filling-plasticizing process and the properties of the resulting materials. Particularly, the use of petroleum jelly imparts hydrophobic properties to the leather, hemp oil – hydrophilic properties with a high vapor capacity, and flaxseed oil allows obtaining a flexible leather with a high vapor permeability. Additionally, the use of special liposome fillers with antibacterial properties – essential oils of *Monarda fistulosa*, tea tree, Tagetes, polyhexamethylene guanidine, and others – allows producing leather with a high resistance against biological deterioration. The significantly smaller particles, compared to fatliquor, have a higher diffusivity and, therefore, a higher plasticizing effect which contributes to the strength and elongation at low loads that match the deformation requirements to the material during its performance. The possibility of intensifying the filling-fatliquoring technology by combination of processes and saving chemical materials and energy deserves special attention.

According to the publication [25], members of the Lanxess corporation have designed new polymer materials using polyamide-carboxylic acid in filling-fatliquoring different types of leather that are recommended for the production of footwear, apparel, leather goods, furniture, and automotive leather. The advantages of this polymer compared with natural fatliquoring reagents include its heat resistance and lightfastness, high color intensity, and resistance to the fogging effect to which leather materials are vulnerable.

The authors of another study [26] showed that upon a semi-finished leather soaking with dispersions of polymaleate and polyacrylates of different molecular weights with the increase in the particle size from 17 to 562 nm, the porosity and the vapor permeability of the untreated chrome-tanned bovine leather for shoe uppers decreases when a polymer is added at the beginning of the process. If polymers are used at the stage of the completing dyeing, the above characteristics slightly increase, and the hygienic properties of such leather materials is getting improved according to a complex of properties. Thus, the lining leather of an equine origin has a comprehensive assessment of 98.5 %, and the shoe lining leather of a bovine origin – 46.8 % when as the standard material a natural non-dyed lining leather of a porcine origin is used.

Therefore, the analysis of technological studies shows that in most cases synthetic reagents or compositions are recommended as fillers and plasticizers in the formation of leather materials. Regarding the higher environmental requirements for manufacturing processes, the necessity to save energy, improve the quality of leather materials, and reduce their cost, there should be further research in the development of new efficient filling-plasticizing compositions based on primarily natural reagents for the combined technological processes and production of high-quality multifunctional leather materials.

The Purpose and Objectives of the Study

The goal of this work is to study the processes of filling-plasticizing using organomineral compositions at the final stages of manufacturing leather produced from hides with different ratios of papillary and reticular dermis layers. To achieve this goal, the following tasks were set:

– to study the technological efficiency of the filling-plasticizing compositions;

– to study the impact of a filling-plasticizing composition content of physicochemical properties of semi-finished leather;

– to investigate the effect of a highly-dispersive aluminosilicate on the bulk formation and elastic properties of the resulting leather;

– to study the structural characteristics of a leather material during its formation.

Materials and Methods

We used a 0.9–1.6 mm thick semi-finished product of chrome tannage made of green-salted raw hide of bovine origin and 1.1–1.2 mm thick sheepskin obtained by a method of producing leathers for shoe uppers. Before the filling-plasticizing processes, raw hides were subjected to a number of technological treatments such as: restoring the hydrophilic state of the dermal structure after its preservation; removing hair and epidermis; dividing the fibrous macrostructure through alkaline processing and simultaneous removal of non-fibrous components; and acid-salt processing followed by chemical structuring with chemical compounds of chromium (III).

In the combined process of filling and plasticizing, the developed technology of forming elastic leathers for shoe uppers involved both natural and synthetic materials. Particularly, this includes vegetable tannins from mimosa and acid hydrolysis product of secondary resources for manufacturing semi-finished products of chrome tannage (edge cuts and trim): a protein hydrolysate [27, 28] with 41.3 % of solids and density of 1.21 g/cm^3, pH of 6.5–7.0, and the molecular weight of collagen hydrolysate products 12–14 kDa. The activity of protein oligomers is defined by the presence of imino-, amino hydroxyl, carboxyl, and hydroxyl functional groups [29].

The mineral filler that we used is the natural highly-dispersed montmorillonite (MM) from the Dashukivsk deposit (Cherkasy region, Ukraine); it has the general formula $Al_2O_3{\cdot}4SiO_2{\cdot}H_2O{\cdot}nH_2O$

and was modified with sodium formate with concentration of 100 g/L at a consumption of 10 % of the montmorillonite mass. The exchange interaction involving sodium cations creates favorable conditions for dispersing montmorillonite aggregates and obtaining a filler of 0.9–1.0 nm in size [30]. Vegetable tannins were dispersed using synthetic condensation product of 2-naphtholsulfonic acid and dioxide phenyl sulfone with formaldehyde – a β-naphthalene sulfonate (BNS).

The process of filling-plasticizing consists in processing the split semi-finished product with composite materials of defined chemical structure after its neutralization [3]. The diffusion of tannins and their mixture with the BNS, as the modifier, in the structure of the chrome-tanned semi-finished product were studied microscopically at the cross section for determining the filler diffusion depth during one hour of processing a 1.6 mm thick semi-finished product. The effect of filling-plasticizing compositions on the formation of leather material was assessed by studying physical, chemical, and technological properties of the final leather using the relevant methods [31]. The substances that are typically extracted with organic solvents (OS) were determined using a mixture of tetrachloromethane and trichloroethylene in the ratio of 1 : 1. The contents of the components in the leather material were calculated on a dry basis.

The mechanical properties of the leather were studied using a tensile testing machine RT-250M at an extension rate of 90 mm/min. The leather stiffness was studied on a device PZhU-12M (Russia) for determining stiffness and elasticity. The leather thickness was measured by a micrometer TR 25-100 with 10 μm scale division value. The leather area was measured on a specialized electromechanical equipment (Svit, Czech Republic; model 07484/P1) after drying-moisturizing and mechanical processing. As a control, the leather produced by the existing industrial technology was used.

The microscopy study was performed using a scanning electron microscope REMMA-102 (Selmi, Ukraine). Leather samples were prepared from a semi-finished product after its alcohol-ether dehydration. To eliminate electrical charges, the surface of each sample was coated with silver film 3–5 nm thick. The depth of the electron beam in scanning the area of a sample according to the method [32] was 3 μm.

The Effect of Organomineral Compositions on the Physicochemical Properties of Leather

When studying the filling-plasticizing process in the technology of manufacturing leather materials, it is essential to consider the peculiarities of interaction between reagents and elements of chemically-structured dermal collagen at macrofibrous and microfibrous levels. The effectiveness of replacing traditional and scarce fillers with newly developed reagents is determined by a specific mechanism of their dynamics in these processes. The results of studying the effect of the mimosa-BNS composition on the formation and properties of chrome-tanned semi-finished product from cattle hides are shown in Fig. 1 and Table I.

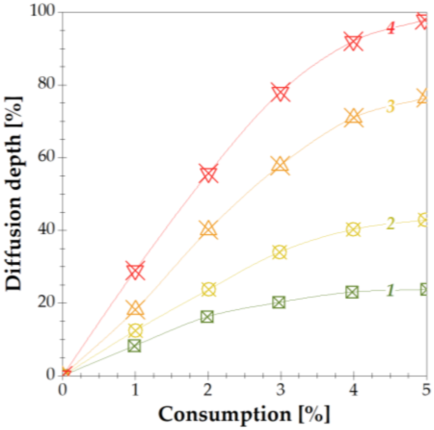

Fig. 1. Dependence of the diffusion depth of mimosa (1 and 3) and mimosa/BNS with the ratio of 1 : 1 (2 and 4) in chrome-tanned semi-finished product from bend (1 and 2) and belly (3 and 4) areas.

The results of the mimosa vegetable tanning and BNS diffusion into the semi-finished product of chrome tannage (Fig. 1) show an acceleration of the filling process if mimosa and BNS are used together.

Table I. *Physicochemical properties of the chrome-tanned semi-finished product (CTSFP) filled with vegetable-based tannin agents.*

Parameter	**CTSFP**	**Mimosa [%]** [1]	**Mimosa-to-BNS ratio and consumption [%]**		
			1:1		**1:2**
		1.2	**2.4**	**3.5**	**3.6**
Mass fraction [%] of					
– proteins †	82.2	78.8	74.4	71.7	71.1
– Cr_2O_3	$\frac{3.6}{5.6}$	$\frac{3.5}{5.3}$	$\frac{3.3}{4.9}$	$\frac{3.0}{4.2}$	$\frac{2.8}{4.0}$
– ash	$\frac{5.4}{6.9}$	$\frac{5.3}{6.7}$	$\frac{4.9}{6.3}$	$\frac{4.6}{5.7}$	$\frac{4.4}{5.3}$
– substances extracted with OS	$\frac{5.6}{9.4}$	$\frac{6.1}{9.9}$	$\frac{6.7}{10.4}$	$\frac{6.9}{11.2}$	$\frac{7.6}{11.8}$
– bound organic substances	0.94	0.81	1.23	1.5	1.38
– tanning composition (filler)	—	3.72	7.51	9.82	10.4
Tensile strength [MPa]					
– whole skin	18.6	18.1	18.2	17.0	18.3
– grain side	17.4	17.1	15.4	15.7	17.4
Elongattion [%]					
– at 9.8 MPa	38.0	34.0	38.0	36.0	29.0
– at break	63.0	59.0	65.0	60.0	56.0

Note: *The numerator and denominator correspond to the values for grain and flesh side, respectively; † denotes that nitrogen content was quantified using Kjeldahl method and recalculated for protein content;* [1] *of the mass of the CTSFP*

This effect was observed both in loose and dense areas of the samples. The depth of diffusion of reagents in loose areas was close to 100 % with a consumption of 5 % of the mass of the semi-finished product; in dense areas even at increased consumption, it was only 80 % of the thickness of the semi-finished product.

At the same time, we observed an increase in the content of the filler in the dermis of the semi-finished product (Table I), which facilitates further formation of its structure. The amount of organic substances that are extracted by solvents increases alongside the filler content in the structure of the semi-finished product. The deformation characteristics of the semi-finished product increase, too.

Considering the chemical similarity between protein hydrolysate and collagen-based semi-finished product of chrome tannage, it is promising to use protein-based filler while forming the product structure and properties in the process of filling and plasticizing. As it is shown in Table II, an increase of the protein hydrolysate content reduces the porosity of the semi-finished product and its post-dehydration shrinkage while increasing the thickness.

The change in the decrease of the area and volume of the semi-finished product with increasing in consumption of protein hydrolysate and with decreasing in consumption of syntan indicates a greater decrease of the area of the leather material. Thus, the filling effect of protein hydrolysate in forming a semi-finished leather product is effectively evident by comparing the properties of the material that has been produced by the developed method and industrial technology of JSC Vozko (Ukraine). It should be noted that the use of protein hydrolysate in the composition with vegetable tannins modified with BNS reduces the stiffness of the final leather.

More efficient filling of the loose sheepskin structure is observed at a higher content of a highly-dispersed montmorillonite (Table III).

Table II. *Physicochemical properties of the chrome-tanned semi-finished product (CTSFP) filled with a composition of vegetable tannins and protein hydrolysate.*

Parameter	Filling option			
	Treatment		control	no filling
	1	2		
Consumption [%]				
– water	150	150	150	—
– protein hydrolysate	2	4	—	—
– mimosa	1	1	3	—
– BNS	3	1	3	—
– Cr_2O_3	5.2	5.4	4.4	4.7
Thickness [mm] of $\frac{\text{bend}}{\text{belly}}$	$\frac{1.23}{1.19}$	$\frac{1.29}{1.26}$	$\frac{1.18}{1.07}$	$\frac{0.91}{0.86}$
Shrinkage [%] of $\frac{\text{area}}{\text{volume}}$	$\frac{5.2}{11.0}$	$\frac{5.9}{10.0}$	$\frac{8.2}{17.0}$	$\frac{13.0}{28.0}$
Tensile strength [MPa]				
– whole ssin	19.0	21.0	17.0	14.0
– grain side	17.0	19.0	14.0	13.0
Elongation at 9.8 MPa [%]	48.0	45.0	43.0	39.0
Porosity of peripheral areas [%]	57.0	55.0	59.0	62.0
Stiffness [cN]	21.0	25.0	39.0	28.0

Note: *The material consumption is proportional to the mass of the semi-finished product.*

As it can be seen from the Table II, the increase in the content of montmorillonite in the filling composition, while the content of protein hydrolysate remains the same, results in an extreme change in the physicochemical properties of the semi-finished product. In this case, the structural and physicomechanical characteristics prevail over the properties of the semi-finished leather product that is obtained by the existing industrial technology of filling sheepskin practiced at the PJSC Chinbar (Kyiv, Ukraine). This especially relates to leather porosity and area yield. Thus, the technology of using a composition containing protein hydrolysate and montmorillonite can be implemented in manufacturing multifunctional leathers.

Table III. *Physicochemical properties of sheepskin filled with a composition of protein hydrolysate and montmorillonite (MM).*

Parameter	**MM [%]**			**control**	**no filling**
	1	***2***	***4***		
Consumption [%]					
– water	100	100	100	150	—
– protein hydrolysate	4	4	4	—	—
– mimosa	2	2	2	3	—
– BNS	2	2	2	5	—
Mass fraction [%] of					
– ash	8.7	9.8	10.2	7.9	7.3
– Cr_2O_3	4.3	4.3	4.6	4.5	4.9
– substances extracted with OS	8.7	8.5	8.1	8.3	7.8
Tensile strength [MPa]	14.7	15.3	15.8	13.6	14.0
Elongation [%]					
– at 9.8 MPa	33.8	31.5	32.3	32.0	29.0
– at the breaking point	68.6	72.0	69.4	66.7	63.0
Stiffness [cN]	16.0	15.3	15.7	21.5	25.0
Porosity [%]	66.3	69.5	67.8	65.4	64.0
Thickness [mm]	1.23	1.28	1.21	1.17	1.03
Volume yield [cm^3 **per 100 g proteins]**	285	309	296	272	253
Leather yield [%] by					
– thickness	102.6	103.9	104.8	100	83.0
– area	104.3	106.8	105.9	100	86.0

To control interaction between an anionic modified montmorillonite (MMM) and a chrome-tanned semi-finished leather under intense filling of the product structure, especially the papillary layer, a preliminary plasticization of the dermal structure is required. To form elastic leather, the filling-plasticizing processes for shoe uppers are carried out according to the chart presented in Table IV. In this case a decrease in interaction between the filling materials and the collagen-based semi-finished chrome-tanned product, if the filling process is effective, can be achieved by utilizing an alkylcarboxylethanolamines (ACEA), which was synthesized from monoethanolamine and synthetic fatty acids of the fraction S7–S9 [33] with a dispersion of modified montmorillonite.

Table IV. *The chart of the filling-plasticizing process to form a semi-finished leather.*

Filling	**Fixation 1**	**Plasticization**	**Fixation 2**
Reagent – consumprion [%] of the semi-finished product mass / processing duration [min]			
Water (100)		Water (100)	
Acrylic polymer Targotan 2MB (1.2 / 40) ACEA (1.0 / 20) BNS (4.0 / 60) Mimosa (2.0 / 30) MDM (4.0 / 40)	Sodium formate (0.4) + potassium alumi (2.5 / 30)	fatliqour (6.0) + ammonium hydroxide (0.3 / 60)	Formic acid (1.0 / 10)

Note: *After fixation procedures 1 and 2, 150 % of water is used to wash the semi-finished leather at 54–56 °C and 23–25 °C for 15 and 10 min, respectively.*

Rational use of cattle raw hides can be achieved by increasing the content of a highly-dispersed mineral. ACEA was utilized to optimize the dispersing effect of mineral on the dermal structure. An effect of increased montmorillonite consumption on the leather properties, similar to the process of filling a semi-finished sheepskin, was observed for the semi-finished leather produced from cattle hides and used for shoe uppers (Table V).

Processing of the semi-finished leather product with ACEA increases the use of the mineral filler up to 4 %. This helps achieve the maximum values of volume and area yield of the final leather by 31 cm^3 per 100 g of the protein substance and by 5.7 % compared to leather obtained by the existing industrial technology of the PJSC Chinbar (Kyiv, Ukraine). The industrial technology does not use the ACEA dispersant and modified montmorillonite.

Table V. *Physicochemical properties of leather for shoe uppers.*

Parameter	**MMM [%]**				**Control**
	1	**2**	***4***	***6***	
Mass fraction [%]					
– ash	8.7	9.3	10.1	11.3	7.7
– Cr_2O_3 [%]	4.3	4.3	4.4	4.3	4.2
– proteins	75.9	73.4	72.7	71.5	76.8
– substances extracted with OS	8.7	8.6	8.6	8.6	8.8
Tensile strength [MPa]	20.3	21.7	22.0	20.1	23.0
Elongation [%]					
– at 9.8 MPa	34.6	33.0	31.7	32.4	30.0
– at break	57.0	54.0	53.0	55.0	59.0
Stiffness [cN]	23.0	21.8	21.0	22.5	25.0
Porosity [%]	55.3	56.8	57.7	56.4	54.0
Volume yield [cm^3 per 100 g proteins]	255.0	268.0	276.0	264.0	245.0
Leather yield [%]					
– by thickness	102.3	103.6	104.5	104.2	100.0
– by area	102.8	104.9	105.7	104.6	100.0

The results of the microscopy study of leather for shoe uppers made of bovine hides according to the developed technology are shown in Fig. 2. The images (Fig. 2*a* and 2*b*) indicate that the grain side of the leather that was obtained by the developed technology using montmorillonite differs from those of the samples that were produced by the industrial technology and reveals depth and consistency of the filler distribution.

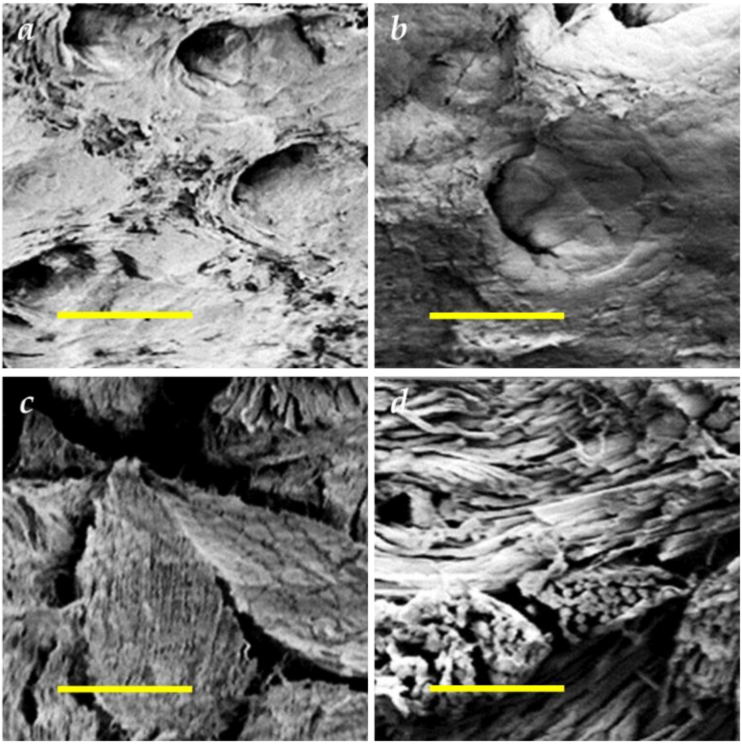

Fig. 2. *Scanning electron microscopy images of the grain side (a and b) and cross section (c and d) of leather filled without a mineral filler (a and c) and with montmorillonite (b and d). Scale bar – 100 μm (a and b) and 50 μm (c and d).*

This may indicate obtaining leather with a denser papillary layer. The images of the internal structure of the dermis in the semi-finished leather without the mineral filler (Fig. 2*c*) display a dense packing of collagen fibers in bundles, and the interbundle intervals are slightly larger than in the samples that were produced utilizing montmorillonite (Fig. 2*d*). In this case, there is some qualitative division of collagen bundles into individual fibers, which indicates uniformity of their distribution throughout the depth of the leather.

Thus, the results of the structural study indicate a correlation between the obtained data and the properties of the leathers that were formed by the developed technology.

Physicochemical Characteristics of Filling-plasticizing Processes

To form multifunctional leather materials out of various hides that differ by the ratio of the papillary and reticular layers of the dermis and by the packing density of fibrillar elements across topographical areas, a semi-finished leather has to be filled with suitable compositions [34, 35]. It is necessary to consider the application of the raw materials and the chrome-tanned semi-finished products and chemocolloidal properties of the filler. A leather material with high elastic-plastic properties can be formed by dispersing the fibrillar structure of the dermal collagen, which is primarily achieved utilizing fatliquor and highly-dispersive reagents with high diffusivity. Effective filling of a semi-finished leather should also primarily ensure formation of a dense grain side of the leather material, and it should even the physicochemical properties of the semi-finished leather product throughout the topographical areas. The first stage of the process should ensure minimum interaction between tannin particles and dermal collagen so that they could be effectively diffused in the structure of the semi-finished product. This process is implemented at a pH of 5.6–5.8; if the pH is higher, there is an increased interaction between tannin particles and dermal collagen, which leads to concentration of tannins on the surface of the semi-finished product. The optimal temperature condition for the process corresponds to 40–45 °C. Higher temperatures reduce the strength of the grain side of the semi-finished product due to fixation of tannins in the papillary layer of the dermis, which causes its cracking. Besides, the grain side of the semi-finished leather product gets separated from the reticular layer. This effect is particularly evident in the filling of loose sheepskin.

On the second stage of the process to ensure efficient fixation of tannins in the fibrillar structure, the pH of the technological solution decreases to 4.2. It facilitates interaction between the filling reagents and collagen in the chrome-tanned semi-finished product as a result of ionization of amino groups of dermal collagen and tannin molecules.

The process of plasticizing is performed at 50–55 °C to increase the mobility of the structural elements as a result of an even distribution of fatliquor components in chrome-tanned leather. To maintain the strength of the collagen fibrillar structure of the semi-finished product and to ensure the necessary technological characteristics of the plasticizer, the process temperature should be in the range of 50–55 °C. This allows creating a highly elastic leather material of a dense structure at a pH of 7.5–7.8. The fatliquor particles are destroyed and fixed in the semi-finished product structure when the filling-plasticizing process of forming multifunctional leather materials finishes at a pH of 4.0–4.2.

Given the low colloidal stability of tannins, their effective diffusion can be achieved through using 2-naphtholsulfonic acid and dioxide phenyl sulfone for modifying the surface of the tannin particles and increasing tanning dispersity. An increase in the evenness of the distribution of tannins in the product layers facilitates the formation of more elastic leather material and increases the rational use of raw hides.

Different types of connections between functional groups of collagen [29] and fewer micropores are possible when the filling composition is supplemented with a reactive oligomeric protein hydrolysate of a chemical nature that is similar to the dermal collagen of the chrome-tanned semi-finished product. Increased dispersibility and stabilization of the fibrillar structure of dermal collagen result in formation of a dense leather material with increased elasticity.

The technological composition was supplemented with a highly-dispersive hydrophilic and previously modified montmorillonite to form a dense grain side of the semi-finished leather derived from raw sheepskin, which is characterized by the deep hair root location (up to 70 % of the thickness of the dermis). The surface of the aluminosilicate particles was modified to improve the dispersibility and the diffusivity. The high degree of absorption of the filling-plasticizing composition can be caused by the effective dispersing and shielding effects of the dispersed montmorillonite particles on the structure of the dermis and their deep diffusion into the intermicrofibrillar space. However, an increased content of montmorillonite in the composition reduces the dispersing effect of montmorillonite particles on the dermis structure due to the decrease in the rate of diffusion of anionic particles as a result of a substantial increase in the number of connections between the montmorillonite particles and the positively charged structural elements of the dermal collagen at the beginning of their interaction.

High dispersibility and diffusivity of the MMM particles in the filling-plasticizing composition facilitate formation of the elastic leather materials with increased volume and area yield. Preliminary plasticization of the semi-finished product of chrome tannage is necessary to ensure an effective degree of filling the structure of a cattle hides, which has a denser packing of collagen fiber bundles, especially in the bend area, compared to sheepskin. If ACEA is used, the high surface activity of its molecules promotes diffusion of the components of the technological composition, especially at the initial stage of the process, which helps achieve a higher degree of dispersing the fibrillar collagen structure and distribute the density of the material throughout all topographical areas. These effects ensure formation of elastic materials for shoe uppers with a higher yield in terms of thickness and area.

Thus, the laboratory and semi-industrial research concerned the processes of forming leather materials through using protein hydrolysates and modified montmorillonite. We have determined the technological regimes and composition contents and consequently developed a filling-plasticizing technology of manufacturing multifunctional leather materials from a chrome-tanned semi-finished product.

Conclusion

The study concerned the processes of a filling-plasticizing technology in manufacturing leathers from raw hides of cattle and sheep origins to manufacture multifunctional products utilizing new chemical materials. We have determined how to accelerate the process of filling, especially in the loose topographical areas of chrome-tanned semi-finished products, by using tannin dispersants of various chemical structures.

An acid hydrolysis product produced from chrome-tanned shredded rawhides replaces 66 % of vegetable tannins and synthetic dispersants in the process of filling a semi-finished product and produces elastic leathers of high-quality peripheral areas with a homogeneous and stable structure. We have established an increase in area yield of the semi-finished product by 2.3–3.0 % in comparison with the industrial technology. The developed technology of filling-plasticizing chrome-tanned semi-finished sheepskin was developed utilizing a hydrolysis product of the chrome-tanned shredded rawhides and a modified montmorillonite, which can produce more elastic leather materials for apparel and haberdashery articles and increase the efficiency of using raw materials in comparison with the industrial technology.

The undertaken study of the process of filling-plasticizing the chrome-tanned semi-finished product involved a modified montmorillonite and an alkylcarboxylethanolamines, which has helped to improve the technology of manufacturing elastic leathers for shoe uppers with the necessary set of physicomechanical properties: with the volume yield of 268–276 cm^3 per 100 g of a proteins and the area yield that is by 5.7 % larger compared to the industrial technology.

The scanning electron microscopy was used to study the structure of the semi-finished leather product that had been filled with an organomineral composition containing a highly-dispersed montmorillonite. It was determined a high degree of divisibility of the modified fibrillar structure of the dermal collagen, which ensures its mobility in the deformation processes in forming and using leather products.

The developed technologies have been implemented at industrial companies in Ukraine to ensure efficient use of green-salted hides for manufacturing elastic multifunctional leathers based on environmentally friendly materials.

References

[1]. **Danylkovych A.** Ecologically oriented technologies for production of leather and fur materials for manufacturing of competitive goods (in Ukrainian) in: Ecologically oriented technologies for production of leather and fur materials for manufacturing of competitive goods: monograph (in Ukrainian). Fenix (Publisher «Фенікс») 2011, Kyiv.

[2]. **Danylkovych A.** Efficacy of collagen application in its structuring (in Ukrainian). *Bulletin of the Kyiv National University of Technologies and Design* **1** (2002) 182–185.

[3]. **Danylkovych A., Mokrousova O., and Okhmat O.** Technology and materials for leather production (in Ukrainian). Fenix (Publisher «Фенікс») 2009, Kyiv.

[4]. **Danilin D., Studenikin S., Zykova N., et al.** Effect of distribution of filling polymers in the layers of the split (in Russian). *Shoe Leather Industry* (Publisher «*Коженно-обувная промышленность*») **6** (2009) 46-48.

[5]. **Bao Y., Ma J., and Wang, Y.-L.** Preparation of acrylic resin/montmorillonite nanocomposite for leather tanning agent. *Journal of the American Leather Chemists Association* **104**, 10 (2009) 352–358.

[6]. **Nashy E., Hussein A., and Essa M.** Novel retanning agents for chrome-tanned leather based on emulsion-nano particles of styrene/butyl acrylate copolymers. *Journal of the American Leather Chemists Association* **106**, 9 (2011) 241–248.

[7]. **Vinnitskii B., Lebedev O., Makarov-Zemlianskii Ja., et al.** Filling and retanning of chrome-tanned skins with new generation of polymers (in Russian). *Shoe Leather Industry* (in Russian) **1** (2003) 33–34.

[8]. **Giliasov E. and Ostrovskaia A.** Amino furazan resin as a filling and retanning reagent in the manufacture of leather (in Russian). *Proceedings of the international scientific-practical conference "New technologies and materials for light industry"*, Kazan State Technological University, Kazan; 2010; 77–81.

[9]. **Chernova A., Latfullin I., and Ostrovskaya A.** Modified amino resins as filling and retanning reagents (in Russian). *Proceedings of the international scientific-practical conference "New technologies and materials for light industry"*, Kazan State Technological University, Kazan; 2010; 120–124.

[10]. **Jaisankar S., Gupta S., Lakshminarayana Y., et al.** Water-based anionic sulfonated melamine formaldehyde condensate oligomer as retanning agent for leather processing. *Journal of the American Leather Chemists Association* **105** (2010) 289–296.

[11]. **Iurasova O.** Development and application of retanning composition in leather industry (in Russian). *Leather and shoe* (Publisher «*Кожа и обувь*») **3** (2008) 30–33.

[12]. **Iurasova O.** The effect of retanning and filling agents on the leather properties (in Russian). *Natural and technical sciences* **3**, 35 (2008) 382.

[13]. **Iurasova O.** Synthesis of a tanning agent for the leather industry based on sulfoaromatic compounds (in Russian). *Biotechnology* (in Russian) (2008) 34.

[14]. **Iurasova O.** The influence of "RKF-1" on the exploitation properties of the leather semi-finished product (in Russian) *Leather and shoe* (Publisher «*Кожа и обувь*») **1** (2010) 48.

[15]. **Ramazonov B., Kadirov T., Toshev A., et al.** Filling leathers with nitrogen-containing polymers (in Russian). *Reports of the Academy of Sciences of the Republic of Uzbekistan* (in Russian) **2** (2008) 64–67.

[16]. **Chursin V.** The effect of the starting components on the leather-technological properties of polymer-tannids (in Russian). *Leather and shoe* (Publisher «*Кожа и обувь*») **1** (2009) 20–22.

[17]. **Chursin V., Bordunova E., and Osipov A.** Effect of biopolymer compositions on the elastic-plastic and strength properties of leathers (in Russian). *Leather and shoe* (Publisher «*Кожа и обувь*») **2**, 29 (2008) 16–18.

[18]. **Mariliz G., Silva D., and Vigannico I.** Leather retanning with hydrolyzed protein. *Journal of the American Leather Chemists Association* **105** (2010) 195–202.

[19]. **Balada E., Taylor M., Brown E., et al.** Whey protein isolate: a potential filler for the leather industry. *Journal of the American Leather Chemists Association* **104** (2009) 122–130.

[20]. **Wang C., Feng S., and Wu J.** Preparation of organosilicon modified palm oil fatliquor. *Journal of the American Leather Chemists Association* **106** (2011) 161–169.

[21]. **Baiandin V., Klenovskaia N., Zhivova Z., et al.** Intensification of dyeing and fatliquoring processes by the combined method (in Russian). *Shoe Leather Industry* (Publisher «*Кожевенно-обувная промышленность*») **4** (2003) 25–26.

[22]. **Baiandin V., Klenovskaia N., Zhivova Z., et al.** Intensification of dyeing-fatliquoring processes by the combined method (in Russian). *Shoe Leather Industry* (Publisher «*Кожевенно-обувная промышленность*») **5** (2003) 37–38.

[23]. **Goriacheva L., Chirkova N., Chibotareva O**. Leather filling with liposome compositions (in Russian). *Shoe Leather Industry* (Publisher «*Кожевенно-обувная промышленность*») **2** (2011) 33–34.

[24]. **Chirkova N., Esina G., Chubatova S., et al.** Application of liposome compositions in the production and exploitation of leather and fur (in Russian). *Technology and Design* (in Ukrainian) **3** (2013) 1–8.

[25]. **Tysoe Ch. and Reiners J.** Technologie zur Weichmachung von Leder. *IDC Leder und Haute Markt* **1** (2009) 26–30.

[26]. **Fordzyun Yu., Andreyeva O., and Maistrenko L.** Level of comfort: artificial and natural shoe materials. A comprehensive assessment. *Key Engineering Materials.* **559** (2013) 25–30; 10.4028/www.scientific.net/kem.559.25

[27]. **Glubysh P. and Teslia O.** Investigation of the process of hydrolysis of collagen-containing recyclables to obtain new agents for the intended purpose (in Ukrainian). *Bulletin of the Kyiv National University of Technologies and Design* **4** (2007) 255–259.

[28]. **Kerner S., Glubysh P., Danylkovych A., et al.** Acid-alkaline properties of collagen sols as a polyfunctional material of leather production. *News of the Academy of Engineering Sciences of Ukraine* (in Ukrainian) **2** (1995) 58–65.

[29]. **Teslia O., Mokrousova O., Kovtunenko O., et al.** IR spectroscopic studies of the interaction of econate composition with collagen of chromium dermis (in Ukrainian). *Bulletin of the Kyiv National University of Technologies and Design* **6** (2009) 95–99.

[30]. **Tarasovych Ju. and Ovcharenko F.** Adsorption on clay minerals (in Russian) Naukova dumka 1975, Kyiv, 351 p.

[20]. **Danylkovych A.** Practicum in chemistry and technology of leather and fur. Fenix (Publisher «Фенікс») 2006, Kyiv.
[31]. **Goldstein J., Newbury D., Echlin P., et al.** Scanning electron microscopy and x-ray microanalysis (in Russian). Mir (Publisher «Мир») 1984, Moscow, Vol. **1** 343 p. & Vol. **2** 351 p.
[32]. **Danylkovych A., Omelchenko N., and Brailko A.** Properties of nitrocellulose films modified with alkylcarboxyethanolamine (in Ukrainian). *Problems of the light and textile industry of Ukraine* (in Russian) **1** (2010) 12–15.
[33]. **Stirtz T.** Treatise of Collagen. *Leder und Hautemarkt* **26**, 9 (1975) 155–168.
[34]. **Mihailov A.** Chemistry and physics of skin collagen (in Russian). Light Industry (in Russian) 1980, Moscow, 232 p.

13. RESEARCH OF CONSUMER PROPERTIES OF LEATHER FILLED UTILIZING ELECTROACTIVATED AQUEOUS SOLUTIONS [9]

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Abstract: *Consumer properties of the filled macroporous chrome-tanned semi-finished leather produced by the developed technology utilizing electrochemically activated aqueous solutions for the filling composition containing acrylamide modified with xanthan gum were studied. Sorption-desorption properties of different sections of the filled material, relaxation and deformation characteristics, differential moisture content, and volume yield were determined. It was found that the leather material produced by the developed technology has higher elastic and plastic strain by 1.7 and 1.3 times, respectively, compared with the current technology. Porosity, volume yield, and hygroscopic properties of resulting leather exceed those of the experimental technology by 4.5, 19.0, and 9.8–11.3 %, respectively. The technology of filling of chrome-tanned leather derived from porcine hide is based on the diffusion of the composition ingredients in the anolyte solution at pH 4.2–4.4 with the decrease of surface tension and the formation of mostly hydrogen bonds between the elements of the modified structure of collagen and the filler reagents. The interaction with water results in partial disruption of bonds that are restored after moisture removal. Optimal consumer properties are achieved at a certain ratio of the hydrophilicity and the differential porosity of the leather material. The use of the filling composition based on xanthan acrylamide in the anolyte results in*

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[9] *The title has been modified; the original title is "Research of consumer properties of leather filled with the use of electroactivated water reagent solutions".*

effective distribution of pores in different sections of the semi-finished product due to preferred filling of large pores and increasing the specific volume of smaller pores. The resulting fine-pored leather material with the split fibrillar structure causes a smaller loss of its area by 0.3 % after moisturizing-drying processes compared with the current technology. The leather material formed using the developed technology due to the complex of consumer properties is recommended for making shoes – insoles and lining, and materials for surface moisture removal in the mechanical cleaning of products and structures.

Keywords: *semi-finished leather; filling; activated water; xanthan gum acrylamide; porosity; hydrophilicity; elasticity.*

Introduction

Expanding the range and improving the quality of the leather materials is a prerequisite for the development of modern production and the expansion of economic relations in the domestic and foreign markets. High-quality leather should be characterized by a homogeneous structure and uniform density and thickness at different areas [1, 2]. This applies particularly to porcine hides, which are characterized by the pores which goes through the dermis resulting from the hair removal, intensive development of skin glands and fat cells, and relatively low strength, despite the high density of the intertwining of collagen fibers in bundles with a smaller angle to the surface compared to the structure of cattle hides [3].

In this regard, the filling of leather material with active polymer compositions to improve consumer properties is conducted. The process of filling should provide a complex of physical, mechanical, and hygienic properties of leather material and increase the resistance to external factors, reduce shrinkage during drying, increase the leather yield, especially in the processing of low-quality raw materials and preparation of semi-finished products for effective coating.

Thus, the process of filling is crucial in terms of the formation of technological and consumer properties of the final material during finishing of the chrome-tanned semi-finished leather in production technologies of leather for various purposes. Therefore, the development and research of different chemical compositions for the effective filling of the chrome-tanned semi-finished products are important.

Literature Review and Problem Statement

The use of a wide range of different chemical compositions for filling semi-finished leather is known [4], in which each component must have specific properties that, first of all, consider the structural features of hides. For obtaining high-strength and intensely colored chrome-tanned leather from raw hide, the filling process can be carried out using polymerizing acrylamide in the presence of potassium persulfate [5] followed by retanning with chromium compounds and fatliquoring. The disadvantage of this method is the additional usage of the environmentally harmful chrome tanning agent.

For the filling of semi-finished leather, materials of synthetic and natural origin, including collagen hydrolysate products, can be used. Particularly, the use of compositions of aqueous dispersions of copolymers of diallyl dimethylammonium chloride (DADMAC) and maleic acid in an amount of up to 8 % of the semi-finished product mass is known [6]. The process of filling of semi-finished leather from raw hide can be conducted in a wide temperature range of 30–65 °C for 45–90 min. The resulting semi-finished product is characterized by improved physical and mechanical performance. The use of aqueous dispersions of acrylic copolymers with different ratios of ingredients [7] when combining the processes of filling and retanning of semi-finished materials from rawhides and subsequent retanning with organic tanning agent β-naphthalene sulfonate (BNS) is also known. Application of this processing method enables to produce the elastic semi-finished leather material. The process of filling of the chrome-tanned semi-finished product with a latex of a copolymer of styrene and butyl acrylate [8] synthesized by emulsion polymerization of monomers is also known. The use of the emulsion of copolymers with particles in the nanoscale range made it possible to get an elastic leather material with high hydrothermal stability and mechanical strength.

In the work [9], the authors used anionic sulfonated melamine formaldehyde oligomers with subsequent dyeing and fatliquoring for post-tanning processing of the chrome-tanned semi-finished materials from raw hide. These leather materials are characterized by high elasticity, density, and dyeability. However, the resulting leather contained up to 10 mg/kg of free formaldehyde. For filling, retanning, and hydrophobization of vegetable-tanned semi-finished products, particularly in manufacturing technology of harness leather, the authors [10] recommend the use of amino furazan resin. Because its particles acquire a positive charge as a result of protonation, they actively interact with negatively charged functional groups of dermal collagen, accompanied by the additional structuring of semi-finished leather. It is found that the use of such copolymer containing 10 % of polyoxyethylene lauryl provides an improved physical and mechanical properties of leather material – abrasion resistance, transverse and longitudinal tensile and tearing strength and elasticity, and reduce shrinkage of semi-finished products after finishing compared with the control treatment. According to the previously published results [11], the leather properties can be improved by the use of nitrogen-containing water-soluble polymers used for the semi-finished leather filling, together with acrylic emulsion A.

In the technology of post-tanning processes, filling materials of natural origin, including protein mixtures derived from whey in the manufacture of cheese with gelatin in the ratio of 10 : 1 are more promising from an ecological perspective [12]. The pretreatment of semi-finished leather with microbiological enzyme – transglutaminase, makes it possible to increase the rate of the process by four times. The resulting material for shoe uppers and upholstery filled with the protein/gelatin mixture has the improved coloration, flexibility, and high degree of draping.

The uniformity of semi-finished leather structure can be increased by filling with the use of sodium caseinate and gelatin, modified with microbial transglutaminase [13]. However, the leather material after this treatment has a high density and smoothness of the grain side, while the physical and mechanical properties of the filled material are practically identical to the samples derived by the current technology.

The possibility of using environmentally friendly reagents – genipin and modified gelatin at various stages of processing of semi-finished leather – retanning, dyeing, and fatliquoring, have been previously described [14]. The resulting material is characterized by the uniform distribution of the complex filler in the semi-finished product structure, better organoleptic properties (thickness and color) compared to the control group of samples. At the same time, there is an increase in shrinkage temperature of semi-finished leather when using genipin-gelatin treatment. The results of the scanning electron microscopy study revealed that the effect achieved is due to the coating of fibers of the fibrillar structure of the dermal collagen with a complex modifier.

As a result of the study of the process of filling chrome-tanned semi-finished product derived from cattle rawhide with natural aluminosilicates – bentonite, modified sodium polyphosphate [15], and sodium carbonate and basic chromium sulfate [16], elastic leather materials are formed with increased volume and area yield, improved elastic-plastic properties, and increased permeability of water vapor and air.

Given the large volume of water needed in the production of leather materials, the works, which examine the role of electroactivated water in terms of increased technological and consumer properties of the finished leather materials are of special interest. It is shown [17, 18] that the use of activated water solutions of benzyl alcohol, glycerol, and glyoxal can increase the flexibility of leather [17] and corium of fur during dyeing [18]. Plasticizing leather materials derived from raw hides with electrochemically activated water in drying-moisturizing processes of forming shoe uppers makes it possible to increase the deformability of shoe pieces and reduce the consumption of leather by 1.5–5.0 % [19, 20], depending on the production technology.

Consequently, most of the analyzed works are related to the manufacture of leather materials, mainly from raw hide, whereas virtually no work has been done on post-tanning formation of semi-finished products derived from porcine hides and especially utilizing activated water solutions of chemical reagents in processing technologies. Significant technological difficulties in the processing of raw materials and large volumes of production determine the prospects of work in this direction.

The Goal and Objectives of Research

The aim was to study consumer properties of the chrome-tanned semi-finished leather from porcine hides using electro-chemically activated aqueous solutions for the filling composition containing xanthan gum acrylamide (XGAAm).

To achieve this goal, the task was set to study the effect of the filling composition on consumer specifications of the split chrome-tanned semi-finished leather, including:

– porous structure;
– absorption properties;
– strain-relaxation dependencies;
– volume and areal yield of the material.

Materials and Methods

For experiments, we selected the chrome-tanned semi-finished porcine hide (technical specification, TU U 00302391-03-98) after shaving to the thickness of 1.4 mm, obtained by the method of PJSC Chinbar (Kyiv, Ukraine), which are characterized not just by the deep hair follicles but also by large structural defects.

Variants for the filling technology were practiced on three experimental groups of 120×150 mm samples each containing seven specimens arranged into the groups by the previously described method [21]. Before the filling process, the semi-finished product was neutralized with formate (technical specification, TU 21-249-00204168-92) and sodium carbonate in a ratio of 1 : 1. In the course of the semi-finished product filling, preliminary plasticization with fatliquor Trupol RA (Trumpler, Germany), due to its electrolyte stability, was conducted.

The active component of the filling composition for the semi-finished product processing was a copolymer of exopolysaccharide of bacterial origin (technical specification, TU U 88-105-002-2000) – xanthan gum modified with acrylamide (technical specification, TU 6-01-1049-92) (XGAAm, Ukraine) [22].

The semi-finished product was processed using the XGAAm composition according to the current technology, instead of anionic acrylic-based polymer Retanal RCN-40 (Cromogenia-Units, Spain) in the electrochemically activated water – anolyte and catholyte [23].

Properties of the resulting semi-finished product were studied by the relevant methods [21]. Particularly, physical and mechanical properties of the leather material were determined on the tensile-testing machine RM-50M at the sample deformation rate of 90 mm/min, while stiffness – on the PZhU-12M device. Relaxation and deformation properties of semi-finished leather were determined on using a previously described methodology [24]. The sample was under stress corresponding to 9.8 MPa. The duration of the sample under load was 30 min. After removing the stress, conventional elastic deformation was determined immediately, after 30 min – high elastic, and after 24 hours – residual deformation.

Volume yield was evaluated by the ratio of the volume of the semi-finished product filled with the composition in cubic cm to the volume of 100 grams of protein substances (PS). The reduction of the surface area [%] of leather material – by the change in the area of the chrome-tanned semi-finished product in the dried state relative to the area before filling.

Moisture content of the semi-finished product samples was determined on a thermogravimetric-calorimetric equipment [25] in the thermogram mode. For this purpose, the samples of the semi-finished product with the size of 40×40 mm were previously hydrated for 24 h at 20 °C. The change in the mass of samples during moisture desorption was determined at 100 °C for 4 h using modified analytical scales ADV-200 and resistance thermometer. Recording of measurement results was conducted on the potentiometer KSP-4. Critical points that correspond to different types of moisture binding with the pore structure of the dermal collagen of the semi-finished product were determined by inflections on the curves of the dependence of the sample weight on the drying duration.

The reduction of the material area was determined after drying-moisturizing processes and operations relative to the unfilled semi-finished leather.

Effect of Composition on the Properties of the Resulting Semi-Finished Product

In the process of this study, filling compositions differing in types of the dispersion medium are used (Table I).

Unlike the current processing technology of semi-finished products, the experimental technology used the compositions based on acrylamide modified with xanthan gum and electrochemically activated (ECA) water.

Table I. *Chemical components of filling composition.*

Component	Producing country	Material consumption [%] † by			
		experimental technology			current technology
		1	*2*	*3*	
Trupon DL	Germany	2	2	2	2
Retanal RCN-40	Spain	—	—	—	3
XGAAm	Ukraine	5	5	5	—
Trupotan AG	Germany	2	2	2	2
Tergotan PMB	Poland	2	2	2	2
Quebracho	China	3	3	3	3
Water	Ukraine				tap water
– anolyte		+			
– catholyte			+		
– distilled				+	

Note: *† stands for % of mass of shaved semi-finished product.*

The process of filling the chrome-tanned semi-finished leather was carried out after washing for 30 min at the ratio of water and semi-finished product, liquid coefficient (LC), 2:1 with increasing temperature from 35–40 to 55–60 °C and addition of the filling composition. The processing duration was 1 h. The use of anolyte provided the pH of the working solution within 4.2–4.4, distilled water – 4.7–4.9, while catholyte – 6.7–7.0. Subsequently, for the structure plasticizing, processing of the semi-finished product with the fatliquor (6 % consumption) for 1 h was conducted. Ten minutes before the filling-fatliquoring process completion, fixing with 10 % formic acid at a consumption of 1 % of the semi-finished product mass was performed.

Given the essential role of moisture exchange for chromium-tanned leather material derived from porcine hides, when it is used for making the insides of shoes, the study of the interaction of the material with water is of significant interest. The results of this study are shown in Fig. 1.

Water sorption by semi-finished leather filled using the experimental anolyte composition indicates the effective interaction of the modified dermal collagen with water in the first two hours. With further soaking, the moisture content of the samples increases. This process occurs more rapidly when using the filling composition with the catholyte.

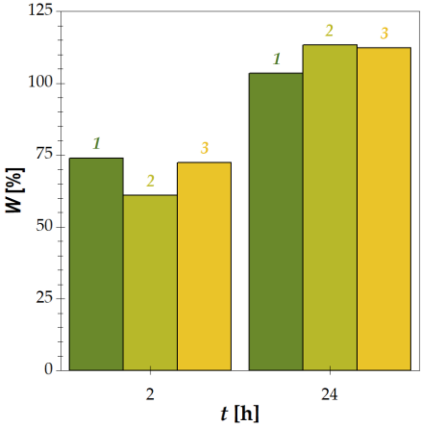

Fig. 1. *Dependence of soaking of the filled semi-finished leather at 20 °C on the duration of the process using in anolyte (1), catholyte (2), and distilled water (3).*

Thus, at the initial stage of the interaction of the filled chrome-tanned semi-finished leather with water, the samples produced using a composition where the dispersion medium is the anolyte display greater sorption capacity. However, according to the experimental results (Table II), forming of semi-finished leather using XGAAm in the anolyte solution provides a leather material with the volume yield greater by 19.0 % compared with the current technology (control). When using a filling composition based on the catholyte, the volume yield decreases by 12.0 %. It should be noted that application of the experimental composition based on distilled water practically does not change this technological parameter of the semi-finished product. The results of the study of the content of unused reagents in the working solution demonstrate the effectiveness of using the filling composition based on the anolyte.

Table II. *Technological properties of the filled semi-finished leather.*

Parameter	**Semi-finished leather produced by**			
	experimental technology			**current technology**
	1	*2*	*3*	
Volume yield [cm^3 per 100 g PS]	258.9	197.1	224.4	217.4
Solids [mg/L]	1.7	3.9	2.3	2.6

The resulting leather material filled with the experimental composition using the anolyte is characterized by a high content of bound organic substances (Table III) and a slightly higher content of plasticizing substances extracted with organic solvents (OS) and, accordingly, a lower content of proteins. Thus, the obtained leather material tends to increase in elasticity compared with the sample obtained by the current technology and is characterized by a decrease in stiffness by 12.0 %.

According to the results of the research of relaxation and deformation properties of semi-finished leather (Fig. 2), the use of the anolyte-based filling composition gives a material with improved deformation properties. This includes elastic and plastic components of deformation which are higher by 1.7 and 1.3 times, respectively, compared to the semi-finished product, filled using the catholyte-based composition. This effect may be due to the greater porosity of the samples in the former case.

It should be noted that the porosity of semi-finished leather obtained by the experimental technology using the anolyte is higher by 4.5 % compared with the samples obtained by the current technology. This also applies to air permeability of the resulting leather material. However, such an important technological parameter as the area reduction during drying-moisturizing processes is minimal when the anolyte is used in the experimental technology.

Table III. *Physical and chemical properties of semi-finished leather.*

Parameter	**Semi-finished leather produced by**			
	experimental technology			**current technology**
	1	2	3	
Mass fraction [%] [†] of				
– moisture	14.1	13.9	13.5	13.4
– Cr_2O_3	4.1	4.7	4.3	4.4
– substances extracted with OS	8.9	7.9	8.1	8.3
– bound organic substances	11.2	7.9	10.4	10.5
– protein substances	68.2	69.9	68.2	69.1
T_S **[°C]**	115.0	112.0	114.0	114.0
Tensile strength [MPa]	19.7	18.0	18.6	18.8
Elongation at 10 MPa [%]	35.8	28.0	32.0	33.2
Belly porosity [%]	54.6	45.7	49.8	50.1
Air permeability $[cm^3/(cm^2\cdot h)]$	324.0	269.0	301.0	308.0
Stiffness [cN]	37.0	48.0	42.0	43.0
Area reduction [%]	1.9	1.1	1.5	1.4

Note: *[†] on a dry basis.*

Given the crucial sorption capacity of the leather material for the insides of shoes produced from macroporous materials – porcine hides, the study of differential porosity by the areas after filling chrome-tanned semi-finished leather by the experimental and current technologies is of considerable interest (Table IV). The above data show that the moisture sorption of the samples filled using the experimental composition is characterized by the lower values of moisture content compared to the control samples. The sorption of water in the polylayer and monolayer in dense and loose areas is greater at lower values of these parameters in the former case.

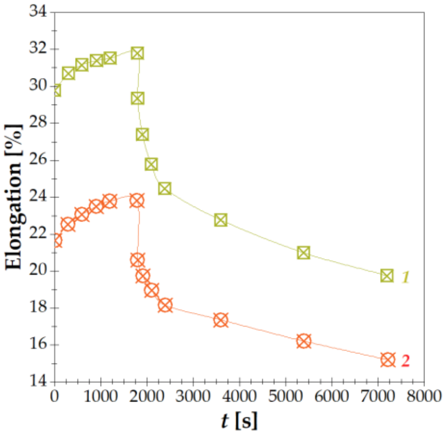

Fig. 2. *Relative elongation of semi-finished leather before and after removal of the load using anolyte (1) and catholyte (2).*

Table IV. *Differential moisture content of the filled semi-finished leather.*

Area	Moisture content [%]	Water soaking [%]	Differential water content [%]			Specific pore volume [%] corresponding to water	
			hygroscopic	polylayer	monolayer	soaking	hygroscopic
Butt	$\frac{107.2}{113.0}$	$\frac{51.9}{60.6}$	$\frac{55.3}{52.4}$	$\frac{18.1}{14.2}$	$\frac{4.6}{4.1}$	$\frac{48.41}{53.63}$	$\frac{52.59}{46.37}$
Belly	$\frac{121.4}{130.6}$	$\frac{66.5}{75.8}$	$\frac{54.9}{53.8}$	$\frac{21.8}{16.3}$	$\frac{4.8}{3.7}$	$\frac{54.78}{58.81}$	$\frac{45.22}{41.19}$

Notes: *The water of the polylayer and monolayer is part of the hygroscopic water. Numerator – semi-finished leather samples filled using the anolyte and XGAAm;*

denominator – control samples of semi-finished leather obtained by the technology of PJSC Chinbar.

The mass of the sorbed water in the polylayer of the filled semi-finished leather obtained by the experimental technology is higher by 27–34 % compared with the samples of the current technology.

It should be noted that the data relate to water desorption from previously maximally hydrated samples of semi-finished leather. However, the pore volume corresponding to the hygroscopic water in the process of moisture removal by drying the experimental semi-finished leather is higher by 9.8–11.3 % compared to the leather material obtained by the current technology.

Physicochemical Characteristics of the Semi-Finished Leather Filling Process

To form the leather material with a complex of sorption and desorption properties of the chrome-tanned semi-finished leather out of macroporous raw materials, the process of filling that provides an optimal combination of hydrophilicity and porosity of the material is of significant importance. The effectiveness of the process increases with decreasing difference between the properties of dense and loose areas of the semi-finished product. Through the use of electrochemically activated aqueous solutions of reagents with negative oxidation-reduction potential, in non-thermodynamic equilibrium [26], and low surface tension, the filling composition with the anolyte easily penetrates the cells. Thus, there is a significant structural change in the chrome-tanned semi-finished leather as a result of accelerating the diffusion of chemicals within the dermis and the formation of chemisorptive bonds of the physical and ionic type by molecules of the modifier with functional groups of collagen at the microfibrillar level. These are the results of IR spectroscopic studies [27]. Similar effects were also observed when filling the chrome-tanned semi-finished leather materials produced from heifer rawhides by using the xanthan gum – acrylamide copolymer [28] with different chemical composition. This changes the nature of the porous structure with increasing volume of micropores with a radius of less than 10^{-7} m. This feature of the semi-finished leather structure formation is confirmed by the change of solids in the spent solution depending on the content of the filling composition that reaches the maximum value for the catholyte-based composition.

Effective diffusion and interaction of the components of the filling composition of the chrome-tanned semi-finished leather is promoted by an optimal pH when using the anolyte, which provides even distribution of the filler ingredients in the dermis of the leather material. This ensures the formation of highly porous material with the split microfibrillar structure, due to its additional plasticizing during filling-fatliquoring and after water removal from the semi-finished product in the process of drying-moisturizing remains in a mobile state. This structure formation of the material enhances water sorption in the first two hours of its contact with water. While the structure of the semi-finished leather product, formed using the composition in the presence of catholyte is characterized by a greater density, caused by the stronger interaction of the ingredients of the filling composition with the structural elements of the modified dermal collagen and their uneven distribution in the material volume. This is reflected in the lower activity of leather material at the initial stage of getting wet. Later in contact with water due to the disruption of the formed mainly hydrogen bonds, water sorption is almost equated with the samples obtained by the current technology. Prolonged contact of the material with water results in partial destruction of bonds between the collagen fibers and ingredients of the filling composition.

A significant difference of the porous structure, particularly microporous, of leather material obtained by the developed technology using the composition of anolyte from the current technology is indicated by the lower water absorption values at maximum water content, rate of shrinking of the sample of the filled semi-finished leather, and higher values of elasticity and plastic deformation.

Therefore, a comprehensive study of porosity, sorption-desorption, and physical and mechanical properties of the leather material obtained by different technologies, shows that the material with a larger volume of microstructure and high sorption capacity and plasticity can be formed by the developed technology using xanthan gum – acrylamide in the anolyte solution.

Conclusions

Consumer properties of the filled chrome-tanned semi-finished leather materials from macroporous raw material obtained by the developed technology using electrochemically activated aqueous solution containing acrylamide modified with xanthan gum were determined. Replacement of acrylic polymer in the current technology of PJSC Chinbar with xanthan gum – acrylamide in the electroactivated aqueous solution of anolyte at pH 4.2–4.4 provided for semi-finished leather with increased by 4.5 % porous structure using the developed technology.

Semi-finished leather formed in the presence of activated anolyte solution is characterized by higher content of micropores by 10–11 % compared to the current technology of PJSC Chinbar and accordingly water sorption capacity, as evidenced by a differential moisture content of the filled semi-finished leather and reduced soaking by 12–14 % due to the increase of small pores in the structure.

The advantages of the developed manufacturing technology of semi-finished leather are also indicated by increased strain-relaxation properties by 19 %, due to the higher elasticity of the material because of the mobility of the fibrillar structure.

Higher volume yield by 41.5 cm^3 per 100 g of proteins compared with the current technology contributes to the formation of a material with high hygienic properties and lower area reduction by 0.5 %.

The advantages of the developed technology with a complex of sorption-deformation characteristics of the resulting semi-finished product make it possible to recommend it for making the insides of shoes and cleaning material.

References

[1]. **Danylkovych A.** (ed.) Innovative technologies of production of leather and fur materials and products: monograph (in Ukrainian). Fenix (Publisher «Фенікс») 2012, Kyiv, 344 p.

[2]. **Danylkovych A.** Ecologically oriented technologies for production of leather and fur materials for manufacturing of competitive goods: monograph (in Ukrainian). Fenix (Publisher «Фенікс») 2011, Kyiv, 437 p.

[3]. **Andreieva O. and Tsemenko G.** Commodities of leather and fur raw materials (in Ukrainian). Kondor (Publisher «Кондор») (2012), Kyiv, 360 p.

[4]. **Danylkovych A., Mokrousova O., and Okhmat O.** Technology and materials for leather production (in Ukrainian). Fenix (Publisher «Фенікс») 2009, Kyiv, 578 p.

[5]. **Chursin V. and Lvova A.** Method of leather production (in Russian). RU patent 2113493; June 20, 1998.

[6]. **Kunakova R., Vorobyova A., and Abramov V.** Method for the production of leather (in Russian). RU patent 2145978; February 27, 2000.

[7]. **Vinnitskii B., Lebedev O., Studenikin S., et al.** Method of leather processing (in Russian). RU patent 2186116; July 27, 2002.

[8]. **Nashy E., Hussein A., and Essa M.** Novel retanning agents for chrome tanned leather based on emulsion-nano particles of styrene/butyl acrylate copolymers. *Journal of the American Leather Chemists Association* **106**, 9 (2011) 241–248.

[9]. **Jaisankar S., Gupta S., Lakshminarayana Y., et al.** Water-based anionic sulfonated melamine formaldehyde condensate oligomer as retanning agent for leather processing. *Journal of the American Leather Chemists Association* **105** (2010) 289–296.

[10]. **Chernov A., Latfullin I., and Ostrovskaya A.** Modified amino resins as filling and retanning reagents (in Russian). *Proceedings of the international*

scientific-practical conference "New technologies and materials for light industry", Kazan State Technological University, Kazan; 2010; 120–124.

[11]. **Ramazonov B., Kadirov T., Toshev A., et al.** Filling leathers with nitrogen-containing polymers (in Russian). *Reports of the Academy of Sciences of the Republic of Uzbekistan* (in Russian) **2** (2008) 64–67.

[12]. **Balada E., Taylor M., Brown E., et al.** Whey protein isolate: a potential filler for the leather industry. *Journal of the American Leather Chemists Association* **104**, 4 (2009) 122–130.

[13]. **Liu Q., Liu L., Li J., et al.** Influence of microbial transglutaminase modified gelatin-sodium caseinate, as a filler, on the subjective mechanical and structural properties of leather. *Journal of the American Leather Chemists Association* **106**, 6 (2011) 200–207.

[14]. **Taylor M., Bumanlag L., Marmer W., et al**. Potential Application for Genipin in Leather Processing. *Journal of the American Leather Chemists Association* **104**, 3 (2009) 79–91.

[15]. **Mokrousova O. and Danylkovych A.** Filling a leather semi-finished product. Modification and use of bentonite dispersions (in Ukrainian). *Bulletin of the Khmelnytskyi National University* **3** (2008) 239–244.

[16]. **Mokrousova O. and Moraru V.** Polyfunctional materials for liquid finishing of skin. Influence of montmorillonite modification by Cr (III) compounds on the electro-surface and structural properties of dispersions (in Ukrainian). *Bulletin of the Kyiv National University of Technologies and Design* **1** (2011) 84–93.

[17]. **Zorina E., Zeleva G., and Nagornaya Z.** The effect of the nature of tanning agents and water on the plastic properties of the skin tissues of fur and leather (in Russian), *Omsk Scientific Bulletin* **19** (2002) 140–141.

[18]. **Zorina E. and Zeleva G.** Dying of fur with various dyes (in Russian), *Omsk Scientific Bulletin* **19** (2002) *138–139*.

[19]. **Lutsyk R., Matvienko O., and Bovsunovskyi O..** Possibilities of using electroactivated water in technological processes for shoe production (in Ukrainian), *Bulletin of the Kyiv National University of Technologies and Design* **2** (2005) 53–58.

[20]. **Zlotenko B., Romaniuk O., Danylkovych A., et al.** Eco-friendly light industry technologies based on the use of activated aqueous solutions (in Ukrainian). *Bulletin of the Kyiv National University of Technologies and Design* **1** (2008) 127–130.

[21]. **Danylkovych A.** Practicum in chemistry and technology of leather and fur. Fenix (Publisher «Фенікс») 2006, Kyiv, 338 p.

[22]. **Gvazdiak R., Matyshevskii M., Grigorev E., et al**. The microbial polysaccharide xanthan gum (in Russian). Naukova dumka (Publisher «Наукова думка») 1989, Kyiv, 212 p.

[23]. **Prilutskii V. and Bakhir V.** Electrically activated water: anomalous properties, mechanism of biological effect (in Russian). VNIIIMT (Publisher «ВНИИИМТ») 1997, Moscow 244 p.

[24]. **Lutsik R., Melnikova A., and Movchanova A**. Automatic installation for studying the relaxation properties of polymers in a wide range of temperatures and humidity (in Russian). *Mekhanika polimerov* (Publisher «Механика полимеров») **3** (1978) 553–556.

[25]. **Lutsik R., Malkin E., and Abarzhi I.** Heat and mass transfer in the processing of textile materials: monograph (in Russian). Naukova dumka (Publisher «Наукова думка») 1993, Moscow, 344 p.

[26]. **Plutakhin G., Aider M., Koshchaev A., et al.** Theoretical foundations of electrochemical treatment of aqueous solutions (in Russian). *Journal of the Kuban State Agrarian University* **8** (2013) 1–25.

[27]. **Tsemenko I., Danylkovych A., and Tsemenko G.** Copolymer of xanthan gum – acrylamide-collagen-chromium compounds. Investigation of system interaction by IR spectroscopy (in Ukrainian). *Bulletin of the Kyiv National University of Technologies and Design* **6** (2005) 100–103.

[28]. **Danylkovych A. and Tsemenko G.** The role of xanthan gum – acrylamide in forming the consumption properties of a leather semi-finished product (in Ukrainian). *Technology and Design* (Publisher «Технології та дизайн») **4** (2013) 1–8.

14. IMPROVING WATER RESISTANCE OF CHROME-TANNED LEATHER BY ALKENYL MALEIC ANHYDRIDE COMPOSITION [10]

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Abstract: *To solve the problem of improving the performance properties of hydrophobic leather materials and products, a wide range of chemical reagents and methods are used in manufacturing technologies of leather for various purposes. The effect of alkenyl maleic anhydride composition (AMAC) used during processing semi-finished leather on the chemical composition and physicochemical properties of hydrophobized material was determined in the paper. Hydrophobization of semi-finished product was performed after its neutralization by formate and sodium bicarbonate, washing, dyeing, and retanning by the mixture of vegetable-mineral tannins. Fatliquoring-hydrophobization was performed after increasing the temperature of the solution containing alkenyl maleic anhydride polymer, formic acid, and fish oil or sunflower oil. Further fixation was performed by potassium alum in the presence of masking solution – sodium formate. Using AMAC compared to the traditional fatliquoring leads to an increase in the amount of bound fatty substances in the semi-finished product by 1.7–2.0 times and a corresponding decrease in the amount of substances, extracted by organic solvents. The semi-finished product obtained using this technology is characterized by higher deformability and water permeability in dynamic conditions. The obtained results confirm that using alkenyl maleic anhydride composition in manufacturing*

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[10] *The title has been modified; the original title is "Improving water resistance of chrome-tanned leather by alkene-maleic composition". The original paper was published in Ukrainian.*

technology of leather materials allows producing leather with high hydrophobicity and a complex of necessary physicochemical properties. The alkenyl maleic anhydride composition, developed and implemented in the leather production, is a promising water-repellent reagent that can be effectively used in manufacturing technologies of shoe leather which can be used in extreme conditions.

Keywords: *chrome-tanned leather; water resistance; fatliquor composition; alkenyl maleic anhydride polymer; processing; hydrophobization.*

Introduction

In the process of using leather products, their resistance to prolonged periodic exposure to water is extremely important. At the same time, an important requirement for leather materials is the preservation of their water resistance (hydrophobicity) and, consequently, thermophysical properties for a long time. To solve the problem of improving the exploitational properties of hydrophobic leather materials and products, a wide range of chemical reagents [1] and methods are used. Hydrophobic reagents include derivatives of fatty acids and alcohols of different chemical composition, nitrogen-containing compounds, salts of transition metals and their complexes with hydrocarbon compounds, modified complexes of chromium and fatty acids, polymerized fatty acids and their salts, silicates, polysiloxanes, isocyanates, fluorocarbon derivatives, and others [2]. It should be noted that the hydrophobization of natural leather by treating its surface with silicon and fluorine-containing polymers, derivatives of fatty acids, and other hydrophobic reagents is accompanied by a significant deterioration in its sanitary and hygienic properties.

The greatest hydrophobic effect is observed when the reagent diffuses into the volume of fine fibrillar structure of the leather semi-finished product with its subsequent active interaction with the functional groups of the biopolymer during fatliquoring.

Despite the significant variety of known hydrophobic reagents, the development of new methods for their use in the production of hydrophobic leather for domestic production remains relevant.

Literature Review and Problem Statement

Hydrophobization of a leather semi-finished product can be performed at various stages considering the chemical agent composition, the technological process, and its interaction with the dermal collagen and other components of the working solution. In this respect, polyorganosiloxane with polyacrylates or amides of higher fatty acids can be effectively used when processing semi-finished product of chrome-free tannage [3], followed by fixation with aluminum or zirconium salts, and adjusting drying conditions. A method of hydrophobization of a semi-finished leather product which includes leather post-tanning with chromium compounds, the following neutralization, washing, and twofold vegetable tanning, which is carried out by polymers and a mixture of synthetic and vegetable tannins, is known. At the same time, neutralization, twofold vegetable tanning, and dying is carried out at a consumption of 50–70 % of the mass of the semi-finished product [4]. The hydrophobizing fatliquoring is performed in the presence of a 20 % solution of the products of the reaction of amino alcohol, fatty acids of vegetable oils (C_{12-22} fraction), and boric acid at a molar ratio of 2 : 1 : 1 in mineral oil. The final stage of the treatment is post-tanning with chromium compounds. Alkyl alkoxysilane of the general formula $R_1R_2Si(OR_3)(OR_4)$, where R_1 is an aliphatic hydrocarbon residue with C_{6-20}, R_2, R_3, and R_4 are aliphatic hydrocarbon residues of different chain length (C_{1-10}), are used in this process [5].

Hydrophobization of the leather with amide derivatives of fatty acids [6] is also utilized. These derivatives can coordinate with chromium compounds and form complexes with functional groups of collagen. In the work [7], the effect of water repellent agent Synthol EW-321 (Smith & Zoom) on the hydrophobization of leather of various thicknesses, especially the thick one, without additional neutralization is studied. Despite the fact that the fat is fixed by formic acid in the surface layers, its main hydrophobic effect is achieved in the presence of salts of transition metals which are sensitive to changes in pH.

For the hydrophobization of semi-finished leather products, fluorine-containing compounds such as tridecafluoro-*N*-[3-(triethoxysilyl)propyl]-heptanamide which has the structural formula $CF_3(CF_2)_5–C(O)–NF–(CH_2)_3–Si(OC_2H_5)_3$ are also used [8]. In this case, ethyl alcohol, which is used as the solvent, is removed during heat treatment. The use of fluorosilane and fluorosiloxane [9], which provide a long-lasting hydrophobic effect, increase leather strength, and reduce the hygroscopicity of the pelage. Hydrophobic, tanning, and film-forming effects are observed in the treatment of the semi-finished product with polyethylhydroxysyloxanoacrylates [10] due to the presence of active siloxane, carboxyl, hydroxyl, and other functional groups that interact with the amino groups of the dermal collagen. The hydrophobization of the semi-finished leather product can be carried out with the emulsion of the products of the reaction of organopolysiloxanes containing *Si-H* groups and polyhydroxyalkenyl ethers or glycerin monoalkyl ester in the presence of a platinum or rhodium catalyst followed by blocking of *OH* groups with organic acid anhydrides [11]. Application of this reagents make it possible to reduce the water sorption of the leather during 6 and 24 h, respectively, from 103 and 190 % to 72–80 and 121–130 %.

Companies specialized in leather and fur manufacturing for the production of hydrophobic materials and products utilize imported reagents and compositions, predominantly of unknown chemical composition. This creates objective difficulties for the effective use of such reagents considering the specifics of the existing production technologies for polyfunctional leather materials.

The Goal and Objectives of the Research

The goal of the research is to develop a method of fatliquoring-hydrophobization [12] which provides a significant increase in the water-repellent properties of chrome-tanned leathers and the improvement of their properties.

The objectives of research are:

- to determine and investigate the ingredients of the alkenyl maleic anhydride polymer composition and parameters of the processing of the semi-finished leather product;
- to determine the effect of the processing regime of semi-finished leather product, using the alkenyl maleic anhydride polymer with fish or sunflower oil, on the chemical composition and physicochemical properties of the hydrophobized material;
- to develop (*i*) an optimal hydrophobic composition based on alkenyl maleic anhydride polymer and (*ii*) a process for fatliquoring-hydrophobization for increasing water resistance of chrome-tanned leathers.

Methodology for Studying the Effect of Hydrophobic Treatment

In this study we used a semi-finished chrome-tanned product obtained from a cattle rawhide with an average weight of fresh green 22 kg according to the procedure [13]. Processing of raw hide included soaking, dehairing, liming, fleshing, deliming-softening, pickling, tanning, and shaving for a thickness of 2.0 mm. The hydrophobization of the semi-finished product was carried out after its neutralization with formate and sodium bicarbonate, washing, dying, retanning with a mixture of vegetable and mineral tanning agents at water consumption of 60 % of the mass of the semi-finished product. All technological processes were carried out in a drum. For the hydrophobization, compositions listed in Table I (treatments *1–4*) at a consumption of 7 % of the mass of the semi-finished product were used. Control treatments are *5* and *6*.

Table I. *Compositions for treatment of a semi-finished leather product.*

Component	**Treatment**					
	1	***2***	***3***	***4***	***5***	***6***
Alkene-maleic polymer	67.0	65.0	63.0	65.0	—	—
Fish oil	33.0	35.0	37.0	—	63.0	10.0
Sulphited fish oil	—	—	—	—	—	40.0
Sunflower oil	—	—	—	35.0	—	—
Synthetic fat	—	—	—	—	—	50
Oleic acid	—	—	—	—	17.0	—
Paraffin	—	—	—	—	5.0	—
Potassium alum	3	3.5	4	3.5	13.6	—
Bentonite	—	—	—	—	1.4	—

Note: *In treatments 1–4 the compositions of potassium alum are given as a percentage of the mass of the shaved semi-finished product.*

After the complete dying of the semi-finished product with vegetable tanning agents at 30–35 °C for 45 minutes the temperature of the solution was increased to 60–65 °C by adding hot water. The volume of technological solution was brought up to 140 % of the mass of the semi-finished product.

After 60 min of rotating in a drum 85 % formic acid diluted with water 1 : 10 in an amount of 1.7–2 % of the mass of the semi-finished product was added. The drum rotation was continued for another 30–40 min until the pH of the spent solution increased to 3.5–3.8 and the alkenyl maleic anhydride composition (AMAC) emulsion got completely absorbed. In this case, the surface of the semi-finished product should not be oily. The fixing treatment with potassium alum is performed in a fresh solution at 35 °C with the consumption of water – 100 %, potassium alum – 3–4 %, and sodium formate – 0.3–0.4 % of the mass of the semi-finished product.

The drum was rotating for 30 min until the pH of spent solution reaches 3.9–4.1 with following draining of the solution and washing the semi-finished product with water for 10–15 min at 23–25 °C with a water consumption of 150 %. The following drying-moisturizing treatments were carried out according to the previously described technology [13]. Analysis of the chemical composition and physicomechanical properties was carried out according to the methods described in the work [14]. Water penetration under dynamic conditions was investigated using the PVD-2 device at the sample deformation rate of 70 min^{-1}. The determination of the physicomechanical characteristics of the samples was carried out at a rate of 90 mm/min. The stiffness of samples 160 mm long was determined using PZhU-12M device.

Research Results of the Leather Properties

The process of fatliquoring-hydrophobization of semi-finished leather products was carried using four treatments which differed in the content and composition of the AMAC in the spent solution. To determine the effectiveness of the composition, a comparison was made between the hydrophobized leather materials obtained using the developed composition and the leather material hydrophobized according to the method [15]. The latter method uses the following composition for hydrophobization: fish oil – 18.5 %, oleic acid – 5 %, paraffin – 1.5 %, bentonite – 1.4 %, potassium alum – 4 %, water – remaining (treatment *5*), and fatliquoring composition containing sulphited fish oil – 40 %, fish oil – 10 %, and synthetic fat (GOST 11010-84) – 50 % (treatment *6*).

The use of AMAC in comparison with traditional fatliquor (treatment *6*) indicates an increase in the amount of bound fatty substances in the semi-finished product by 1.7–2.0 times (Table II) and a corresponding decrease in substances extracted with organic solvents (OS). This results in a slight decrease in the moisture content, which is caused by the active interaction of oxygen atoms with the components of the dermal structure and with the further orientation of alkyl radicals in inter structural spaces.

Table II. *Chemical composition of semi-finished leather product.*

Parameter	**Treatment**					
	1	**2**	***3***	***4***	***5***	***6***
Mass fraction [%]						
– moisture	12.15	10.91	11.32	11.27	11.86	12.91
– Cr_2O_3	4.05	4.17	4.09	4.25	3.95	4.24
– ash	6.92	6.63	6.41	6.59	6.97	5.89
– substances						
extracted with OS	8.83	9.32	10.97	9.19	11.86	11.58
not extracted with OS	4.27	4.36	4.93	4.42	3.74	2.51

Note: *The results of the analysis are calculated on a dry basis.*

The resulting semi-finished product is characterized by an increased deformability (Table III) and lower stiffness by 45–48 times compared to the materials obtained by control treatment 6. Compared to the similar method of hydrophobic treatment *5*, this this value is higher by 18–20 %. The hydrophobic effect is manifested by the increased separation of the structural elements of the dermis in the presence of AMAC due to the effective diffusion of its emulsion and the corresponding plasticizing effect on the structure of the dermis. This can be seen in a significant increase in the deformation of leather at 9.81 MPa load.

Table III. *Physicochemical properties of semi-finished leather products.*

Parameter	**Treatment**					
	1	**2**	***3***	***4***	***5***	***6***
Dynamic water wetting [min]	228	238	240	234	200	5.0
Tensile strength [MPa]	22.5	23.8	23.6	23.9	21.5	22.0
Elongation at 9.81 MPa [%]	26.0	28.0	29.5	29.4	23.0	21.0
Stiffness [cN]	51.2	48.0	45.4	50.0	78.0	86.0

Thus, the use of the alkenyl maleic anhydride composition in the technology of manufacturing leather makes possible to produce highly hydrophobic leather materials with a complex of necessary physicochemical properties.

The method of imparting hydrophobic properties to leather materials using a composition consisting of an alkenyl maleic anhydride polymer is protected by the Ukrainian patent for Utility Model No. 70418, “Fatliquoring-Hydrophobization Method”. PJSC Chinbar (Kyiv, Ukraine) has been licensed to use this technology for the purpose of manufacturing, applying, selling, and other applications.

Conclusions

To improve the water resistance of chrome-tanned leathers, a method of fatliquoring-hydrophobization is proposed. The method includes fatliquoring-hydrophobization and fixation of potassium alum in two stages. Before the fatliquoring, retanning is carried out with acrylic, synthetic, and vegetable tanning agents at 30–35 °C, while the fatliquoring-hydrophobization is carried out after the solution is heated up to 60–65 °C using the emulsion containing the following components: alkenyl maleic anhydride polymer (100 %), formic acid (85 %), and fish oil or sunflower oil. The mentioned ingredients are consumed based on the mass of the shaved semi-finished product in amount of 4.0–4.5 %, 2.0–2.5 %, and 1.7–2.0 %, respectively. The fixation with potassium alum is performed in the presence of a masking solution – sodium formate. Additionally, the fixation of potassium alum in the second stage is carried out in a fresh solution at 30–35 °C with potassium alum consumption of 0.3–0.4 %, based on Al_2O_3, and sodium formate consumption – 0.3–0.4 %.

Based on the results of the effect of the alkenyl maleic anhydride composition on the physicochemical properties of the hydrophobic semi-finished leather product, it is established that the water resistance and elasticity of the obtained chrome-tanned leathers, manufactured according to the developed technology of fatliquoring-hydrophobization, exceed the leather obtained according to the existing technologies, respectively, by 18–20 and 33 %. The developed technology was implemented in the PJSC Chinbar (Kyiv, Ukraine).

The alkenyl maleic anhydride composition is a promising reagent for hydrophobization and it can be effectively utilized in the technologies for the production of shoe leather which can be used in extreme conditions.

References

[1]. **Danylkovych A., Lishchuk V., and Khliebnikova N.** The problem of improving the hydrophobic properties of leather and fur materials (In Ukrainian). *Lehka Promyslovist* (Publisher «*Легка промисловість*») **3** (2011) 27–29.

[2]. The use of hydrophobizing compositions for water and dirt-repellent impregnation of textile products in dry cleaning, available at: http://www.travers.su/, Accessed on May 5, 2015).

[3]. **Meyndt R. and Germann H.-P.** Investigations on the hydrophobing of chrome-free leather. *World Leather* **8** (2007) pp. 49–50 and 52–54.

[4]. **Studenikin S., Iakovlev K., Bogomolov V., et al.** The method of producing hydrophobic skin (in Russian). RU patent 2404260, November 20, 2010.

[5]. **Reiners J., Kleban M., and Bley M.** Process for the hydrophobization of leather by means of alkyl alkoxysilanes and hydrophobized leather. DE patent DE102005012329A1; September 28, 2006.

[6]. **Ramazonov B.** Investigation of the processing of leather and leather products by some polymer binders (in Russian). *Proceeding of the International scientific-practical conference "Theoretical knowledge on practice"*, Omsk, Russia; March 25, 2008; 260–261.

[7]. **Drik von Ber**. Optimization of the process of hydrophobization of the leather with Synthol EW-321 (in Russian). *Kozhevenno-Obuvnaia Promyshlennost* (Publisher «Кожевенно-Обувная Промышленность») **2** (2008) 17–20.

[8]. **Muzafarov A., Serenko O., Myshkovskii A., et al.** The method of hydrophobization of leather and fur semi-finished product (in Russian). RU patent 2390567; May 27, 2010.

[9]. **Evsiukova N., Vorobeva I., Polukhina L., et al.** Hydrophobization of leather and fur semi-finished product with fluorine-containing functional

silanes and siloxanes (in Russian). *Dizain i Tekhnologii* (Publisher «Дизайн и технологии») **11** (2009) 68–72.

[10]. **Akhmedov V., Dzhuraev A., Toshev A., et al.** Polyethylhydroxysyloxanoacrylate polymers to enhance the effect of hydrophobization (in Russian). *Khimicheskaia Tekhnologiia* (Rushian publisher «Химическая технология») **5** (2007)145–146.

[11]. **Maurer T., Herrwerth S., Koenig F., et al.** Novel polycarboxy-functional organosiloxanyl derivatives and their use for the treatment of leather. DE patent DE102006042869A1; March 27, 2008.

[12]. **Lishchuk V., Danylkovych A., Omelchenko N., et al.** Method of leather fatliquoring-hydrophobization (in Ukrainian). UA patent for Utility Model No. 70418; June 11, 2012.

[13]. **Danylkovych A., Mokrousova O., and Okhmat O.** Technology and materials for leather production (in Ukrainian). *Fenix* (Publisher «Фенікс») 2009, Kyiv, 578 p.

[14]. **Danylkovych A.** Practicum in chemistry and technology of leather and fur (in Ukrainian). *Fenix* (Publisher «Фенікс») 2006, Kyiv, 340 p.

[15]. **Mokrousova O., Oliinyk M., Danylkovych A.** Method of fatliquoring-hydrophobization of semi-finished leather (in Ukrainian). UA patent for Utility Model No. 33010; June 10, 2008.

15. A COMPREHENSIVE ANALYSIS OF CONSUMER PROPERTIES OF NUTRIA VELOUR HYDROPHOBIZED WITH ALKENYL MALEIC ANHYDRIDE – ACRYL SYNTAN COMPOSITION [11]

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Abstract: *A set of consumer properties of hydrophobized nutria fur velour obtained with the use of alkenyl maleic anhydride – acryl syntan composition has been studied. Components of this composition included alkenyl maleic anhydride and polyacrylic polymers, and synthetic tanning agent. The process of filling-hydrophobizing nutria fur velour was carried out at pH 6.8–7.0 and at 40–43 °C for three hours and completed at pH 3.8–4.0. Hydrophobized nutria fur velour was obtained from raw materials with low hair quality, heterogeneous structure in different areas, and low density, but with satisfactory physicomechanical properties of the skin tissue. Influence of the component ratio of the filling-hydrophobizing composition on the physicochemical properties of fur velour was investigated. Specifically, the following characteristics have been studied: thermal resistance, dynamic water wetting, water drop absorption, wetting angle, wetting, vapor permeability, air permeability, etc. Optimal component ratio of the alkenyl maleic anhydride – acryl syntan composition has also been established which ensures formation of a modified nutria fur velour with a set of improved consumer properties compared with the sheepskin velour. Particularly, the decrease in the thermal resistance and vapor permeability of the hydrophobized nutria fur velour by 9.7 and 1.7 times compared to the*

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[11] *The title has been modified; the original title is "A comprehensive analysis of consumer properties of nutria velour hydrophobicized with alkenmalein-acrylsyntane composition"*

sheepskin velour is observed during hydroprocessing. At the same time, aesthetic indicators of the nutria velour (coloristic design and quality of leather dressing were higher by 39–41 % than those of the sheepskin velour. The obtained results on hydrophobizing fur velour with a set of required consumer properties indicate the possibility of expanding the range of products made from fur raw materials with poor-quality hair but satisfactory physicomechanical properties of skin tissue. Fur products manufactured from hydrophobized nutria velour will be suitable for wearing in high humidity.

Keywords: *nutria fur velour; filling-hydrophobizing; alkenyl maleic anhydride – acryl syntan composition; consumer properties.*

Introduction

Present-day fur production involves fabrication of a wide range of furs and fur coat materials including velour. Sheepskin is mainly used in production of fur velour considering the features of skin tissue and hair. At the same time, considering conditions for wearing the fur velour products, physicomechanical properties of skin tissue are essential. Fur velour is obtained from wool sheepskins after their wet-polishing and discarding unusable semi-finished sheepskins for velour production [1]. Considering the shortage of such raw materials in Ukraine [2], there is an objective necessity and urgency in a search for other types of fur raw materials with a corresponding set of consumer properties. In this regard, male nutria skins with low-grade guard hair cannot be used for the production of fur material and are of interest. They can be effectively used for the production of fur velour after the removal of guard hair and the improvement of physicomechanical properties of the skin tissue by applying new chemical filling materials followed by hydrophobization.

Literature Review and Problem Statement

Structure of fur skin materials is hydrophobized using monomeric and polymeric reagents with a wide variety of chemical compositions, particularly, silanes, fluorocarbon resins, polydimethylsiloxane rubbers, complexes of aluminum and wax or paraffin compounds [3] etc. Improvement of water resistance of the skin is also achieved by coating dying which results in a formation of a multilayer protective film coating during multiple application of a coating composition followed by drying, pressing, and use of a special equipment [4, 5]. It should be noted that such technology is highly complex, time-consuming, and labor intensive.

Semi-finished fur skin materials are modified with nitrogen-containing compounds, derivatives of hydroxycarboxylic acids, fatty acid esters, etc. Among the most common hydrophobizing agents, organosilicon compounds including silanes and silicones and paraffins are used. A copolymer of acrylic acid and hydrophobic acrylate monomers of various chemical compositions were used in the previous work [6] at the stage of post-tanning and filling chrome-tanned semi-finished products. At the same time, the degree of filling increases and water resistance, plasticity, and mechanical strength get improved. Considerable effect of copolymers with straight hydrocarbon chains on these properties has been established. The highest hydrophobic effect was achieved at a side chain length above C_{16}.

Emulsion of fluorine-containing copolymer [7] based on maleic anhydride and rapeseed or fish oil with addition of dodecafluorheptanol and octadecyl alcohol make it possible to obtain chrome-tanned leather with increased water resistance. In this case, the maximum effect was achieved at a 5 % content of fluorine in the copolymer molecules. The resulting skin was characterized by wetting angle of 155°, a static water absorption coefficient of 9 %, and dynamic water permeability of 55 min. Use of hybrid polyfunctional polyurethanes of organo-inorganic amphiphilic polymers with hydrophobic and hydrophilic moieties to improve water resistance and dirt repulsion is known

[8]. However, after such modification, the hardness of the skin increases and its appearance deteriorates.

The studies that results in increasing water resistance of skin materials due to the use of combined treatment with low-temperature plasma and chemical reagents are of significant scientific and technical interest. For example, when applying hexamethyldisiloxane and tetraethylorthosilicate [9], the water resistance of the skin increases. Authors of works [10, 11] investigated influence of organic-silicone polymer A-187 and conditions of plasma treatment on physical, mechanical, and hygienic properties of leather obtained from cattle hide and sheepskin raw materials. The materials produced according to the proposed technology were characterized by a 23 % higher strength after integrating plasma treatment. In this case, duration of absorption of water drops increased by 86 % and hygroscopicity decreased by 87 and 76 % [10] for sheep skin and cattle hide, respectively.

It should be noted that the overwhelming number of these studies relate to the skin hydrophobicity. At the same time, due to the considerable difference between tissues of fur skin and leather consisting in its increased plasticity and structural features, this fact determines high demands to the technological process. Particularly, this refers to the process of filling and hydrophobizing fur velour with preservation of elastic properties of the skin tissue.

Thus, combination of hydrophobization of fur skin materials with other technological processes is considered an effective method. At the same time, quality of the resulting natural material featuring water resistance essentially depends on chemical structure of reagents, development of new compositions, and technologies of their application. In determining water resistance of the skin tissue and hence thermal protection properties of the fur velour with polished pelage, significant difficulties arise in objective determination of these parameters. Therefore, it is necessary to use a system of structural and chemocolloidal properties of the investigated materials. Therefore, solution of these issues becomes especially important in the development of technologies for manufacturing fur velour from raw materials with a specific structure of skin tissue which can be used effectively in products worn in high humidity.

The Goal and Objectives of the Study

The goal of the study was to obtain a fur velour from nutria skins with low-grade guard hair by hydrophobizing the skin tissue with alkenyl maleic anhydride – acryl syntan composition.

To achieve the goal, the following tasks were set:

– to analyze technological features of production of hydrophobic velour from nutria skins;

– to determine the effect of the component ratio of the filling-hydrophobizing composition on physicochemical properties of nutria fur velour;

– to determine essential consumer properties of fur velour obtained from nutria skins processed using an optimal component ratio of the filling-hydrophobizing composition.

Materials and Methods

Male nutria skins with area of 24–25 dm^2 and rough guard hair were used to produce hydrophobic nutria fur velour (NFV) 22–24 h after chrome tannage, centrifugation, and tumbling [1].

The process of filling-hydrophobizing of the semi-finished nutria skins was carried out in a stationary apparatus with a horizontal stirrer with a solution of alkenyl maleic anhydride (AMA) polymer at a temperature of 40–43 °C and stirring for 20 min. After 1 h, a filling mixture of Melio Resin A-821 polyacrylic emulsion from Clariant (Germany) and a synthetic tannin *β*-naphthalene sulfonate (BNS; technical specification TU 17-06-165-89) was added to the technological solution (Table I). After 40 min of stirring, the rest of the hydrophobizing AMA polymer (60 %) was added. The polyacrylic emulsion had dry residue of 24 % and density of $1.03 \cdot 10^3$ kg/m^3, while the BNS syntan contained 62 % of tannins. A composition based on $C_{20–24}$ α-alkenes and maleic anhydride which is a 50–52 % aqueous-organic polymer solution with a mean weight-average molecular weight of 38 kDa was used for hydrophobizing of NFV.

The pH of the technological solution was 6.8–7.0. After 30 min of stirring, the pH of the solution was adjusted with formic acid to 3.8–4.0. Subsequent wringing and unstretched drying of the semi-finished product were carried out at 20–23 °C. Guard hair was removed by epilation. The obtained hydrophobized semi-finished nutria skins were subjected to polishing by No. 4 abrasive cloth.

The filled and hydrophobized NFV was characterized by a set of physicochemical properties after pre-conditioning samples using a desiccator method at normal conditions.

Thermoprotective ability of the fur velour was determined on whole skins using PTS-225 device (Russia) as a total thermal resistance [12]. Samples of fur velour were tested without and with blowing at a speed of 5 m/s and 45° air flow direction to the sample surface. Total thermal resistance, R, [(m^2 °C)/W] was calculated as

$$R = \frac{3C_1}{3FKC_1z - a - C_2},$$

where C_1 is the total heat capacity of the instrument plate [J/°C]; F is the plate constant [(J·°C)/m^2]; K is the coefficient of dissipation of heat flow over the fur sample; z is the rate of cooling of the instrument plate [s]; a is the correction for dissipation of the heat flux in the device [s^{-1}]; and C_2 is the total heat capacity of the plate and the sample [J/°C].

The total heat capacity is calculated using the following equation:

$$C_2 = CqA,$$

where C is the specific heat of the material of organic origin which is equal to $1.675 \cdot 10^3$ J/(kg·°C); q is weight of 1 m^2 of sample [kg]; and A is the device plate area [m^2].

Water absorption under dynamic conditions was determined on a PVD-2 (Russia) instrument. Air permeability, vapor permeability, and other parameters were determined by the previously described methods [13]. Water resistance of NFV was determined after its hydrotesting according to ISO 4920:2012 standard "Textile fabrics — Determination of resistance to surface wetting (spray test)" for 10 min in the same way as textile materials by spraying water at 24–26 °C. Tensile strength and elongation of velour under 4.9 MPa load and uniaxial tension were determined on a tensile testing machine RT-250M, belt A, at a deformation rate of 80 mm/min.

Thus, a set of physicochemical parameters including thermoprotecting and hygienic properties was used to assess the consumer properties of hydrophobized nutria fur velour.

Effect of Component Ratio of Alkenmaleic-Acrylsyntan Composition on Properties of Nutria Fur Velour

Results of the study of the effect of chemical composition of filling-hydrophobizing agents (Table I) on physicochemical properties of NFV are given in Table II. Filling-hydrophobizing treatments of nutria skins are characterized by different consumption of ingredients of technological solution at a sevenfold water excess relative to the skin mass. Moreover, the treatment *3* differs from the treatment *1* by 1.7 and 3 times higher values of consumption of alkenyl maleic anhydride polymer and acryl syntan component, respectively. Filling-hydrophobizing ingredients in the structure of nutria skin tissue were fixed by reducing pH to 3.8–4.0 with formic acid. Sheepskin fur velour (SFV) whose semi-finished product was re-tanned using chrome tanning agent with basicity of 35–40 % and BNS syntan according to the current technology was used as a control sample [1]. At the same time, spending of the technological solution in all studied technologies exceeded the existing technology by 5–15 %.

Table I. *Consumption of alkenyl maleic anhydride – acryl syntan complex ingredients in filling of semi-finished nutria skins.*

Treatment	**Material consumption [g/L]**					**Solution Spending [%]**
	AMA polymer	**Polyacrylic emulsion**	**BNS**	**AMA polymer**	**Formic acid**	
1	2	4	3	5	0.5	86
2	5	9	6	7	0.5	80
3	5	12	9	7	0.5	76

As it can be seen from Table II, with an increase in consumption of hydrophobizing-filling ingredient, physicochemical properties of NFV varied drastically. Particularly, duration of dynamic water wetting and water drop absorption by samples processed by the treatment *2* increased 2.8 and 2.65 times, respectively, compared with the treatment *1*. Compared to the control treatment, 17 and 106 times increase in these parameters was observed. It should be noted that at the same time, air permeability of the NFV reached the maximum value for the treatment *3* (1.8 times increase) at a slight decrease in vapor permeability compared to the treatment *1*.

The obtained data show a considerable effect of filling and hydrophobizing ingredients on structure and physicochemical properties of the fur velour due to their interaction with fibrous collagen of the NFV skin tissue and corresponding decrease in fibrillar interactions. This effect was accompanied by 1.80 and 1.97 times increase in area for the semi-finished product obtained by treatment 2 and *3*, respectively, as compared with the minimum consumption of the filling component (treatment *1*).

Table II. *Physicochemical properties of nutria fur velour.*

Parameter	**Treatment**			
	1	***2***	***3***	***control***
Shrinkage temperature [°C]	63	64	64	61
Dynamic water wetting [s]	360	1,020	720	60
Water drop absorption [s]	1200	3180	2940	30
Wetting angle [°]				
– in 1 min	110	130	130	—
– in 30 min	—	120	120	—
Soaking [%]				
– in 2 h	142	123	131	197
– in 24 h	184	160	172	213
Vapor permeability:				
– absolute, 10^{-6} [kg/(m^2·s)]	5.28	4.72	4.44	5.83
– relative [%]	54	48	45	59
Air permeability:				
– absolute [s]	11	13	16	9
– relative, 10^{-6} [m^3/(m^2·s)]	0.16	0.13	0.11	0.19
Increase in area [%]	3.2	5.8	6.3	0

Thus, the results of physicochemical studies allow determining the content of the filling-hydrophobizing composition for production of fur velour with a set of improved properties from nutria skins.

In further studies to establish the most important exploitational and aesthetic properties of hydrophobized fur velour of nutria skins obtained by the developed technology, *a priori* ranking was carried out [14]. As a result of this ranking, 10 significant parameters were established with coefficient of concordance of 0.894. Statistical significance of this coefficient was confirmed by the χ^2 criterion which was equal to 136.8 at its critical value of 27.6 at the level of significance 0.05.

Results of the experimental studies of the effect of ingredients of the filling-hydrophobizing complex on essential consumer properties of the NFV are given in Table III and in Fig. 1 and Fig. 2. Treatment of NFV with alkenyl maleic anhydride polymer is accompanied by a sharp increase (24 times) of duration of dynamic water wetting of NFV (Table III) compared with non-hydrophobized SFV which indicates its significant hydrophobizing effect on hydrophilic structure of the material. Accordingly, if the hydrophobized NFV revealed somewhat lower values of total thermal resistance in its initial state (Fig. 1) in comparison with SFV, this parameter increased 2.1 times after hydroprocessing. In this case, deformation properties after NFV hydroprocessing were characterized by significantly greater stability compared to SFV which, accordingly, had almost twice the value of residual elongation. The results indicate that the products made from hydrophobized NFV will ensure high stability of their shape, even after 10 min of being exposed to water.

Effect of hydrophobizing of NFV is revealed in analysis of its hygienic properties (Fig. 2).

Thus, hydrophobized NFV is characterized by 53 and 60 % higher values of vapor permeability and air permeability parameters, respectively, compared with SFV. Difference between these parameters significantly increases by 4.7 and 2.5 times after hydroprocessing. It should be noted that hydrophobized NFV also has a clear advantage in aesthetic parameters after hydroprocessing (Table III). This is manifested in a smaller loss of quality of leather dressing and coloristic design of the skin tissue.

Thus, processing of fur velour from nutria skins with the developed filling-hydrophobizing composition provides formation of a modified material with a complex of improved consumer properties in comparison with the fur velour produced from wool sheepskins. This effect significantly increases after hydroprocessing.

Table III. *Consumer properties of fur velour obtained from nutria and sheep skins before and after hydroprocessing.*

Parameter	**Fur velour**			
	nutria		**sheepskin**	
	hydroprocessing			
	before	**after**	**before**	**after**
Tensile strength [MPa]	0.69	0.63	0.94	0.82
Dynamic water wetting [s]	1380	870	57	0
Elongation [1] [%]	21	23	22	29
Elastic elongation [1] [%]	12	12	10	8
Residual elongation [1] [%]	9	11	12	21
Coloristic design [units]	1.00	0.85	0.95	0.61
Dressing quality [units]	1.00	0.85	0.90	0.60

Note: *[1] at 4.9 MPa load.*

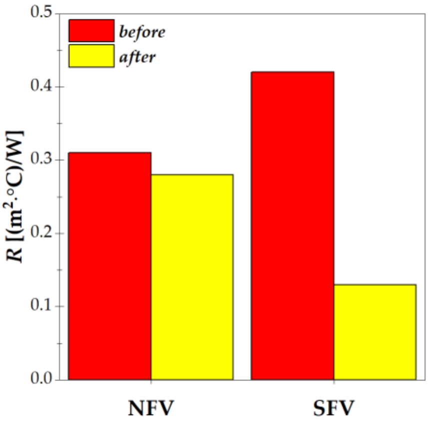

Fig. 1. *Dependence of the total thermal resistance for NFV and SFV on condition of fur velour – before and after hydroprocessing.*

Discussion of the Results on the Consumer Properties of Nutria Fur Velour

To improve water resistance and other consumer properties of natural leather and fur materials, surface and bulk processing was applied using a wide range of chemical reagents. Volumetric hydrophobizing modification of the semi-finished products is used in the processes of filling, re-tanning, fatliquoring, and coating dying. Given the heterogeneous and reduced density of nutria skin tissue in both volumetric and topographic areas, its structure has to be filled. This will increase density of the skin tissue and improve its physicomechanical properties. To improve thermoprotective and hygienic properties and keep the shape of the product during its exploitation in high humidity, it is necessary to hydrophobize the semi-

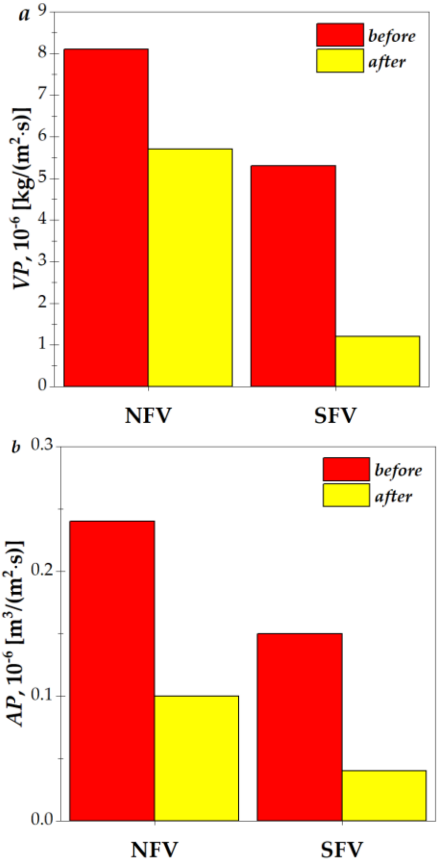

Fig. 2. Dependence of vapor permeability (VP, a) and air permeability (AP, b) of NFP and SFP on condition of fur velour hydroprocessing: before and after.

finished products. Significant advantages of volumetric processing of semi-finished products without intermediate drying [1] during implementation of the NFV manufacturing cycle should be noted.

To effectively carry out the NFV filling-hydrophobizing process, introduction of AMA polymer in the technological solution in two steps (before and after filling) was used in the study. Primary treatment of NFV with AMA polymer ensures its deep diffusion in the intermicrofibrillar structure of the semi-finished product and promotes distribution of polyacrylic polymer and the BNS followed by their sorption. After filling the interfibrillar gaps in the structure of the semi-finished product, it is necessary to reintroduce AMA polymer for its sorption by the modified surface of the fibrillar structure of the semi-finished product and achieving the hydrophobic effect. When using an optimal amount of alkenyl maleic anhydride – acryl syntan composition, maximum value of water resistance of NFV is achieved. However, the hydrophobic effect decreases when amount of hydrophilic filler is increased. At the same time, maximum hydrophobic effect causes increased mobility of elements of the fibrillar structure in the NFV skin tissue and its plasticization and, accordingly, increased yield of the material area.

An adequate change in porosity of the hydrophobized NFV skin tissue occurs which is expressed by the change in air and vapor permeability. With an increase in the filler concentration at an optimal content of AMA composition, the effect of distribution of structure of the semi-finished product and hence air permeability grows. Difference in the vapor permeability is due to the different mechanism of diffusion of water vapor through the porous structure of NFV skin tissue, particularly, due to different contribution of the pore size and shape, the character of the pore size distribution, and hydrophobic-hydrophilic nature of the surface in the process of sorption-desorption of water molecules during their transportation through the material structure.

The effect of using the alkenyl maleic anhydride – acryl syntan composition with an optimal content of elements in the NFV manufacture was well observed in comparative study of the set of essential consumer properties after hydroprocessing. The hydrophobic-hydrophilic character of structure of the modified nutria fur velour is expressed in the practically stable elastic elongation of the skin tissue at 4.9 MPa load or a slight increase in elongation at the practically unchanged strength. At the same time, considerably larger changes in deformation parameters of SFV skin tissue and especially residual elongation are explained by its higher water sensitivity connected with increased hydrophilicity of its structure. This is also reflected in significantly higher dynamic water resistance of the hydrophobized NFV in comparison with the sheepskin velour. Significantly higher value of the SFV wetting causes low value of its total thermal resistance. At the same time, this important consumer parameter decreases less in the hydrophobized NFV indicating its high thermoprotective properties.

In future, it is necessary to perform computer multicriteria optimization of the alkenyl maleic anhydride – acryl syntan composition and conditions of its effective use in the technology for industrial testing of the developed process of filling-hydrophobizing of nutria fur velour. To do this, it is necessary first to work out a corresponding plan of an experiment to determine element content of the composition and properties of the nutria fur velour and then determine type of a plan of establishing filling-hydrophobizing technology and elucidating properties of the obtained velour. After realization of corresponding experiments, mathematical models shall be constructed and used to determine the parameters of optimal element content of the composition and its use in the technological process.

As a result of the studies to be conducted, permissible limits of element contents in the alkenyl maleic anhydride – acryl syntan composition and the process factors shall be established. The obtained results of optimization will be used for testing the developed technology in semi-industrial conditions. After development of technological regulations, the process of filling-hydrophobizing nutria fur velour can be implemented under industrial conditions.

Consequently, proceeding from the discussed set of essential consumer properties, the hydrophobized nutria fur velour obtained by the developed technology can be used as an effective material for replacing sheepskin fur velour in the manufacture of water-resistant products.

Conclusions

To manufacture nutria fur velour with a set of consumer properties suitable for use in high humidity, it is necessary to carry out filling-hydrophobizing of the semi-finished product in a single technological cycle of material production. The process of filling-hydrophobizing of nutria fur velour is carried out in two stages. About 40 % of the alkenyl maleic anhydride polymer is introduced in the technological solution at the first stage and the rest after filling of the skin tissue with the acryl syntan component. This process gives a significant compaction of the skin tissue structure and increases its water resistance and shape stability of the products made from nutria fur velour.

It was established that duration of dynamic water wetting and water drop absorption of the skin tissue of the hydrophobized nutria fur velour increased with increasing content of alkenyl maleic anhydride polymer in the filling-hydrophobizing composition. These indicators reached maximal value at the polymer consumption of 12 g/L. After increasing the content of acryl syntan tanning agent from 15 to 21 g/L, the wetting angle reaches 130 and 120° in 1 and 30 minutes, respectively. Air permeability of nutria velour increases by 23 % at practically the same vapor permeability with a 5.8 and 6.3 % increase in area compared with the control treatment.

Ten essential consumer properties of nutria fur velour were determined by the method of *a priori* ranking. They most fully and objectively characterize exploitational and aesthetic properties of the material. Application of the optimal component ratio in the alkenyl maleic anhydride – acryl syntan composition in the manufacture of modified nutria fur velour contributes to formation of a material with increased total thermal resistance and vapor permeability after hydroprocessing of the material. These parameters are 2.1 and 4.7 times higher than those of the sheepskin fur velour. At the same time, aesthetic parameters of nutria fur velour (coloristic design and quality of leather dressing) also exceed those of sheepskin fur velour by 39–41 %.

The results on hydrophobizing fur velour with a set of necessary consumer properties indicate the possibility of expanding the range of materials produced from fur skins with low hair quality but satisfactory physicomechanical properties of skin tissue. The fur products made from hydrophobized nutria velour will be suitable for use in high humidity.

References

[1]. **Danylkovych A., Lishchuk V., and Strembulevych L.** Modern fur production (in Ukrainian). *Fenix* (Publisher «Фенікс») 2006 2015, Kyiv, 320 p.

[2]. **Hryshchenko I.** (ed.). Fur market of Ukraine: monograph (in Ukrainian). *Svit Uspikhu* (Publisher «Світ Успіху») 2016, Kyiv, 280 p.

[3]. **Boinovich L. and Emelianenko A.** Hydrophobic materials and coatings: principles of design, properties and applications (in Russian). *Uspekhi himii* (Publisher «Успехи химии») **7**, (2008) 619–638.

[4]. **Hryshchenko I., Zvarych I., and Okhmat O.** Technological equipment for fur and leather production in the innovative economy: a monograph (in Ukrainian). *Svit Uspikhu* (Publisher «Світ Успіху») 2018, Kyiv, 272 p.

[5]. **Shestov A.** Production of leather materials with improved protective and physicochemical characteristics (in Russian). *Vestnik tekhnicheskogo universiteta* (Publisher «Вестник технического университета»), **8**, 14 (2015) 137–139.

[6]. **Du J., Huang C., and Pen B**. Influence of hydrophobic side chain structure on the performance of amphiphilic acrylate copolymers in leather-making. *Journal of the Society of Leather Technologists and Chemists* **100**, 2 (2016) 67–72.

[7]. **Zhaoyang L., Haojun F., and Yan L**. Fluorine-containing aqueous copolymer for waterproof leather. *Journal of the Society of Leather Technologists and Chemists* **92**, 3 (2008) 107–113.

[8]. **Casas C., Bou J., Ollé L., et al.** Development of nanocomposites with self-cleaning properties for textile and leather. *Journal of the Society of Leather Technologists and Chemists* **102**, 1 (2018) 33–41.

[9]. **Koizhaiganova M., Meyer M., Junghans F., et al.** Surface activation and coating on leather by dielectric barrier discharge (DBD) plasma at atmospheric pressure. *Journal of the Society of Leather Technologists and Chemists* **101**, 2 (2017) 86–93.

[10]. **Shataeva D., Kulevtsov G., and Abdullin I.** Production of leather materials from the skins of sheepskin and cattle hides with improved hygienic properties by processing NNTP and organosilicon compounds (in Russian). *Bulletin of Kazan Technological University* **17**, 11 (2014) 86–87.

[11]. **Shataeva D., Kulevtsov G., and Abdullin I.** Investigation of the effect of the interaction of non-equilibrium low-temperature plasma and organosilicon compounds on the physicomechanical properties of cattle hides (in Russian). *Bulletin of Kazan Technological University* **17**, 11 (2014) 73–74.

[12]. **Danylkovych A.** Practicum in chemistry and technology of leather and fur (in Ukrainian). *Fenix* (Publisher «Фенікс») 2006, Kyiv, 340 p.

[13]. **Danylkovych A. and Chursin V.** Analytical control in leather and fur production: a laboratory practicum (in Russian), Infra-M, Moscow, 2016, 176 p.

[14]. **Statiukha H., Skladannyi D., and Bondarenko O.** Introduction to planning the optimal experiment (in Ukrainian). NTUU «KPI» 2011, Kyiv, 125 p.

16. CONSUMER PROPERTIES OF LEATHER MATERIALS HYDROPHOBIZED BY ALKENYL MALEIC ANHYDRIDE COMPOSITION [12]

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Abstract: *The complex of consumer properties of leather obtained by the technology for fatliquoring-hydrophobizing with alkenyl maleic anhydride composition (AMAC) was studied. It is shown that hydrophobization of hides with an AMAC provides a substantial increase in water-resistance of leather materials with an increase in their air permeability compared to leathers obtained by hydrophobization using the fatliquoring composition with a 1 : 4 : 5 ratio of fish oil, sulphited fish oil, and synthetic oil.*

Keywords: *hydrophobization; semi-finished leather; alkenyl maleic anhydride (AMA) polymer; composition; hygienic and physicomechanical properties.*

Introduction

In the process of exploitation, leather products are exposed to various external influences and especially to water, both in vapor and liquid form. Thus, when manufacturing various types of products from leather materials, including products for special purposes, the problem of increasing the water-resistance or hydrophobicity is of great practical importance. The process of hydrophobization of leather materials is directly related to significant changes in the complex of all consumer properties.

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[12] *The title has been modified; the original title is "Consumer properties of leather materials, hydrophobized by alkenyl maletnatnym composites". The original paper was published in Russian.*

Therefore, when developing technologies for fatliquoring-hydrophobization of leather semi-finished product that require optimization of the production process, it is necessary to conduct not only a scientifically justified choice of hydrophobizing reagents and compositions, but also considering the effect of the hydrophobization on the consumer properties of the final material. In this regard, research on improving the exploitational characteristics of leather materials while maintaining a sufficiently high level of sanitary and hygienic properties is of great importance.

Analysis of technical and patent literature indicates that there are a large number of chemical reagents used for the hydrophobization of leather materials. Among the known hydrophobizing chemical reagents, the most widely used are organosilicon compounds and compositions based on them. The use of the organosilicon composition of polyalkylsiloxane liquid PMS-200, hydrophobizing polyethylhydroxysiloxane liquid 136-41, and organophosphorus substance as an activating additive made it possible to improve dynamic water wetting by 18–21 times, and decrease water absorptivity by 50–75 % [1, 2]. At the same time, the hydrophobizing leather treatment with powder slightly reduces the dynamic water wetting and does not affect the leather stiffness [2]. The modification of the structurally inhomogeneous surface of the split with a fluorine-containing silane and a formulation based on fluorocarboxylic acid [3] prevents the rapid penetration of moisture inside the material structure and thereby improves the exploitational characteristics of the footwear. Small addition of octafluorotoluene to organosilicon compounds at the stage of fatliquoring semi-finished product leads to a decrease in its dynamic water wetting up to 40 times, water penetration up to 5 times, and an increase in heat resistance [4, 5].

The use of products of reaction of polyorganosiloxanes with glycerol esters results in the decrease of water absorption by the treated leather by 1.5 times after 6 h of being in contact with water [6]. The treatment of the leather semi-finished product with a copolymer based on the maleic acid ester and α-oxypropyldimethylsiloxane at a ratio of 2 : 1, acrylic acid, and 1-octadecane [7, 8] increases the water-resistance and elasticity of the leather material. The increase in the hygienic properties of hydrophobic leathers is achieved during fatliquoring in the presence of a 20 % solution of the products of the reaction between amino alcohol, fatty acids of vegetable oils of the C_{12-22} fraction, and boric acid at their molar ratio of 2 : 1 : 1 in mineral oil [9].

Despite the large number of hydrophobizing reagents cited in the literature, the technologies utilize only their limited number, moreover in domestic technologies imported material products are predominantly used. Since the chemical composition of such reagents is largely unknown, effective use of these reagents is complicated and limited. Thus, there is an urgent need to develop new domestic hydrophobizing materials based on environmentally friendly reagents.

Problem Statement

In this paper, the effect of the developed composition based on alkenyl maleic anhydride (AMA) polymer on the consumer properties of leather during its exploitation is investigated.

Materials and Methods

The leather samples of chrome-tannage with the thickness of 1.2–2.4 mm obtained from cattle rawhide - heifer of 22 kg weight, were used in the study. The manufacturing technology of hide processing was previously described [10]. Hydrophobizing composition has a 2 : 1 ratio of alkenyl maleic anhydride polymer and fish oil. Samples for treatment *1* and *2* were 1.8 and 2.4 mm thick. Treatment *3* was a control with a 1.8 mm thick sample obtained by the same technology but using the fatliquoring composition with 1 : 4 : 5 ratio of fish oil, sulphited fish oil, and synthetic fat (GOST 11010-84). For cyclic tests of stiffness and elasticity, both hydrophobized and control samples of 1.2 mm thick leather were also used. All samples were subjected to 10-fold hydration for 24 h at 20 ± 3 °C and dried unstretched for 24 h at 20 ± 3 °C with further maintaining under normal conditions for a day.

The chemical composition of the leather, their sorptivity and diffusivity, and physicomechanical characteristics were determined by standard methods. Dynamic water penetration of the leather was determined on samples 80×90 mm using a PVD-2 equipment and a device produced by Giuliani at deformation rates of 24, 70, 120, and 52 min^{-1}, respectively. Tests on the spherical stretching of the obtained leathers were carried out on a POIK (in Russian "ПОИК" – "Прибор Оперативного Испытания Кож") device using a punch with a hemisphere radius of 5 mm [11]. Determination of the stiffness and elasticity for repeated moisturizing-drying cycles of leather samples of 20×(70, 95, or 160) mm was carried out on a device PZhU-12M [12].

Chemical Composition and Sorption-Diffusion Properties of Leathers

The proposed hydrophobization method provides a deep penetration of substances that are part of the hydrophobizing emulsion. For the purpose of determining chromium (III) oxide, substances extracted with organic solvents (OS; unbound fatty substances) and mineral substances in the inner and outer layers of hydrophobized samples 2.4 mm thick was performed (Table I). Considering the effect of the thickness of leather materials on its chemical composition, it can be noted that the experimental data differ only in the amount of unbound fatty substances with the maximal amount corresponding to a sample with smaller thickness.

Table I. *Chemical composition of leather for the top of the shoe*

Parameter	**Treatment**			**Leather layer**		
	1	*2*	*3*	**grain**	**middle**	**flesh**
Thickness [mm]	1.8	2.4	1.8	0.8	0.8	0.8
Mass content [%] of						
– moisture	11.26	11.98	12.32	11.98	11.98	11.98
– Cr_2O_3	4.38	4.32	4.43	4.49	3.21	4.18
– total ash	6.53	6.36	6.18	6.17	5.93	6.49
– substances extracted with OS	9.12	8.37	8.34	9.93	4.86	7.97
– bound fatty substances	4.18	4.08	2.42	4.57	2.03	3.73
– proteins	60.66	62.53	64.36	—	—	—

Note: *The mass composition of leather components is calculated on a dry basis.*

As a result of the examination of leather layers, it was found that the content of unbound fatty substances is the highest in the grain layer, and it is the least, including bound fatty substances, in the middle layer. Such distribution of fatty substances is due to the structural features of the grain layer after removal of the pelage during chemical destruction of the hair follicles located in the papillary layer. The content of bound fatty substances in this layer is 2.2 times less compared to the substances extracted with OS, but 1.9 times more than in control samples (treatment *3*). This can be due to more efficient diffusion of the components of the developed composition into the structure of the semi-finished leather material and subsequent active interaction with structured macromolecules of collagen. Similarly, the distribution of chromium (III) oxide in the layers of the hydrophobized sample is observed.

The nature of the porosity variation, depending on the composition of the fatliquoring composition, indicates that the use of the hydrophobic composition based on alkenyl maleic anhydride promotes the formation of a more developed fibrous structure as compared to the control treatment of fatliquoring (Table II). This is explained by a 17–24 % increase in the volume yield of semi-finished leather material and it is due to the preservation of the divided fibrous structure of natural material after moisture removal from it.

Table II. *Sorption-diffusion properties of leather for shoe uppers.*

Parameter	**Treatment**		
	1	***2***	***3***
Porosity [%]	55.0	57.0	51.0
Volumetric area yield [%]	253.0	270.0	217.0
Vapor permeability [mg/(cm^2·h)] of			
– flesh side	11.2	6.1	14.0
– grain side	2.3	1.9	3.9
Air permeability [cm^3/(cm^2·h)] of			
– flesh side	790.0	540.0	370.0
– grain side	630.0	360.0	290.0
Hygroscopicity [%]	12.1	13.3	11.7
Moisture release [%]	5.3	4.9	2.6

A significant increase in the air permeability of hydrophobized leather compared with the control sample by 2.1–2.2 and 1.2–1.5 times, respectively, for 1.8 and 2.4 mm thick samples indicates the presence of a significant number of through pores. The higher relative air permeability of the leather from the flesh side as compared to the control sample indicates an increased porosity of this layer of hydrophobized leathers.

The observed effect of the vapor permeability of hydrophobized leather samples in comparison with the leather of treatment *3* may be due to the complicated mechanism of water vapor transport, which is based on the successive processes of condensation and evaporation of condensed water. This may indicate the presence of a significant number of pores of smaller radius in the samples of treatment *1*, which facilitate the condensation of water vapor, on the one hand, and make it difficult to transport them through the thickness of the sample, on the other hand. This is confirmed by the character of the dependence of vapor permeability on the thickness of the sample.

Peculiarities of the porous structure of the samples of treatment *1* and *2* explain the nature of the change in hygroscopicity and moisture release of the hydrophobized leather material, which depend on the thickness and composition of the fatliquoring composition. Thus, the moisture release of leather material fatliquored by hydrophobic AMA composition is 1.9–2.0 times higher than the control leather samples.

The deformation rate of the hydrophobic leather material significantly affects its moisture absorption and water penetration (Fig. 1). At the same time, an increase in the rate of deformation by a factor of five is accompanied by a 1.8-fold decrease in the water wetting time for samples with a thickness of 1.8 mm, and to a lesser extent this is observed for the thicker samples.

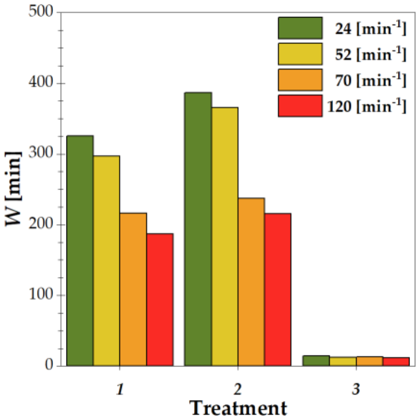

Fig. 1. *Dynamic water wetting of leather material at different deformation rates: 24, 52, 70, and 120 min*$^{-1}$.

Water penetration at minimum and maximum deformation rates in comparison with the control leather material decreases by 46–54 and 36–42 times, respectively. The effect of the deformation rate on the water penetration of control leather samples is less pronounced due to their increased hydrophilicity of the sample as a result of treatment with a fatliquor composition containing molecules with sulfo groups.

Similarly, the wetting properties of hydrophobized leather samples change. The experimental samples absorb an insignificant amount of water during the first 5 h of contact with water, while the control samples absorb 11–14 times more during the first hour (Fig. 2). Over time, this difference increases and after 8 h the leather obtained by the control technology absorbs practically the maximal amount of water, in contrast to the hydrophobized leather material for which water absorption increases slowly.

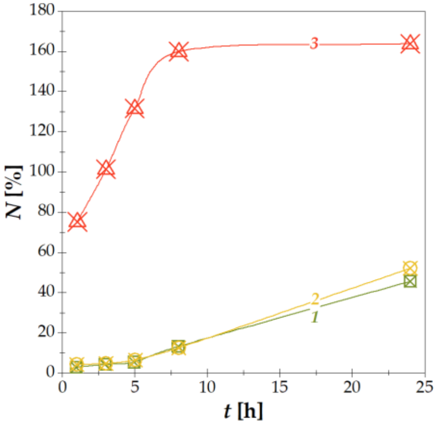

Fig. 2. *Wetting kinetics of leather materials obtained by treatment 1, 2, and 3.*

Thus, the bulk hydrophobization with AMA composition of leather materials with different thickness results an increased water resistance compared to the control samples for which a traditional fatliquor is used. At the same time, due to the preservation of the well-formed porous structure of the resulting hydrophobized natural material, its sanitary and hygienic properties remain sufficiently high.

Physicomechanical Properties of Hydrophobized Leathers

The objective information on the consumer properties of leather materials can be obtained as a result of their testing under the influence of various external factors, such as interaction with water and complex deformations, including cyclic and combined ones. The physicomechanical properties which depend on the state of the leather samples are presented in Table III.

Table III. *Physicomechanical properties of leathers under uniaxial tension.*

Parameter	**Treatment of**					
	dry sample			**wet sample**		
	1	**2**	***3***	***1***	**2**	***3***
Tensile strength [MPa]	22.0	25.5	23.2	20.3	23.0	20.5
Strength at break onset of grain side [MPa]	22.0	25.0	21.0	19.3	22.5	18.2
Elongation at 9.8 MPa load [%]	36.0	34.0	37.0	39.0	37.8	42.0
– at break	46.0	43.0	55.0	54.0	52.0	63.0
– residual	8.7	9.9	10.2	18.3	21.4	22.1
– elastic	37.3	33.1	44.8	35.7	30.6	40.9

From the data it can be seen that after wetting the hydrophobized leather samples their mechanical strength decreases on average by 11–13 %, while the deformation characteristics increase by 17–21 %. At the same time the elastic elongation slightly decreases. This is due to the plasticizing effect of moisture on the structure of the dermis.

For complex deformation of the leather samples – spherical stretching, the strength of the leather grain layer and elongation change in a similar way (Table IV). In this case, the meridional elongation of moistened leather samples increases by 13–15 %, and after drying both strength and elongation practically corresponds to the initial values of the physicomechanical parameters of the samples.

The stiffness (S) and the elasticity (E) of the hydrophobized samples with different lengths and thicknesses under cyclic moisturizing is given in Table V. The data show that with increasing length of a specimen of the same thickness the stiffness decreases by 3.8–6.1 times, with the largest changes related to the sample thickness of 1.8 mm. At the same time, the elasticity increases only by 0.09–0.18 times. In the moisturized state, the control samples become more elastic. With cyclic moistening, the elasticity and stiffness of the leathers are reduced to a greater extent for shorter samples, and with decreasing thickness this difference decreases. Therefore, for an objective assessment of the stiffness and elasticity of leather materials, it may be recommended to carry out tests using the PZhU-12M instrument on samples with a length of 70 mm.

Table IV. *Physicomechanical properties of leathers under spherical tension.*

Parameter	**Treatment of**								
	dry sample			**wet sample**			**after drying**		
	1	**2**	***3***	***1***	**2**	***3***	***1***	**2**	***3***
Tensile strength [N]									
– whole sample	580	720	540	545	680	475	570	710	560
– grain layer	580	710	430	510	630	380	580	710	420
Meridional elongation [%]									
– at break onset of grain side	57.0	48.0	32.0	66.0	58.0	34.0	62.0	48.8	30.0
– at break of the whole sample	59.0	52.0	43.0	67.0	60.0	49.0	58.0	54.0	43.0

From the obtained data it follows that samples of hydrophobized leather after cyclic moisturizing-drying are characterized by a decrease in stiffness, while the control leather samples – by its increase, and consequently also by a decrease in the elastic properties. This can be explained by the plasticizing effect of water molecules in the control samples that affect the hydrophilic structural elements of the dermis and the formation of additional hydrogen bonds between them after drying. In this regard, the hydrophobized leather after cyclic moisturizing-drying restores the physicochemical characteristics, while the leather obtained with sulphited fish oil undergoes deeper structural changes which is manifested in the tendency to increase their stiffness and elasticity.

Table V. *Stiffness and elasticity of the leather after a cyclic moisturizing.*

Thickness [mm]	Length [mm]	Leather state					
		dry		moisturized		after drying	
		S [cN]	E [%]	S [cN]	E [%]	S [cN]	E [%]
2.4	70	529	90	460	76	498	84
	95	238	82	199	73	213	75
	160	110	78	90	71	98	74
1.8	70	316	92	268	66	287	76
	95	109	83	92	68	104	76
	160	44	78	36	73	42	73
1.2	70	107	76	78	69	89	74
	95	51	72	42	66	47	69
	160	19	70	14	63	17	67
1.2 (control)	70	127	75	75	82	136	85
	95	76	71	38	75	103	76
	160	33	68	20	71	38	73

Conclusions

The complex of consumer properties of leathers, obtained by the technology of bulk fatliquoring-hydrophobization with the use of alkenyl maleic anhydride composition, has been investigated. It has been shown that the hydrophobization of leather by alkenyl maleic anhydride composition provides an increase in the water resistance of leather materials under dynamic conditions by 36–54 times, depending on their thickness, with an increase in air permeability by 1.5–2.1 times compared to with leather samples obtained by the control technology. It has been established that the physicomechanical properties of the leathers obtained with the use of alkenyl maleic anhydride composition have improved characteristics and better recovery of structure and properties during modeled conditions for exploitation of shoe materials compared to control samples. The manufactured leathers meet the technical standards for leather for the shoe upper: GOST 939-88 and DSTU 2726-94. The obtained results give the basis for the use of alkenyl maleic anhydride composition in the technology of producing hydrophobized leather materials for the production of everyday and special items.

References

[1]. **Zakharov S., Slobodskikh L., Vakhromeeva N., et al.** The effect of organophosphorus additives on the hide hydrophobic properties (in Russian). *Kozhevenno-Obuvnaia Promyshlennost* (Publisher «*Кожевенно-Обувная Промышленность*») **2** (1998) 28–29.

[2]. **Zurabian K.** Development of a composition for hydrophobic hide treatment (in Russian). *Kozhevenno-Obuvnaia Promyshlennost* (Publisher «*Кожевенно-Обувная Промышленность*») **5–6** (1995) 33–35.

[3]. **Nizamova Z., Kalinin M., Evsiukova N., et al.** Evaluation of the effectiveness of compositions for surface hydrophobization of split (in Russian). *Kozhevenno-Obuvnaia Promyshlennost* (Publisher «*Кожевенно-Обувная Промышленность*») **2** (2012)18–19.

[4]. **Ermolenko N., Platonov V., Gurianova T., et al.** The method of hydrophobization of the hides (in Russian). RU patent 2000332; September 07, 1993.

[5]. **Ermolenko N.** On the effect of fluorine-containing compounds on the hydrophobic properties of hides (in Russian). *Kozhevenno-Obuvnaia Promyshlennost* (Publisher «*Кожевенно-Обувная Промышленность*») **3** (2003) 30–31.

[6]. **Maurer T., Herrwerth S., Koenig F., and Stadtmueller S.** Novel polycarboxy-functional organosiloxanyl derivatives and their use for the treatment of leather. DE patent DE102006042869A1; March 27, 2008.

[7]. **Dahmen K. and Mertens R.** Use of siloxane copolymers for treating leather and pelts. *Leather Science Abstract* **1** (1995) 9–10.

[8]. **Kovacevic V. and Babic R.** Postizavanje otpornosti na vodu koze za specijalne namjene. *Koza i obuca* **42**, 11–12 (1993) 127–128.

[9]. **Studenikin S., Iakovlev K., Bogomolov V., et al.** The method of producing hydrophobic leathers (in Russian). RU patent 2404260; November 20, 2010.

[10]. **Lishchuk V., Danylkovych A., Omelchenko N., et al.** Method of leather fatliquoring-hydrophobization (in Ukrainian). UA patent for Utility Model No. 70418; June 11, 2012.

[11]. **Iagoda L. and Ostrovskii V.** Equipment and methodology for testing leather (in Russian). *Kozhevenno-Obuvnaia Promyshlennost* (Publisher «*Кожевенно-Обувная Промышленность*») **7** (1978) 52–55.

[12]. GOST 8977-74 (1998). Artificial leather and films. Methods for determination of flexibility, hardness and elasticity.

17. APPLICATION OF GRADIENT METHOD FOR SOLVING CONSTRAINED OPTIMIZATION TASKS

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Abstract: *The constrained optimization task of wool sheepskin tanning–fatliquoring is solved by the gradient method. The optimality criterion is formulated as a generalized additive objective function. The modified gradient method algorithm was used in a software module. Mathematical description for a low-waste technology using chrome tanning agent is obtained and its constraints are determined.*

Keywords: *optimal task; objective function; algorithm; wool sheepskin; tanning.*

Introduction

Formalization of the problem of chemical engineering and the selection of an optimization method is very challenging as many processes are characterized by a large number of physical, chemical, thermophysical, and structural parameters, which significantly complicates the task. Difficulties occurring at this stage are, first of all, associated with obtaining the description of the process and the definition of the boundary conditions.

Vast experience in solving optimization problems allows receiving a solution for specific applications [1] and in a generalized form [1, 2]. However, a number of technological problems require special consideration. Quite often under the real conditions of production, the object quality which is getting optimized is estimated not by one, but by a set of criteria. At the same time, all these criteria are important. This leads to the necessity of finding optimal operating conditions based on a compromise scheme. Therefore, when choosing a solution for the vector criterion, we can limit the search of the optimal area of compromise. This allows applying conventional optimization methods for solving multi-objective optimization of chemical engineering for many feasible solutions to get the best ones [3, 4].

This paper deals with the efficiency of the gradient method for the development process of tanning–fatliquoring of wool sheepskins, which is the main process determining the structure and properties of the finished material. Optimization of tanning–fatliquoring process of semi-finished product will significantly reduce the cost of chemical reagents and their concentration in the spent solutions and will result in production of wool sheepskins with a given set of physicomechanical properties.

Analysis of Studies and Publications

The analysis of publications relating to the development of resource-saving and environmentally efficient technologies in the treatment of cattle hides has shown that the mathematical description of typical processing technologies is mainly obtained using the methods of experiment design [5, 13–15]. The optimization criterion is formed using desirability functions and for the finding of the extremum, the method of scanning is applied [5, 6]. Thus, the search for optimal solutions is based mainly on experimental and statistical approaches, and the general optimization criterion is formed using the Harrington's desirability function.

Such an approach to solving the optimization tasks is related to the complexity of formalizing criteria and requires significant amount of computation. In this case, the choice of the method depends on the experience of the researcher, and in some cases requires special mathematical training. The choice of optimization method and the method of forming the optimality criterion have a significant impact on the quality of the obtained decisions. Application of the gradient method [3, 7] allows achieving the optimum as soon as possible since the gradient vector points in the direction of the fastest growth of the objective function.

Formulation of the Problem

In this paper we solved the problem of multi-objective optimization process of wool sheepskin tanning–fatliquoring using a chrome tanning agent (technical specification, TU 2141-033-541386-2003) which takes into account technological constraints of the parameters and an application of the method of gradient. It involves the replacement of environmentally hazardous industrial oil I-12A, a plasticizer, used together with non-ionic surfactants for its emulsification on the sulfonated di(propylene glycol) ether (DPGE). The idea of this complex process is to process wool sheepskins with a structuring agent – basic chromium sulfate (BCS) and DPGE emulsion with a molecular weight of 705 Da. Carrying out of tanning–fatliquoring process involves the preparation of wool sheepskins by previous acid-salt treatment (pickling) lasting for 6–8 h at 313 K with the ratio of water volume to the mass of flint-dried sheepskins of 7 : 1.

After completing the pickling process, a plasticizer and BCS are added into the system. In the developed technology the plasticizer I-12A replacement is carried out, which is caused by its considerable usage in the process – 10 g/L with 10 % of non-ionic surfactant for its emulsification, while DPGE is a self-emulsifying agent. The previous studies have also shown, that the use of DPGE can be reduced by more than 50 % due to its high absorptivity by the sheepskins. It is also found that consumption of BCS together with DPGE ranges from 0.9 to 1.3 g/L (recalculated for Cr_2O_3), which corresponds to the reduced consumption of chrome-tanning agents by 60 %. The effectiveness of the tanning process strongly depends on pH of the technological solution, which directly affects its basicity [13] and therefore BCS chemical activity that requires controlled regulation of the technological process. As the acid-salt treatment forms the structure of wool sheepskins before tanning, opening it up, and subsequently affects the basicity of chrome tanning agents reducing it, these parameters are fixed as technological requirements. This also applies to the concentration of sodium chloride and acid when pickling sheepskins [8]. The mechanism of tanning–fatliquoring process of the semi-finished product is based on the diffusion of tanning chromium compounds in the structure of a semi-finished product to the active groups of collagen macromolecules, their subsequent reaction with carboxyl groups, the degree of ionization of which is determined by pH of the technological solution, and the formation of spatial chemical bonds of interacting components. Thus, the given set of elastic-plastic properties of the finished wool sheepskins can be achieved only at optimal content of the plasticizer [5, 6]. When hydrocarbon plasticizer I-12A in the form of an emulsion is used, its deep diffusion and its uniform distribution in the fibrous structure of skin tissue is not occurring. This is associated with its excessive consumption and its high residual concentration in the spent solutions. Application of hydrophilic DPGE is characterized by its high compatibility with collagen of skin tissue, allowing to achieve high plasticizing effect with significantly lower consumption. Final wool sheepskins are obtained as a result of drying-moisturizing processes and finishing operations of skin tissue and fur by a typical technology at the final stage.

Based on the analysis of the existing technologies, the main factors that significantly affect the tanning–fatliquoring process are the concentration of BCS with the specified initial basicity 35–

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[13] *The degree of basicity is the relation of the number of associated with chromium OH groups to the oxidation degree of chromium.*

40 % – x_1 [g/L], based on Cr_2O_3; concentration of electrolyte resistant sulfonated DPGE – x_2 [g/L]; concentration of fat substances (FS) at constant liquid coefficient and pH at the final stages of tanning – x_3 [g/L] [5].

Since the efficiency of the technology depends not only on the exploitational properties, but also on its environmental friendliness, the output variables are: the shrinking temperature of semi-finished products – y_1 [K]; the concentration of tanning agent and DPGE in the spent solutions – y_2 [g/L], based on Cr_2O_3; the concentration of FS in the spent solutions – y_3 [g/L]; tensile strength – y_4 [MPa]; and elongation at 4.9 MPa load – y_5 [%].

Solution for Multi-Objective Optimization Task

An important element in solving the problems of multi-objective optimization is the correct formation of the optimality criterion. In general, the multi-objective optimization task is formulated as follows. The quality of the optimization object is estimated by a vector function

$$f(\bar{x}) = (f_1(\bar{x}), f_2(\bar{x}), \dots, f_k(\bar{x}),) \qquad (1)$$

the components of which $f_i(\bar{x})$, (i = 1, 2, …, k) – specified functions of the vector $\bar{x} = (x_1, x_2, \dots, x_n)$. Linear or non-linear constraints are usually imposed on the variables x_i, ($i = \overline{1,n}$). Thus, the vector x belongs to the set X of its possible values. We need to find a point that will provide the optimal value of the functions $f_1(\bar{x}), f_2(\bar{x}), \dots, f_k(\bar{x})$. Criteria $f_i(\bar{x})$, ($i = \overline{1,k}$) usually have different physical nature and, accordingly, different dimension. Therefore, when solving the problem of multipurpose optimization, normalization of local criteria is used, with the help of which instead of $f_i(\bar{x})$ value, its relation to some regulatory value, which is measured in the same units as the criterion itself, is considered [1, 3, 9]. As a result of this operation, all criteria $f_i(\bar{x})$, ($i = \overline{1,k}$) are the dimensionless quantities. In this paper, the dimensionless criteria $f_i(\bar{x})$ are determined by the formula:

$$f_i^*(\bar{x}) = \frac{f_i(\bar{x})}{f_{i\,max}(\bar{x}) - f_{i\,min}(\bar{x})} \tag{2}$$

where $f_i(\bar{x})$ – value of i criterion.

To solve the problem of multi-objective optimization of the process of tanning–fatliquoring wool sheepskins in the given formulation, the following method for constructing generalized optimality criterion was used:

$$f(\bar{x}) = \sum_{i=1}^{k} \alpha_i f_i^*(\bar{x}) \tag{3}$$

where α_i – weight coefficients, $\sum_{i=1}^{k} \alpha_i = 1$. As a rule, α_i is determined based on expert estimates [2, 3, 5].

To solve the problem of multi-objective conditional optimization eq. 1–3, the gradient method was used [2, 7]. The algorithm of the method is shown in Fig. 1. The selected method was applied successfully for solving various problems of non-linear programming as the extreme value search is performed in the direction of the fastest change in the objective function. The method uses information about the objective function and constraints of the task at every stage.

Suppose you want to maximize the function. The formulation of the optimization problem is as follows:

$$f(\bar{x}) = f(x_1, x_2, \dots, x_n) \tag{4}$$

where $\bar{x} = (x_{1,} x_{2,} \dots, x_n)$ is determined by the explicit constraints:

$$l_j \leq x_j \leq u_j \; (j = 1, 2, \dots, n) \tag{5}$$

and implicit constraints:

$$q_i(\bar{x}) \leq b_i (i = 1,2, \dots m) \tag{6}$$

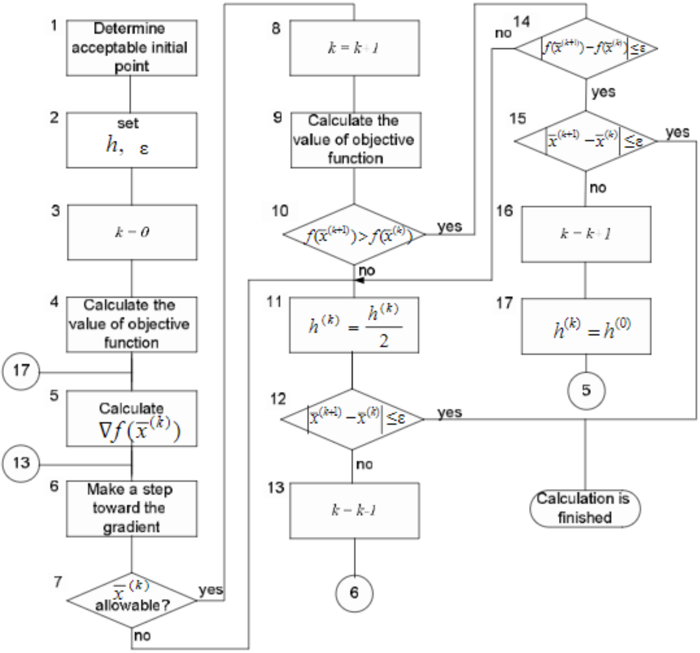


Fig. 1. Algorithm of the gradient method.

The method of gradient indicates the direction of the fastest growth of the objective function. In this paper, the method was modified taking into account the technological constraints (eq. 5 and eq. 6).

The first stage involves finding acceptable initial point. The point that satisfies the conditions (eq. 5 and eq. 6) is allowable.

The initial allowable point $\bar{x}^{(0)} = (x_1^{(0)}, x_2^{(0)}, \dots, x_n^{(0)})$, if possible, can be specified, or the following formula can be used:

$$x_j = l_j + r_j(u_j - l_j), (j = 1,2, \dots, n) \tag{7}$$

where r_j – random numbers uniformly distributed in the interval (0; 1).

Thus, the point obtained is checked for permissibility by calculating the function $q_i(\bar{x})$, $(i = 1,2, \dots, m)$ within the limits (6).

The process continues until the point is found that satisfies all the constraints of the task. At this stage, as well, the precision of optimization ε, the magnitude of the stage in the direction of the gradient $h^{(0)}$, and the number of optimization stages, $k = 0$, are set.

At the second stage, the value of the objective function $f(\bar{x}^{(k)})$ and partial derivatives value $\nabla f\left(\bar{x}^{(k)}\right)$ of all variables at the point $\bar{x}^{(k)}$ are calculated:

$$\frac{\partial f(\bar{x}^{(k)})}{\partial x_1}, \frac{\partial f(\bar{x}^{(k)})}{\partial x_2}, \dots, \frac{\partial f(\bar{x}^{(k)})}{\partial x_n} \qquad (8)$$

At the third step, the direction of movement toward the gradient is changed. The coordinates of the new point are calculated by the formula:

$$x_j^{(k+1)} = x_j^{(k)} + h^{(k)} \frac{\partial f(\bar{x}^{(k)})}{\partial x_j}, (j = 1,2, \dots, n) \qquad (9)$$

The value of the function $f(\bar{x}^{(k+1)})$ are calculated as well.

At the fourth stage $f(\bar{x}^{(k)})$ and $f(\bar{x}^{(k+1)})$ are compared:

- if $f\left(\bar{x}^{(k+1)}\right) < f\left(\bar{x}^{(k)}\right)$, then the initial value of the stage is reduced by half ($h^{(k)} = h^{(k)}/2$) and the calculations are repeated, starting from the third stage;
- if $f\left(\bar{x}^{(k+1)}\right) > f\left(\bar{x}^{(k)}\right)$, then the stage toward the gradient is successful, and the conditions of the end are checked: $\left|\bar{x}^{(k+1)} - \bar{x}^{(k)}\right| \leq \varepsilon$;
- if the inequality is performed, the calculation is stopped, otherwise the iteration number is increased by one: $k = k + 1$, $h^{(k)} = h^{(0)}$, and the calculations of the second stage are repeated.

Experimental Section

The described algorithm was the basis for the software module that is implemented using object-oriented programming language "Visual Basic for Application". The developed software module is used to find the optimal values of the generalized objective function.

The task of determining the optimal composition of the ternary mixture that is used in tanning-fatliquoring of wool sheepskins was considered as the task of non-linear programming. The meaning of the factors X_1, X_2, X_3 varied at two levels with the correspondent interval: 0.5, 1.0, and 0.25, and a plan center is situated in a factor space with the point: 1.0, 4.0, and 3.5 (Table I).

Table I. *The experimental plan.*

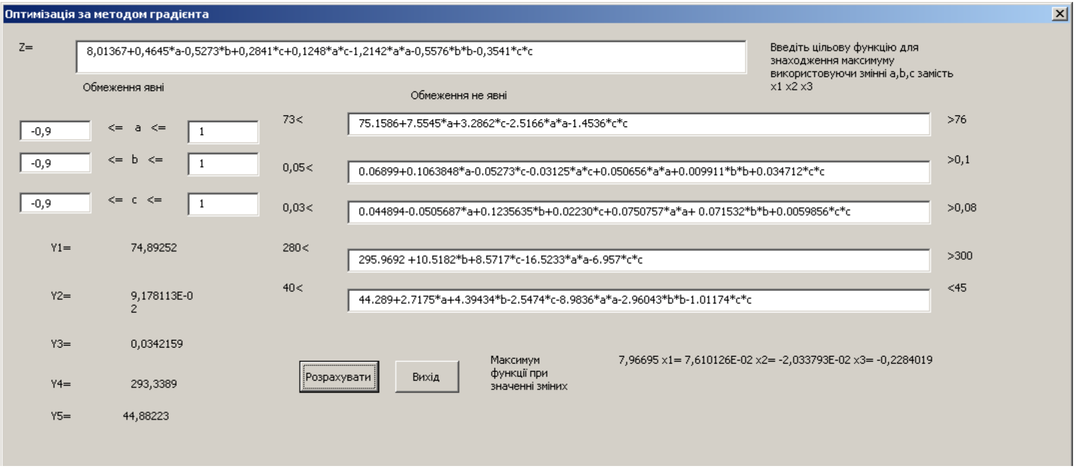
Factor	Experimental point																			
	1	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**	**13**	**14**	**15**	**16**	**17**	**18**	**19**	**20**
x_1	+	–	+	–	+	–	+	–	$+a$	$-a$	0	0	0	0	0	0	0	0	0	0
x_2	+	+	–	–	+	+	–	–	0	0	$+a$	$-a$	0	0	0	0	0	0	0	0
x_3	+	+	+	+	–	–	–	–	0	0	0	0	$+a$	$-a$	0	0	0	0	0	0

Note: *The corresponding +1 and –1 levels are marked by the signs "+" and "–", and the value of an axial distance is $a = 1.682$.*

Results and Discussion

The experimental results of studying the effect of technological parameters of wool sheepskin treatment on the physicochemical properties of the finished wool sheepskins are listed in Table II.

The developed software module is applied in the study of low-waste technology of semi-finished leather tanning [10]. The main window of non-linear programming software is shown in Fig. 2 and enables visualization of the initial data and the results of calculation. When developing a software module, the ability to work with explicit and implicit constraints and calculation unit of statistical indicators to assess the adequacy of the model is provided.



```
Оптимізація за методом градієнта

Z=  8,01367+0,4645*a-0,5273*b+0,2841*c+0,1248*a*c-1,2142*a*a-0,5576*b*b-0,3541*c*c
    Введіть цільову функцію для знаходження максимуму використовуючи змінні a,b,c замість x1 x2 x3

Обмеження явні
-0,9  <=  a  <=  1
-0,9  <=  b  <=  1
-0,9  <=  c  <=  1

Обмеження не явні
73<    75.1586+7.5545*a+3.2862*c-2.5166*a*a-1.4536*c*c    >76
0,05<  0.06899+0.1063848*a-0.05273*c-0.03125*a*c+0.050656*a*a+0.009911*b*b+0.034712*c*c    >0,1
0,03<  0.044894-0.0505687*a+0.1235635*b+0.02230*c+0.0750757*a*a+ 0.071532*b*b+0.0059856*c*c    >0,08
280<   295.9692 +10.5182*b+8.5717*c-16.5233*a*a-6.957*c*c    >300
40<    44.289+2.7175*a+4.39434*b-2.5474*c-8.9836*a*a-2.96043*b*b-1.01174*c*c    <45

Y1=  74,89252
Y2=  9,178113E-0
     2
Y3=  0,0342159
Y4=  293,3389
Y5=  44,88223

Максимум функції при значенні змінних   7,96695 x1= 7,610126E-02 x2= -2,033793E-02 x3= -0,2284019
```

Fig. 2. Main window of software module (in Ukrainian).

Table II. *Experimental results for output variables (y_i).*

y_i	Experimental point									
	1	***2***	***3***	***4***	***5***	***6***	***7***	***8***	***9***	***10***
y_1	82.0	67.0	80.0	66.0	73.0	62.0	74.0	63.0	84.0	53.0
y_2	0.23	0.07	0.18	0.05	0.32	0.10	0.39	0.07	0.38	0.01
y_3	0.31	0.39	0.07	0.11	0.22	0.34	0.06	0.09	0.13	0.38
y_4	13.3	15.0	13.9	14.1	14.4	14.6	13.0	12.4	12.1	11.0
y_5	32.0	28.0	25.0	23.0	42.0	29.0	34.0	26.0	24.0	18.0

y_i	***11***	***12***	***13***	***14***	***15***	***16***	***17***	***18***	***19***	***20***
y_1	76.0	74.0	78.0	65.0	75.0	76.0	76.0	75.0	76.0	74.0
y_2	0.07	0.09	0.04	0.26	0.08	0.06	0.07	0.08	0.06	0.05
y_3	0.47	0.02	0.10	0.02	0.06	0.04	0.05	0.05	0.04	0.06
y_4	15.0	13.1	14.0	11.7	14.5	14.7	14.8	14.6	13.9	14.3
y_5	49.0	27.0	40.0	47.0	45.0	44.0	43.0	43.0	45.0	42.0

The mathematical description of the process of tanning was obtained from the composite Box-Hunter central rotatable plan of the second-degree of 6 experimental points in the center of the plan and presented by the following regression equation [11]:

$$y_1 = 75.1587 + 7.5545x_1 + 3.2862x_2 - 2.5166x_3 - 2.5166x_1^2 - 1.4537x_3^2;$$

$$y_2 = 0.068995 + 0.1064x_1 - 0.0527382x_3 - 0.03125x_1x_3 + 0.0099113x_2^2 + 0.034713x_3^2;$$

$$y_3 = 0.044894 - 0.050568x_1 + 0.1236x_2 - 0.022309x_3 + 0.075076x_1^2 + 0.071533x_2^2 + 0.0059857x_3^2;$$

$$y_4 = 295.97 + 10.5183x_2 + 8.5718x_3 - 16.5234x_1^2 - 6.957x_3^2;$$

$$y_5 = 44.289 + 2.7175x_1 + 4.3943x_2 - 2.5475x_3 - 8.9837x_1^2 - 2.9604x_2^2 - 1.0117x_3^2.$$

Checking the adequacy of the obtained equations was performed by the Fisher's criterion. The calculation results show that the resulting equation describes the abovementioned experimental data rather precisely, that is the calculated Fisher criterion value does not exceed the tabulated ones.

The restriction of the optimization task is selected according to technological reasons:

$$
\begin{array}{ll}
 & 73 < y_1 < 76 \\
0.9 < x_1 < 1.3 & 0.05 < y_2 < 0.10 \\
3.7 < x_2 < 4.2 & 0.03 < y_3 < 0.08 \\
3.6 < x_3 < 3.8 & 280 < y_4 < 300 \\
 & 40 < y_5 < 45
\end{array}
$$

Based on the requirements of the process, both technological and economic, the output values y_1, y_4, and y_5 are maximized and y_2 and y_3 are minimized.

To calculate the weighting coefficients the method of peer review is used, namely ranking method [12], which is based on assigning by experts the individual factors that affect the process with a sequence number of their importance. In this case, the most important criterion is assigned with number one, then the second one, etc. These ranks are converted as follows: rank 1 receives an estimate *m* (the number of partial criteria), rank 2 – assessment of *m–1*, etc. denoting the estimates r_{ik} (where *i* – the number of *i*th expert, *k* – the number of *k*th criterion). The results of the expert survey were entered into a spreadsheet and the total score for each criterion was calculated:

$$r_j = \sum_{j=1}^{L} r_{ji} \; (i \; = \; 1, 2, \ldots, m),$$

where *L* – the number of experts.

The weights for each criterion are defined as follows:

$$\alpha_i = \frac{r_i}{\sum_{i=1}^{m} r_i}, (i = 1,2, \ldots, m).$$

According to this method the processed results of the survey of seven experts in this field were used. The weight coefficients of the function α_i are derived from expert ratings $\alpha_1 = 0.2$; $\alpha_2 = 0.2$; $\alpha_3 = 0.3$; $\alpha_4 = 0.15$; and $\alpha_5 = 0.15$. The generalized objective function is obtained by the eq. 3, where$f_i^*(\bar{x}) = y_i^*$ and $y_i^* = y_i/(y_{i\,max} - y_{i\,min})$:

$$f(\bar{x}) = 8.0137 + 0.4645x_1 - 0.5273x_2 + 0.2841x_3 + 1.2142x_1^2 - 0.5576x_2^2 - 0.3541x_3^2.$$

According to the formulated optimization task, the derived generalized objective function is maximized.

As a result, the optimal values of the factors and output variables that meet these criteria are found: $x_1 = 1.20$; $x_2 = 3.46$; $x_3 = 3.71$; $y_1 = 75.912$; $y_2 = 0.0686$; $y_3 = 0.0383$; $y_4 = 296.24$; and $y_5 = 43.82$.

Thus, as a result of the performed calculations, the optimal values of the parameters of the process of wool sheepskin tanning-fatliquoring and corresponding values of the objective function are found.

In this way, the extremum of the objective function found with regard to the conditions form eq. 5 and eq. 6. Thus, the gradient method can be effectively used to solve the tasks of conventional optimization.

The disadvantages of this method include the need to find partial derivatives of the objective function, which complicates the programming and requires appropriate mathematical manual training. In some cases, the objective function is not given analytically, which is quite typical for the problems of chemical technology, then the partial derivatives that define the gradient can be calculated in the desired points with approximation by replacing them with corresponding difference relations:

$$\frac{\partial f}{\partial x_i} \approx \frac{f(x_1, \ldots, x_i + \Delta x_i, \ldots, x_n) - f(x_1, \ldots, x_i, \ldots, x_n)}{\Delta x_i}$$

Thus, Δx_i is not recommended to be too small, and the value of the function should be calculated with a sufficiently high precision exponent, otherwise when calculating the difference $\Delta f = f(x_1, \ldots, x_i + \Delta x_i, \ldots, x_n) - f(x_1, \ldots, x_i, \ldots, x_n)$ a significant error may appear.

Conclusions

The problem of multi-objective optimization of conventional wool sheepskin tanning-fatliquoring process using the method of gradient is solved and the parameters of the process to ensure the maximal output of semi-finished product by the area are set.

The optimality criterion for chrome-tanning process of semi-finished product represented as a generalized objective function for which the calculation with the values of weight coefficients, provided by experts, is made. According to the chosen criterion the optimal values of the process of wool sheepskin tanning are determined.

The proposed algorithm of a modified method of gradients, which is utilized in the developed software module can significantly reduce the time of searching an optimal solution and can be used without a fundamental change to determine the optimal parameters of similar technological processes.

The developed technology allowed the replacement of environmentally hazardous industrial oil plasticizer I-12A with surfactant-free sulfonated di(propylene glycol) ether at its substantially reduced consumption, and yields wool sheepskins with improved plasticity. In this case, almost complete absorption of chromium tannins and fatty substances from the technological solutions are achieved, which increases the sustainability of the developed technology of the wool sheepskin processing.

References

[1]. **Ostrovskii G. and Berezhinskii T.** Optimization of chemical-technological processes. Theory and practice (in Russian). Khimiia (Publisher «Химия») 1984, Moscow, 240 p.

[2]. **Bunday B.** Optimization methods. Introductory course (in Russian, translated from English; original title "Basic optimization methods"), Radio i sviaz (Publisher «Радио и связь») 1988, Moscow, 128 p.

[3]. **Steuer ·R.** Multiple criteria optimizations. Theory, Computation, and Applications (in Russian, translated from English). Radio i sviaz (Publisher «Радио и связь») 1992, Moscow, 504 p.

[4]. **Boiarinov A. and Kafarov V.** Optimization methods in chemical technology (in Russian). Khimiia (Publisher «Химия») 1975, Moscow, 575 p.

[5]. **Danylkovych A.** Innovative technologies for production of leather and fur materials and products: monograph (in Ukrainian). Fenix (Publisher «Фенікс») 2012, Kyiv, 344 p.

[6]. **Danylkovych A.** Ecologically oriented technologies for production of leather and fur materials for manufacturing of competitive goods: monograph (in Ukrainian). Fenix (Publisher «Фенікс») 2011, Kyiv, 437 p.

[7]. **Vasilev F.** Optimization methods (in Russian). Faktorial Press (Publisher «Факториал Пресс») 2002, Moscow, 824 p.

[8]. **Grigorev B., Vasileva A., Loznevaia E., et al.** Technology of woolskin processing (in Russian). Central Scientific Research Institute of Information and Technical and Economic Research of Light Industry (Publisher «ЦНИИТЭИлегпром») 1988, Moscow, 200 p.

[9]. **Kafarov V.** Cybernetics methods in chemistry and chemical technology (in Russian). Khimiia (Publisher «Химия») 1971, Moscow, 496 p.

[10]. **Danylkovych A.** Fundamentals of scientific research in higher education (in Ukrainian). Kyiv National University of Technologies and Design 2010, Kyiv, 296 p.

[11]. **Danylkovych A. and Vasyliuk O.** Development of technology of tanning-fatliquoring of wool sheepskin and its multicriteria optimization (in Ukrainian). Problemy legkoi i tekstilnoi promyshlennosti Ukrainy (Publisher «Проблемы лёгкой и текстильной промышленности Украины») **3** (2000) 82–84.

[12]. **Taha H.** Operations Research: an introduction (6th edition) (in Russian, translated from English). Williams (Publisher «Вильямс») 2001, Moscow, 912 p.

[13]. **Danylkovych A., Omelchenko N., and Shakhnovskii A.** Optimization of the composition for hydrophobization of elastic materials (in Russian). *Bulletin of the Khmelnytskyi National University* **1** (2012) 74–78.

[14]. **Lishchuk V., Voitsekhovska T., and Danylkovych A.** Using multicriteria optimization to determine the optimal parameters for the liming process (in Ukrainian). *Lehka Promyslovist* (Publisher *«Легка промисловість»)* **1** (2007) 37–39.

[15]. **Danylkovych A., Brailko A., and Omelchenko N.** Improving the quality of the secondary coating by optimizing the coating composition (in Ukrainian). *Bulletin of the Khmelnytskyi National University* **3** (2010) 129–134.

18. OPTIMIZATION OF LEATHER FILLING COMPOSITION CONTAINING SiO_2 NANOPARTICLES [14]

Danylkovych A. & Korotych O.

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Abstract: *The global leather industry is looking for a cleaner leather processing technology to overcome its negative environmental impact. As an alternative to conventional processing, an eco-friendly filling composition based on fumed silica was developed and tested for the production of leather materials. Polycriterial optimization of the filling composition containing silica nanoparticles was conducted using the McLean-Anderson method by considering the type of mathematical model of the process "content-properties". For optimization of the experimental conditions a multithreaded program based on calculation of informative and dispersive matrices and their determinants was developed. The optimal formulation of filling composition for the production of flexible leather materials was established and experimentally tested. The developed technology yields leather materials with increased volumetric yield and elasticity and more homogeneous microstructure when compared to the current company technology. The mathematical modelling discussed in the paper can be also used to solve similar problems for other technological processes.*

Keywords: *leather material; optimization of filling composition containing silica nanoparticles; experiment design; McLean-Anderson method; multithreaded program; informative and dispersive matrices.*

Introduction

While improving existing and developing innovative technologies for the production of high-quality leather materials

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[1], a prerequisite condition is to find an effective set of eco-friendly reagents for leather production [2, 3] and to optimize reagent formulations using mathematical modeling. During multistep processing of leather materials, filling step plays an important role given that final properties of processed materials are determined by the formulation of filling composition. Different mathematical modeling techniques, which consider the peculiarities of the chemical ingredients of the composition, have been used to compute and optimize the filling composition. While solving this problem, significant difficulties arise due to the limited content of ingredient in the composition which is determined by its physicochemical properties.

In mathematical modeling of technological compositions in form of "content-properties", methods such as simplex-lattice, simplex-centroid, or D-optimal designs are usually used [4, 5]. However, sometimes there are compositions in which component fractions cannot be changed continuously in a whole range from 0 to 1, for example, due to the limited solubility of some ingredients. In such cases, methods of imposition of restrictions on the factors are applied. For example, McLean-Anderson method [6], D-optimal design, or pseudo-components method can be used in such situations. However, the well-known McLean-Anderson method for design of the experiment does not consider a type of mathematical model and it often results in getting a degenerate plan when choosing experimental points from a candidate set of points. Direct design of the experiment according to the Fedorov theory does not always allow defining the experimental area/region which indicates a non-optimality of the method [7].

For experiment optimization of silica-silver nanosupplement content in polypropylene fibers, a simplex-lattice design with pseudo-components using a Harrington criterion was applied [8]. Herewith, a mathematical model of "content-properties" of modified filaments made it possible to compute the optimal content of binary polypropylene-nanosupplement composition which provides high mechanical strength of yarns and their bactericidal capacity. Despite that this method allows displaying an optimal area geometrically, it is not possible to choose the experimental set of parameters (which has to be similar to simplex for a given constrains on mixture ingredients) and due to the loss of a set of points.

A simplex-lattice method is used for modeling the composition of ternary integumentary polymer compositions and composition optimization [9, 10]. Herewith, a mathematical model of composition of polyvinyl alcohol – urethane fluoropolymers – toluene diisocyanate was obtained using the modified Scheffe design by applying polynomial of the fourth-degree. An optimized composition of exopolysaccharide-polyacrylate-polyurethane system was computed by using Kiefer D-optimal design. The application of optimized composition results in increased physicomechanical properties of final leather materials. But despite of mentioned advantageous it was impossible to get the coverage of pure components because the design described in these publications does not include restrictions on the components.

With the help of the linear programming method using a computer program Simplex Win, a composition of the grain and fruit mixture of 9 ingredients was optimized by minimizing cost ratios and caloricity [11]. However, this method cannot be applied to optimize the composition because it does not consider the content condition – a sum of all ingredients must be equal to one. For composite materials based on epoxy resin ED-20 and polyethylene polyamine the content of two-component filler composition based on aluminum oxide and crystalline boron was optimized to form a protective coating surface layer with enhanced physicomechanical properties [12]. The optimal content of filler was determined by mathematical modeling and using orthogonal central composite design [12]. However, this method is only effectively used in “technology-properties” modeling.

Simplex-lattice modeling method can be used as well [13, 14]. Studying the degree of soil salinization by natural minerals in system “sodium chloride – magnesium sulfate – calcium sulfate”, the ratio between the ingredients at which the highest degree of soil salinity is reached was defined [13]. In another study, the authors investigated the selective extraction by natural zeolitic tuff of mixed rare earth elements from its mixtures [14]. The resulting mathematical model gives the opportunity to predict the optimal conditions for extracting of lanthanum, praseodymium, and ytterbium ions.

In paper by Rezanova et al. [15] the method of penalty functions and the gradient method for optimization of polymer composition based on four components were used to obtain the ultrathin nanofibers with high exploitational properties. Herewith, only one quality of polymer composition was modeled.

It should be noted that in most studies on content optimization of composite materials with the usage of mathematical modeling, the problem is solved by considering only one property of composite system. However, given a complex and sometimes even contradictory dependence of system properties on the composition, a several output variables (properties) were applied to optimize the filling composition containing silica nanoparticles to obtain more reliable data. In this respect, inorganic fillers are very promising to solve the problem during filling stage and develop new innovative and eco-friendly technologies for leather and fur production.

Highly-dispersed minerals have been used previously in processing of leather and fur [16, 17]. Particularly, it has been shown that the application of modified montmorillonite can increase the thickness, volume yield, and improve the physicomechanical properties of materials compared to the ones processed using existing technology. Among inorganic fillers synthetic silica nanoparticles or fumed silica due to its colloid and physicochemical properties are considered to be a promising reagent for production of elastic leather materials [18]. In a review on recent progress on cleaner preservation of hides and skins [3], one of the discussed *NaCl*-less curing method contains silica gel and appears to have environmental advantage over the conventional method by reducing a pollution from chlorides up to 80–85 %. Silicon-containing flame retardants are considered as very promising alternatives to halogenated compounds [19] as they do not release corrosive smoke during combustion and at the same time are considered to be an environmentally friendly for its application in coating. Incorporation of silica nanoparticles may also improve mechanical properties and aging- and climate-resistance of final materials [20]. The method of chemical modification of silica nanoparticles by poly(methacrylic acid) was developed by Pan et al. [20] and applied as leather finishing agent in leather tanning process. Additionally, silica-based colorant nanoparticles were developed for sustainable dyeing of leather [21].

Herein we are going to utilize silica nanoparticles as one of the components of leather filling composition. Determination of the optimal formulation of filling composition containing silica nanoparticles by using modified McLean-Anderson method in modelled system "content-properties" will have a significant importance from practical point of view in process intensification. But to achieve this, an optimal design of the experiment with restrictions on ingredients have to be generated and computed first.

Thus, the goal of the study was to improve the physicochemical properties of leather materials by using the optimized formulation of eco-friendly filling composition containing silica nanoparticles. Optimization of filling composition was performed based on McLean-Anderson method by selecting the best experimental points from the candidate set of points according to the D-optimality criterion. To achieve the goal, we (1) developed a computer algorithm which allows calculating automatically plan based on McLean-Anderson method, checking the adequacy of the mathematical model, and carrying out the optimization according to the desirability function; (2) designed mathematical model for the formulation of the filling composition – quality of leather material; (3) determined optimal content of the ingredients of filling composition based on silica nanoparticles; and (4) tested experimentally the developed and optimized formulation for filling the semi-finished leather product and the final properties of leather materials.

Materials and Methods

Filling composition containing silica nanoparticles was studied for improving physicochemical properties and technological quality of semi-finished leather product made of chrome-tanned green-salted heifer hides. Semi-finished leather product was produced at PJSC Chinbar (Kyiv, Ukraine) using an established technology for shoe leather production after shaving to 1.4–1.5 mm. Effect of formulation of the filling composition on the final properties of leather material was studied in 10 batches each containing 8 samples of 8×25 cm semi-finished product. The samples were selected in two rows on both sides of the vertebral column [22].

The formulations of filling composition contained the following components: nanosized (32.4 ± 1.1 nm for n = 50) fumed silica A-300 with specific surface area 300 m^2/g (Fig. 1) produced by pilot plant (Kalush, Ukraine) of the Chuiko Institute of Surface Chemistry; lightfast resin tanning agent Relugan D (BASF,

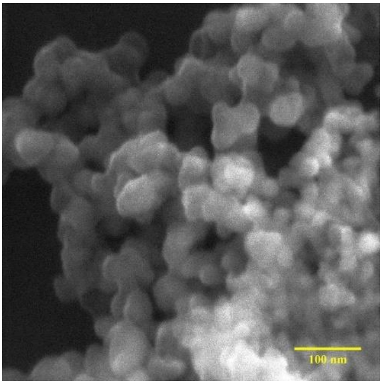

Fig. 1. *Microphotograph (SEM) of fumed silica A-300. Scale bar – 100 nm.*

Germany); Truposol GF (Trumpler, Germany); and quebracho extract (China) as a natural vegetable tannin for leather materials.

Filling of semi-finished leather product was carried out after washing and neutralizing with a 1 : 1 (weight ratio) mixture of sodium formate and sodium bicarbonate until the pH of a semi-finished product reached 5.8–6.0. The process was carried out for an hour in a drum with the inner diameter of 30 cm and volume 18 L with a weight ratio of technological solution to semi-finished product (hereinafter, the liquid coefficient, LC) fixed to 1.

Washing and neutralizing was carried out at 28–30 °C with constant rotational speed of 18–20 rpm (Fig. 2). The total weight of the filling composition was 11 % from the mass of semi-finished leather product. Previously to washing and neutralizing step, semi-finished leather product was incubated for an hour with Trupol RA (Trumpler, Germany) reagent in the amount of 1 % of the mass of semi-finished leather product. This reagent was also used for the next fatliquoring of the semi-finished leather product after increasing the volume of the technological solution

Fig. 2*. Photo of the laboratory setup for production of leather materials.*

and temperature to LC 1.5 and 45 °C, respectively. For fixation of filling components distributed within the structure of semi-finished product, we added potassium alum ($KAl(SO_4)_2 \cdot 12H_2O$, equivalent to 0.3 % Al_2O_3 of the mass of the semi-finished leather product) to decrease pH from 5.8–6.0 to 4.0–4.2. The total duration of the process was approximately 2 h.

Subsequently, the samples of the semi-finished leather product were vacuum-dried using M1 4025 dryer (Incoma, Italy) to a moisture content of 26 % followed by drying at 40–45 °C to a moisture content of 16 %, and moisturizing back to 22–24 %. The samples were kept for a day under a polyethylene film at 18–22 °C and dried again at 40–45 °C for 45–50 minutes to a moisture content of 16 %. The samples were finally examined after their conditioning for 24 h at 60 % humidity and 20 °C.

Physicochemical properties of the filled leather materials were determined using previously described methods [22–24]. Particularly, for the determination of volume yield [cm^3 per 100 g of proteins], nitrogen content was quantified using Kjeldahl method and converted into protein content. Volume, density, and porosity of leather samples were determined by pycnometry using kerosene. Mechanical properties (tensile stress and elongation) [25] of leather materials were measured using a tensile testing machine RT-250 (range A) at extension rate 80 mm/min. Initial length of the leather samples (10 mm in width) between clamps was 50 mm. Stiffness measurements were carried out using a device PZhM-12M for determination of stiffness and elasticity. Stiffness was characterized by the load in [N] required to deform the sample (20×160 mm) bent into a ring by 1/3 of its initial diameter.

Scanning electron microscopy (SEM) study was performed on silica nanoparticles, dehaired semi-finished leather product, and final leather materials. The information about topology, morphology, and microstructure of leather samples was obtained from microphotos taken on a high-resolution field emission scanning electron microscope (FE-SEM) Mira 3 LMU (Tescan, Czech Republic). For the microscopical study the leather specimens were attached to standard stubs with conductive graphite paint and coated with Au film (20 nm thick) using an ion-sputter coater Gatan Pecs 682. Fields of interest were imaged using secondary electron detector with 10 kV accelerating voltage. For elemental analysis and chemical characterization of surface and cross section of leather samples, energy-dispersive x-ray spectroscopy (EDXS) was carried out using Oxford instruments X-max 80 mm^2 detector.

All data is presented herein as an arithmetic mean ± standard uncertainty [25–27].

For the optimization of the formulation of fumed silica filling composition a mathematical model of the incomplete third-degree polynomial function was used:

$$\hat{y} = \sum_{i=1}^{k} b_i x_i + \sum_{i=1}^{k-1} \sum_{j=i+1}^{k} b_{ij}\, x_i x_j + b_{ij\ldots k} x_i x_j \ldots x_k, \qquad (1)$$

where $\hat{y}$ – the predicted output variable; b_i, b_{ij}, $b_{ij\ldots k}$ – the model coefficients; x_i – the relative weight fraction of component in composition ($i = 1, 2, \ldots, k$); k – number of factors; $i, j, \ldots, k$ – factor counters.

The model was normalized using the following condition:

$$\sum_{i=1}^{k} x_i = 1 \qquad (2)$$

From technological point of view restrictions on the numerical values of the ingredients x_i were imposed:

$$0 \leq \alpha_i \leq x_i \leq \beta_i \leq 1 \; (i = 1, 2, \ldots, k),$$

where α_i and β_i – are the restrictions of ingredient composition.

Thus, a mathematical model for system composed of three ingredients can be written in the form:

$$\hat{y} = b_1x_1 + b_2x_2 + b_3x_3 + b_{12}x_1x_2 + b_{13}x_1x_3 + b_{23}x_2x_3 + b_{123}x_1x_2x_3, \quad (3)$$

where $\hat{y}$ – the predicted output variable; x_1 – the weight fraction of fumed silica; x_2 – the weight fraction of mixture of Relugan D and Truposol GF with weight ratio 2 : 3; x_3 – the weight fraction of quebracho extract.

The effect of the formulation of filling composition on the final properties of leather materials was evaluated using the following criteria:

y_1 – the volume yield of the leather material [cm^3 per 100 g of proteins];

y_2 – the porosity of samples [%];

y_3 – the stiffness [cN];

To get a mathematical model which can describe the properties of system depending on its formulation, it is necessary to compute an experimental plan based on the criterion of the D-optimality with the imposed restrictions on the composition components. After the implementation of the plan and processing of the experimental data, the model coefficients should be determined and checked for its adequacy in the control points. Developed mathematical model will be further used for optimization of the composition using the desirability function.

Results and Discussion

Mathematical Model: Definition

In our previous research we defined the concentration range (as weight ratio) for each component in the filling composition (Table I) [22].

To determine the model coefficients from the candidate set of points (Table II), McLean-Anderson method (without considering the model type) based on maximal distance of candidate point from the center of the design and from each other was used. For generating the design multithreaded computer algorithm developed by authors have been applied.

Table I. *Concentration range for components of filling composition.*

x_i	Concentration restrictions	
	lower limit	**upper limit**
x_1	0	0.25
x_2	0.14	0.42
x_3	0.22	0.50

The *n* points for the design of the experiment were chosen from N candidate points using the D-optimal criterion. To select the points for the experiment the combination was calculated using the following formula:

$$\mathrm{C}(N,n)=\frac{N!}{n!\,(N-n)!}, \tag{4}$$

for which the determinant is approaching a minimal value

$$det|D| \to \min,$$

where $D = (F^T F)^{-1}$ – the dispersion matrix of design (determinant *det* $|I| \to$ *max* of informational matrix $I = F^T F$);

F – the matrix for the design generalized by the type of the model $\overline{f^0}(\bar{x})$with size $n{\times}l$;

l – the number of model coefficients;

T – the matrix transposition operation.

Table II. *Candidate set for variables* x_1, x_2, *and* x_3.

x_i	Theoretical points of experimental plan															
	1	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**	**13**	**14**	**15**	**16**
x_1	0.20	0.20	0	0.30	0	0.30	0.20	0.25	0.10	0.10	0.25	0	0.15	0.30	0.15	0.17
x_2	0.20	0.50	0.40	0.40	0.50	0.20	0.35	0.20	0.30	0.50	0.45	0.45	0.45	0.30	0.35	0.37
x_3	0.60	0.30	0.60	0.30	0.50	0.50	0.45	0.55	0.60	0.40	0.30	0.50	0.45	0.40	0.50	0.47

To determine the coefficients for three-component model an optimal design of the experiment was computed (Table III) in a limited area of simplex (Table I) taking into account the normalization condition.

Table III. *Design of the experiment.*

x_i	Experimental points						
	1	**2**	**3**	**4**	**5**	**6**	**7**
x_1	0.25	0.10	0.10	0.25	0	0.30	0.17
x_2	0.20	0.30	0.50	0.45	0.45	0.30	0.37
x_3	0.55	0.60	0.40	0.30	0.55	0.40	0.47

Note, that the points presented in Table II and in Table III were rounded to 2 decimal places, what caused an apparent deviation in total sum of components for #16 and #7, respectively.

Thus, from 16 candidate points (Table II) obtained by McLean-Anderson method and D-optimal criterion, 7 points (Table III) were selected and tested experimentally. The effect of formulation of filling composition on final properties of leather materials was determined experimentally and corresponding data is presented in Table IV.

Table IV. *Physicochemical properties of leather materials filled with silica nanoparticles.*

Technological index	Experimental points						
	1	**2**	**3**	**4**	**5**	**6**	**7**
y_1	237	243	227	215	203	219	238
y_2	54	60	49	46	42	41	56
y_3	28	31	39	33	36	32	23

The coefficients of three component mathematical model are defined using the method of least squares in a matrix form

$$B = (F^T F)^{-1} F^T Y, \tag{5}$$

where B – the vector of unknown coefficients; Y – column of values of the dependent variable which were observed in the experiments.

The adequacy of the model was checked using the formula below at each control point of interest:

$$t_p = \frac{|y_i - \hat{y}_i|\sqrt{m}}{s_{exp}\sqrt{1+\zeta}} < t_T\,\{q;\ f\}, \tag{6}$$

where t_p – the calculated critical value of two-tailed t-distribution; y_i and $\hat{y}_i$ – the experimental and calculated output variable at the i-control point; m – number of parallel experiments; t_T – the theoretical critical value of two-tailed t-distribution; q – the level of significance; $f = z(m-1)$ – the number of degrees of freedom; z – the number of control points; s_{exp} – the experimental uncertainty which was calculated using the following formulas:

$$s_{exp} = \sqrt{\frac{1}{z(m-1)}\sum_{i=1}^{z}\sum_{j=1}^{m}(y_{ij} - \bar{y}_i)^2}, \tag{7}$$

$$\bar{y}_i = \frac{1}{m}\sum_{j=1}^{m} y_{ij}\,; \tag{8}$$

where ζ – output variable uncertainty depending on the location of the checkpoints in simplex was calculated as

$$\zeta = \bar{f}^T(\bar{x})D\bar{f}(\bar{x}), \tag{9}$$

where $\bar{f}(\bar{x})$ – the vector-function depending on the type of the model and coordinates of the checkpoints.

To test the adequacy of the mathematical model, two parallel experiments at three randomly selected control points were carried out (Table V).

Based on the experimental and control data (Table IV and Table V) a non-linear mathematical model of property dependence of leather materials on the formulation of fumed silica filling composition was computed (eq. 10).

Table V. Physicochemical properties of leather materials filled with silica nanoparticles at different control points.

Check points	**Component**			**Technological index**					
	x_1	x_2	x_3	y_1		y_2		y_3	
1	0.09	0.46	0.46	227	226	52	51	30	31
2	0.14	0.41	0.46	234	234	55	56	24	26
3	0.18	0.37	0.46	237	239	55	54	23	23

$$
\begin{aligned}
\hat{y}_1 = {} & -111.8828211x_1 + 323.0428301x_2 + 344.450159x_3 \\
& - 372.0384108x_1x_2 + 1.109933603x_1x_3 \\
& - 532.5933776x_2x_3 + 3198.150111x_1x_3x_3; \\
\hat{y}_2 = {} & -463.49878x_1 - 11.12395548x_2 + 63.98313724x_3 \\
& + 888.5407893x_1x_2 + 701.6063908x_1x_3 \\
& + 47.73759388x_2x_3 - 336.0106514x_1x_3x_3; \\
\hat{y}_3 = {} & 899.6635109x_1 + 443.93978861x_2 + 265.4472965x_3 \\
& - 2493.618612x_1x_2 - 1984.054048x_1x_3 \\
& - 1251.59158x_2x_3 + 3762.312302x_1x_3x_3;
\end{aligned} \tag{10}
$$

The results of the validation of mathematical model "formulation of the filling composition – properties of leather materials" at control points are given in Table VI.

As it can be seen from Table VI the resulting mathematical model of the formulation of fumed silica filling composition adequately describes the properties of leather materials.

Mathematical Model: Optimization

To optimize the content of the composition $\bar{x} = |x_1, x_2, x_3|$ which is characterized by g initial physicochemical characteristics of the resulting mathematical model, the desirability function is used [23]:

$$D_f = \sqrt[g]{d_1 d_2 \dots d_g} \tag{11}$$

where d_i $(i = 1, 2, \ldots, g)$ – the partial function of desirability of the technological index y_i which can take any value in the range from 0 to 1 and it is determined as

$$d_i = \exp[-\exp(-y_i')], \tag{12}$$

where y_i' – dimensionless value of the technological index, defined by a linear correlation:

$$y_i' = b_0^{(i)} + b_1^{(i)} y_i. \tag{13}$$

Table VI. *Results of mathematical model validation* [15].

y_{ij}	$\overline{y}_i$	$\hat{y}_i$	ζ	$\lvert\overline{y}_i - \hat{y}_i\rvert$	t_p	**Adequacy**
y_{11}	226.5	227.8	0.6	1.3	2.238	1
y_{12}	234.0	234.7	0.8	0.7	1.179	1
y_{13}	238.0	237.3	1.0	0.7	1.094	1
y_{21}	51.5	51.1	0.6	0.4	0.960	1
y_{22}	55.5	54.7	0.8	0.8	1.666	1
y_{23}	54.5	55.3	1.0	0.8	1.698	1
y_{31}	30.5	31.4	0.6	0.9	1.522	1
y_{32}	25.0	25.6	0.8	0.6	1.003	1
y_{33}	23.0	23.0	1.0	0	0.065	1

Coefficients $b_0^{(i)}$ and $b_1^{(i)}$ of the above equation are defined from the following system of equations:

$$\begin{cases} y_i'^{worse} = b_0^{(i)} + b_1^{(i)} y_i^{worse} \\ y_i'^{better} = b_0^{(i)} + b_1^{(i)} y_i^{better} \end{cases}, \tag{14}$$

---

[15] *All theoretical points presented in Table VI were rounded to 1 decimal place for calculated output variables and its uncertainties, and to 3 decimal places for calculated critical values of t-distribution.*

where y_i^{worse} and y_i^{better} $(i = 1, 2, \dots, g)$ – the worse and the better value of a criterion y_i which is established by the researcher and by the reasons of the technological character cannot be reduced or increased; $y_i'^{\,worse}$ and $y_i'^{\,better}$ $(i = 1, 2, \dots, g)$ – the worse and the better value of the dimensionless quality criterion which can be calculated based on the eq. *12* as follow:

$$\begin{aligned} y_i'^{\,worse} &= -\ln(-\ln d_{worse}), \\ y_i'^{\,better} &= -\ln(-\ln d_{better}), \end{aligned} \qquad (15)$$

where d_{worse} and d_{better} – the worse and the better value of the desirability function (D_f) which are equal to 0.2 and 0.8, respectively [28].

Maximum of the desirability function D_f corresponds to the optimal formulation $\overline{x^{opt}}$ which has the best compromise values of physicochemical properties y_i $(i = 1, 2, \dots, g)$.

Thus, based on the desirability functions an optimal formulation of the filling composition characterized by three best technological indexes are determined.

The resulting regressive equations of the mathematical model are used for a multicriteria determination of the optimal content of the fumed silica filling composition using the generalized functions of desirability. Desirability function are composed based on the resulting equations of the mathematical models in the x-coordinates with the restrictions on the output variables which correspond to the worst and the best values: y_1 – 230 and 243, y_2 – 55 and 60, y_3 – 30 and 23. By the screening using an 0.01 increments, an optimal mass fraction of the composition in was obtained: $x_1 = 0.165$, $x_2 = 0.340$, and $x_3 = 0.495$ [29]. Herewith, the output variables become: $y_1 = 240.27$ cm^3 per 100 g of proteins, $y_2 = 57.27$ %, and $y_3 = 22.68\ cN$ with the desirability function $D_f = 0.6706216$. Thus, to prepare 100 kg of the silica nanoparticle-based filling composition one should take 16.5 kg of fumed silica A-300; 34.0 kg of mixture of Relugan D and Truposol GF with 2 : 3 weight ratio; and 49.5 kg of quebracho extract.

Mathematical Model: Testing

We approbated the developed technology for the production of flexible leather material by filling the semi-finished leather product with optimized formulation of fumed silica-based composition at PJSC Chinbar. Using the developed technology 60 m^2 for upper shoe parts were produced. A company current technology was used as a control. It should be noted that the formulation of the company current filling composition differs from the described filling composition containing silica nanoparticles. The former filling composition did not contain nanosized fumed silica and has higher content of quebracho extract (5.1 % more). The developed technology was tested by performing the filling in the drum with the volume of 9.2 L. The properties of the resulting leather materials are depicted in Fig. 3 and shown in Table VII.

As it can be seen from the Fig. 3 volumetric yield and porosity of leather materials filled with fumed silica composition is increased by 28 cm^3 per 100 g proteins and 11 %, respectively, compared to the control group, while stiffness is decreased by 8 %. From SEM photos one can directly see the increase in thickness for both leather materials obtained using current (Fig. 4*b*) or developed (Fig. 4*c*) technology in comparison to semi-finished leather product (Fig. 4*a*). The largest interfibrillar pores have a control sample as a result of agglomeration of collagen fibers during processing. The semi-finished leather product after chrome tannage has a relatively smaller size of collagen fiber bundles (Fig. 5*a*). Filling the chrome-tanned leather product with a nanocomposite composition results in more homogeneous and highly-dispersed structure of collagen bundles, which is clearly visible at cross section (Fig. 5*b*). In general, the microstructure of the leather material obtained by the developed technology is

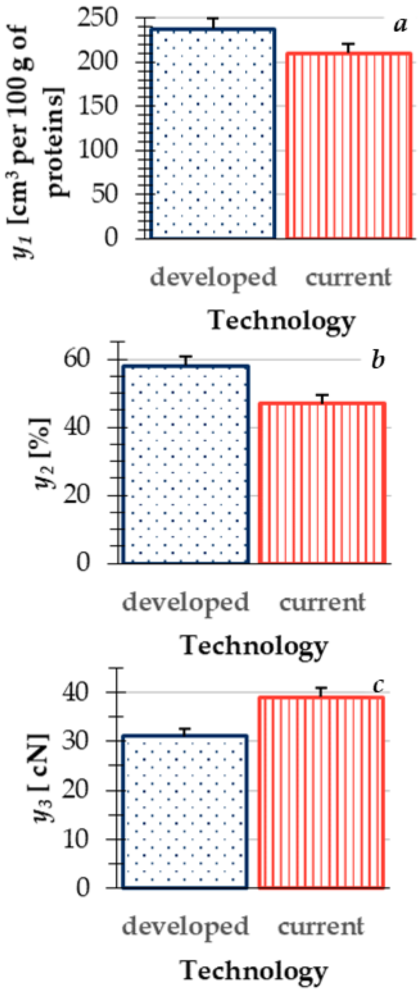

Fig. 3. Properties of the leather materials obtained using developed or current technology: volumetric yield (a), porosity (b), and stiffness (c).

more homogeneous compared to the structure of leather material obtained by current technology.

According to the data listed in Table VII the obtained leather materials have improved mechanical characteristics (tensile strength and elongation), but the difference is not statistically significant.

The results may be explained by the diffusion of silica nanoparticles deep inside the structure of semi-finished leather product which may help to distribute uniformly other ingredients of filling composition into the microstructure of the leather materials (Fig. 5*a*). After removing the water from the leather during the drying-moisturizing processes the presence of silica nanoparticles in the interfibrillar space increases its elasticity and ensures that the mobility of the entire fibrous structure is preserved.

Table VII. *Physicochemical properties of leather materials obtained by developed and current technologies.*

Parameter	**Parameter values for leather materials obtained by**	
	developed technology	**current technology**
T_S [°C]	113.0 ± 0.2	112.0 ± 0.2
Thickness [mm]	1.15 ± 0.01	1.09 ± 0.01
Tensile strength [MPa]	28.5 ± 0.2	27.0 ± 0.2
Elongation at 10 MPa [%]	30.0 ± 0.1	27.0 ± 0.1
Elongation at break [%]	62.5 ± 0.1	58.0 ± 0.1

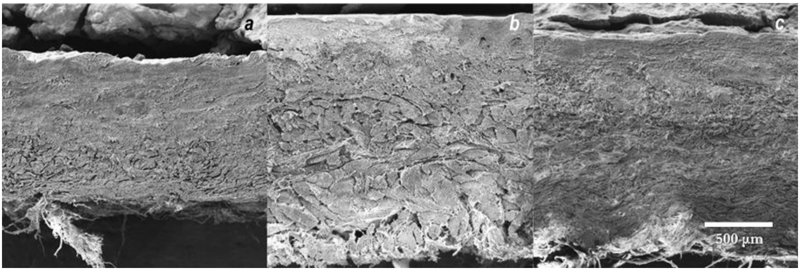

Fig. 4. *Microphotographs (SEM) of cross section of semi-finished leather product (a) and leather materials obtained using current (b) or developed (c) technology at 181× magnification.*

SEM analysis also showed that hair pores were free of any hair residues in dehaired bovine pelts after conventional dehairing process (Fig. 6*a*). The grain structure of all thee samples was also found clean and without any damages. Silica nanoparticles are found to cover the entire surface homogeneously and evenly distributed within the volume of final leather sample (Fig. 5).

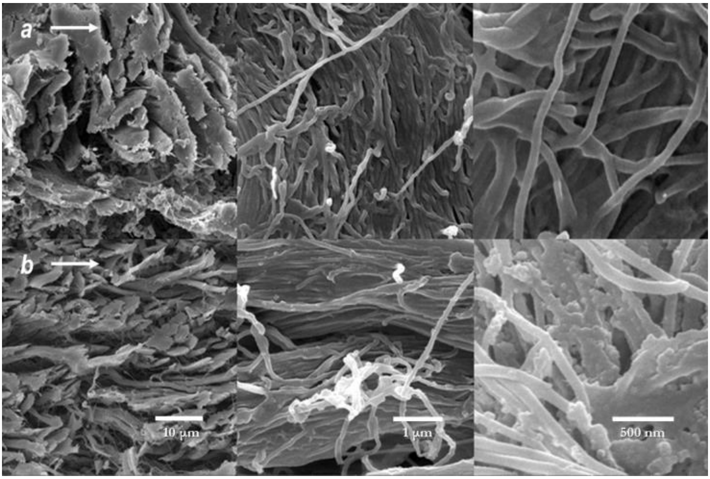

Fig. 5. *Microphotographs of cross section of semi-finished leather product (a) and leather materials obtained using developed (b) technology at three magnifications: 7 220× (column on the left), 90 300× (middle column), and 120 000× (column on the right).*

The filling of the chrome-tanned semi-finished leather product in various degrees changes the atomic ratio between the C, O, and N. This is due to the difference in the chemical formulation of the filling compositions. According to the developed technology filling of semi-finished leather product with composition containing silica nanoparticles and its further fixation with potassium alum results in appearance of Si within leather structure, fivefold increase in Al, and increase in O by 3.2 %. The decrease in Cr content may be due to the active interaction of $-OH$ groups of silica nanoparticles [30] with unilaterally bound to collagen ($-COO^{-} \cdot Cr^{3+}$) or even unbound chromium (III) compounds and it further removing from leather structure during filling.

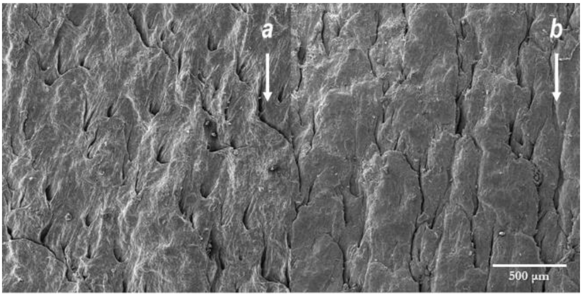

Fig. 6. *Microphotographs of surface of semi-finished leather product (a) and leather materials obtained using developed (b) technology at 181× magnification.*

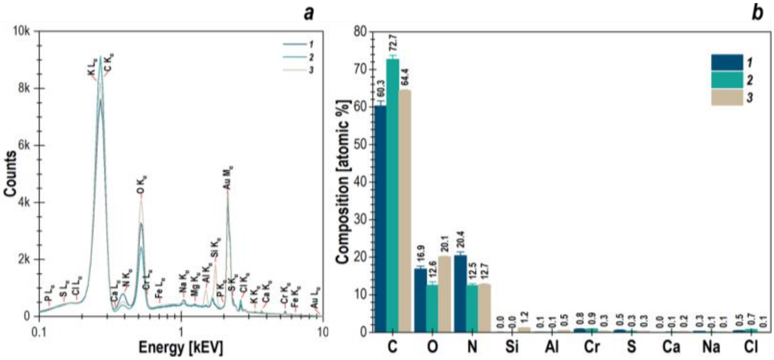

Fig. 7. EDXS spectrum (a) and results of elemental analysis (b) of surface of semi-finished leather product (1) and leather materials obtained using current (2) or developed (3) technology. Analysis was performed at 1 810× magnifications (200 µm field of view) for three different areas.

Conclusions

The optimal design of the experiment has been generated by using McLean-Anderson method which takes into account the type of mathematical model "content of the filling composition – properties of leather materials" and multithreaded program. The latter one provides the parallel calculations of the informative and dispersive matrices and their determinants for the design of multicomponent system. The described mathematical model can be used to solve similar problems in leather and fur production, or other industries.

The optimal formulation of the composition used in the developed technology of filling the semi-finished leather product was determined as well. The mass ratio between fumed silica A-300, Relugan D, Truposol GF, and quebracho extract corresponds to 1.2 : 1.0 :1.5 : 3.6. This formulation allows obtaining the leather materials for production of flexible leather materials with enhanced volumetric yield and porosity in comparison to the current company technology.

Besides, industrial testing of the developed technology of filling the semi-finished leather product allows reducing the usage of natural tannins by 5.1 %, and results in the leather materials with increased volumetric yield and elasticity by 13 and 25 %, respectively, and more homogeneous microstructure. Physicomechanical properties of the obtained leather materials meets the requirements for leather materials for sewing wares (GOST 3115-95), standard for shoe upper leather (GOST 939-88), and quality management systems (ISO 9001:2008).

References

[1]. **Saravanabhavan S., Thanikaivelan P., Rao J., et al.** Reversing the Conventional Leather Processing Sequence for Cleaner Leather Production. *Environ. Sci. Technol.* **40**, 1069, 2006.

[2]. **Mortuza M., Rahman M., Rahman M., et al.** Isolation, Biochemical and Genetic Characterization of Extracellular Protease Producing Cattle Hide Dehairing Bacterium – A Potential Alternative to Chemical Dehairing. *Ecol. Genet. Genomics* **2**, 3, 2017.

[3]. **Wu J., Zhao L., Liu X., et al.** Recent Progress in Cleaner Preservation of Hides and Skins. *J. Clean. Prod.* **148**, 158, 2017.

[4]. **Zedginidze I.** Planning of the Experiment for Studying the Multicomponent System (in Russian), Nauka: Moscow, 1976.

[5]. **Novik F.** Planning of the Experiment on the Simplex for Studying Metallic Systems (in Russian), Metalurgiia: Moscow, 1985.

[6]. **Anderson V. and McLean R.** Design of Experiments: A Realistic Approach, Marcel Dekker: New York, Basel, Hong Kong, 1974.
[7]. **Fedorov V.** Theory of Optimal Experiment (in Russian), Nauka: Moscow, 1971.
[8]. **Rezanova V., Shchotkina V., and Tsebrenko M.** Planning the Experiment and Optimization of the Content of Nanoaddition in Polypropylene Monothreads. *Bull. Kyiv Natl. Univ. Technol. Des.* **2**, 42, 2014.
[9]. **Ivanov S., Trachevskyy V., Hetmanchuk I., et al.** Optimization of Polymer Composition Content by the Method of Mathematical Planning (in Ukrainian). *Proc. Natl. Aviat. Univ.* **4**, 199, 2006.
[10]. **Kondratiuk O. and Kasian E.** Optimization of the Content of Coating Compositions (in Russian). *Proceedings of the International conference "Modelling in Engineering and Economics"* 91, 2016.
[11]. **Machinko L., Machinko V., and Doroshenko E.** Optimization of the Content of Fruit Cereal Mixtures Using Simplex Method (in Ukrainian). *Food Sci. Technol.* **1**, 124, 2012.
[12]. **Sapronov O.** Optimization of the Content of Protective Coatings for the Elements of Ship Power Plants Using the Mathematic Planning of the Experiment (in Ukrainian). *Sci. Bull. Kherson State Mar. Acad.* **1**, 237, 2014.
[13]. **Madizhan A. and Nasarov E.** Simplex-Lattice Design of $NaCl–MgSO_4–CaSO_4$ System According to the Degree of Soil Salinity (in Russian) 1, 2008.
[14]. **Dampilova B. and Zonkhoeva E.** Investigation of Extraction by Zeolite Tuff of La, Pr, and Yb Ions from Mixed Solutions Using Simplex-Lattice Design (in Russian). *Sorption Chromatogr. Process.* **12**, 439, 2012.
[15]. **Rezanova V.** Optimization of the Content of Four Component Polymer Blends Using the Method of Penalty Function (in Ukrainian). *Bull. Kyiv Natl. Univ. Technol. Des.* **2**, 59, 2016.
[16]. **Jianzhong M., Xinjiang C., Yun C., et al.** The Preparation and Application of a Montmorillonite-Based Nanocomposite in Leather Production. *J. Soc. Leather Technol. Chem.* **87**, 131, 2003.
[17]. **Mokrousova O. and Danylkovych A.** Formation of Collagen Structure of Derma by Mineral Dispersions. *Sci. Proc. Riga Tech. Univ.* **1**, 83, 2007.
[18]. **Ma J., Hu J., Zhang Z., et al.** The Acrylic Resin Leather Coating Agent Modified by Nano-SiO_2. *J. Compos. Mater.* **40**, 2189, 2006.
[19]. **Liang S., Neisius N. M., and Gaan S.** Recent Developments in Flame Retardant Polymeric Coatings. *Prog. Org. Coatings* **76**, 1642, 2013.
[20]. **Pan H., Li G., Liu R., et al.** Preparation, Characterization and Application of Dispersible and Spherical Nano-SiO_2 Copolymer Nanocomposite in Leather Tanning. *Appl. Surf. Sci.* **426**, 376, 2017.
[21]. **Ramalingam S., Sreeram K., Raghava Rao J., et al.** Organic Nanocolorants: Self-Fixed, Optothermal Resistive, Silica-Supported Dyes for Sustainable Dyeing of Leather. *ACS Sustain. Chem. Eng.* **4**, 2706, 2016.

[22]. **Danylkovych A. and Chursin V.** Analytical control in leather and fur production: a laboratory practicum (in Russian), Infra-M, Moscow, 2016, 176 p.

[23]. **Danylkovych A., Bilinskii S., and Kudzieva A.** Application of Highly Dispersed Silicon Dioxide in the Technology for Production of Semi-Finished Leather Products (in Ukrainian). *Herald of Khmelnytskyi National University. Technical Sciences* **6**, 112, 2016.

[24]. **Fan H., Ling L., Shi B., et al.** Characteristics of Leather Tanned with Nano-SiO_2. *J. Am. Leather Chem. Assoc.* **100**, 22, 2005.

[25]. **Samchenko Y., Korotych O., Kernosenko L., et al.** Stimuli-Responsive Hybrid Porous Polymers Based on Acetals of Polyvinyl Alcohol and Acrylic Hydrogels. *Colloids Surfaces A Physicochem. Eng. Asp.* **544**, 91, 2018.

[26]. **Taylor B. and Kuyatt C.** Guidelines for Evaluating and Expressing the Uncertainty of NIST Measurement Results. *NIST Tech. Note* **1297**, 20, 1994.

[27]. **Korotych O., Mondal J., Gattás-Asfura K., et al.** Evaluation of Commercially Available Styrene-Co-Maleic Acid Polymers for the Extraction of Membrane Proteins from Spinach Chloroplast Thylakoids. *Eur. Polym. J.* **114**, 485, 2019.

[28]. **Akhnazarova S. and Kafarov V.** Methods for Experiment Optimization in Chemical Engeneering (in Russian), 2nd ed., Vusshaya Shkola: Moscow, 1985.

[29]. **Branovitska S., Medvedev R., and Fialkov Y.** Computational Mathematics in Chemistry and Chemical Engeneering (in Russian), Vusshaya Shkola: Moscow, 1986.

[30]. **Danylkovych A., Lischuk V., and Zhyhotsky O.** Structuring of Collagen of the Dermis during Rawhide Formation. *Chem. Chem. Technol.* **11**, 81, 2017.

19. IMPROVING SKIN CONSUMER PROPERTIES BY OPTIMIZING FILLING COMPOSITION FOR LEATHER MANUFACTURING TECHNOLOGY [16]

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Abstract: *The filling process is studied in the manufacture of elastic leather by optimizing the filling composition. At the same time, the four-component composition includes oligomers and polymers of natural and synthetic origin. The process of filling the semi-finished leather is carried out using the technology of PJSC Chinbar (Ukraine, Kyiv). The goal of the research is to produce highly elastic leather from the semi-finished product of chrome tannage, obtained from the porcine raw hides, with a complex of improved consumer properties by optimizing the ingredient concentrations in the filling composition. For studying the effect of composition, we used a mathematical model for four-component composition, developed a multithreaded program using the McLean-Anderson method, considered the type of the model, and determined the experimental compositions by the D-optimality criterion. The optimum composition is defined at the maximum of the desirability function, which corresponded to the best compromise value of the consumer leather properties – volume yield of the material, its stiffness, and sample density. The technology of filling is developed to ensure the formation from porcine hides a more homogeneous in different areas leather material with a complex of improved consumer properties. At the same time, the produced leather material by its deformability under 9.8 MPa load exceeds by 15 % the leather manufactured using the technology of*

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[16] *The title has been modified; the original title is "Increasing of skin consumer properties by optimization of filling composition in its manufacturing technology".*

PJSC Chinbar. According to physicomechanical characteristics the produced leather meets the requirements for the properties of garments (GOST 3115-95) and the quality management system (ISO 9001:2008).

Keywords: *MacLean-Anderson method; design synthesis; filling composition; composition optimization; consumer properties; leather material.*

Introduction

Improving consumer properties of leather material has a particular importance in recent years due to the expansion of markets for both leather materials and products from them. At the same time, much attention is paid to the complex of their quality characteristics. This is especially important for leather materials produced from a specific macroporous raw material, in particular, porcine hides. Moreover, leather materials from such raw materials occupy the second place in terms of production volume [1] after materials obtained from cattle rawhides. It should be noted that the raw materials of porcine skins are characterized by a considerable heterogeneity of the structure in different areas. Thus, the problem of formation of a quality material by area arises. Formation of quality materials can be achieved, first of all, by performing the process of filling the structure of a semi-finished product efficiently using developed composite reagents. In this case, the concentration of chemical ingredients of the filling composition should be optimized by mathematical modeling using the MacLean-Anderson method [2], improved by authors, and the desirability function [3]. Due to the complex pore size distribution in porcine hides processed into chrome-tanned leather semi-finished product and the impossibility of changing the content of the components of the filling composition within the range of 0–1, the optimization of the composition based on “composition-properties” relations should be connected to obtaining an experiment design with the McLean-Anderson method considering the mathematical model.

Literature Review and Problem Statement

In the technology of manufacturing of elastic leather materials, the stage of filling the structure of the semi-finished product is especially important, since after tanning processes an effective yield of the material over the area is achieved. At the same time, a complex of sorption-mechanical properties is formed.

A wide range of chemical reagents of synthetic and natural origin is used to fill the leather semi-finished product [4]. From an ecological point of view, the technology of filling a semi-finished product with a mixture of sodium caseinate, obtained from waste products of the food industry, with gelatin in a ratio of 10 : 1 can be considered as a promising coenzyme [5, 6]. In this case, the use of microbial trans-glutaminase for gelatin modification speeds up the process four times, and the resulting material is characterized by high density, smoothness of the grain side, elasticity, and high degree of draping. The resulting leather material when filled with gelatin modified with genipin [7] is characterized by a uniform distribution of the complex filler in the semi-finished product due to its sorption on the fibers of the fibrillar structure of the dermis. The use of genipin-gelatin treatment of the semi-finished product also contributes to an increase in the hydrothermal stability of the material.

Uniformity of the structure of the dermis of the semi-finished product of chrome tannage can be improved by filling with the sulphonated oligomers based on melamine and formaldehyde [8]. Copolymer of styrene and butyl acrylate was used previously to fill the chrome-tanned semi-finished product [9]. Filling the semi-finished product with aqueous dispersions of synthesized copolymers with nano-sized particles makes it possible to form a leather material with increased hydrothermal stability and improved physicomechanical properties.

Elastic leather materials obtained by filling the chrome-tanned semi-finished product with montmorillonite, modified by sodium polyphosphate and sodium carbonate with basic chromium sulphate [10,11], are characterized by increased volume yield, and improved elastic-plastic and sanitary-hygienic properties. It has been previously shown [12] that the use of a copolymer of sodium maleate and 10 % of polyoxyethylene lauryl ether makes it possible to form an elastic semi-finished product from the porcine raw hides. The resulting material has enhanced physicomechanical properties and increased area yield compared to control technology.

Thus, the analysis of the literary data indicates the use of a wide range of chemical reagents in the composition for filling the leather semi-finished product of chrome tannage. In this case, the consumer properties of the material depend on the type of the composition and the ratio of the components. Thus, the search for a quasi-optimal composition is performed using a passive experiment. Investigation of a material that is structurally heterogeneous in different areas, with both varied porosity and physicomechanical properties, can be considered promising for mathematical modeling, imposing restrictions on the components of the composition with subsequent multicriteria optimization.

The Goal and Objectives of the Research

The goal of the research is to produce a highly elastic leather material with a complex of improved consumer properties from a porcine chrome-tanned semi-finished product by optimizing the composition of the filling composition. To achieve the goal, the following tasks were set:

- computing of the experiment design “composition of filling mixture – properties of leather material” using MacLean-Anderson method;
- obtaining an adequate mathematical model of the experiment based on the experimental data and establishing the optimal

composition of the filling composition using the desirability function;
- determination and analysis of physicomechanical properties of the filled leather material obtained at the experimental points of the computed design.

Materials and Methods

Samples of the semi-finished product of chrome tannage (technical specification, TU U 00302391-03-98) is used after its shaving for the thickness 1.3–1.4 mm. Semi-finished product was produced according to the method of the PJSC Chinbar (Ukraine, Kyiv). According to the previously described method [13], 14 groups of 20×120 mm samples, each group contained 12 samples, were selected from the semi-finished product. Each group consists of samples of semi-finished products selected from the belly and the bend – 6 of each.

Samples of the semi-finished product were neutralized with sodium formate (technical specification, TU 21-249-00204168-92) and sodium bicarbonate (GOST 2156-76) with the mass ratio of 1 : 1. To study the process of filling the leather semi-finished product, a composition with the following ingredients were used:

- copolymer of exopolysaccharide of bacterial origin (technical specification, TU U 88-105-002-2000) – xanthan gum, modified with acrylamide (XGAAm; technical specification, TU 6-01-1049-92) [14];
- Trupotan AG (Trumpler, Germany) – composition based on a modified plant extract and pyrocatechine;
- Tergotan SMU (Clariant, Poland) – copolymer based on synthetic and natural reagents;
- Quebracho extract (China).

In the control technology of PJSC Chinbar instead of the copolymer XGAAm, the anionic acrylic polymer Retanal RCN-40 (Cromogenia Units, Spain) was used.

The process of filling the semi-finished product was carried out using the solutions based on the fraction of electrochemically activated water – catholyte [15]. Filling process using the control technology (in a laboratory setup) was performed in solutions based on distilled water. The total consumption of the components was 11.5 % of the mass of the wringed semi-finished product at a 1.2 : 1 ratio of water volume to the semi-finished product mass. The temperature of the medium and the duration of the process correspond to the control technology and are 28–30 °C and 2.0 h with constant mixing of the components at a rate of 8–10 rpm. The leather samples were treated with a fatliquor at a consumption of 7 % of the mass of semi-finished product, dried unstretched at 20–23 °C, kneaded, wringed, kept in a desiccator over calcium chloride, and tested in laboratory conditions.

Consumer properties of leather semi-finished products were determined by the previously published methods [13] using samples from the belly area, since it is more structurally and kinetically sensitive to the filling process. We determine the volume yield of the leather material as volume of the semi-finished product per 100 g of proteins, the leather stiffness using a PZhU-12M device, and also sample density. The physicomechanical properties of the samples from the bend area were determined on a tensile testing machine RT-250 at a deformation rate of 80 mm/min, as it is required by the standard for leather for garments (DSTU 3115-95). At the same time, the samples obtained in each experimental point of the design were analyzed according to the following parameters:

σ_s – tensile strength [MPa];
ε_t – elongation at 9.8 MPa load [%];
ε_b – elongation at break [%].

Previous studies [16] established the possible intervals of consumption of the components of the composition (Table I) for the filling process.

Table I. *Restrictions on the concentration of ingredients in the filling composition.*

i	Limits of the change of the ingredient concentrations			
	true X_i		encoded x_i	
	min	max	min	max
1	2	6	0.17	0.52
2	1	3	0.09	0.26
3	1	3	0.09	0.26
4	2	5	0.17	0.43

Note: *i is the sequence number of the ingredient of the filling composition; true values for the ingredients are given in % of the mass of the semi-finished product.*

Since $\sum_{i=1}^{k} X_i \neq 1$, where *k* is the number of the components, the problem "composition-property" is reduced to encoded factors x_i by the dependence:

$$X_i = 1.337 \cdot 10^{-10} + 11.5x_i$$

The composition of the filling composition is determined by a second-degree mathematical model:

$$\hat{y} = \sum_{i=1}^{k} b_i x_i + \sum_{i=1}^{k-1} \sum_{j=i+1}^{k} b_{ij} x_i x_j$$

where $\hat{y}$ – the predicted value of the output variable; b_i and $\sum_{i=1}^{k} x_i$ – coefficients of the model; *i, j* – the sequence numbers of the components.

For the above model, the normalization condition is used:

$$\sum_{i=1}^{k} x_i = 1.$$

In experiments because of technological reasons, the following restrictions are imposed on the numerical values of the x_i components:

$$0 \leq x_i^{min} \leq x_i \leq x_i^{max} \leq 1 \ (i = 1, 2, \dots, k).$$

The mathematical model of a general form for a four-component composition acquires the form:

$$\hat{y}_i = b_1x_1 + b_2x_2 + b_3x_3 + b_4x_4 + b_{12}x_1x_2 + b_{13}x_1x_3 + b_{14}x_1x_4 + b_{23}x_2x_3 + b_{24}x_2x_4 + +b_{34}x_3x_4,$$

where, $\hat{y}_i$ – the predicted value of the consumer property of the leather material, $i = 1 \div 3$;

x_1 – copolymer XGAAm;

x_2 –composition Trupotan AG;

x_3 – copolymer Tergotan SMU;

x_4 – quebracho extract.

The effect of the concentration of ingredients of the filling composition on the consumer properties of the leather material is evaluated according to the following parameters:

y_1 – volumetric yield of leather material [cm^3/100 g of protein];

y_2 – material stiffness [cN];

y_3 – sample density [kg/m^3];

To obtain a mathematical model that describes the consumer properties of the leather material depending on the ingredient concentrations in the composition, it is necessary to synthesize the experiment design according to the D-optimality criterion with imposed restrictions on the components of the composition. After the implementation of the experiment design and the processing of the obtained data, the coefficients of the model are calculated and its adequacy at the control points is checked. The obtained "composition-property" models are used to optimize the ingredient concentrations of the filling composition using the desirability function.

Mathematical Model for the Ingredient Concentration of the Filling Composition

Previous studies [16] made it possible to determine the boundaries (mass fraction) of the variation of these ingredients in the filling composition (Table I).

Table II. *Theoretical points of the design.*

x_i	Theoretical points of the design													
	1	*2*	*3*	*4*	*5*	*6*	*7*	*8*	*9*	*10*	*11*	*12*	*13*	*14*
x_1	0.22	0.22	0.39	0.30	0.48	0.48	0.17	0.52	0.17	0.52	0.17	0.52	0.22	0.35
x_2	0.09	0.26	0.09	0.26	0.09	0.26	0.13	0.22	0.26	0.09	0.26	0.09	0.17	0.09
x_3	0.26	0.09	0.09	0.26	0.26	0.09	0.26	0.09	0.13	0.22	0.26	0.09	0.17	0.26
x_4	0.43	0.43	0.43	0.17	0.17	0.17	0.43	0.17	0.43	0.17	0.30	0.30	0.43	0.30

x_i	*15*	*16*	*17*	*18*	*19*	*20*	*21*	*22*	*23*	*24*	*25*	*26*	*27*	*28*
x_1	0.30	0.20	0.35	0.20	0.30	0.46	0.24	0.39	0.39	0.48	0.50	0.50	0.17	0.17
x_2	0.09	0.11	0.26	0.26	0.17	0.09	0.26	0.26	0.17	0.17	0.09	0.24	0.20	0.20
x_3	0.17	0.26	0.09	0.11	0.09	0.09	0.26	0.17	0.26	0.17	0.24	0.09	0.26	0.20
x_4	0.43	0.43	0.30	0.43	0.43	0.37	0.24	0.17	0.17	0.17	0.17	0.17	0.37	0.43

x_i	*29*	*30*	*31*	*32*	*33*	*34*	*35*	*36*	*37*	*38*	*39*	*40*	*41*
x_1	0.52	0.52	0.17	0.52	0.43	0.27	0.23	0.27	0.43	0.46	0.17	0.52	0.35
x_2	0.15	0.15	0.26	0.09	0.09	0.17	0.17	0.26	0.18	0.18	0.22	0.13	0.17
x_3	0.09	0.15	0.20	0.15	0.18	0.26	0.17	0.17	0.09	0.18	0.22	0.13	0.17
x_4	0.24	0.17	0.37	0.24	0.30	0.30	0.43	0.30	0.30	0.17	0.39	0.22	0.30

To determine the coefficients of the model *4* from the defined theoretical candidate points (Table II) and compute the experimental design, MacLean-Anderson method based on the maximal distance of candidate point from the center of the design and from each other was used [2] and the multithread program was developed. Next, we selected from *N* theoretical points the best *n* experimental points of the design according to the D-optimality criterion.

In order to determine the experimental points of the design, all possible combinations from *N* to *n* points are calculated

$$C(N,n) = \frac{N!}{n!\,(N-n)!}$$

And a combination is calculated in which the determinant

$$\det|D| \to min,$$

where $D = (F^T F)^{-1}$ is the dispersion matrix of the design; F is the matrix for the experiment design X generalized by the type of the model $\overline{f^0}(\bar{x})$ with size $n \times l$ with l being the number of model coefficients; T is the matrix transposition operation.

To obtain the coefficients of the four-component composition model, an optimal experiment design was computed (Table III) in a limited region of the simplex (Table I), considering the normalization condition.

Table III. *Experiment design.*

x_i	Experimental point									
	1	***2***	***3***	***8***	***10***	***11***	***22***	***23***	***28***	***41***
x_1	0.22	0.22	0.39	0.52	0.52	0.17	0.39	0.39	0.17	0.35
x_2	0.09	0.26	0.09	0.22	0.09	0.26	0.26	0.17	0.20	0.17
x_3	0.26	0.09	0.09	0.09	0.22	0.26	0.17	0.26	0.20	0.17
x_4	0.43	0.43	0.43	0.17	0.17	0.30	0.17	0.17	0.43	0.30

Thus, from the theoretical points obtained by the MacLean-Anderson method and the D-optimality criterion, 10 experimental points were selected for further research. The obtained experimental results of the effect of the ingredient concentration of the filling composition according to the design of Table III on consumer properties of leather material are given in Table IV.

Table IV. *Physicochemical properties of the filled leather material.*

Parameters	Experimental point									
	1	***2***	***3***	***8***	***10***	***11***	***22***	***23***	***28***	***41***
y_1	260	222	184	162	175	168	170	178	227	158
y_2	22	24	29	37	32	30	32	34	24	33
y_3	0.580	0.594	0.615	0.629	0.634	0.626	0.630	0.632	0.587	0.639

The coefficients of the four-component mathematical model are determined by the method of least squares in a matrix form:

$$B = (F^T F)^{-1} F^T Y,$$

where B is the vector of the coefficients we have been looking for; Y is the column of the values of the dependent variable, which are observed in the experiments.

The adequacy of the model is verified by the Student's criterion [2] at each control point that the researcher is interested in. To test the adequacy of the mathematical model, two parallel experiments are performed at three arbitrarily chosen control points (Table V).

Table V. *Physicochemical properties of the filled leather material in control points of the ingredient concentrations in the filling composition.*

Control point	**Composition**				**Technological parameter**					
	x_1	x_2	x_3	x_4	y_1		y_2		y_3	
1	0.3478	0.087	0.2174	0.3478	190	195	30	28	0.623	0.629
2	0.2609	0.087	0.2609	0.3913	230	237	25	22	0.598	0.595
3	0.4348	0.1739	0.087	0.3043	147	153	33	35	0.643	0.638

Based on the experimental and control data from Table IV and Table V, a non-linear mathematical model of the dependences of the technological consumer properties of leather material on the ingredient concentration of the filling composition is obtained:

$$\begin{aligned}\hat{y}_1 = {} & 200.4072406x_1 + 817.284176x_2 + 794.772566x_3 \\ & + 1156.822057x_4 - 281.5242594x_1x_2 \\ & - 222.1743473x_1x_3 - 2008.642258x_1x_4 \\ & - 2586.624701x_2x_3 - 2367.360642x_2x_4 \\ & - 1842.679728x_3x_4;\end{aligned}$$

$$\begin{aligned}\hat{y}_2 = {} & 33.33858726x_1 - 182.0446065x_2 + 102.5243729x_3 \\ & - 69.85634247x_4 + 287.9413363x_1x_2 \\ & + 182.396578x_1x_3 + 184.1415527x_1x_4 \\ & + 252.758817x_2x_3 + 440.0149701x_2x_4 \\ & - 5.857645514x_3x_4;\end{aligned}$$

$$\begin{aligned}\hat{y}_3 = 0.524937846x_1 + 0.380750396x_2 + 0.412988324x_3 \\ - 0.075938768x_4 + 0.134947852x_1x_2 \\ + 0.252701323x_1x_3 + 1.518567636x_1x_4 \\ + 0.737231397x_2x_3 + 1.435059291x_2x_4 \\ + 1.11690889x_3x_4.\end{aligned}$$

The results of the determination of the adequacy of the mathematical model of the "ingredient concentration of the filling composition – the properties of the leather material" at the control points are given in Table VI.

Table VI. *Results of checking the adequacy of the mathematical model.*

y_{ij}	$\bar{y}_i$	$\hat{y}_i$	ξ	$\lvert\bar{y}_i - \hat{y}_i\rvert$	t_o	**adequacy**
y_{11}	187.8	192.5	1.4	4.7	1.425	1
y_{12}	28.6	29.0	1.3	0.4	0.307	1
y_{13}	0.628	0.626	1.5	0.002	0.667	1
y_{21}	229.4	233.5	1.4	4.1	1.261	1
y_{22}	25.3	23.5	1.3	1.8	1.421	1
y_{23}	0.603	0.597	1.5	0.007	2.522	1
y_{31}	141.8	150.0	1.4	8.2	2.420	1
y_{32}	36.7	34.0	1.3	2.7	2.015	1
y_{33}	0.645	0.641	1.5	0.004	1.523	1

Thus, from the Table VI, it can be seen that the obtained mathematical model adequately describes the consumer properties of the leather material with the corresponding concentration of the ingredients in the filling composition.

Optimization of Ingredient Concentrations in the Filling composition

To optimize the ingredient concentrations of the four-component composition $\bar{x} = ||x_1, x_2, x_3, x_4||$, which is characterized by g output of the computed mathematical model by consumer parameters, the desirability function [3] is used:

$$D_f = \sqrt[g]{d_1 d_2 \dots d_g},$$

where d_i $(i = 1,2, \dots, g)$ is the partial function of the property desirability of the leather material y_i, which takes values in the interval [0; 1] and is determined by the dependence:

$$d_i = \exp[-\exp(-y_i')],$$

where y_i' is the dimensionless value of the material property y_i which is determined by the linear relationship:

$$y_i' = b_0^{(i)} + b_1^{(i)} y_i.$$

The coefficients $b_0^{(i)}$ and $b_1^{(i)}$ from the above equation are determined from the following system of equations:

$$\begin{cases} y_i'^{worse} = b_0^{(i)} + b_1^{(i)} y_i^{worse} \\ y_i'^{better} = b_0^{(i)} + b_1^{(i)} y_i^{better} \end{cases},$$

where $y_i'^{worse}$ and $y_i'^{better}$ $(i = 1,2, \dots, g)$ is the worse and better values of the criterion y_i which is established by the researcher and by the reasons of the technological character cannot be reduced or increased; $y_i'^{worse}$ and $y_i'^{better}$ is worse and better values of the dimensionless quality criterion which is determined by the formulas:

$$y_i'^{worse} = -\ln(-\ln d_{worse}),$$
$$y_i'^{better} = -\ln(-\ln d_{better}),$$

where d_{worse} and d_{better} is the worse and better values of individual desirability functions. Accordingly, the values 0.2 and 0.8 are adopted values of the consumer parameters y_i.

So, based on the desirability function, the optimal ingredient concentrations of the filling composition which was characterized by three best consumer properties are determined. At the same time, the increased yield of the leather material and the minimal values of sample density and stiffness are considered as the best values.

The obtained mathematical models of consumer properties are used for multicriteria search of the ingredient concentrations in the filling composition using the generalized desirability function, compiled from the corresponding mathematical models in x-coordinates with constraints on the output variables corresponding to the worst and best values: y_1 – 200 and 260, y_2 – 30 i 22, y_3 – 0.630 and 0.580. Using the scanning method [17] in 0.01 increments, the optimal ingredient concentrations in the filling composition are founds: $x_1 = 0.222$ %, $x_2 = 0.087$ %, $x_3 = 0.257$ %, and $x_4 = 0.434$ %, or as a percentage of the mass of the semi-finished product: X_1 = 2.55 %, X_2 = 1.00 %, X_3 = 2.96 %, and X_4 = 4.99 %. In this case, the consumer properties of the leather material take the values: $y_1 = 257.4$ cm^3 per 100 g of protein, $y_2 = 22.1\ cN$, and $y_3 = 0.581$ kg/m^3 when a desirability function D_f is equal to 0.7896.

Physicomechanical Properties of the Filled Leather Material

The research results of the physicomechanical properties of the samples at 10 experimental points (Table III), corresponding to the ingredient concentrations in the filling composition, are given in the Table VII. As it can be seen from the data, the deformability is the most indicative parameter of the leather material characterizing its consumer properties in the investigated interval of the ingredient concentrations. At the same time, the deformability of the material samples at 9.8 MPa load increases by 47 % with a change of the ingredient concentrations, while the tensile strength changes 2.6 times less. It should be noted that the volumetric yield and stiffness of the leather material from the belly area, respectively, change by 64 and 68 %.

With the optimum composition of the filling composition, which practically corresponds to the first experimental point, the physical and mechanical parameters reach the maximum values.

The research results of the physicomechanical properties of the filled semi-finished product produced by using the developed and control filling compositions are shown in the Fig. 1.

Comparative analysis of the samples produced by the developed technology using the optimal filling composition and the control technology of PJSC Chinbar, demonstrates the advantages of replacing the anionic acrylic polymer Retanal RCN-40 with a copolymer of exopolysaccharide of bacterial origin, xanthan gum modified with acrylamide. At the same time, the deformability at 9.8 MPa load of the material produced by the optimized technology exceeds the control samples by 15 %.

Table VII. *Physicomechanical properties of the filled leather material.*

Parameter	**Experimental point**				
	1	***2***	***3***	***8***	***10***
σ_s [MPa]	19.0 ± 0.9	18.0 ± 0.9	17.0 ± 0.8	16.0 ± 0.8	16.0 ± 0.8
ε_t [%]	34.0 ± 2.0	32.0 ± 2.0	29.0 ± 1.7	23.0 ± 1.4	25.0 ± 1.5
ε_b [%]	66.0 ± 4.6	64.0 ± 4.5	57.0 ± 4.0	51.0 ± 3.6	53.0 ± 3.7

Parameter	***11***	***22***	***23***	***28***	***41***
σ_s [MPa]	18.0 ± 0.9	17.0 ± 0.8	17.0 ± 0.8	18.0 ± 0.9	18.0 ± 0.9
ε_t [%]	27.0 ± 1.6	23.0 ± 1.4	24.0 ± 1.4	35.0 ± 2.1	23.0 ± 1.4
ε_b [%]	58.0 ± 4.1	51.0 ± 3.6	52.0 ± 3.6	64.0 ± 4.5	56.0 ± 4.0

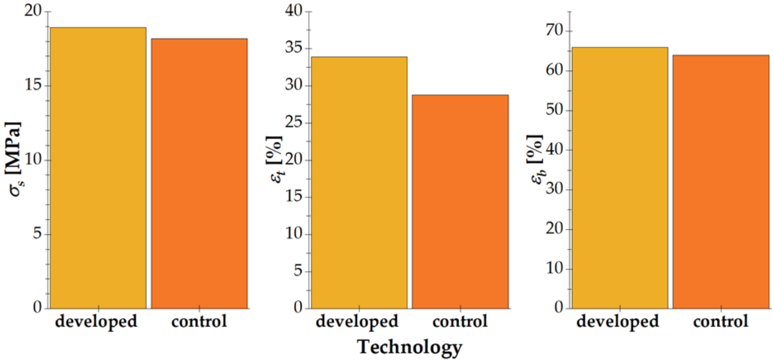

Fig. 1. *Physicomechanical characteristics of leather material produced by the optimized (left) and the control (right) technology.*

Thus, according to the set of consumer characteristics, the optimal ingredient concentrations in the filling composition is established based on the mathematical model and the generalized desirability function. The developed filling composition provides an efficient filling process in the production of elastic chrome-tanned leather material from porcine hides with a complex of improved exploitational properties.

Conclusion

For the formation of leather material with improved consumer properties from the chrome-tanned semi-finished porcine hide, an experiment design for the ingredient concentrations of the filling composition by the improved MacLean-Anderson method is computed and implemented considering the type of the mathematical model using the developed multithread program. The developed program reduces the duration for the computation of the D-optimal design twice (to 24 h) compared to a single-threaded program. Based on the computed mathematical model for consumer properties of leather material, a multifactor optimization of the ingredient concentrations in the filling composition using the desirability function is carried out. The optimal ingredient concentration of the four-component filling composition is established, which ensures the formation of a more homogeneous leather material with a complex of improved consumer properties. According to physicomechanical characteristics, the produced leather material meets the requirements for the properties of garments (GOST 3115-95) and the quality management system according (ISO 9001:2008).

References

[1]. **Khludeev K. and Gordienko I.** Commodity and expertise of leather raw materials (in Russian). Koloss S (Rushing publisher «КолосС») 2013, Moscow; http://www.studentlibrary.ru/book/ISBN9785953206204.html.

[2]. **Anderson V. and McLean R.** Design of experiments: a realistic approach. *Marcel Dekker* 1974, New York and Basel, 418 p.

[3]. **Akhnazarova S. and Kafarov V.** Methods of optimizing the experiment in chemical technology: textbook (in Russian). *Vysshaia shkola* (Publisher «Высшая школа») 1985, Moscow, 320 p.

[4]. **Danylkovych A., Mokrousova O., and Okhmat O.** Technology and materials for leather production (in Ukrainian). Fenix (Publisher «Фенікс») 2009, Kyiv, 578 p.

[5]. **Balada E., Taylor M., Brown E., and Liu C.** Whey protein isolate: a potential filler for the leather industry. *Journal of the American Leather Chemists Association* **104** (2009) 122–130.

[6]. **Liu Q., Liu L., Li J., et al.** Influence of microbial transglutaminase modified gelatin-sodium caseinate, as a filler, on the subjective mechanical and structural properties of leather. *Journal of the American Leather Chemists Association* **106** (2011) 200–207.

[7]. **Brown E.** Potential application for genipin-modified gelatin in leather processing. *Journal of the American Leather Chemists Association* **104** (2009) 79–91.

[8]. **Jaisankar S., Gupta S., Lakshminarayana Y., et al.** Water-based anionic sulfonated melamine formaldehyde condensate oligomer as retanning agent for leather processing. *Journal of the American Leather Chemists Association* **105** (2010) 289–296.

[9]. **Nashy E., Hussein A. and Essa M.** Novel retanning agents for chrome tanned leather based on emulsion-nano particles of styrene/butyl acrylate copolymers. *Journal of the American Leather Chemists Association* **106** (2011) 241–248.

[10]. **Maruhlenko M., Palamar V., and Mokrousova O.** Stabilizing derma collagen structure with modified dispersions of montmorillonite. *IOP Conference Series: Materials Science and Engineering* **111** (2016) 1–8.

[11]. **Danylkovych A., Mokrousova O., and Zhyhotsky A.** Improvement of the filling and plasticization processes of forming multifunctional leather materials. *Eastern-European Journal of Enterprise Technologies* **80** (2016) 23–31.

[12]. **Wang X.-C., Zhao Y., and Li T.** Preparation of microemulsion polymer and its influence on softness and physical-mechanical properties of chrome tanned leather. *Fine Chemicals* **8** (2008) 784–789.

[13]. **Danylkovych A. and Chursin V.** Analytical control in leather and fur production: a laboratory practicum (in Russian), Infra-M, Moscow, 2016, 176 p.

[14]. **Gvazdiak R., Matyshevskii M., Grigorev E., et al.** Microbial polysaccharide xanthan gum (in Russian). Naukova Dumka (Publisher «Наукова думка») 1989, Kyiv, 212 p.

[15]. **Prilutskii V. and Bakhir V.** Electrically activated water: anomalous properties and the mechanism of biological effect (in Russian). *VNIIIMT* (Rushing publisher «ВНИИИМТ»)1997, Moscow, 244 p.

[16]. **Danylkovych A., Lishchuk V., and Romaniuk O.** Use of electrochemically activated aqueous solutions in the manufacture of fur materials, *SpringerPlus* **5**, 214 (2016); doi.org/10.1186/s40064-016-1784-6

[17]. **Branovitska S., Medvedev R., and Fialkov Y.** Computational mathematics in chemistry and chemical technology (in Russian). *Vysshaia shkola* (Publisher «Высшая школа») 1986, Kyiv, 216 p.

20. OPTIMIZATION OF FILLING-FATLIQUORING PROCESS OF LEATHER SEMI-FINISHED PRODUCT WITH NANO-SILICA [17]

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Abstract: *The optimization of the ingredient concentration of the filling-fatliquoring composition containing nano-sized fumed silica during the processing of chrome-tanned semi-finished product into light-colored leather was carried out. A second-degree mathematical model was developed using a central composite rotatable plan for the three input variable components of the filling-fatliquoring composition, namely, the concentration of Aerosil A-300, acrylic dispersion 2037, and Trupol RA fatliquoring reagent and three physicochemical parameters to assess the quality of the produced leather. The multicriteria optimization of the filling-fatliquoring process of leather semi-finished product using the desirability function and the limitations on the concentration of ingredients, considering their desirable values, was carried out. The optimal concentration of the ingredients in the filling-fatliquoring composition were determined. To investigate the effect of the ingredient concentration on the physicochemical properties of leather, the semi-finished product of chrome-tannage (20 samples) was used for filling-fatliquoring after its shaving to a thickness of 1.5-1.6 mm. The developed technology of the filling-fatliquoring process utilizing nano-sized fumed silica in the formation of light-colored leather was tested in the semi-industrial conditions at PJSC Chinbar on half-skins. This technology allows us to produce leather material with improved elasticity and*

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[17] *The title has been modified; the original title is "Optimization of the filling-greasing process of the leather semi-finished products with the use of nano-silica".*

durability. The filling-fatliquoring technology also yields leather material with a 2.6 % increase in area compared with the current technology which involves the formation of leather materials using a colored tanning agent. The produced light-colored leather meets the requirements for elastic leather for sewing products according to DSTU 3115-95 and the requirements of the international standard of quality management systems ISO 9001: 2008. The availability of the developed filling-fatliquoring process is stipulated due to the possibility of its use on chrome-tanned semi-finished products to manufacture light-colored leather of wide use.

Keywords: *leather semi-finished product; chrome tannage; filling-fatliquoring process.*

Introduction

Improvement of current technologies and development of innovative technologies for production of various elastic leather materials (especially light-colored ones) can be considered an objective necessity in the modern conditions of technological progress. Due to the fact that in the technologies of leather production tannage with chromium compounds provides leather materials with improved elastic-plastic properties, the actual problem is the implementation of retanning-filling processes of leather semi-finished product with the exclusion of naturally colored reagents for production of light-colored leather. In this case, the search for effective chemical reagents for filling leather semi-finished product of chrome tannage in the retanning processes can be effective. At the same time, such reagents, due to their chemocolloidal properties, should be characterized by high diffusivity within the microfibrillar structure of the dermal collagen and their even distribution in the structure of semi-finished product and, thus, provide a complex of improved physicochemical properties of light-colored leather.

In the processes of retanning-filling of leather semi-finished product, a wide range of chemical reagents of natural and synthetic origin are used. It is known the usage of aqueous emulsions of copolymers synthesized based on acrylic acid [1] and butyl acrylate and styrene [2] for the formation of leather semi-finished product with the required hydrothermal stability. The recommended techniques provide the decrease of contamination of spent solutions.

In the post-tanning processing of leather semi-finished product of chrome tannage, dispersions of water-soluble polyacrylates, including amino resins [3,4], are also used. In this case, amino resins effectively diffuse into the structure of leather semi-finished product. The resulting leather is characterized by an increased density and durability of the grain layer. Dicyandiamide polymers [5] combined with inorganic, vegetable, or synthetic reagents are used to fill the semi-finished product. The usage of a sulfonated melamine formaldehyde oligomer for retanning chrome-tanned semi-finished product improves the filling of leather structure, but the resulting leather material can contain up to 10 mg/kg of free formaldehyde.

The work [2] presents the results of the effect of polymaleate and polyacrylate on the porosity and vapor permeability of leather semi-finished product. At the same time a certain increase of these parameters is observed when at the final stage of finishing the dispersions of polymers is used.

In the technology of leather production for retanning-filling the combination of vegetable and synthetic tannins are the most commonly used. To obtain the necessary technological effect and given the variety of leathers, the processes of retanning and filling are carried out separately. This paper describes the technology of combined processing of leather semi-finished product of chrome tannage using mimosa extract with oxazolidine [6] which results in the leather with the necessary complex of physicomechanical properties that meet the standard requirements.

The effect of the particle size (in the range of 60–150 nm) of a composition based on nano-sized SiO_2 and oxazolidine with a wide range of concentrations on the uniformity of ingredient distribution in the structure of semi-finished product was investigated [7]. At concentration of SiO_2 more than 7 % the agglomeration of the particles in clusters up to 400 nm is observed. At the same time, leather with the increased resistance to mold is obtained.

Therefore, the analysis of scientific papers indicates that the usage of a wide range of natural and synthetic reagents at the stage of retanning-filling practically does not allow producing light-colored leather with the necessary complex of exploitational properties. Thus, a very promising filler can be a highly-dispersed hydrophilic aluminosilicate – Aerosil, which can be combined with a polymer dispersion when producing a light-colored leather. Although, to form leather with a complex of improved physicochemical properties while using nano-silica, it is necessary to optimize the technological process of retanning-filling of leather semi-finished product of chrome tannage.

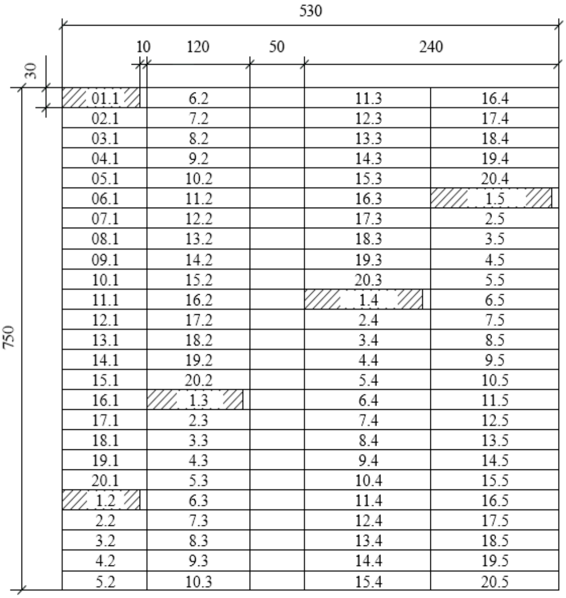
Problem Definition

The goal of the work is to optimize the process of filling-fatliquoring of leather semi-finished product of chrome tannage using nano-silica for manufacturing light-colored leather. To achieve this goal the following tasks were determined:

1. Obtain a mathematical model of the filling-fatliquoring process of semi-finished product of chrome tannage by using the central composite rotatable plan (CCRP) of the second-degree;
2. Perform multicriteria optimization of the filling-fatliquoring process utilizing nano-silica;
3. Test the developed technology of filling-fatliquoring of leather semi-finished product in semi-industrial conditions.

Materials and Methods

To investigate the effect of concentration of ingredients on the physicochemical properties of leather material, a semi-finished product of chrome tannage from calfskin was used after its shaving to a thickness of 1.5–1.6 mm. Using the previously described method [8], we selected 20 samples from the bend (Fig. 1). In this case, the numbered strips, 10×30 mm in size, from the right side of each sample were used to determine the volumetric yield of leather.



01.1	6.2		11.3	16.4
02.1	7.2		12.3	17.4
03.1	8.2		13.3	18.4
04.1	9.2		14.3	19.4
05.1	10.2		15.3	20.4
06.1	11.2		16.3	1.5
07.1	12.2		17.3	2.5
08.1	13.2		18.3	3.5
09.1	14.2		19.3	4.5
10.1	15.2		20.3	5.5
11.1	16.2		1.4	6.5
12.1	17.2		2.4	7.5
13.1	18.2		3.4	8.5
14.1	19.2		4.4	9.5
15.1	20.2		5.4	10.5
16.1	1.3		6.4	11.5
17.1	2.3		7.4	12.5
18.1	3.3		8.4	13.5
19.1	4.3		9.4	14.5
20.1	5.3		10.4	15.5
1.2	6.3		11.4	16.5
2.2	7.3		12.4	17.5
3.2	8.3		13.4	18.5
4.2	9.3		14.4	19.5
5.2	10.3		15.4	20.5

Fig. 1. *Schematic representation of the selection of 20 samples.*

To obtain a mathematical model, the experiments were carried out in the laboratory at the Department of Biotechnology, Leather, and Fur according to CCRP [9], as the advantage of the chosen plan is the approach of the information surface to the spherical one. In this case, accuracy for all points that are at the same distance from the center of the plan is practically the same.

The approbation of the optimized filling-fatliquoring process was performed in semi-industrial conditions using alternating half-skins of leather semi-finished product of chrome tannage.

The following chemical reagents have been used for retanning-fatliquoring:

1. Nano-silica Aerosil A-300 with a particle size of 4–50 nm, a specific surface of 300 g/m^2, and a mass fraction of silicon oxide more than 99.9 %, produced by pilot plant (Kalush, Ukraine) of the Chuiko Institute of Surface Chemistry;
2. Acrylic anionic polymer Retanal RCN-40 (Cromogenia Units, Spain) with pH 6.8, 39.8 % of dry residues, and a viscosity of $12 \cdot 10^3$ sP s;
3. Fatliquor Trupol RA (Trumpler, Germany) – a mixture of sulphated and sulphited synthetic and natural anionic fatty substances with an active substance content of 70 % and a pH of 10 % emulsion of 7.5;
4. Quebracho extract (China) containing 80.5 % of vegetable tanning agents (on a dry basis).

The filling of the leather semi-finished product was performed after its complete neutralization at 1 : 1 ratio of the volume of working solution to the mass of semi-finished product, rinsing for 10 min, at the consumption of the ingredients of the composition with the content corresponding to the experimental point, at 28–30 °C, and a constant rotation at 18–20 rpm. Aerosil A-300 was used in a mixture with the Trupol RA fatliquor (50 % of the mass of nano-silica). After15 min of the semi-finished product processing, the acrylic dispersion 2037 was added into the technological solution, and in 30 min the rest of the fatliquor was added. The process of filling leather semi-finished product was completed at pH 4.4. The following technological processes and operations of retanning-filling of leather semi-finished product were performed according to the technology of PJSC Chinbar (Ukraine, Kyiv).

Physicochemical properties of the filled leather material were determined according to the established methods [8]. In particular, the volumetric yield of the material was estimated by the ratio of the material volume in the finished form, filled with the composition, to the volume of the semi-finished product of chrome tannage on the cut-off samples (Fig. 1). The physicomechanical properties of the filled leather material were determined on a tensile testing machine RT-250 at a compression rate of 90 mm/min. The leather stiffness was determined using a PZhU-12M device.

CCRP of the second-degree is based on a full factorial experiment supplemented by the n_α tests at the star points (points 9–14 in Table II) and n_0 tests in the center of the plan, which allow us to estimate the uncertainty of the experiment [10]. The mathematical model of the process looks like this:

$$\hat{y} = b_o + \sum_{i=1}^{n} b_i x_i + \sum_{i=1}^{n-1} \sum_{j=i+1}^{n} b_{ij} x_i x_j + \sum_{i=1}^{n} b_{ii} x_i^2 , \qquad (1)$$

where $\hat{y}$ is the predicted value of the dependent variable; x_i is the factors (concentrations); n is the number of factors; b_o, b_i, b_{ij}, b_{ii} is the coefficients of the model; and i and j are indexes.

While optimizing the filling-fatliquoring process of semi-finished product of chrome tannage, the effect on the leather properties of three factors (in % of the mass of the semi-finished product) was investigated:

x_1 – Aerosil A-300;

x_2 – acrylic polymer Retanal RCN-40;

x_3 – fatliquor.

To obtain a mathematical model of the process, a zero level of the selected factors and their variation interval (Table I) was established. The experiment plan in the encoded and true values is given in the Table II.

The transition from encoded $x_i$to the technological values X_1 is carried out according to the formula:

$$x_i = \frac{X_i - X_{i0}}{\Delta X_i}, \qquad (2)$$

where X_{i0} is zero factor level and ΔX_i is the variation interval.

Table I. *Options of the experiment plan.*

Name	**Values of the factor**		
	$\mathbf{X_1}$	$\mathbf{X_2}$	$\mathbf{X_3}$
Zero level	2.0	6.0	7.0
Variation interval	1.0	1.5	1.5

Table II. *Experiment plan.*

#	**Factors that affect the process in**					
	Encoded values			**True values [% of the mass of semi-finished product]**		
	$\boldsymbol{x_1}$	$\boldsymbol{x_2}$	$\boldsymbol{x_3}$	$\mathbf{X_1}$	$\mathbf{X_2}$	$\mathbf{X_3}$
1	–1	–1	–1	1.0	4.5	5.5
2	–1	–1	1	1.0	4.5	8.5
3	–1	1	–1	1.0	7.5	5.5
4	–1	1	1	1.0	7.5	8.5
5	1	–1	–1	3.0	4.5	5.5
6	1	–1	1	3.0	4.5	8.5
7	1	1	–1	3.0	7.5	5.5
8	1	1	1	3.0	7.5	8.5
9	0	0	–1.682	2.0	6.0	4.477
10	0	0	1.682	2.0	6.0	9.523
11	0	–1.682	0	2.0	3.477	7.0
12	0	1.682	0	2.0	8.523	7.0
13	–1.682	0	0	0.318	6.0	7.0
14	1.682	0	0	3.682	6.0	7.0
15	0	0	0	2.0	6.0	7.0
16	0	0	0	2.0	6.0	7.0
17	0	0	0	2.0	6.0	7.0
18	0	0	0	2.0	6.0	7.0
19	0	0	0	2.0	6.0	7.0
20	0	0	0	2.0	6.0	7.0

Mathematical Model of the Filling-Fatliquoring Process

According to the CCRP, different variations of the filling-fatliquoring processing of the semi-finished product of chrome tannage with the corresponding consumption of the composition ingredients at 20 experimental points were carried out (Table I). The obtained values of physicochemical properties of the leather materials samples are given in Table III.

Table III. *Results of filling-fatliquoring of semi-finished product of chrome tannage.*

y_i	Experimental points																			
	1	***2***	***3***	***4***	***5***	***6***	***7***	***8***	***9***	***10***	***11***	***12***	***13***	***14***	***15***	***16***	***17***	***18***	***19***	***20***
y_1	21	25	22	28	24	30	26	32	25	36	30	27	25	29	32	33	30	31	32	30
y_2	38	35	36	34	31	29	28	29	34	28	27	30	37	30	26	26	28	27	27	29
y_3	52	54	55	57	56	63	58	65	55	68	57	59	57	67	64	66	62	63	64	63

At the same time, the effect of the concentration of ingredients of the filling composition on the leather physicochemical properties was assessed by the following indicators:

y_1 is the elongation of leather at 10 MPa load [%];
y_2 is the material stiffness [cN];
y_3 is the volumetric yield of leather material [%].

Results and Discussion

Filling-Fatliquoring of Semi-Finished Product of Chrome Tannage

To find the coefficients of the model (1), the least squares method in the matrix form was used:

$$B = (F^T F)^{-1} F^T Y = D F^T Y, \qquad (3)$$

where B is the vector of the model coefficients we have been looking for; F is the matrix of the experimental data of plan X generalized by model type $\tilde{f}^T$ at $\bar{x} = ||x_1, x_2, x_3||$ [10]; T is the matrix transposition operations; and Y is the vector-column of the dependent variable.

The experimental uncertainty S_{exp}^2 is calculated using the experimental points of the center of the plan by the formula:

$$S_{exp}^2 = \frac{1}{n_0 - 1}\sum_{i=1}^{n_0}(y_{i0} - \bar{y}_0)^2 \ \mathit{if}\ \bar{y}_0 = \frac{1}{n_0}\sum_{i=1}^{n_o} y_i. \qquad (4)$$

The significance of the coefficients of the mathematical model is verified according to Student's criterion according to the formula:

$$t\{b_j\} = \frac{|b_j|}{s\{b_j\}} > t_{tab}[q;\ f_{exp}]\ \mathit{is}\ s\{b_j\} = \sqrt{d_{jj}S_{exp}^2}, \qquad (5)$$

where q is the level of the criterion significance; $f_{exp} = n_0 - 1$ is the number of degrees of freedom; and d_{jj} is the corresponding diagonal element of the dispersive matrix D.

The coefficient of a model is considered significant when the calculated value of the Student's criterion is bigger than the one from the table. After excluding the insignificant coefficients, the adequacy of the model according to Fisher's criterion is determined. For this, the dispersion of adequacy is calculated according to the formula:

$$S_{ad}^2 = \frac{S_{res} - S_{exp}}{f_{ad}}\ \mathit{at}\ S_{res}^2 = \frac{\sum_{i=1}^{n}(y_i - \hat{y}_i)^2}{n - 1}, \qquad (6)$$

where $f_{ad} = f_{res} - f_{exp}$ and $f_{res} = n - 1$ are the number of degrees of freedom of dispersions.

Verification of the model adequacy is carried out by the formula:

$$F_{cal} = \frac{S_{ad}^2}{S_{exp}^2 \geq} F_{tab}[q;\ f_{ad}; f_{exp}], \qquad (7)$$

where F_{cal} and F_{tab} is the calculated and tabulated values of Fisher's criterion.

After calculation of the CCRP, the coefficients of the modelb_js and the corresponding estimated values of the Student's coefficients $t\{b_j\}$ are given in Table IV, and the parameters of the model adequacy is listed in Table V.

Table IV. *The coefficients of the models and the calculated values of the Student's criterion.*

b_j	Model $\hat{y}_1$		Model $\hat{y}_2$		Model $\hat{y}_3$	
	b_j	$t\{b_j\}$	b_j	$t\{b_j\}$	b_j	$t\{b_j\}$
b_0	31.4168015	—	27.1246128	—	63.7602158	—
b_1	1.6651034	5.0787764	–2.7673550	8.7441406	2.9901500	8.0843134
b_2	0.2169325	0.6616715	–0.0703569	0.2223099	0.9791284	2.6472187
b_3	2.9666979	9.0488043	–1.1784708	3.7236695	2.9197938	7.8940949
b_{12}	0.0	0.0	0.0	0.0	–0.25	0.3030457
b_{13}	0.25	0.3418818	0.5	0.7083376	1.25	1.5152286
b_{23}	0.25	0.3418818	0.5	0.7083376	0.0	0.0
b_{11}	–2.0644879	1.3310804	2.5105045	14.2742853	–1.1835907	5.7582803
b_{22}	–1.5330223	8.4140959	0.7389672	4.2016373	–2.6008203	12.6532364
b_{33}	–0.8244048	4.5248008	1.6247383	9.2379751	–1.3607414	6.6201353

Note: *the insignificant coefficients of models are highlighted in gray.*

In such way, the obtained mathematical model (8)

$$\begin{aligned} \hat{y}_1 = 31.4268 + 1.665103x_1 + 2.966698x_3 \\ - 2.064488x_1^2 - 1.533022x_2^2 \\ - 0.8244048x_3^2, \\ \hat{y}_2 = 27.12461 - 2767355x_1 - 1.17847x_3 \\ + 2.510504x_1^2 + 0.7389672x_2^2 \\ + 1.624738x_3^2, \\ \hat{y}_3 = 63.76022 + 2.99015x_1 + 0.9791284x_2 \\ + 2.91979x_3 - 1.18359x_1^2 \\ - 2.60082x_2^2 - 1.360741x_3^2, \end{aligned} \tag{8}$$

adequately describes the process of filling-fatliquoring the leather semi-finished product of chrome tannage to produce white leather. The given mathematical model was used for optimization of the investigated process.

Table V. Estimation of the model adequacy.

Parameter	Model		
	$\hat{y}_1$	$\hat{y}_2$	$\hat{y}_3$
Experimental uncertainty S_{exp}^2	1.466667	1.366667	1.866667
Tabulated Student's criterion t_{tab} [5, 5 %]	2.571	2.571	2.571
Adequacy dispersion S_{ad}^2	5.736937	4.474275	8.3434
Fisher's criterion			
– **calculated F_{cal}**	3.911548	3.27386	4.469678
– **tabulated F_{tab} [5 %; f_{ad}; f_{exp}]**	4.78 (9; 5)	4.78 (9; 5)	4.82 (8; 5)

Optimization of the Filling-Fatliquoring Process

The use of the mathematical model (8) as a target function involves solving the problem of multicriteria conditional optimization. As the resulting model includes three optimization parameters and each of them has three factors affecting the process, then the desirability function [11] was used to solve this problem:

$$D_f = \sqrt[g]{d_1 d_2 \ldots d_g}, \tag{9}$$

where g is the number of dependent variables affecting the filling-fatliquoring process; d_i $(i = 1,2, \ldots g)$ is the partial desirability function of the i-th parameter y_i, which takes values in the interval [0; 1], and it is determined by the formula:

$$d = \exp[-\exp(-y_i')], \tag{10}$$

where y_i' is the dimensionless value of quality parameter y_i, determined by the linear dependence:

$$y_i' = b_0^{(i)} + b_1^{(i)} y_i. \tag{11}$$

Coefficients $b_0^{(i)}$ and $b_1^{(i)}$ are determined from a system of equations:

$$\begin{cases} y_i'^{worse} = b_0^{(i)} + b_1^{(i)} y_i^{worse} \\ y_i'^{better} = b_0^{(i)} + b_1^{(i)} y_i^{better} \end{cases} \quad (12)$$

where y_i^{worse} and y_i^{better} $(i = 1,2, \dots g)$ is the worse and better values of the criterion of the leather semi-finished product quality y_i which is established by the researcher; and $y_i'^{worse}$ and $y_i'^{better}$ is the worse and better values of the dimensionless quality criterion which is determined based on the formula (10) according to the following equations:

$$y_i'^{worse} = -\ln(-\ln d_{worse}),$$
$$y_i'^{better} = -\ln(-\ln d_{better}), \quad (13)$$

where d_{worse} and d_{better} is the worse and better values of partial desirability functions (10) which are equal to 0.2 and 0.8, respectively.

The maximum of the desirability function F constructed according to equation (9), corresponds to the optimal filling-fatliquoring process $\bar{x}^{opt}$ which has the best compromise values of the output variables y_i $(i = 1,2, \dots, g)$.

By using the obtained mathematical model (8) and the formulas of the desirability function (9) – (12) by the scan method within [–1.68; +1.68] the optimal values for the implementation of the process are found (Table VI).

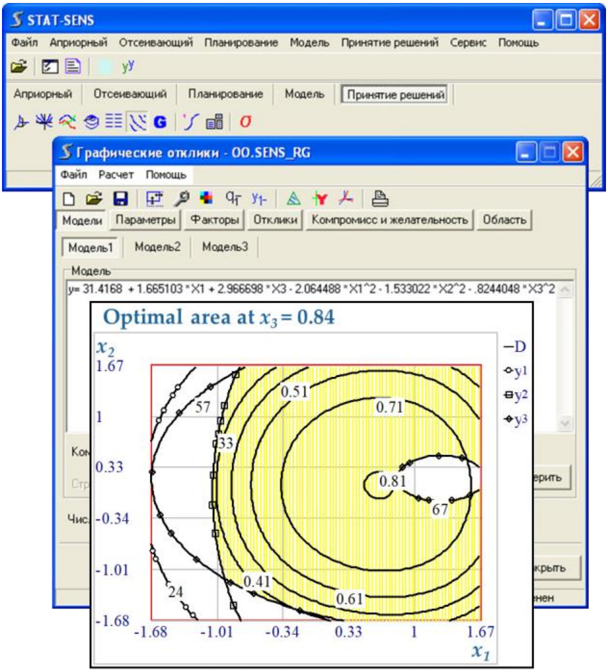
To determine the intervals of the consumption of ingredients of the filling-fatliquoring composition, it is necessary to find an optimal part of the implementation of the technological process. To do this, we need to define a compromised area of the process, namely, all possible values of the ingredients of the composition at which simultaneously the physicochemical parameters will acquire the values at given intervals of the Table VI. The compromise area, in which the isolines of the function of desirability correspond to its maximum value, is optimal for the implementation of the process and it is shown in Fig. 2 and Fig. 3.

Table VI. *The result of the process optimization by scanning method.*

i	**Coordinates of the optimum**		**Input optimization parameters**		**The optimal value of the output variable y_i**
	x_i	X_i	y_i^{worse}	y_i^{better}	
1	0.6399984	2.6399984	24	33	33.53185
2	0.09999872	6.14999808	33	27	26.54569
3	0.8399982	8.2599973	57	67	66.7535

$$D_f = 0.8119443\ ^*$$

Note: ** The number of calculations of the values of the desirability function is 37933056.*



y= 31.4168 + 1.665103 *X1 + 2.966698 *X3 - 2.064488 *X1^2 - 1.533022 *X2^2 - .8244048 *X3^2

Fig. 2. *Construction of the optimal area in $x_1 \times x_2$ at $x_3 = 0.84$.*

At the same time, when we are increasing the values of the desirability function, the values of factors and physicochemical parameters of the quality of leather material are getting improved. It should be noted that the construction of the optimal area is performed in the program STAT-SENS [12]. As it can be seen from Fig. 2 and Fig. 3, the intervals of the optimal values of the factors are within the encoded values: $x_1 = 0.5 - 0.7$, $x_2 = 0 - 0.2$, and $x_3 = 0.8 - 0.9$.

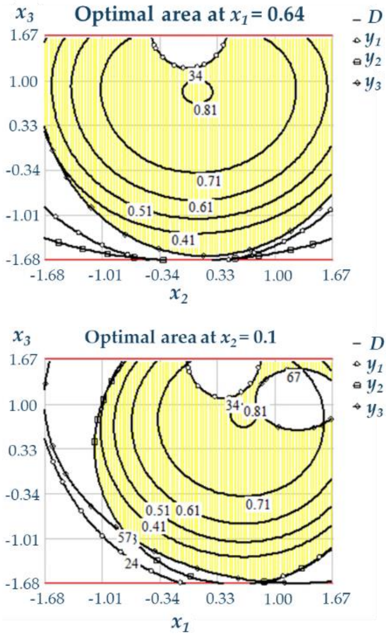


Fig. 3. *Optimal area of the filling-fatliquoring process in the coordinates:* $x_1 \times x_3$ *(a) and* $x_2 \times x_3$ *(b).*

Consequently, the optimal values of the consumption of the ingredients of the filling-fatliquoring will be equal to [in % of the mass of the semi-finished product]: 2.5–2.7 for Aerosil A-300, 6.0–6.3 for acrylic polymer Retanal RCN-40, and 8.20–8.35 for fatliquor. At the same time, the physicochemical parameters of the resulting semi-finished product acquire the following values:

elongation at 10 MPa load – 33.3–33.7 %, leather stiffness – 26.3–26.7 cN, and volumetric yield 66.5–66.8 %.

Semi-Industrial Testing of the Filling-Fatliquoring Technology

The technology of filling-greasing of leather semi-finished product of chrome tanning by using the certain optimal expenses of ingredients is tested in the conditions of the research department of PJSC Chinbar (Ukraine). In order to compare the developed technology, a production technology which involves the use of quebracho plant extract and acrylic dispersion with consumption at the stage of filling-greasing, is used, % of the semi-finished product mass: (Table 7)

Table VII. *Physicochemical properties of the filled leather semi-finished product of chrome tannage.*

Parameter	Technology	
	optimized	**current**
Color	white	light-brown
Tensile strength [MPa]	23.0	21.0
Tensile strength, grain side [MPa]	23.0	19.0
Elongation at 10 MPa load [%]	31.0	29.0
Elongation at break [%]	59.0	55.0
Stiffness [cN]	28.0	31.5
Volume yield [%]	65.0	66.0
Area yield [%]	102.6	100.0

According to the results, leather produced using Aerosil A-300 at the filling-fatliquoring stage according to the experimental technology is characterized by white color, has a higher strength of the grain side, which corresponds to the strength of the leather, and the increased elasticity compared with leather produced by using the technology of PJSC Chinbar. At the same time, due to the higher elasticity, the resulting leather has a 2.6 % increase in area, which can be explained by the more effective diffusion of highly-dispersed nano-silica into the structure of the dermis and the even distribution of the ingredients of the filling-fatliquoring composition in the structure of the formed leather.

Conclusion

The mathematical model of the second-degree of the technological process of filling-fatliquoring based on central composite rotatable plan with three input variable components of the filling composition and three physicochemical parameters of the resulting leather material was developed. The multicriteria optimization of the filling-fatliquoring process of leather semi-finished product using the desirability function and limitations of the parameter values considering their desirable values was performed. The optimal values of the consumption of the ingredients of the filling-fatliquoring composition for the light-colored leather produced from the semi-finished product of chrome tannage using Aerosil A-300 and acrylic dispersion were established. The developed technology of the filling-fatliquoring process in the formation of light-colored leather results in the production of leather material with increased elasticity, durability, and a 2.6 % increase in area yield compared with the current technology which utilizes colored tanning agents for the formation of leather materials. The resulting light-colored leather meets the requirements for elastic leather for sewing products according to DSTU 3115-95 and the requirements of the international standard of quality management systems ISO 9001: 2008. The availability of the developed filling-fatliquoring process is stipulated due to the possibility of its use in the technologies of the manufacture of light-colored leather of wide use from chrome-tanned semi-finished product.

References

[1]. **Ma J.** Elasticity studies on leather retained with various types of acrylic polymers. *Journal of the American Leather Chemists Association* **103** (2008) 363–369.

[2]. **Nashy E.** Novel retanning agents for chrome-tanned leather based on emulsion – nano particles of styrene/butyl acrylate copolymers. *Journal of the American Leather Chemists Association* **106** (2011) 241–248.

[3]. **Ostrovskaya A., Chernova A., and Latfullin I.** Fluorinated amino resins and their use in leather production (in Russian). *Bulletin of Kazan Technological University* **11** (2010) 584–585.

[4]. **Giliasov E., Petrova A., Ostrovskaia A.** Amino furazan resin as a filling and retanning reagent in the production of leather (in Russian). *Novye tekhnologii i materialy legkoi promyshlennosti* (Publisher «Новые технологии и материалы легкой промышленности») (2009) 36–40.

[5]. **Jaisankar S., Gupta S., Lakshminarayana Y., et al.** Water-based anionic sulfonated melamine formaldehyde condensate oligomer as retanning agent for leather processing. *Journal of the American Leather Chemists Association* **105** (2010) 289–296.

[6]. **D'aquino A., Barbani N., D'elia G., et al.** (2004) Combined organic tanning based on mimosa and oxazolidine: development of a semi-industrial scale process for high-quality bovine upper leather. *Journal of the Society of Leather Technologists and Chemists* **88** (2004) 47–55.

[7]. **Yan L., Zhaoyang L., Haojun F., et al.** NaNO-SiO_2/oxazolidine combination tannage: potential for chrome-free leather. *Journal of the Society of Leather Technologists and Chemists* **92** (2008) 252–257.

[8]. **Danylkovych A. and Chursin V.** Analytical control in leather and fur production: a laboratory practicum (in Russian), Infra-M, Moscow, 2016, 176 p.

[9]. **Statiukha H., Skladannyi D., and Bondarenko O.** Introduction to planning the optimal experiment (in Ukrainian). NTUU «KPI» 2011, Kyiv, 125 p.

[10]. **Danylkovych A. and Zlotenko B.** (2017) Methodology of scientific research with the fundamentals of intellectual property: textbook. Fenix (in Ukrainian) (Publisher «Фенікс») 2017, Kyiv, 433 p.

[11]. **Akhnazarova S. and Kafarov V.** Methods of optimizing the experiment in chemical technology: textbook (in Russian). *Vysshaia shkola* (Publisher «Высшая школа») 1985, Moscow, 320 p.

[12]. **Statiukha G., Kamal M., and Petran A.** The application of CAE in Polymer Processing System. CHISA’98, Prague: Process Systems Engineering 67.

21. OPTIMIZATION OF LEATHER FILLING-PLASTICIZING PROCESS USING DISPERSED SYSTEM [18]

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Abstract: *The second-degree mathematical model is obtained based on the experimental data from the PJSC Chinbar (Ukraine, Kyiv) via the experiment design. The model adequately describes the filling-plasticizing process of the semi-finished leather. The leather material was obtained from cattle raw hides of chrome tannage after its shaving to the thickness of 1.5–1.6 mm. The dispersed system of natural fats and oils: beef tallow, sunflower oil, and fish oil in a ratio of 1 : 1.75 : 2.25 % was used for plasticizing the semi-finished product. The non-ionic surface-active agent was used to emulsify the fats. The diagrams of single-factor dependencies for simulation models are obtained. The effect of the ingredients (plasticizer, modified filler, and non-ionic surfactant) of the dispersed system based on the technological properties (area yield, total content of fatty substances, and stiffness) of the leather material is investigated. The software calculation module in the Visual Basic for Application was developed to automate the calculation of the optimal composition of the dispersed system. To solve the optimization task, the module allows converting multi-criteria task into single-criterion task using maximin convolution and Hooke-Jeeves method. As a result, the optimal values of the factors that affect the filling-plasticizing process of semi-finished leather are found. The optimal values of the ingredient concentrations of dispersed system using multi-criteria constrained optimization task of the filling-plasticizing process are found. The area yield of the leather material with a minimum stiffness of 19.0 cN is*

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[18] *The title has been modified; the original title is "Optimization of leather material filling-plasticizing process using disperse system".*

increased, as compared to the control technology, by 7.0 % at the concentrations of plasticizer, modified filler, and non-ionic surfactant of 115.3, 22.5, and 23.9 g/L, respectively. Additionally, the content of fatty substances in the finished material was 7.6 %, that complies with DSTU 3115-95 "Leather for Garments. General Specifications". The developed software module can be applied for the optimization of similar technological processes.

Keywords: *Hooke-Jeeves method; optimization of filling-plasticizing process; leather material; technological property.*

Introduction

Development of innovative technologies of the leather and fur materials formation requires application of a wide range of new synthetic and natural reagents [1, 2] in the filling-plasticizing process. The efficient implementation of the process requires creating conditions for a deep diffusion of chemical particles into a microfibrillar collagen structure of the dermis. This can be performed due to the application of well-dispersed plasticizing reagents of hydrophilic and hydrophobic nature and will result in improving features of elastic polyfunctional leather materials [3, 4]. Considering the wide range of interactions between components of a filling-plasticizing system and interactions between ingredients and collagen of semi-finished structured material during the tanning process, it is necessary to create conditions for the efficient diffusion of reagents inside the structure. Thus, in the beginning of the process, the minimal interaction of the system components is provided.

Optimization of chemical composition of the above-mentioned systems is an important aspect of the problem. At the same time, it is promising to use natural materials, such as natural fats of animal and plants and natural aluminosilicates which depending on the stage of their application in the technological process are subjected to modification [4]. This is an important problem both in terms of obtaining aggregation-stable colloidal systems used in leather production technology and increasing diffusivity of reagents into semi-finished leather.

The complex ingredient composition of the filling-plasticizing dispersed system and multiple stages of structuring and formation of properties of the leather material require the use of multi-criteria optimization approach. Such an approach promotes the rational use of leather raw materials and chemical reagents. In this case, minimax convolutional optimization of the criteria of filling-plasticizing process has been used. This method allows improving the worst indicator among the technological properties of the material. After such a convolution of criteria, single-criteria optimization problem has been solved by the method of Hooke-Jeeves. This method consists of two main stages – the exploring search and pattern search (accelerating search). Accelerating search allows finding the global optimum of the function faster.

Literature Review and Problem Statement

The analysis of publications devoted to the development of innovative technologies of leather and fur materials formation showed that researchers mainly use the experiment design methods to obtain a mathematical description of the mentioned processes. In the work [5] it is shown that the theoretical model and optimal area of the chrome tanning process were obtained by using Mathcad software where the non-composite symmetric quasi-optimal plan was implemented. The mentioned software is not typically used at Ukrainian leather factories. Thus, such solution cannot be used to correct the optimum area of the process in operating mode under changing production conditions.

Plackett-Burman plan is used to decrease the number of factors from 7 to 4 [6]. The survey of the full factorial experiment to study the process of chrome tannage utilizing modern polymer material – a derivative of maleic acid was reported [7]. The adequate simulation model that describes the dependencies of semi-finished leather indicators on the consumption of basic materials and processing time is obtained. The rational conditions of tanning are identified. It should be noted that the Harrington's desirability function used for the formation of the generalized criterion of optimization is performed in the papers [6, 7]. With this approach, the formation of optimization criterion depends on the experience of the researcher [8]. The application of SWOT-analysis methods [9] in the marketing strategies area, connecting the factors of threats and opportunities, allows us to solve the problematic issues. However, it contains subjective evaluation of the company's management. It may adversely affect the activity of the company in terms of dynamics and uncertainty.

The approach proposed previously [5–8] for solving the optimization problem is associated with the complexity of the formalization and requires performing substantial calculation. In papers [10, 11] it is shown that in some cases the wrong selection of driving directions to the optimum does not lead to the desired result. The choice of the optimization method and the optimality criterion formation method have a decisive impact on the quality of the obtained solutions. Application of the modified method of Hooke-Jeeves [12] allows us to solve constrained optimization problems and to optimize the investigated processes with a higher degree and achieve the optimal area more rapidly.

Goal and Objectives of the Study

The goal of this paper is an improvement of basic technological properties of leather material formed by optimized filling-plasticizing process using the disperse system ingredients.

In accordance with the goal, the following research tasks are identified:

- to obtain simulation models that adequately describe the effect of the filling-plasticizing process using dispersed system on the technological properties of the leather material;
- to develop software module allowing automation of the calculation of the required ingredient concentration of the dispersed system;
- to optimize ingredient concentration for the filling-plasticizing process using the developed software module.

Materials and Methods

To optimize the filling-plasticizing process, semi-finished leather product is used. The semi-finished product was obtained from cattle raw hides using chrome tannage and shaved to 1.5–1.6 mm thickness. Fine-dispersed aluminosilicate (FA), modified by sodium format, was used as a filler of semi-finished product. The dispersed mixture of natural fats and oils: beef tallow, sunflower oil, and fish oil in a mass ratio of 1 : 1.75 : 2.25 % [13] is used for plasticizing the semi-finished product. The non-ionic surface-active agent was used to emulsify the fats.

The process of filling-plasticizing semi-finished product was carried out at PJSC Chinbar (Ukraine, Kyiv) at 1 : 1 ratio of water to semi-finished product at 55–60 °C. The concentrations of the plasticizer, surfactant, and aluminosilicate filler were varied, respectively, within the range: 49.6–140.4, 4.4–31.6, and 15.0–30.0 g/L.

The effectiveness of the filling-plasticizing process was determined by the concentration of the following substances which affect the technological properties of the materials [g/L]:

- plasticizer (X_1);
- modified filler (X_2);
- non-ionic surfactant (X_3).

The technological effect of the ingredients of filling-plasticizing on the properties of leather material, compared to the control technology, was evaluated by the following quality parameters:

- area yield [%] (y_1);
- the total content of fatty substances [%] (y_1);
- leather stiffness [cN] (y_3).

The area yield of the leather material was calculated as the area ratio of the produced samples of the finished leather materials to the finished leather produced by the current technology. The total content of fatty substances in the finished leather was determined as a sum of the fat in the sample extracted by the mixture of organic solvents and after the sample hydrolytic destruction by alkali solution followed by the extraction of fatty acids with ether [14]. The stiffness was measured on the PZU-12M equipment after drying-moisturizing followed by keeping samples in a desiccator at 20–22 °C and 16 % humidity for 24 h.

The central composite rotatable plan of second-degree was designed to conduct the experiment. The plan is based on the full factorial experiment, complemented by experiments in the center of the plan which allow evaluating the dispersion of reproducibility and asterisk points [15, 16]. The area of the experiment is described by the following model (1):

$$\hat{y} = b_0 + \sum_{i=1}^{n} b_i x_i + \sum_{i=1}^{n-1} \sum_{\substack{j=i+1 \\ i \neq j}}^{n} b_{ij} x_i x_j + \sum_{i=1}^{n} b_{ii} x_i^2 \tag{1}$$

where x_i and x_j are factors; n is the total number of factors b_i, b_{ij}, b_{ii} are coefficients.

This model includes the first-degree coefficients with even and quadratic interaction effects. The results of the experiment are shown in Table I.

Factors x_1, x_2, and x_3 are equal to 0 at the following ingredient concentrations: plasticizer – 90 g/ L, modified filler – 18 g/L, and non-ionic surfactant – 22.5 g/L, respectively, within their variation interval of 30, 8.1, and 4.5.

Table I. *Central composite rotatable plan of the second-order with encoded values of factors.*

#	x_0	x_1	x_2	x_3	x_1x_2	x_1x_3	x_2x_3	x_1^2	x_2^2	x_3^2
1	1	1	1	1	1	1	1	1	1	1
2	1	–1	1	1	–1	–1	1	1	1	1
3	1	1	–1	1	–1	1	–1	1	1	1
4	1	–1	–1	1	1	–1	–1	1	1	1
5	1	1	1	–1	1	–1	–1	1	1	1
6	1	–1	1	–1	–1	1	–1	1	1	1
7	1	1	–1	–1	–1	–1	1	1	1	1
8	1	–1	–1	–1	1	1	1	1	1	1
9	1	β	0	0	0	0	0	α	0	0
10	1	$-\beta$	0	0	0	0	0	α	0	0
11	1	0	β	0	0	0	0	0	α	0
12	1	0	$-\beta$	0	0	0	0	0	α	0
13	1	0	0	β	0	0	0	0	0	α
14	1	0	0	$-\beta$	0	0	0	0	0	α
15	1	0	0	0	0	0	0	0	0	0
16	1	0	0	0	0	0	0	0	0	0
17	1	0	0	0	0	0	0	0	0	0
18	1	0	0	0	0	0	0	0	0	0
19	1	0	0	0	0	0	0	0	0	0
20	1	0	0	0	0	0	0	0	0	0

Note: *The encoded values –1, 0, and 1 correspond to the bottom, zero, and top levels of the plan; –1.68 and 1.68 correspond to the asterisk points on the bottom and top levels of the plan; α and β are equal to 2.8224 and 1.68, respectively.*

The transition from the technological values X_1 to the encoded x_1 parameters is carried out using the formula (2):

$$x_i = \frac{X_i - X_{i0}}{\Delta X_i} \tag{2}$$

where X_{i0} is factor zero value and ΔX_i is the variation interval.

Model of the Filling-Plasticizing Process

To study the effect of input variables on the technological properties of the leather material, 20 batches were collected according to the experiment plan. For this reason, the method of alternating half-skins [14] was used for semi-finished chrome-tanned leather with 3 samples in a batch. The values obtained for the technological properties of semi-finished chrome-tanned leather after the filling-plasticizing process are given in Table II.

Table II. *The experimental results.*

#	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20
Y_1	105.6	98.7	103.8	96.5	101	95.1	98.4	93.2	104.7	93.7	104.3	100.9	99.3	93.6	105.9	105.2	105.1	104.3	105.6	105.4
Y_2	7.3	5.9	6.7	3.9	5.6	4.8	5.1	3.7	6.7	4.7	7.8	5.7	4.3	2.8	7.5	6.4	7.2	6.1	7.4	6.9
Y_3	24.5	28.5	23	29	22.5	24.5	32	37.5	25.5	31	17	19	33	43	17.5	20	18	22	19	21

The coefficients of the simulation model (1) were calculated using the least squares method in a matrix form (3):

$$B = (X^T X)^{-1}(X^T Y) \tag{3}$$

Using the experimental points in the center of the plan, the reproducibility dispersion is defined as

$$S_0^2 = \frac{1}{N_0 - 1}\sum_{u=1}^{N_0}(y_{u0} - \overline{y}_o)^2 \tag{4}$$

The value of the simulation model coefficients was tested by the Student's criteria:

$$t_{p_i} > t_T(f_0, q) \tag{5}$$

The criterion impact was considered significant if its estimated value exceeded a tabulated value. After the elimination of non-significant coefficients, an adequacy of the model was determined by the Fisher criterion. For this purpose, two dispersions were calculated: the residual dispersion and dispersion of adequacy using the equations (6) and (7).

$$S_{res}^2 = \frac{\sum_{u=1}^{N}(\overline{y_u} - \hat{y}_u)^2}{N - l} \tag{6}$$

$$S_{adeq}^2 = \frac{S_{res} - S_0}{f_{adeq}} \tag{7}$$

The Fisher criterion was calculated using the equation (8).

$$F_p = \frac{S_{adeq}^2}{S_0^2} \tag{8}$$

The tabulated values of the Fisher criterion were taken according to the degree of freedom of dispersions of adequacy, dispersion, and value level q, $F_T\ (f_{adeq} f_0, q)$.

As the elimination of insignificant coefficients from the obtained model led to inadequate model $F_p > F_T$, the final model includes all the factors (Table III).

Table III. *Coefficients of the simulation model.*

b_{ij}	b_0	b_1	b_2	b_3	b_{23}	b_{11}	b_{22}	b_{33}
Y_1	105.2504	3.208548	1.041569	1.940373	−0.0625[1]	−2.14613	−0.94148	−3.12048
Y_2	6.911947	0.715291	0.56637	0.521811	0.125[1]	−0.40115	−0.0291[1]	−1.16292
Y_3	19.61442	−1.95972	−1.82194	−2.07405	2.9375	2.873593	-0.75807	6.328099

Note: *The impact of factors on the technological properties of the material is insignificant.*

In this case, the calculated value of the Fisher's criterion was less than the tabulated values $F_p > F_T$, for the specified degrees of freedom (Table IV). Thus, the resulting model was adequate.

Table 4. *Determination of the model adequacy.*

Model	Y_1	Y_2	Y_3
Dispersion			
– residual	0.12902	0.03702	2.63670
– adequacy	0.22691	0.19585	4.15753
Fisher criterion			
– calculated	0.4315	0.1165	0.8669
– tabulated	4.9503	4.7351	4.7351

Thus, the mathematical model adequately describes the process of filling-plasticizing of semi-finished leather. The following mathematical model (9) was used to optimize the composition of the dispersed system:

$$\begin{aligned} y_1 &= 105.2504 + 3.208549x_1 + 1.041569x_2 + 1.940374x_3 \\ &\qquad - 2.146144x_1^2 - 0.9414786x_2^2 - 3.120475x_3^2 \\ y_2 &= 6.888165 + 0.7152907x_1 + 0.5663697x_2 + 0.5218105x_3 \\ &\qquad - 0.398291x_1^2 - 1.1600545x_3^2 \\ y_3 &= 19.61442 - 1.959721x_1 - 1.821939x_2 - 2.07405x_3 \\ &\qquad + 2.9375x_2x_3 + 2.87359x_1^2 - 0.7580667x_2^2 \\ &\qquad + 6.328101x_3^2 \end{aligned} \tag{9}$$

Optimization of the Filling-Plasticizing Composition

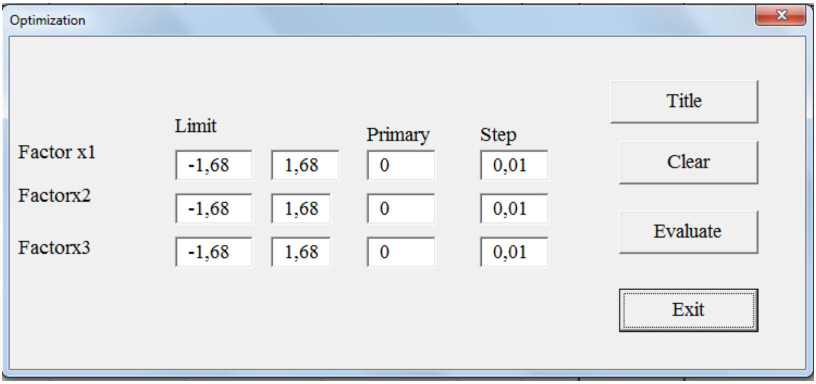
Using the simulation model (9) as an objective function specifies the solution of the multiobjective constrained optimization problem. First of all, we need to obtain a compromise solution to solve this problem. Specifically, to find values of the factors where the technological properties parameters of the material take the same values in the given range of values. The methods of the main criterion, additive and multiplicative convolution of criteria, generalized Harrington's desirability function [12, 17] can be used. In addition, the papers that describe the alternative compromise optimizing modern methods [18] are known. However, the mentioned methods are not applicable to the solution of chemical engineering problems.

In this paper, the maximin convolution of optimization criteria were used as it provides the best value of the worst criterion (10).

$$Y(x_1, x_2, x_3) = \text{minmax}\, y_1(x_1, x_2, x_3) \qquad (10)$$

According to the formula (10), the minimum value of each parameter y_1 is calculated, and the corresponding factors are determined. Optimum values of factors are defined as the maximum of the minimum value of the output variables. The method of Hooke-Jeeves, which is referred to the zero-order direct methods [12, 19], is used to solve this task. The Hooke-Jeeves method algorithm consists of two stages – the exploring search and the pattern search. The Hooke-Jeeves method specifies the starting point near the center of the test range. The starting point can be set as a random value. After that, the exploring search was conducted in the vicinity of the starting point, which allows to determine the direction of the function steepest ascent. Then, the accelerating search was carried out in the identified direction. If the function value ceased to increase, the search is conducted around the new point. If the exploring search failed in all directions and if the predetermined calculation accuracy is not reached, the step is narrowed down. The search is carried out until the optimum is found with a given accuracy [17, 18].

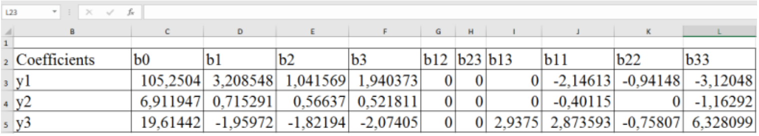
As the obtained model includes three optimization parameters and each of them contains all three factors, the software module in the Visual Basic for Application was developed to automate the calculation. It allows to specify the starting point, step size, and the factors boundaries. The main window of the module is shown in Fig. 1.



	Limit		Primary	Step
Factor x1	-1,68	1,68	0	0,01
Factorx2	-1,68	1,68	0	0,01
Factorx3	-1,68	1,68	0	0,01

Fig. 1. Main window of software module.

A user places initial data on the MS Excel sheet (Fig. 2), and then can run the calculation of the simulation model (9).



Coefficients	b0	b1	b2	b3	b12	b23	b13	b11	b22	b33
y1	105,2504	3,208548	1,041569	1,940373	0	0	0	-2,14613	-0,94148	-3,12048
y2	6,911947	0,715291	0,56637	0,521811	0	0	0	-0,40115	0	-1,16292
y3	19,61442	-1,95972	-1,82194	-2,07405	0	0	2,9375	2,873593	-0,75807	6,328099

Fig. 2. Coefficients of the simulation model in MS Excel.

As a consequence of solving the multicriteria optimization task using the software module, the factors optimal values of the leather material filling-plasticizing process were obtained. The 115.267, 22.492, and 23.883 g/L concentration of plasticizer, modified filler, and surfactant should be set, respectively.

Thus, the maximum leather material area yield $y_1 = 107.0393\ \%$, the material hardness $y_3 = 18.986$ cN, and the total content of fatty substances in the material $y_2 = 7.565\ \%$ are provided.

Analysis of the Semi-Finished Leather Filling-Plasticizing Process Simulation Model

Presented graphical diagrams (Fig. 3*a* and 3*b*) demonstrate the technological properties of leather materials and the composition of the dispersed system relationships. Namely, the increase in the plasticizer concentration in the system leads to increase in the material area yield up to the saturation point 115.27 g/L. Further increase of the plasticizer content decreased the area yield. The reason for this is that the mobility of the collagen dermis structure fibers increased up to the critical plasticizer concentration in the material during its deformation in different directions. After water removing, the degree of deformation of semi-finished leather structure was stabilized.

Influence of the modified filler and a non-ionic surfactant concentration on the leather material area yield is symbatical as compared to the plasticizer influence. However, the non-ionic surfactant provides the plasticizer and the filler particles diffusion to the product structure and their uniform distribution in the material by layers.

Effective implementation of the process of filling-plasticizing of semi-finished leather can be carried out at the optimal concentration of surfactants in the disperse system. Insufficient amount of surfactant in the system does not provide effective plasticizer particles dispersion. However, the plasticizer overdosage increases the stability of disperse system. In the former case, the plasticizer is deposited in the surface layer of the material. In the latter case, the plasticizer does not provide an active diffusion that leads to increased material shrinkage. Effect of filler on the material area yield is due to its reduction resulted from increase in thickness at a concentration above the critical value.

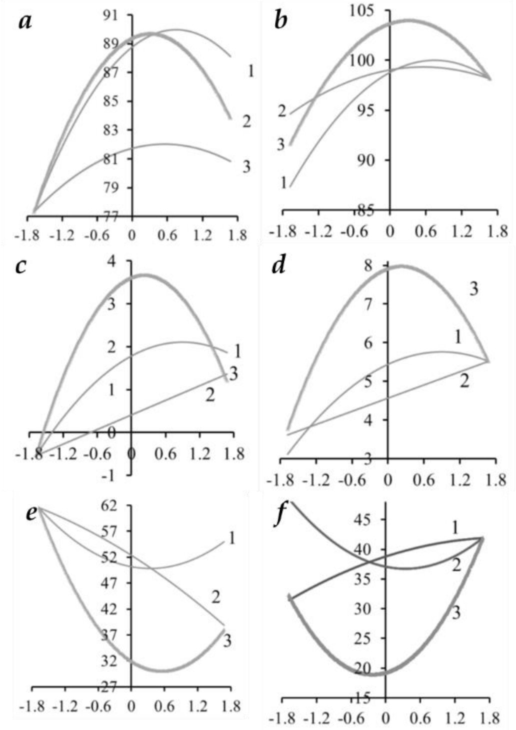


Fig. 3. *Single-factor dependency for technological properties of leather material y_1 (a, b), y_2 (c, d), y_3 (e, f) in minimum and maximum concentration area [g/L]: 1 – plasticizer, 2 – modified filler, 3 – non-ionic surfactant: a, c, e – valley region; b, d, f – peak region.*

The increase of the plasticizer concentration from 49.6 to 119.05 g/L leads to an increase of the total content of fatty substances in the leather (Fig. 3*c* and 3*d*). Further increase of fatty substances concentration in the system leads to a reduction of the total content of the plasticizer in the material. As a result, the degree of emulsification is reduced and the content in the disperse system is increased. An increase of the modified filler concentration due to the increased diffusion capacity of the hydrophilic filler leads to an increase of fatty substances content in the leather material.

The major impact on the leather hardness is caused by non-ionic surfactant concentration (Fig. 3*e* and 3*f*). The increase of concentration from 15 to 24.95 g/L leads to an increase of material elasticity that is caused by aggregate stability increase of disperse systems and reduction of diffusion of the plasticizer and filler particles in the leather structure. In this connection, the increase of surfactant concentration above the critical value leads to a decrease of the plasticizing effect of fatliquoring substances in the material structure. At the same time, the hardness of the leather material was increased.

To evaluate the influence of each factor on the area yield of leather material $W(x_i)$, the single-factor dependencies for x_1, x_2, x_3 were obtained using the equation (11).

$$W_i = (b_i + b_{ij}x_j)x_i + b_{ii}x_i^2 \qquad (11)$$

For this purpose, each plot contained only analyzed factor index effects, and the other factors were fixed at zero level. The diagrams of obtained dependencies (Fig. 4) have a similar nature.

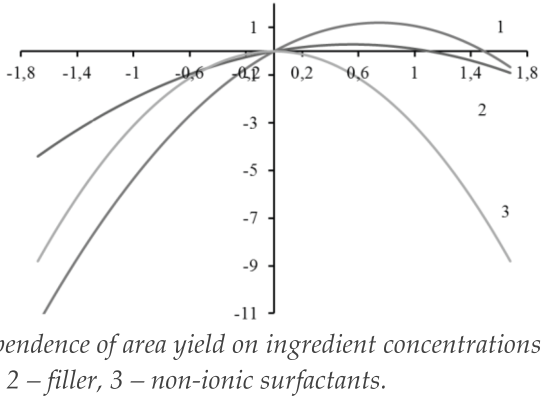


Fig. 4. *Dependence of area yield on ingredient concentrations [g/L]: 1 – plasticizer, 2 – filler, 3 – non-ionic surfactants.*

Thus, the leather material area yield is mainly affected by the concentration of plasticizer and a non-ionic surfactant. The stabilization of the filler concentration at zero level provides the optimal area of the process (Fig. 5).

Fig. 5 shows that the optimal area of the filling-plasticizing process of semi-finished chrome-tanned leather produced from cattle raw material. The optimal area is located within the plasticizer and the non-ionic surfactant concentration 84.2–123.1 and 21.8–26.6 g/L, respectively. The maximum area yield of the leather material is achieved.

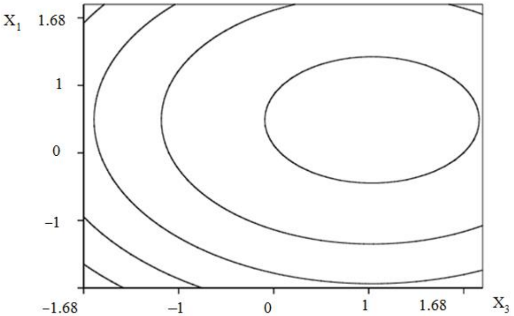


Fig. 5. Optimal area of semi-finished leather filling-plasticizing process.

Discussion of the Study Results of the Leather Filling-Plasticizing Process

The obtained optimal area of the process of filling-plasticizing of the semi-finished leather allows to increase technological properties of the product, decrease the stiffness of the leather material, and to maximize the area yield of the semi-finished product.

The area yield of leather material with a minimum hardness of 19.0 cN is increased as compared to the control technology by 7.0 % using 115.3, 22.5, and 23.9 g/L in the studied solution of plasticizer, modified filler, and non-ionic surfactant, respectively. Wherein fatty substances content in the finished material is 7.6 %, that complies with DSTU 3115- 95 “Leather for Garments. General Specifications”.

The developed software module can be used to successfully optimize technological processes of forming various composite materials.

Conclusions

The second-order mathematical model is obtained based on experimental data acquired at the PJSC Chinbar (Ukraine, Kyiv). The model describes filling-plasticizing process of the semi-finished leather adequately. The diagrams of single-factor dependencies for simulation models are obtained, and the influence of disperse system ingredients on fundamental technological properties of the leather material are analyzed.

To convert multi-criteria task into single-criterion task using maximin convolution and Hooke-Jeeves method to solve the optimization task, a software module in the VBA environment (Visual Basic for Application) was developed. The developed module implements the considered computational schemes of a compromise solution. As a result, the optimum values of the factors that influence the semi-finished leather filling-plasticizing process conditions are found.

The optimum values of the concentration parameters of disperse system ingredients using multi-criteria constrained optimization of the filling-plasticizing process are found. The area yield of leather material with a minimum hardness of 19.0 cN is increased as compared to the control technology by 7.0 % with 115.3, 22.5, and 23.9 g/L of plasticizer, modified filler, and a non-ionic surfactant, respectively. In addition, the content of fatty substances in the finished material is 7.6 % and meets the standard requirements. The developed software module can successfully be applied for the optimization of technological processes of composite materials formation.

References

[1]. **Danylkovych A., Mokrousova O., and Okhmat O.** Technology and materials for leather production (in Ukrainian). Fenix (Publisher «Фенікс») 2009, Kyiv, 578 p.

[2]. **Grigorev B.** Chemical materials and technological processing of fur and sheepskin raw materials (in Russian). OOO «Alkon Prestizh» (Publisher «Алькон Престиж») 2004, Moscow, 48 p.

[3]. **Danylkovych A.** Innovative technologies for production of leather and fur materials and products: monograph (in Ukrainian). Fenix (Publisher «Фенікс») 2012, Kyiv, 344 p.

[4]. **Hryshchenko I., Danylkovych A., and Mokrousova O.** Multifunctional leather materials (in Ukrainian). Fenix (Publisher «Фенікс») 2013, Kyiv, 268 p.

[5]. **Nikonova A., Andreyeva O., and Maistrenko L.** Application of advanced polymeric compounds for development of leather production. *IOP Conference Series: Materials Science and Engineering* **111**, 1 (2016) 012024.

[6]. **Gomes C., Piccin J., and Gutterres M.** Optimizing adsorption parameters in tannery-dye-containing effluent treatment with leather shaving waste. *Process Safety and Environmental Protection* **99** (2016) 98–106.

[7]. **Maistrenko L., Andreieva O., and Koliada M.** Investigation of the process of chrome tanning using a polymeric material - a derivative of maleic acid (in Ukrainian). *Tekhnolohii ta dyzain* (Publisher «Технології та дизайн») **4** (2013).

[8]. **Onem E., Gulumser G., Akay S., and Yesil-Celiktas O.** Optimization of tannin isolation from acorn and application in leather processing. *Industrial Crops and Products* **53** (2014) 16–22.

[9]. **Solomenko O. and Cherniuk Yu.** SWOT-analysis as the tool of marketing strategies determination (in Ukrainian). *Bulletin of the Kyiv National University of Technologies and Design* **2**, 58 (2011) 7–11.

[10]. **Kuznetsov A.** Flexible Technology Options Assessment in the Case of Complex Criteria. *Bulletin of SIBGUTI* **1** (2012) 13–22.

[11]. **Lutsenko I.** Systems engineering of optimal control. Synthesis of the structure of the technological product conversion system (part 1). *Eastern-European Journal of Enterprise Technologies* **6**, 2 (72) (2014) 28–37.

[12]. **Branovitska S., Bondarenko S., Danylkovych A., et al.** Application of modified Hooke-Jeeves method for multi-objective optimization. *Research Bulletin of the National Technical University of Ukraine "Kyiv Polytechnic Institute"* **1**, 26 (2014) 24–30.

[13]. **Mokrousova O. and Oliinyk M.** (2007). Composition for processing leather semi-finished products (in Ukrainian). UA patent for Utility Model No. U200613912; May 10, 2007.

[14]. **Golovteeva A., Kutsidi D., and Sankin L.** Laboratory practicum in chemistry and technology of leather and fur (in Russian). Legkaia i Pishchevaia Promyshlennost (Publisher «Легкая и пищевая промышленность») 1982, Moscow, 312 p.

[15]. **Adler Ju., Markova E., and Granovskii Ju.** Design of the experiment to find optimal conditions (in Russian), Nauka (Publisher «Наука») 1986, Moscow, 278 p.

[16]. **Montgomery D**. Design and analysis of experiments (in Russian). Sudostroenie (Publisher «Судостроение») 1980, Leningrad, 384 p.

[17]. **Ehrgott M.** Multicriteria optimization. Springer (2005) 328 p.

[18]. **Novakova A., Davidenko A., Kats M.** The method of compromise suboptimization for solving multicriteria problems (in Russian). *Eastern-European Journal of Enterprise Technologies* **5**, 4 (41) (2009) 39–44.

[19]. **Hamdy A.** Operation research an introduction. Prentice Hall (2005) 898 p.

22. SELECTING THE NOMENCLATURE OF QUALITY INDICATORS OF HYDROPHOBIZED FUR VELOUR BY EXPERT METHOD [19]

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Abstract: *We developed the expenditure model for fur product made of the hydrophobized fur velour which can be used at low temperatures, under large dynamic loads, and high humidity (rain and snow). Scientific and regulatory documentation on existing nomenclature of quality indicators of fur semi-finished products was analyzed. A common list of quality indicators of the fur velour was compiled. Questionnaires and instructions were developed and an expert group was formed. The results of the performed survey were processed using the author's application program. Significance of quality parameters of the hydrophobized fur velour was defined. To assess the hydrophobized fur velour, the questions about which properties new materials should have and which indicators will determine the formation of the quality semi-finished product remain relevant. Significance of indicators, characterizing the hydrophobized fur velour quality was determined. Nomenclature of these indicators includes the finishing, color design of skin tissue and hair, dynamic water permeability, vapor and air permeability, total thermal resistance, tensile strength, and total, residual, and elastic elongation at 4.9 MPa load. For further research, in the process of ranking, three groups of indicators that characterize the functional (exploitational), aesthetic, and ergonomic (hygiene) properties were selected and their significance was defined. For the consumer it is important that clothes, made of fur velour, which is exploited not only at low temperatures and dynamic loads, but also in*

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[19] *The original paper was published in Ukrainian.*

conditions of specific precipitations such as rain, sometimes even snow, had proper moisture resistance. The nomenclature of indicators of consumer properties is sufficient for an objective assessment of complex quality indicator of hydrophobized fur velour, which is confirmed by the high concordance of opinions of specialists, who participated in the expert survey (concordance coefficient was 0.894).

Keywords: *hydrophobized fur velour; quality indicator; water permeability of skin tissue.*

Introduction

The quality problem remains one of key problems and it is still relevant today. Final products should be endowed with the properties in which the potential consumer is interested and should satisfy the customer needs in full.

Any research in the field of commodity science is conditioned by the peculiarities of the structure, properties, technological processing, and operating conditions of the final product. Each researcher, while solving scientific task, must consider this. Today, various methods, one of which is hydrophobization, are used to improve the consumer properties of fur materials used for the production of clothing exploited in conditions of low temperatures, dynamic loads, and high humidity. This method acquires further development, through the introduction of new approaches and technologies that require checking the quality indicators of the final product for compliance with established regulations and consumer needs. To ensure an objective assessment of the quality of the product, it is important to select and determine the significance of consumer characteristics considering the conditions under which the product will be used.

In order to evaluate the semi-finished product, it is necessary to determine the nomenclature of these indicators, which is one of the most important stages in the process of such assessment, according to experts. The questions of which properties new materials should have and which indicators will determine the formation of the quality semi-finished product remain relevant.

Literature Review and Problem Statement

Ensuring an objective assessment of the quality of any product requires, first of all, an analysis of the conditions of its exploitation. Considering the results of the performed analysis, it is possible to develop the nomenclature of indicators of consumer properties necessary for performing commodity evaluation. The properties and quality of materials having a complex structure and a heterogeneous composition, can be characterized by a large number of indicators. Fur materials have certain structural features that should be considered during quality assessment. The main structural elements, skin tissue and hair, are characterized by a number of individual indicators. These two components should be considered as a system of interconnected components, characterized by the integrity and the specificity of the manifestation of qualitative properties.

The quality of fur velour, provided that it meets the existing standards, is determined by the characteristics of the hair and skin tissue. The nomenclature of indicators of consumer properties for fur products is fixed in regulatory documentation [1] and includes 36 indicators divided between five groups of properties. Numerous works have been devoted to the development of the classification of consumer properties for fur. An attempt to develop a unified nomenclature of fur properties based on the analysis of more than 350 terms, used to characterize the consumer properties and characteristics, was carried out by Russian scientists [2]. Based on an analysis of all existing classifications, a standard classification of the properties of a fur semi-finished product for the automated design of fur garments was proposed [3, 4]. A nomenclature of property indicators was proposed for assessing the quality of industrial products, including raw fur materials [5]. At the same time, each researcher solved a particular scientific task. Any commodity research study determines its goal and objectives, and therefore often requires a well-founded approach to choosing of nomenclature of indicators of consumer properties.

The Goal and Objectives of the Research

The goal of the research was to determine by an expert method the significance of quality indicators of hydrophobized fur velour used at low temperatures, high humidity, and under dynamic loads. The objective was set to choose individual indicators characterizing hydrophobic fur velour and their ranking and to determine the significance of indicators.

The following objectives were determined:

- to build a consumption model for a fur product from hydrophobic fur velour exploited at low temperatures, high humidity (snow and rain), and under significant dynamic loads;
- to analyze scientific and regulatory documentation on available nomenclatures of quality indicators of fur semi-finished products;
- to make a general list of quality indicators of fur velour;
- to develop questionnaires, instructions, and form an expert group;
- to conduct questionnaires and process questionnaires;
- to determine the significance of quality indicators of hydrophobized fur velour;
- to establish consistency of expert's opinions and determine the statistical significance of the results on the importance of quality indicators for hydrophobized fur velour.

Materials and Methods

Materials Used in the Experiment

In the experiments we used hydrophobized sheepskin [6] and nutria [7] fur velour. Semi-finished product from sheepskin with inconsistency in the wool and from male nutria was treated with an abrasive cloth [8] of grain 4–5. Fur velour based on the quality of skin meets all the requirements [9, 10]. For the hydrophobization of velour we used a composition based on α-alkenes C_{20-24} polymerized with maleic anhydride and a few chemical reagents [11].

Methods for Determining the Significance of Quality Indicators for Hydrophobized Fur Velour

To achieve the goal, we used the following methods in the work. The analytical method of investigation was applied for:

- constructing a consumption model for a fur product from hydrophobized fur velour exploited at low temperatures, high humidity (snow and rain), and under significant dynamic loads;
- analysis of scientific and regulatory documentation on the available nomenclatures of quality indicators of fur semi-finished products and compiling a general list of quality indicators of fur velour.

To determine the most significant individual quality indicators for hydrophobized fur velour we used an expert method based on considering and generalizing the opinions of experts in the field of technology and commodity management of fur products. The expert method was implemented in the process of developing questionnaires, instructions, and forming an expert group. Highly qualified scientists of the Departments of Leather and Fur Technology and the Department of Design and Technology of Leather Products at the Kiev National University of Technology and Design, the Department of Expertise and Customs at the Poltava University of Economics and Trade, and specialists of the private JSC Chinbar took part in the survey. The expert group of specialists ensured the formation of a qualified judgment on the system of indicators which would allow providing an objective assessment of the quality of hydrophobic fur materials. The specialists of the expert group has a thorough knowledge of the range of fur materials, their manufacturing techniques, methods of properties assessment and quality control, requirements, and needs of consumers [12, 13].

The method of ranking, in which specialists determined the place of a certain individual quality index of hydrophobized fur velour in the system of these indicators, was applied at the stage of processing the questionnaires. Based on the available knowledge and experience, experts on the proposed methodology ranked each indicator, which entered the selected list in accordance with their weighted opinions. At the same time, the most important indicator got 1 point. Since the specialists, in some cases, did not give preferences to these or other individual indicators, they provided them with the same ranks. To obtain a normal ranking of the quality indicators, which have been studied, by the algorithm of the rank correlation method [14], the indicators, which had the same ranks, were provided the ranks equal to the average value of the places. The process of ranking becomes clear from the calculations based on the data of the first expert (Table I): the individual indicators $x_{1.5}$ and $x_{3.2}$ got the first and second places, therefore they were given the rank (1 + 2) / 2 = 1.5 (Table II); the indicators $x_{1.6}$, $x_{1.8}$, $x_{2.1}$, $x_{2.4}$, $x_{3.1}$ got places from 3 to 7, accordingly they were given the rank (3 + 4 + 5 + 6 + 7) / 5 = 5, etc.

Mathematical and statistical methods were used at the final stages of the study to determine the significance of the quality indicators of hydrophobized fur velour, establishing the consensus of experts' opinions by calculating the concordance coefficient, and solving the question of the statistical significance of the obtained results.

To establish the consistency of opinions of experts, the concordance coefficient [15] was used using the following formula:

***Table I**. Output matrix of ranking of individual quality indicators of fur velour.*

Indicator		**The rank of the indicator assigned by the expert**								
number	**designation**	***1***	***2***	***3***	***4***	***5***	***6***	***7***	***8***	***9***
1	x_1	1	1	1	1	1	1	1	1	1
1.1	$x_{1.1}$	5	11	13	12	13	8	10	11	13
1.2	$x_{1.2}$	3	6	3	4	7	4	5	5	6
1.3	$x_{1.3}$	5	6	9	7	6	9	7	9	10
1.4	$x_{1.4}$	3	9	6	4	4	7	4	8	5
1.5	$x_{1.5}$	1	2	1	2	1	1	1	2	3
1.6	$x_{1.6}$	2	3	5	3	2	3	3	2	4
1.7	$x_{1.7}$	5	7	8	8	8	7	6	8	7
1.8	$x_{1.8}$	2	1	2	1	1	1	2	1	1
2	x_2	2	2	1	2	1	1	2	1	1
2.1	$x_{2.1}$	2	4	7	5	4	7	4	4	5
2.2	$x_{2.2}$	3	2	6	2	3	4	3	3	4
2.3	$x_{2.3}$	5	7	7	8	9	6	8	7	8
2.4	$x_{2.4}$	2	2	4	2	3	3	3	3	3
2.5	$x_{2.5}$	4	8	8	9	10	9	9	10	11
2.6	$x_{2.6}$	4	3	10	10	11	10	9	11	10
2.7	$x_{2.7}$	4	10	14	11	12	11	10	12	12
3	x_3	3	2	3	3	2	3	3	3	3
3.1	$x_{3.1}$	2	1	2	1	2	2	1	2	2
3.2	$x_{3.2}$	1	5	8	6	5	6	5	6	8
3.3	$x_{3.3}$	6	12	15	13	14	12	11	13	14

$$W = \frac{S}{\frac{1}{12}\left[m^2(k^3 - k) - m\sum_{j=1}^{m} T_j^{(i)}\right]} \qquad (1)$$

where $S = \sum_{j=1}^{k}\left(\sum_{i=1}^{m} r_{ij} - \bar{r}\right)^2$, $\bar{r} = 1/k\sum_{i=1}^{m}\sum_{j=1}^{k} r_{ij}$ is the average sum of ranks; $T_j^{(i)} = \sum_{j=1}^{p}(t_j^3 - t_j)$ is the index of fractional ranks; t_j is the number of identical (related) ranks in the p-group of i-ranging; p is the number of groups of related ranks in the i-row;

m is the number of experts; k is the number of individual quality indicators.

Table II. *Matrix of transformed individual quality indicators of fur velour and calculation of the results of the expert estimation.*

Expert	Indicator rank r_{ij}																			
	x_1	$x_{1.1}$	$x_{1.2}$	$x_{1.3}$	$x_{1.4}$	$x_{1.5}$	$x_{1.6}$	$x_{1.7}$	$x_{1.8}$	x_2	$x_{2.1}$	$x_{2.2}$	$x_{2.3}$	$x_{2.4}$	$x_{2.5}$	$x_{2.6}$	$x_{2.7}$	x_3	$x_{3.1}$	$x_{3.2}$	$x_{3.3}$
1	1	15.5	9	15.5	9	1.5	6	15.6	5	2	5	9	15.5	5	12	12	12	3	5	1.5	18
2	1	17	10.5	10.5	15	4	6.5	12.5	1.5	3	8	4	12.5	4	14	6.5	16	2.5	1.5	9	18
3	1.5	16	4	14	7.5	1	6	12	2.5	2	9.5	7.5	9.5	5	12	15	17	3	2.5	12	18
4	1	17	7.5	11	7.5	4	6	12.5	1.5	2	9	4	12.5	4	14	15	16	3	1.5	10	18
5	1.5	17	11	10	7.5	1.5	3.5	12	1.5	2	7.5	5.5	13	5.5	14	15	16	3	3.5	9	18
6	1.5	13	6.5	14.5	11	1.5	4.5	11	1.5	2	11	6.5	8.5	4.5	14.5	16	17	3	3	8.5	18
7	1	16.5	9.5	12	7.5	1.5	5	11	3	2	7.5	5	13	5	14.5	14.5	16.5	3	1.5	9.5	18
8	1.5	15.5	8	13	12	3	3	11.5	1	2	7	5.5	10	5.5	14	15.5	17	3	3	9	18
9	1.5	17	9	13.5	7.5	3.5	5.5	10	1	2	7.5	5.5	11.5	3.5	15	13.5	16	3	2	11.5	18
$\sum r_{ij}$	12	145	75	114	84	21.5	45	108	18.5	16	72	52.5	106	42	124	123	144	27	23.5	80	162
$\sum r_{ij} - \bar{r}$	-6.5	59	-10.5	28.5	-1.5	-64	-40.5	22.5	-67	-2	-13.5	-33	20.5	-43.5	38.5	37.5	58	8.5	-62	-5.5	76.5
Δ_j^2	42	3481	110	812	2.3	4096	1640	506	4489	4	182	1089	420	1892	1482	1406	3364	72	3844	303	5852
$\sum \tilde{r}_{ij}$		36	106	66.5	97	159	135.5	72.5	162		109	128	74.5	138.5	56.5	57.5	37		157	101	18.5

Note: $\Delta_i = \sum r_{ii} - \bar{r}$; $\sum \tilde{r}_{ii} = \left(\sum r_{ii}^{max} + \sum r_{ii}^{min}\right) - \sum r_{ii} = (\mathbf{162} + \mathbf{18.5}) - \sum r_{ii}$.

To simplify the processing of the results of the quality of the hydrophobized fur velour and the implementation of complex mathematical calculations, the applied author's program was developed and used based on the Microsoft Excel software.

Results of Determining the Significance of Quality Indicators of Hydrophobized Fur Velour

According to the regulatory nomenclature of quality indicators [1], it is problematic to carry out studies on assessing the quality of natural fur materials. A large number of quality indicators complicate, increase the cost, and slow down the process of evaluating and comparing the quality of fur velour of various types of processing. Therefore, it is important, first of all to establish a nomenclature of properties sufficient to assess the complex quality indicator of the studied materials [16].

For the main indicators that determine the quality of fur velour were taken the quality indicators of the dressed undyed fur skins for the case when the product is used flesh-side up [1]. The group of indicators of resistance to external influences concerning the resistance of the film coating and the resistance of hair to friction and their lightfastness has been replaced by ergonomic (hygienic) indicators [17]. Given that the individual hygienic indicators, which are determined in static conditions, are not significant for the chosen object of research, because the fur velour is used under dynamic loads of the external environment and must be protected from moisture, therefore, in determining the complex quality indicator, they were not considered [17]. Also, the composition and structure indicators [1] have not been considered, because in the manufacture of fur materials, their control and reliability indicators are specified as a part of production technology, characterizing the average shelf life.

The overall nomenclature of individual indicators provided to experts for ranking included

– indicators of functional properties:

1.1 load at skin tissue fracture [N];
1.2 tensile strength of skin tissue [MPa];
1.3 elongation of skin tissue at break [%];
1.4 total elongation of skin tissue at 4.9 MPa load [%];
1.5 residual elongation of skin tissue at 4.9 MPa load [%];
1.6 elastic elongation of skin tissue at 4.9 MPa load [%];
1.7 coefficient of ductility of skin tissue;

1.8. total heat resistance of the fur skins [°C m^2/W).

– indicators of ergonomic (hygienic) properties:

2.1 air permeability [$m^3/(m^2 \cdot s)$];

2.2 vapor permeability [$kg/(m^2 \cdot s)$];

2.3. steam capacity [g/s];

2.4 water wetting in dynamic conditions [s];

2.5 water permeability in dynamic conditions [kg];

2.6 moisture capacity under 2 h dynamic conditions [%];

2.7 moisture transfer [%].

– indicators of aesthetic properties:

3.1. coloring of the dermal tissue and hair of the fur velour;

3.2 finishing of dermal tissue;

3.3 finishing of hair.

The results of the ranking by experts of individual quality indicators of fur velour were summarized in Table I.

The opinions of experts are considered more consistent when the concordance coefficient approaches unity. Calculation of the concordance coefficient was performed based on the data of Table II.

According to the Table II, the average amount of ranks was $\bar{r} = 1/18 \cdot 1539 = 85.5$. The auxiliary calculations of $\sum r_{ij} - \bar{r}$ and Δ_j^2 were also listed in the Table II. Given that the experts assigned to the separate individual quality indicators the same ranks, the calculation were performed to determine the sum of fractional ranks $\sum_{j=1}^{m} T_j^{(i)}$. The results of the calculation are given in Table III.

The value of the concordance coefficient $W = 0.894$ indicates a high consistency of opinions of specialists whose statistical significance is confirmed by the Pearson criterion, χ^2 was determined by the following formula:

$$\chi_c^2 = m(k-1)W > \chi_T^2(f, q) \qquad (2)$$

where χ_c^2 and χ_T^2 are the calculated and tabular critical value of the Pearson test; $\chi_T^2(f, q)$ is the tabular critical value of Pearson's criterion for $f = k\!-1$ degrees of freedom and significance level $q = 0.05$.

$$\chi_c^2 = 136.7726 > \chi_T^2(18-1=17, 5\ \%) = 27.587$$

Table III. *Calculation of fractional ranks* $T_j^{(i)}$.

Expert	t_j						t_j^3						$t_j^3 - t_j$						$T_j^{(i)}$
1	4	3	2	5	3	0	64	27	8	125	27	0	60	24	6	120	24	0	234
2	2	3	2	2	2	0	8	27	8	8	8	0	6	24	6	6	6	0	48
3	2	3	2	2	0	0	8	27	8	8	0	0	6	24	6	6	0	0	42
4	2	3	2	2	0	0	8	27	8	8	0	0	6	24	6	6	0	0	42
5	2	2	2	2	0	0	8	8	8	8	0	0	6	6	6	6	0	0	24
6	2	2	3	2	2	2	8	8	27	8	8	8	6	6	24	6	6	6	54
7	2	2	2	2	3	2	8	8	8	8	27	8	6	6	6	6	24	6	54
8	2	2	3	2	0	0	8	8	27	8	0	0	6	6	24	6	0	0	42
9	2	2	2	2	2	0	8	8	8	8	8	0	6	6	6	6	6	0	30
$\sum_{j=1}^{m} T_j^{(i)}$																			5

Discussion of Results

Considering the significance of concordance coefficient, a rank diagram was constructed in which the quality indicators are plotted along the abscissa and the sum of ranks, $\sum \tilde{r}_{ij}$, are plotted along the ordinate. If the diagram is constructed in the coordinates "quality indicators – the sum of the ranks ($\sum r_{ij}$)", then the smallest sum of ranks corresponds to the more influential quality indicator. Therefore, for clarity, the diagram is constructed in the coordinates "quality indicator – $\sum \tilde{r}_{ij}$" (Fig. 1), so that the most significant quality indicator corresponds to the largest amount of ranks $\sum \tilde{r}_{ij} = 180.5 - \sum r_{ij}$.

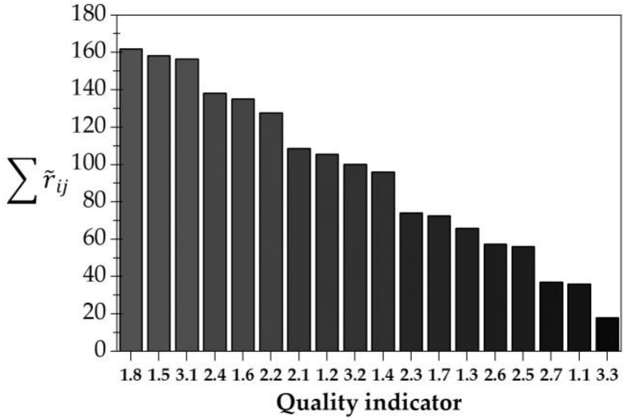

Fig. 1. *Histogram of ranking of individual quality indicators of fur velour.*

From Fig. 1 it can be seen that the individual indicators that affect the quality of fur velour and can be divided into five groups: I – $x_{1.8}$, $x_{1.5}$, $x_{3.1}$; II – $x_{2.4}$, $x_{1.6}$, $x_{2.2}$; III – $x_{2.1}$, $x_{1.2}$, $x_{3.2}$, $x_{1.4}$; IV – $x_{2.3}$, $x_{1.7}$, $x_{1.3}$, $x_{2.6}$, $x_{2.5}$; V – $x_{2.7}$, $x_{1.1}$, $x_{3.3}$, between which there are transitions, respectively, 18.5, 19.5, 22.0 and 19.5 ranks. Significant indicators of quality include the indicators of the first three groups due to a slightly increased rank between them.

The obtained results of calculations (Table II) by groups of indicators prove that the most important indicators of quality are indicators of functional (exploitational) properties x_1. This is also confirmed by the calculations of the average ranks of the separate groups – the first place is occupied by the indicators of functional (exploitational) properties whose average rank is 44.8, the intermediate place belongs to the indicators of aesthetic properties with an average rank of 51.8, and the indicators of ergonomic (hygienic) properties took the third place with an average rank 55.5.

According to the research results, it is established that a water wetting in dynamic conditions is one of the main indicators of the quality of the materials being studied. After all, for the consumer it is important that the clothes made from fur velour, which is used not only at low temperatures and dynamic loads, but also when it is snowing, and sometimes even raining, had an adequate resistance to moisture. This quality indicator is directly related to the aesthetic properties (coloring of skin tissue and hair, dressing of flesh side), and significantly affects its functional (exploitational) properties.

Conclusions

According to the results of the expert examination, individual indicators have been established that significantly affect the quality of fur velour. Those indicators include the total thermal resistance of the fur skin, the relative residual, elastic, and total elongation of skin tissue at 4.9 MPa load, the coloring of skin tissue and hair, water wetting of skin tissue in dynamic conditions, vapor and air permeability, and tensile strength of skin tissue.

The significance of indicators for calculating the complex quality indicator of hydrophobized fur velour is determined. The significance of the essential quality indicators μ_i, which is determined as a fraction from the division of the corresponding to the significant individual indicator of the sum of ranks $\sum \tilde{r}_{ij}$ to the total sum of ranks of significant individual quality indicators.

In future studies, we are going to calculate a complex quality indicator of fur velour based on the significance of important quality indicators.

References

[1]. GOST 4.420-86. The system of indicators of product quality. Fur dressing. Nomenclature of indicators (1986), 21 p.

[2]. **Ganz S., Kotova N., Tsvetkov L., and Bessedin A.** Terminology – the most important factor in the formation of information technology fur (in Russian). Proceedings of the Interregional Scientific and Practical Conference; Moscow; 2002; 100–104.

[3]. **Filimonov V., Shalmina I., and Dolgacheva O.** Classification of fur semi0finished product for semi-automated design of fur garments (in Russian). Proceedings of the Interregional Scientific and Practical Conference "The development of the fur industry in Russia"; Moscow; 2003; 63–69.

[4]. **Shitnik Y.** Development of classification of fur raw materials for garment design using rational assortment series (in Russian). *Legkaia Promyshlennos*t (Publisher «*Легкая промышленность*»), **3** (2000).

[5]. **Lifits I.** Formation of competitiveness of goods and services (in Russian). *Iurait-Izdat* (Publisher «*Юрайт-Издат*») 2004, Moscow, 335.

[6]. GOST 28509-90. Sheepskin not dressed. Specifications (in Russian), (2006), 13 p.

[7]. GOST 2916-84. Nutria pelts not dressed. Specifications (in Russian), (1997), 9 p.

[8]. GOST 5009-82. Fur, polished tissue- and paper-based. Specifications (in Russian). (2002), 11 p.

[9]. GOST 1821-75. Wool sheepskin dressed. Specifications (in Russian). (1997), 12 p.

[10]. GOST 12133-86. Nutria fur dressed. Specifications (in Russian) (2002), 12 p.

[11]. **Danylkovych A., Khliebnikova N., Mokrousova O., and Petko I.** Composition for hydrophobization of fur skins, fur velour, wool sheepskin and products made from them (in Ukrainian). UA patent for Utility Model No. 38472; January 12, 2009.

[12]. **Danylkovych A.** Innovative technologies for production of leather and fur materials and products: monograph (in Ukrainian). *Fenix* (Publisher «*Фенікс*») 2012, Kyiv, 344 p.

[13]. **Bereznenko M., Savchuk N., Bereznenko S., *et al.*** Certification of quality systems and products in light industry (in Ukrainian). *Logos* (Publisher «*Логос*») 1996, Kyiv, 229 p.

[14]. **Kendall M.** Rank Correlation Methods. Hafner Manufacturing Company. 1955, New York, 196 p.

[15]. **Danylkovych A. and Shkaranda I.** (1983). Optimization of the tanning process using water-soluble oil refining products (in Russian). *Tekhnologiia Legkoi Promyshlennosti* (Publisher «*Технология легкой пром-сти*») **1**, 47–50.

[16]. **Danylkovych A., Omelchenko N., and Khliebnikova N.** Determination of consumer properties of waterproof wool sheepskin (in Ukrainian). *Tovaroznavchyi Visnyk* (Publisher «*Товарознавчий вісник*»), **3**, (2011) 73–78.

[17]. GOST 4.11-81. System of product quality indicators. Leather. Nomenclature of indicators (in Russian). (1981), 16 p.

23. ASSESSMENT OF HYDROPHOBIC SHEEPSKIN FUR VELOUR QUALITY [20]

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Abstract: *We have determined the scope of dimensional quality indicators for sheepskin fur velour according to the desirability scale based on specifications, technical documentation, expert assessments, scientific publications, and research findings. Based on the dimensionless parameters of quality, we calculated desirability functions for individual quality indicators and a complex quality indicator for hydrophobic sheepskin fur velour produced according to a developed technology. We have also compared its qualities to those of fur velour obtained by traditional technology. In terms of the increasing necessity to satisfy the Ukrainian consumer, we have attempted to predict the possibility of using hydrophobic sheepskin fur velour in conditions of high humidity. It is determined that a complex quality indicator for hydrophobic fur velour is significantly higher than a complex quality indicator for fur velour produced according to a typical technology, especially after its exposure to rain. Before the test, the hydrophobic fur velour was rated as excellent. The impact of rain on the hydrophobic fur velour has led to a slight decrease of the complex quality indicator. It was rated as good, which is close to excellent. After exposure to rain, fur velour treated with alkenyl maleic anhydride composition completely satisfies consumer needs and can be used in wet conditions, low temperatures, and under dynamic loads. It is determined that a perspective direction in producing high-quality sheepskin fur velour involves using a technology of its finishing with alkenyl maleic anhydride composition, which is aimed at better exploitational, hygiene,*

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[20] *The original paper was published in Ukrainian.*

and aesthetic properties. This will specify new directions and spheres of using sheepskin fur velour, expand the assortment, increase the competitiveness of sheepskin products of Ukrainian origin, and shape the export potential, which is conditioned by the free trade zone, Agreement on association with EU, and modern world integration processes.

Keywords: *complex quality indicator; hydrophobic sheepskin fur velour.*

Introduction

The main aspect of the quality of any product is to focus on the consumer needs. Thus, the quality is determined by a set of properties that are aimed at meeting the customer needs. The complexity of the problem is that not only the properties of products but also the corresponding consumer needs change independently of each other. Ensuring the satisfaction of real and potential needs of consumers is possible through, in particular, by introducing new technological solutions.

The relevance of the proposed study is based on the fact that the justification of the feasibility of introducing new types of processing into production is possible by assessing the level of quality of the final products based on a comprehensive assessment of quality indicators of tested and control samples.

Analysis of Literary Data and Problem Statement

In recent years, the importance of quality as an important component of the activity of companies and society as a whole is increasing [1]. Therefore, there is a need to develop objective methods of quality assessment. Priority of comprehensive assessment, which was based on the procedure of comprehensive quality assessment, known from qualimetry [2], within the methodological complex “Assessment of shoe comfort”, from the standpoint of the authors [3] will help in organizing and implementing product quality management system.

The article [4] considers the introduction of a product quality management system at companies based on international standards ISO 9000 series. The standard will ensure product quality control at all stages of production, simplify and accelerate customer interaction procedures, increase customer satisfaction, significantly reduce the number of defects and production costs, increase profits, improve the organization of enterprise management, and attract investment.

The article [5] explores ways to improve product quality. An algorithm for improving product quality has been developed, which allows comparison of current values of quality indicators with the planned ones considering the proposed quality limits. The advantage is considering the level of satisfaction of requirements and consumer expectations regarding product quality. Using the developed algorithm, each consumer has the opportunity to choose products depending on the proposed limits of quality improvement, set by qualified experts. Quality limits are chosen based on the Kano model, which characterizes the level of consumer satisfaction, and decisions are made on the adequacy of the level of product quality improvement. To improve product quality, it is necessary to assess the level of quality of the product, which should be based primarily on a careful study of current and future demand for products, analysis of consumer feedback, opinion of competent experts and qualified personnel, and more. For this purpose, it is expedient to form processes and indicators of product quality to define ways of achievement of a necessary level of quality and competitiveness of production.

Ecologically-oriented technologies of retanning processes during leather production, using a series of multifunctional materials based on natural minerals montmorillonite and zeolite, are proposed. As a result, the leather with improved performance and hygiene properties can be produced with increased efficiency of utilization of raw materials and chemicals, while the burden on the environment can be reduced. These technologies also increase the competitiveness of the manufacturing industry domestically and globally [6].

The proposed structural diagram of ergonomic indicators will allow improving the quality of clothing development and conducting quality assessment considering the complex indicator of ergonomic requirements. The structure and model of the system for assessing the complex ergonomic quality indicator of clothing can be the basis for the development of a draft standard for determining the nomenclature of clothing quality indicators. The suggested methodical recommendations can be applied when conducting scientific and technical examination of standards for the nomenclature of product quality indicators and assessing the scientific and technical level of standards for the development of methodological documents for assessing the technical level and quality of products and developing automated information systems for managing product quality [7].

In work [8] the technique for estimating the quality of process of chrome tannage of hides is discussed. Ways of improving the control process by analyzing the factors that affect the possibility of the appearance of defects are suggested. The classification of defects and the algorithm for prevention of various defects at each stage of technological process is developed. This approach improves the quality of controlling chrome tannage of hides and ensures the quality of the final product.

Recently, the quality of clothing has become critical [9]. To ensure the entry of quality products to the domestic market and to promote competition, domestic producers need to use high-quality raw hides and materials. The article proves the necessity and carries out a comprehensive assessment of the quality of materials for clothing.

As a material for the production of clothing fur velour can be used. The quality of fur velour from sheepskin, like any other fur material, is formed in the production process and is ensured by the properties of raw hides, chemical materials, the type of technology used, the qualifications of workers, the organization of production, etc. In particular, the quality of fur materials meeting the requirements of standards is determined by the presence of defects and determining the quality level of the fur semi-finished product [10]. However, such assessment does not provide a complete description of the product, which must have properties that correspond to both the material and social needs of the consumer, and the properties that meet the timely demands.

The Goal and Objectives of the Study

Since during the exploitation of the products a whole set of needs are getting satisfied, the product must have such a set of properties that are able to satisfy all the needs in full. Considering the effect of all properties is possible only by combining individual indicators of properties into a complex quality indicator. Quality assessment is performed to determine the consumer value of the product. During the differentiated assessment, individual properties and parameters of the product are analyzed, which does not allow to unambiguously answer the question about the quality degree of the product as a whole. A more effective method of assessing the improvement in the technical level and quality of goods, improving technology, and organization of production is a comprehensive assessment of the quality of final products. The goal of the study is to conduct a comprehensive assessment and determine the quality level of hydrophobized sheepskin fur velour produced by a developed technology [11].

The objectives of the study are:

- to determine limits of dimensional quality indicators of sheepskin fur velour on a scale of desirability;
- to calculate the functions of desirability of individual quality indicators based on dimensionless quality indicators;
- to calculate a complex quality indicator for hydrophobized sheepskin fur velour and other samples under study;
- to predict the possibility of using hydrophobized sheepskin fur velour in conditions of high humidity.

Materials and Methods for Assessing the Quality of Hydrophobized Sheepskin Fur Velour

As the object of the study, we selected hydrophobized fur velour from sheepskins [12]. For hydrophobizing fur sheepskin velour, we used a composition which includes α-alkenes $C_{20–24}$ polymerized with maleic anhydride and a number of chemicals reagents [11, 13].

Comprehensive assessment of sheepskin velour was carried out using a generalized desirability function, which is widely used for various research objects [14–16]. The effectiveness of the complex quality indicator is due to the following:

- allows one numerical value to express the degree of product quality, which is characterized by a set of individual indicators;
- brings the consumer assessment closer to the psychometric understanding of quality given that its limitation on the top and bottom by the desirability function provides a positive value of the indicator and the its monotonic increase with improving the quality of the evaluated product;
- eliminates the compensation of the low level of some properties due to the high level of others by generalizing the various individual quality indicators by the method of average harmonic evaluation and bringing the overall result to a lower level;

- has a high level of objectivity in the formation of the nomenclature of properties of a particular type of product and assessing the importance of its indicators in a complex quality indicator through the use of the method of expert evaluations;
- provides an opportunity to consider not only the existing needs of the consumer, but also those that are proposed to be achieved in the future.

The complex quality indicator for hydrophobized sheepskin fur velour was calculated according to the formula:

$$K_j = \frac{\sum_{i=1}^{k} \mu_i}{\sum_{i=1}^{k} \frac{\mu_i}{d_i}} \qquad (1)$$

where j is the type of fur velour; μ_i is the importance of ith quality indicator calculated by the ratio of ranks $\sum_{j=1}^{m} r_{ij} / \sum_{i=1}^{k} \sum_{j=1}^{m} r_{ij}$; k is the number of significantly influential indicators of the quality of fur velour; d_i – desirability function of y_i calculated as

$$d_i = \exp[-\exp(-y_i')] \qquad (2)$$

where y_i' is the dimensionless value of the quality indicator y_i calculated from a linear regression:

$$y_i' = b_0^{(i)} + b_1^{(i)} y_i \qquad (3)$$

The coefficients $b_0^{(i)}$ and $b_1^{(i)}$ were determined from a system of equations:

$$\begin{matrix} y_i'^{\,worse} = b_0^{(i)} + b_1^{(i)} y_i^{worse} \\ y_i'^{\,better} = b_0^{(i)} + b_1^{(i)} y_i^{better} \end{matrix} \quad (i = 1,2,\dots,m) \qquad (4)$$

where y_i^{worse} and y_i^{better} are the worse and better values of the quality indicator y_i, respectively, which cannot be neither decreased due to the impossibility of its intended use nor increased due to technological reasons; $y_i'^{\,worse}$ and $y_i'^{\,better}$ are the worse and better values of the dimensionless value of the quality indicator calculates as

$$\begin{aligned} y_i'^{\,worse} &= -\ln(-\ln(d_{worse})) \\ y_i'^{\,better} &= -\ln(-\ln(d_{better})) \end{aligned} \qquad (5)$$

where d_{worse} and d_{better} are the worse and better values of desirability function for individual quality indicators.

An algorithm for calculating the complex quality indicator of sheepskin fur velour provided:

1. Establishing boundaries and gradations of desirability functions from d_{worse} to d_{better} and dimensionless quality indicators from $y_i'^{\,worse}$ to $y_i'^{\,better}$;
2. Determination of gradation of dimensional quality indicators of sheepskin fur velour on a desirability scale based on the worse and better dimensional values of quality indicators y_i^{worse} and y_i^{better}.
3. Calculation of the coefficients of equations of transition from dimensional quality indicators to dimensionless, through the solution of the system of equations.
4. Calculation of dimensionless quality indicators y_i' based on dimensional values of quality indicators y_i.
5. Calculation of functions of desirability d_i of individual quality indicators y_i.
6. Calculation of the generalized desirability indicator K_j considering values of weighting factors μ_i and desirability function d_i of individual quality indicators y_i.
7. Characterization of the equation of the quality of various types of sheepskin fur velour and their comparison using complex quality indicator.

The interval of the desirability function was divided into segments: unsatisfactory, satisfactory, good, and excellent. The boundaries for the desirability function d are chosen in such a way that the dependence between the individual quality indicators y_i and its dimensionless version y_i' was linear. Selection and justification of the boundary values (“satisfactory” and “excellent”) of individual quality indicators y_i was performed based on regulatory and technical documentation, expert assessments, scientific publications, and research results. The limits of “unsatisfactory” were selected based on the values of “satisfactory” limits below which the level was considered unacceptable. The limits of “good” were calculated as an average of the limit values of the levels “satisfactory” and “excellent”.

The Results of Quality Assessment of Hydrophobized Sheepskin Fur Velour

Table I shows the boundary conditions, the gradation of the desirability functions from d_{worse} to d_{better}, the results of calculations of boundaries and gradations of dimensionless quality indicators from $y_i'^{\,worse}$ to $y_i'^{\,better}$ (5). The gradations of dimensional indicators of quality of fur velour from sheepskin are determined on the desirability scale based on the aforementioned methodology.

The boundaries of the dimensionless indicator, given in Table I, were calculated based on the upper boundary of the gradation “unsatisfactory” and the lower boundary of the gradation of the “excellent” desirability function.

The upper limit of “unsatisfactory” gradation is given as

$$y_i'^{\,worse} = -\ln(-\ln 0.37) = 0$$

while the lower limit of “excellent” gradation is

$$y_i'^{\,better} = -\ln(-\ln 0.8) = 1.53$$

Gradations of dimensionless indicators were calculated similarly. The appropriate gradations of the desirability function were used.

Considering the boundaries of the dimensional and dimensionless quality indicators, the coefficients b_0 and b_1 of the functions of the dimensionless output variables were calculated using the system of equations (4). The linear dependencies were determined to convert the dimensional values of the quality index

y_i to the dimensionless y_i'. The following equations were used for the corresponding indicators:

– total thermal resistance of fur velour [(°C·m²)/W]

$$\begin{cases} 0 = b_o + 0.07b_1 \\ 1.53 = b_o + 0.49b_1 \end{cases} \rightarrow \begin{cases} b_o = -0.255 \\ b_1 = 3.643 \end{cases} \rightarrow \quad y_i' = -0.255 + 3.643y_i$$

Table I. *Levels of dimensional important quality indicators of fur velour.*

Indicator (notation and name)		Quality score gradation			
		US	S	G	E
D	Descriptive indicator	< 0.37	0.37–0.62	0.63–0.79	≥ 0.80
y_i'	Dimensionless indicator	< 0	0.00–0.76	0.77–1.52	≥≥ 1.53
$x_{1.8}$	The total thermal resistance [°C m²)/W]	< 0.07	0.07–0.27	0.28–0.48	≥≥ 0.49
$x_{1.5}$	Residual elongation of skin tissue at 9.8 MPa load [%]	> 21	21–14.5	14.4–8.1	≥≤ 8
$x_{3.1}$	Coloristic design [score]	< 0.37	0.37–0.62	0.63–0.79	≥≥ 0.80
$x_{2.4}$	Water wetting of skin tissue under dynamic conditions [s]	< 0	0–839	840–1679	≥≥ 1680
$x_{1.6}$	Elastic elongation of skin tissue at 9.8 MPa load [%]	< 8	8–11.4	11.5–14.9	≥≥ 15
$x_{2.2}$	Vapor permeability of skin tissue, 10^{-6} [kg/(m²·s)]	< 1.2	1.2–4.64	4.65–8.09	≥≥ 8.1
$x_{2.1}$	Air permeability of skin tissue, 10^{-3} [m³/(m²·s)]	< 0.04	0.04–0.154	0.155–0.269	≥≥ 0.27
$x_{1.2}$	Tensile strength of skin tissue [MPa]	< 0.48	0.48–0.79	0.8–1.319	≥≥ 1.32
$x_{3.2}$	Quality of skin tissue finish [score]	< 0.37	0.37–0.62	0.63–0.79	≥≥ 0.8
$x_{1.4}$	Total elongation of skin tissue at 9.8 MPa load [%]	< 19	19–23.9	24–28.9	≥≥ 29

Note: *US, S, G, and E stands for unsatisfactory, satisfactory, good, and excellent.*

– residual elongation of skin tissue [%]

$$\begin{cases} 0 = b_o + 21b_1 \\ 1.53 = b_o + 8b_1 \end{cases} \rightarrow \begin{cases} b_o = 2.472 \\ b_1 = -0.118 \end{cases} \rightarrow \quad y_i' = 2.472 - 0.118y_i$$

– coloristic design of skin tissue and hair [score]

$$\begin{cases} 0 = b_o + 0b_1 \\ 1.53 = b_o + 1b_1 \end{cases} \rightarrow \begin{cases} b_o = -1.317 \\ b_1 = 3.558 \end{cases} \rightarrow \quad y_i' = -1.317 + 3.558y_i$$

– water wetting of dermal tissue under dynamic conditions [s]

$$\begin{cases} 0 = b_o + 0b_1 \\ 1.53 = b_o + 1680b_1 \end{cases} \rightarrow \begin{cases} b_o = 0 \\ b_1 = 0.001 \end{cases} \rightarrow \quad y_i' = 0.001y_i$$

– elastic elongation of skin tissue [%]

$$\begin{cases} 0 = b_o + 8b_1 \\ 1.53 = b_o + 15b_1 \end{cases} \rightarrow \begin{cases} b_o = -1.749 \\ b_1 = 0.219 \end{cases} \rightarrow \quad y_i' = -1.279 + 0.219y_i$$

– vapor permeability of skin tissue [kg/(m^2 s)]

$$\begin{cases} 0 = b_o + 1.2b_1 \\ 1.53 = b_o + 8.1b_1 \end{cases} \rightarrow \begin{cases} b_o = -0.266 \\ b_1 = 0.222 \end{cases} \rightarrow \quad y_i' = -0.266 + 0.222y_i$$

– air permeability of skin tissue [m^3/(m^2 s)]

$$\begin{cases} 0 = b_o + 0.04b_1 \\ 1.53 = b_o + 0.27b_1 \end{cases} \rightarrow \begin{cases} b_o = -0.266 \\ b_1 = 6.652 \end{cases} \rightarrow \quad y_i' = -0.266 + 6.652y_i$$

– tensile strength of skin tissue [MPa]

$$\begin{cases} 0 = b_o + 0.48b_1 \\ 1.53 = b_o + 1.32b_1 \end{cases} \rightarrow \begin{cases} b_o = -0.872 \\ b_1 = 1.821 \end{cases} \rightarrow \quad y_i' = -0.872 + 1.821y_i$$

– quality of skin tissue finish [score]

$$\begin{cases} 0 = b_o + 0b_1 \\ 1.53 = b_o + 1b_1 \end{cases} \rightarrow \begin{cases} b_o = -1.317 \\ b_1 = 3.558 \end{cases} \rightarrow \quad y_i' = -1.317 + 3.558y_i$$

– total elongation of skin tissue [%]

$$\begin{cases} 0 = b_o + 1.9b_1 \\ 1.53 = b_o + 29b_1 \end{cases} \rightarrow \begin{cases} b_o = -2.907 \\ b_1 = 0.453 \end{cases} \rightarrow \quad y_i' = -2.907 + 0.453y_i$$

Substituting the values of experimental dimensional individual quality indicators [13] into equation (3), we obtain dimensionless quality indicators of fur velour from sheepskin (Table II).

The definition of a complex quality indicator involves the calculation of the desirability functions d_i of individual quality indicators that for hydrophobic fur velour from sheepskin after spraying were:

$d_{1.8} = \exp[-\exp(-y'_{1.8})] = \exp[-\exp(-1.494)] = 0.799$

$d_{1.5} = \exp[-\exp(-y'_{1.5})] = \exp[-\exp(-0.942)] = 0.667$

$d_{3.1} = \exp[-\exp(-y'_{3.1})] = \exp[-\exp(-1.886)] = 0.859$

$d_{2.4} = \exp[-\exp(-y'_{2.4})] = \exp[-\exp(-1.239)] = 0.748$

$d_{1.6} = \exp[-\exp(-y'_{1.6})] = \exp[-\exp(-1.530)] = 0.805$

$d_{2.2} = \exp[-\exp(-y'_{2.2})] = \exp[-\exp(-1.042)] = 0.703$

$d_{2.1} = \exp[-\exp(-y'_{2.1})] = \exp[-\exp(-0.998)] = 0.692$

$d_{1.2} = \exp[-\exp(-y'_{1.2})] = \exp[-\exp(-1.439)] = 0.789$

$d_{3.2} = \exp[-\exp(-y'_{3.2})] = \exp[-\exp(-1.708)] = 0.834$

$d_{1.4} = \exp[-\exp(-y'_{1.4})] = \exp[-\exp(-1.377)] = 0.777$

Table II. *Dimensionless quality indicators of fur velour from sheepskin.*

Notation	**Dimensionless values of quality indicators y'_i**			
	hydrophobized		**control fatliquoring**	
	1	***1′***	**2**	**2′**
$x_{1.8}$	1.530	1.494	1.275	0.219
$x_{1.5}$	1.177	0.942	1.059	0
$x_{3.1}$	2.242	1.886	2.064	0.854
$x_{2.4}$	1.530	1.239	0.055	0
$x_{1.6}$	1.530	1.530	0.437	0
$x_{2.2}$	1.397	1.042	0.909	0
$x_{2.1}$	1.530	0.998	0.732	0
$x_{1.2}$	1.530	1.439	1.202	0.984
$x_{3.2}$	2.242	1.708	1.886	0.818
$x_{1.4}$	1.071	1.377	0.459	1.530

Note: *Samples 1 and 2 are before spraying, while 1′and 2′ – after spraying.*

These calculations and calculations of the desirability functions d_i of individual quality indicators for hydrophobized fur velour and control fur velour from the sheepskin before and after spraying are listed in Table III.

To calculate the complex quality indicator of Table IV, we introduced the coefficients of significance [18] and used the calculated information on their relationships with the desirability functions of the individual quality indicators (Table III).

The complex quality indicator was calculated according to equation (1) and is listed in the last row of Table IV.

Table III. *Desirability functions of individual quality indicators of fur velour from sheepskin.*

Notation	**Desirability function d_i**			
	1	***1′***	**2**	**2′**
$x_{1.8}$	0.805	0.799	0.756	0.448
$x_{1.5}$	0.735	0.677	0.707	0.368
$x_{3.1}$	0.899	0.859	0.881	0.653
$x_{2.4}$	0.805	0.748	0.388	0.368
$x_{1.6}$	0.805	0.805	0.524	0.368
$x_{2.2}$	0.781	0.703	0.668	0.368
$x_{2.1}$	0.805	0.692	0.618	0.368
$x_{1.2}$	0.805	0.789	0.740	0.688
$x_{3.2}$	0.899	0.834	0.859	0.643
$x_{1.4}$	0.710	0.777	0.532	0.805

Note: *refer to the notes to Table II.*

Discussion of the Results of Quality Assessment of Hydrophobized Fur Velour from Sheepskin

From the results (Table IV) it follows that the complex quality indicator of hydrophobized fur velour from sheepskin has a significantly higher value compared to the complex quality indicator of fur velour produced by the standard technology, especially after the spray test. Hydrophobized fur velour before spraying was estimated as “excellent” with 0.802 value.

Besides determining the overall quality of the hydrophobized fur velour from the sheepskin, it is possible to see which individual indicator caused an increase in the level of the complex quality indicator and which one caused its decrease. Analyzing the Table II, the hydrophobized velour fur of sheepskins has a “good” quality as indicated by the value of the level of the dimensionless quality indicator based on residual and full elongation. These indicators are higher compared with the fur velour of control fatliquoring, respectively, in 1.1 and 2.3 times, or by 11.1 and 133.3 %. This will provide increased form stability of products made of hydrophobized fur velour from sheepskin.

Table IV. *Calculation of the complex quality indicator of fur velour.*

Indicator (notation and name)		μ_i	μ_i / d_i			
			1	***1′***	***2***	***2′***
$x_{1.8}$	Total thermal resistance	0.125	0.155	0.156	0.165	0.279
$x_{1.5}$	Residual elongation of skin tissue at 9.8 MPa load	0.123	0.167	0.182	0.174	0.334
$x_{3.1}$	Coloristic design of skin tissue and hair [score]	0.122	0.136	0.142	0.138	0.187
$x_{2.4}$	Water wetting of skin tissue under dynamic conditions	0.107	0.133	0.143	0.276	0.291
$x_{1.6}$	Elastic elongation of skin tissue at 9.8 MPa load	0.105	0.130	0.130	0.200	0.285
$x_{2.2}$	Vapor permeability	0.099	0.127	0.141	0.148	0.269
$x_{2.1}$	Air permeability	0.084	0.104	0.121	0.136	0.228
$x_{1.2}$	Tensile strength	0.082	0.102	0.104	0.111	0.119
$x_{3.2}$	Finish quality	0.078	0.087	0.094	0.091	0.121
$x_{1.4}$	Total elongation of skin tissue at 9.8 MPa	0.075	0.106	0.097	0.141	0.093
Total: $\sum_{i=1}^{k} \frac{\mu_i}{d_i}$		1.247	1.310	1.581	2.207	1.247
Complex quality indicator: $\sum_{i=1}^{k} \mu_i \Big/ \sum_{i=1}^{k} \frac{\mu_i}{d_i}$		0.802	0.763	0.633	0.453	0.802

Note: *refer to the notes to Table II.*

The “good” level of quality is confirmed by the desirability function of the specified individual quality indicators for the hydrophobized fur velour of sheepskin, the value of which is 0.735 and 0.710, respectively. The desirability function of the fur velour produced by the standard technology is 0.707 – a “good” level for the indicator of residual elongation and 0.532 – “satisfactory” level for the indicator of total elongation. The vapor permeability indicator of the fur velour of sheepskin is also characterized by a “good” level of quality (Table II) and its dimensionless value compared with the control fur velour from sheepskin is 1.537 times higher. The desirability function for vapor permeability indicator for hydrophobized fur sheepskin velour is 0.781, while the desirability function of fur velour produced according to the standard technology is 0.668 (lower). All other quality indicators of hydrophobized fur sheepskin before spraying have an “excellent” level of quality. Their effect on the complex quality indicator is positive and therefore the effect of the above quality indicators, which have a “good” level of quality, are leveled by the indicators with “excellent” level of quality.

The effect of spraying on hydrophobized fur velour led to a slight decrease in the complex quality indicator – up to 0.763. This is a “good” level of quality, which is closely approximated to an “excellent” level. This indicates that the fur velour treated with alkenyl maleic anhydride composition after spraying completely satisfies the needs of the consumer and can be used in conditions of high humidity, at low temperatures, and under dynamic loads. Such assessment was due to the effect of separate individual quality indicators. Characterizing the hydrophobized fur velour from the sheepskin after spraying, we note that the quality indicators that characterize the aesthetic properties of the fur velour from sheepskin remain “excellent”, namely: the coloristic design of the skin tissue and hair, the quality of the skin tissue finish, and the indicator of the elastic elongation of skin tissue, confirming high performance characteristics of products made of fur velour in the dynamic conditions.

As for other indicators of exploitational properties and indicators characterizing hygienic properties, they have a "good" level of quality, which was obtained due to the hydrophobization of samples of fur velour from sheepskin with an alkenyl maleic anhydride composition, and therefore the effect of spraying on the quality indicators was insignificant compared with the fur velour produced by the standard technology.

Particularly interesting are the indicators of the total thermal resistance of fur velour from sheepskin and water wetting of skin tissue under dynamic conditions. Even in conditions of high humidity (after spraying), hydrophobized samples of fur velour from sheepskin have better thermal protection properties. The dimensionless indicators of the total thermal resistance of the fur velour from sheepskin are 6.8 times higher. This indicates the effectiveness of hydrophobization. Such velour can better protect the human body from unfavorable conditions of the environment: from the cold in the autumn-winter period. As for water wetting of skin tissue under dynamic conditions, it should be noted: if samples of fur velour produced by the standard technology were classified as “unsatisfactory”, which for this indicator did not provide the possibility of its exploitation in conditions of high humidity, after hydrophobization the dimensionless value of the indicator of water wetting of skin tissue under dynamic conditions was 1.239 for hydrophobized fur velour from sheepskin after spraying. On a scale of desirability, such velour on the indicator of water wetting of skin tissue under dynamic conditions has a “good” evaluation.

As for the fur velour produced by the standard technology, its evaluation has a lower quality level – “good”, according to the Harrington desirability scale. The application of the spray test, which simulates the process of exploitation of fur velour from sheepskin in conditions of high humidity, indicates a significant decrease in the quality of fur velour produced by the standard technology and limits its use under certain conditions. A complex quality indicator of fur velour from sheepskin produced by the standard technology after spraying was 0.453. It has less than the average gradation level, “satisfactory”, on the desirability scale. This requires the hydrophobization of fur velour from sheepskin with an alkenyl maleic anhydride composition as a new promising method for processing fur velour, as shown in the preliminary analysis.

Conclusions

Based on regulatory and technical documentation, expert assessments, scientific publications, and the results of the conducted studies, the boundaries of dimensional quality indicators of fur velour from sheepskin were determined according to the desirability scale.

The desirability functions of individual quality indicators were calculated. Seven out of 10 desirability functions of individual quality indicators for hydrophobized fur velour have a value ranging from 0.805 to 0.899, which objectively indicate their “excellent” quality level.

The calculated complex quality indicator of hydrophobized fur velour from sheepskin was much higher and received an “excellent” estimate, which was 0.802 compared with the complex quality indicator of fur velour produced by the standard technology, which received a “good” estimate and was equal to 0.633. Sprinkling hydrophobized fur velour resulted in a slight decrease in the complex quality indicator to the “good” estimate, which is closely approximated to the “excellent” estimate and is equal to 0.763. This provide the possibility of using fur velour treated with an alkenyl maleic anhydride composition in conditions of high humidity, at low temperatures, and under dynamic loads.

It was found out that the promising direction of the formation of high-quality fur velour from sheepskin for the production of products is the use of technology, which involves fur velour treatment with an alkenyl maleic anhydride composition to improve exploitational, hygienic, and aesthetic properties. This will determine new directions and areas of use of fur velour from sheepskin, will promote the expansion of the assortment, increase competitiveness of products of Ukrainian origin, and formation of export potential. It acquires an objective necessity in the formation of a free trade zone, signing an association agreement with the EU, and modern world integration processes.

References

[1]. **Holodiuk H.** Comprehensive assessment of the quality of the dyestuff composition and coatings based on alkyd resins (in Ukrainian). *Tovaroznavchyi Visnyk* (Publisher «*Товарознавчий вісник*») **6** (2013) 38–45.

[2]. **Azgaldov G.** Theory and practice of product quality assessment (in Russian). *Ekonomika* (Rushing publisher «*Экономика*») 1982, Moscow, 250 p.

[3]. **Kostrovskaia T.** PhD thesis “Development of the technique of the automated estimation of comfort of footwear using indicators of physicomechanical properties of packages of upper materials” (in Russian), defended on May 19, 2006; 160 p.

[4]. **Kutakh K.** Implementing quality management system at companies (in Ukrainian). *Tekhnologicheskii Audit i Rezervy Proizvodstva* (Publisher «*Технологический аудит и резервы производства»)* **1**, 5 (15) (2014) 24–26; http://journals.uran.ua/tarp/article/view/21725/19230.

[5]. **Hunkalo A. and Shpak O.** Improvement of the products quality level by competent experts (in Ukrainian). *Tekhnologicheskii Audit i Rezervy Proizvodstva* (Publisher «*Технологический аудит и резервы производства»)* **4** 1 (18) (2014) 36–38.

[6]. **Kozar O. and Mokrousova O.** Eco-friendly technologies of leather manufacturing using natural minerals montmorillonite and zeolite (in Ukrainian). *Tekhnologicheskii Audit i Rezervy Proizvodstva* (Publisher «*Технологический аудит и резервы производства»)* **6** 2(14) (2013) 11–16. Available at: http://journals.uran.ua/tarp/article/view/19499/17168

[7]. **Palahniuk Yu. and Slitiuk O.** Development of a nomenclature of ergonomic indicators of clothing quality (in Ukrainian). *Eastern-European Journal of Enterprise Technologies* **3**, 6 (39) (2009) 26–29; http://journals.uran.ua/eejet/article/view/20393/18021.

[8]. **Khimicheva H.** (2013). Quality control of the leather semi-finished product at the tanning stage (in Ukrainian). *Eastern-European Journal of Enterprise Technologies* **3**, 3 (63) (2013) 34–36; http://journals.uran.ua/eejet/article/view/14679/12448.

[9]. **Suprun N., Osypenko N., and Ostrovetska Yu.** Analytical review of the assortment and comprehensive assessment of the quality of knitted fabrics (in Ukrainian). *Tovaroznavstvo ta Innovatsii* (Publisher «*Товарознавство та інновації*») **4** (2012) 116–124.

[10]. **Zhuravskyi V., Kasian E., and Danylkovych A.** Leather and fur technology (in Ukrainian). *DALPU* (Publisher «*ДАЛПУ*») 1996, Kyiv, 743 p.

[11]. **Danylkovych A., Khliebnikova N., Mokrousova O., and Petko I.** Composition for hydrophobization of fur skins, fur velour, wool sheepskin and products made from them (in Ukrainian). UA patent for Utility Model No. 38472; January 12, 2009.

[12]. GOST 28509-90. Sheepskin not dressed. Specifications (in Russian), (2006), 13 p.

[13]. **Khliebnikova N., Omelchenko N., and Danylkovych A.** Consumer properties of hydrophobized sheepskin velour in conditions of high humidity (in Ukrainian). International scientific-practical conference "Problems of social and economic development of entrepreneurship" 2014, Canada, Montreal.

[14]. **Krasnov B., Bernshtejn M., and Gvozdev Yu.** Comprehensive assessment of the quality of shoe materials (in Russian). *Legkaia Industriia* (Publisher «*Легкая индустрия*») 1979, Moscow, 80 p.

[15]. **Chaikovskaia A., Polishchuk L., Galyk I., and Semak B.** Comprehensive assessment of the quality of textile materials (in Russian). *Tekhnika* (Publisher «*Техника*») 1989, Kyiv, 254 p.

[16]. **Galyk I., Kozmich D., Semak B. et. al.** Optimization of the assortment and quality of textile materials (in Russian). *Tekhnika* (Publisher «*Техника*») 1991, Kyiv, 174 p.

[17]. **Akhnazarova S. and Kafarov V.** Methods for optimizing an experiment in chemical technology. *Vysshaia shkola* (Publisher «Высшая школа») 1985, Moscow, 318 p.

[18]. **Danylkovych A., Khliebnikova N., and Omelchenko N.** Selecting the nomenclature of quality indicators of hydrophobized fur velour by expert method. *Eastern-European Journal of Enterprise Technologies* **5**, 3 (71), (2014) 34–39.

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