

IMPROVEMENT OF PARCHMENT TECHNOLOGY

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Parchment is a unique biogenic material, which essentially differs from other types of leather in its technology, structure and properties. Despite its ancient origin, and today, due to its strength and durability, it is used in producing musical instruments, interior items, decorations, and restoration of rare items. At the same time, the problems of restoring ancient or developing modern technology for maintaining parchment from animal skins for the past decades have not been cared for by anyone due to the limited number of restoration specialists and technologists. Known parchment technologies involve the use of significant amounts of calcium hydroxide in *beamhouse* processes, which leads to the formation of sludge, as well as sodium sulfide, which pollutes industrial wastewater with sulfur-containing compounds harmful to aquatic organisms. The purpose of the work is to improve the parchment technology by reducing the cost or eliminating the use of these environmentally hazardous materials. To achieve this purpose, traditional physical-chemical and modern instrumental methods of analysis are used. Based on the results of laboratory studies and production tests, the sheep parchment technology has been improved, which provides enzymatic soaking and use of the mineral zeolite during liming. Compared with the known technology, the developed technology completely eliminates sodium sulfide from the *beamhouse* processes, reduces the consumption of calcium hydroxide by a third, ensures more rational use of material and raw material resources, and improves the composition of wastewater.

Keywords: parchment, technology, properties

INTRODUCTION

Cultural heritage represents a national treasure evolving from the culture and spirituality of people. Therefore, it should be constantly restored, protected and developed by all generations as a priceless heritage. A very important category of museum cultural heritage are leather and parchment items, which are a source of valuable historical information: book bindings, manuscripts, charters etc. (Miu *et al.*, 2020). However, like any organic structure, this material is subject to destructive processes through physical and chemical (light, humidity, temperature, pollutants, etc.), biological and microbiological factors, leading to changes in the structure of the polypeptide chain (Plavan *et al.*, 2010). The resistance of parchment to negative influences, including aging, is largely determined by the manufacturing technology (Kolesnyk *et al.*, 2018). Considering that parchment is still in demand today for restoration work, production of unique documents, musical instruments, souvenirs, jewelry, etc., there is a need to restore, and even more likely, improve this technology.

An analysis of the technological features of leather parchment (hereinafter simply “parchment”) production has revealed the importance of the hide processing method, the choice of raw materials and chemicals (di Curci, 2003; Dziedzelyuk, 2015; Adakina *et al.*, 2018; Fourneau *et al.*, 2020). Since traditional tanning and post-tanning processes are not required in the manufacture of parchment, special attention should be paid to the soaking and ash processes, which largely determine the properties of the finished leather: its strength, elasticity, density, thickness, and condition of the front surface.

Known parchment manufacturing technologies involve the use of a significant amount of calcium hydroxide in the preparatory processes, which leads to the formation of lime sludge and sodium sulphide, which, although it helps speed up the process and prepare the hide for further processing, significantly pollutes industrial effluents with sulphur-containing compounds harmful to aquatic life. Therefore, there is an urgent need to reduce the consumption of harmful materials and find more environmentally friendly ones.

The studies of many scientists are devoted to the improvement of beamhouse processes (Zhang *et al.*, 2021; Danylkovych and Lishchuk, 2022; Morera *et al.*, 2022; George *et al.*, 2014; Nazer *et al.*, 2006). A generalized analysis of the literature shows that the most promising areas for improving biotechnological processes in the production of natural leather are associated with enzymatic treatments, which improve the quality of products and production culture, and reduce the environmental impact; due to this, they are traditionally classified as “clean technologies” (Saran *et al.*, 2013; Zhang *et al.*, 2022; Nyakundi *et al.*, 2022; Jayakumar *et al.*, 2022). Among the latest developments, the works of Kozar *et al.* (2014), Sepehri *et al.* (2020), Mokrousova *et al.* (2015), Sakalova and Khodanitska (2023) are of interest, devoted to the study of natural minerals in the form of montmorillonite, kaolin, zeolite, which, due to their structural features and high sorption capacity, are successfully used as sorbents, fillers, and various auxiliary materials in the leather, food and other industries.

In previous studies, to expand the range of chemical materials and finished products and increase the level of environmental friendliness of parchment production, the authors have established:

- peculiarities of interaction in the collagen-enzyme preparation system during soaking, which consist in the interaction of the preparation with protein functional groups, which contributes to increased enzyme activity and watering of the hide during soaking (Kolesnyk and Andreyeva, 2020a; Kolesnyk, 2021);

- features of sorption-desorption processes in the calcium hydroxide-zeolite system, which regulate the concentration of calcium hydroxide in the solution, its gradual effect on the skin, resulting in a more uniform distribution and better fixation of reagents in the dermis structure, increased strength and yield of the skin by area (Kolesnyk *et al.*, 2022);

- rational parameters of the preparatory processes: consumption of the proteolytic enzyme preparation Pellvit C during soaking is 0.2-0.8 g/l, and calcium hydroxide and zeolite during ashing is 5.0 and 3.5 g/l, respectively (Kolesnyk and Andreyeva, 2020b).

Taking into account the above, this study aims to improve the sulphide-free technology of parchment production using a modern enzyme preparation and domestic natural mineral zeolite in the preparatory processes in compliance with the principles of environmental protection and resource efficiency while ensuring the quality of this unique type of leather.

MATERIALS AND METHODS

The work used both new and common leather and chemical materials in the tanning industry:

- *model collagen preparation* – high molecular weight fibrous protein preparation “GELIOS 11” (TU U 15.8-13848909-001-2008, TOMIG LLC), obtained from purified untanned shingles from cattle hides; contains about 93 % of purified collagen in dry matter;

- *sheep raw materials* using the wet-salted canning method;

- *finished leather* (parchment);

- *Pellvit C* – proteolytic enzyme preparation (manufacturer TFL Ledertechnik GmbH, Germany). The pH value of a 10% solution is 5,3, the activity by the casein number method is 59.9 units/g. When assessing the ability of the drug to break down certain target substrates

(gelatin, collagen, fibrinogen) using enzyme electrophoresis in polyacrylamide gel, the presence of fragments with a molecular weight MW of 97 units was established. IR spectroscopic studies indicate that the mentioned enzyme preparation has a polyfunctional nature (the presence of hydroxyl, amine, imine, peptide and some other functional groups in the structure), due to which it is able to interact with collagen, the main component of the dermis (Fig. 1, Table 1) (Kolesnyk *et al.*, 2020);

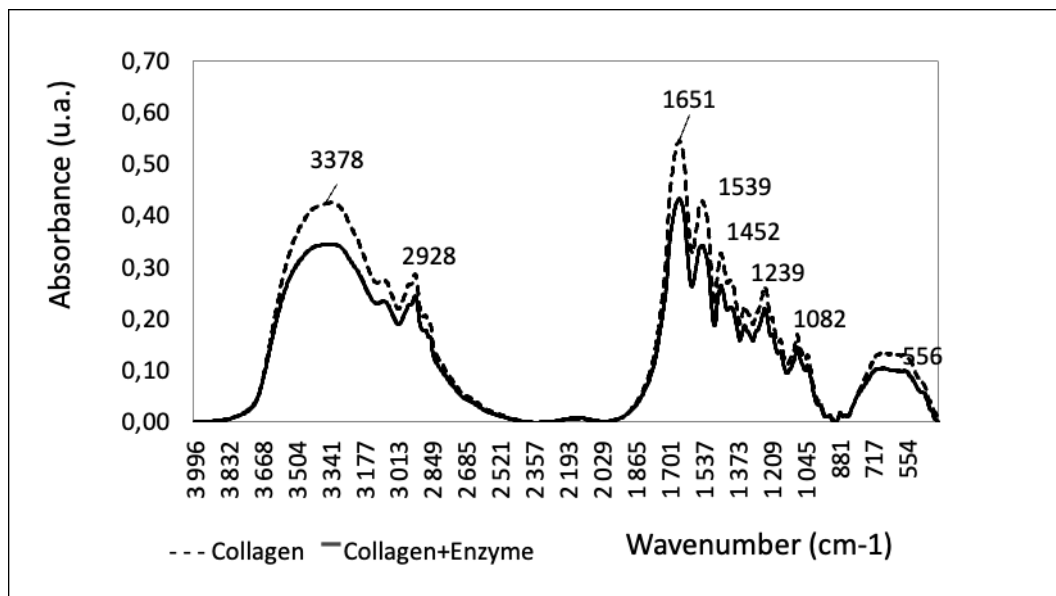


Figure 1. IR spectrograms of collagen preparation before and after treatment with an enzyme preparation

Table 1. Change in relative optical density in IR spectrograms of collagen preparation after treatment with enzyme preparation

Wavenumber (cm ⁻¹)	Interpretation of absorption bands	Experimental data*	
		collagen	collagen + enzyme
3378	Amide A (ν NH); imines (ν C=N), overlapping inter- and intramolecular hydrogen bonds of the side chains; ν OH	<u>3378</u>	<u>3335</u>
		1,74	2,06
2928	Alkanes (CH ₂); alkenes (ν CH)	<u>2928</u>	<u>2928</u>
		1,00	1,00
1651	Amide I, acids and their derivatives (C=O); alkenes (ν C=C)	<u>1651</u>	<u>1651</u>
		3,45	3,50
1539	Amide II; carboxylic acids (COO ⁻)	<u>1539</u>	<u>1542</u>
		2,28	2,28
1452	Alcohols (δOH); substituted alkenes (δ CH); alkanes (ν CH ₃)	<u>1452</u>	<u>1452</u>
		1,57	1,25
1336	Alkanes (δ CH ₃)	<u>1336</u>	<u>1336</u>
		1,00	1,77
1239	Amide III; amini second, third (ν CH); ethers (ν SOS); alcohols (δ C=O, ν C=O)	<u>1239</u>	<u>1238</u>
		1,23	1,17
1082	Primary, secondary, tertiary alcohols (ν CO)	<u>1082</u>	<u>1082</u>
		0,76	0,52
556	Amide VI	<u>556</u>	<u>561</u>
		0,57	0,60

*Note: numerator – frequency λ, cm⁻¹; denominator – relative optical density.

- *zeolite* is a natural mineral of the Sokirnitskoye deposit (Ukraine), which belongs to the group of minerals of volcanic sedimentary origin with similar composition, framework aluminosilicates of alkali and alkaline earth metals. According to energy dispersive X-ray fluorescence analysis, the mineral under study contains 65.88% SiO₂, no less than 8.5% Al₂O₃, is characterized by an average content of Fe₂O₃ (5.66%), a significant content of alkaline earth (CaO, MgO) and alkaline compounds, 68 and 5.27%). Based on microscopic studies carried out using an MBS-9 microscope, it was found that the average particle size of the mineral is 150 microns. It has been experimentally proven that zeolite does not swell either in water or organic solvents. The pH value of an aqueous solution (or rather a suspension), depending on the concentration (2.5-10.0 g/l), is at the level of 5.7-6.0. The mineral content is 88.1%, moisture – 4.9%.

The hypothesis of the delayed effect of calcium hydroxide on leather raw materials with the addition of zeolite as a substance with high adsorption capacity has been investigated. The hypothesis suggests the following mechanism: the absorbing complex of the zeolite sorbs calcium hydroxide ions, and after some time the reverse process gradually occurs – the zeolite gives back Ca²⁺ and OH⁻ ions to the solution. This is confirmed by the results of studying the kinetics of calcium hydroxide sorption-desorption by zeolite depending on the concentration of lime and mineral. In this case, the nature of ion sorption and desorption depends on the concentration of both components of the system. Thus, in calcium hydroxide solutions with a concentration of 5.0 g/l, the lowest degree of lime sorption-desorption is observed at a zeolite concentration of 1.5 g/l; the highest degree of sorption - at a zeolite concentration of 3.5 g/l, and desorption – 5.0 g/l (Figure 2).

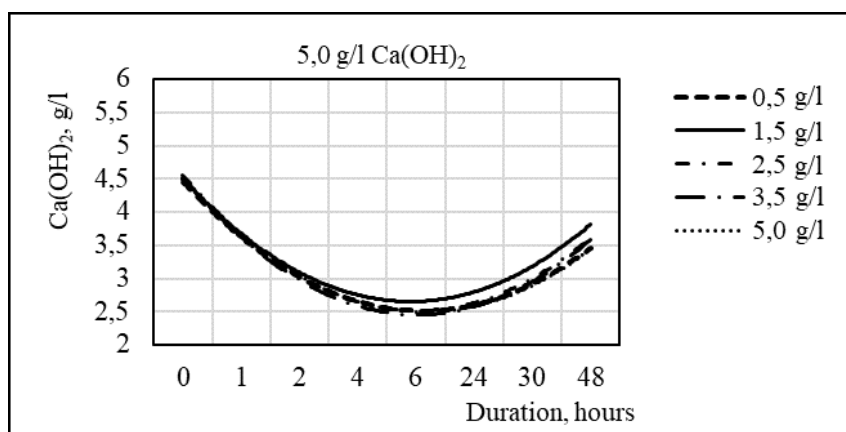


Figure 2. Kinetics of calcium hydroxide sorption-desorption depending on the consumption (concentration) of zeolite

- *other chemical materials common in leather production.*

To achieve these goals, the work uses traditional physicochemical and modern instrumental methods of analysis, including spectroscopic, energy-dispersive X-ray fluorescence (XRF), microscopic, disk electrophoresis in the «enzyme-electrophoresis» modification.

To conduct physical and mechanical tests and chemical analysis, samples of raw materials and finished leather were taken according to the requirements of regulatory documentation: preparation and sampling – ISO 2418:2017; determination of thickness – ISO 2589:2019; determination of tensile strength and relative elongation – ISO 3376:2008; determination of welding temperature (settling) – ISO 3380:2008; determination of the mass fraction of moisture – ISO 4684:2005; determination of the mass part of minerals (ash) – ISO 4047:2006; determination of nitrogen content (mass part of pelt substance – ISO 5397:2006;

determination of the mass part of calcium hydroxide – DSTU 13538-68; determination of the mass part of aluminum oxide – ISO 11885:2007.

RESULTS

Taking into account the results of our research (Kolesnyk *et al.*, 2020; Kolesnyk and Andreyeva, 2020a; Kolesnyk and Andreyeva, 2020b; Kolesnyk, 2021; Kolesnyk *et al.*, 2022), the technology for making parchment from sheep raw materials has been improved (Fig. 3).

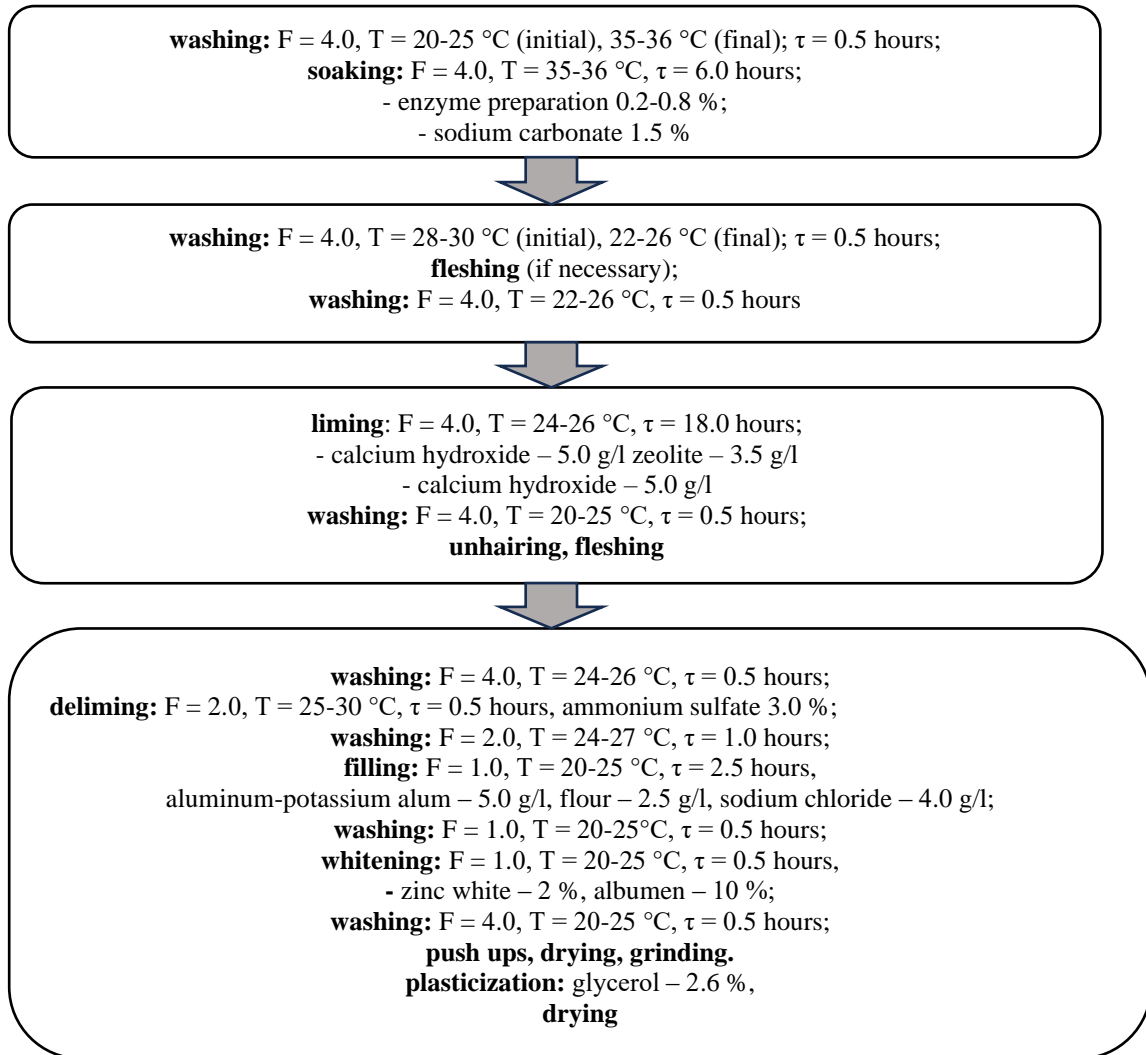


Figure 3. Scheme of improved technology for the production of sheepskin parchment

In the conditions of the Kyiv leather enterprise Chinbar PrJSC, an improved technology for the production of parchment for various purposes (for the manufacture of musical instruments and souvenirs, restoration work) was tested using the wet-salted preservation method of sheepskin as a raw material.

Enzymatic soaking was carried out after washing the raw materials at a float (F) of 4.0 with a gradual increase in temperature to 36 °C for 0.5 hours. First, the enzyme preparation Pellvit C was dosed, and 10 minutes after its dissolution, sodium carbonate; material consumption was determined taking into account the activity of enzyme preparation and the

mass of raw materials. After soaking for 6.0 hours, washing was carried out at F 4.0, temperature 28-30 °C (initial), 22-26 °C (final) for 0.5 hours and fleshing in the raw materials.

The liming-unhairing process was carried out according to the following parameters: F 4.0, temperature 24-26 °C, duration 18.0 hours; consumption of calcium hydroxide 5.0 g/l, natural mineral zeolite – 3.5 g/l; in this case, these materials were previously combined in an aqueous solution for 24.0 hours. In order to increase the degree of the diamond branch and give the parchment the necessary elastic-plastic properties, another 5.0 g/l of calcium hydroxide was dosed 6.0 hours before the end of the liming process. Next, at F 4.0, temperature 20-25 °C, the branch was washed for 0.5 hours. After mechanical removal of the hair and slowing, the branch was washed again (F 4.0, temperature 20-25 °C, duration 0.5 h).

The beamhouse processes in the control batch were carried out using a known technology, therefore the consumption (liquor concentration) of sodium sulfide during soaking and sulfide liming was 0.7 and 9.0 g/l, respectively, and the consumption (liquor concentration) of calcium hydroxide during liming was 15.0 g/l.

Further processes and operations for all batches were carried out according to the well-known technology for the production of parchment, which involves drying of delimiting pelt on frames and final finishing by sanding, plasticizing and bleaching.

The delimiting process was carried out at F 2.0, temperature 25-30 °C, for 0.5 hours using ammonium sulfate – 3.0%. After the latter, washing was performed (F 2.0, temperature 24-27 °C, duration 1.0 hour).

During the next filling, potassium alum was used – 5 g/l, wheat flour – 2.5 g/l and sodium chloride – 4 g/l (F 1.0, temperature 20-25 °C, duration 2.5 hours). At the end of the filling process, washing was carried out (F 1.0, temperature 20-25 °C, for 0.5 hours).

The bleaching process was carried out according to the following parameters: F 1.0, temperature 20-25 °C, duration 0.5 hours; consumption of zinc white – 2.0%, albumin (dry egg white) – 10.0% with the following washing (F 4.0, temperature 20-25 °C, duration 0.5 hours). After washing, squeezing, drying (in a tense state), grinding and plasticization (glycerin – 2.6%) were performed.

Table 2. Comparative assessment of parchment production technologies

Index	Technology	
	famous	new
<i>Leather:</i>		
Tensile strength, 10 MPa	5.80	6.46
Relative elongation at stress 10 MPa, %	20.7	22.5
Thickness, mm	0.69	0.67
Shrinkage temperature, °C	69.0	69.5
Mass part, %:		
- moisture	13.9	14.1
- pelt substance *	84.6	85.4
- minerals *	8.10	7.49
Output by area, %	92.5	93.0
<i>Spent solution after preparatory processes:</i>		
Sodium sulfide content, g/l	2.90	–
Calcium hydroxide content, g/l	4.18	2.66

Note: * in terms of absolutely dry substance

No complications were identified during the processing of the experimental batch. According to organoleptic assessment, indicators of chemical analysis and physical and mechanical tests, pelt and the finished parchment were not inferior to the control ones: thus, pelt had a clean surface grain without hair residues, signs of pipeness, drawn grain and other

defects; the finished leathers were stronger, had a more uniform clean surface grain and a higher yield in area. For the environmental assessment of the developed technology, an analysis of the spent liming solutions was carried out, which revealed (Table 2) an improvement in their composition in the case of the improved technology.

Thus, the test results confirmed the effectiveness of the improved parchment manufacturing technology, which consists of eliminating sodium sulfide from the technological cycle, reducing consumption and more rational use of raw materials (calcium hydroxide consumption decreases by 30%, and area yield increases by 0.5%), improving the physical and mechanical properties of the skin (increasing tensile strength by 10.2%) and the composition of wastewater (lack of sulfides, reducing the calcium hydroxide content in the waste ash solution by 1.6 times).

The technological efficiency of the new development can be explained, firstly, by the peculiarities of interaction in the collagen-enzyme preparation system during soaking, which consist of the interaction of the enzyme with nitrogen-containing substances, hydroxyl and carboxyl groups of the protein, which contributes to an increase in its activity and hydration of the skin; secondly, by sorption-desorption processes in the calcium hydroxide-zeolite system, due to which the concentration of calcium hydroxide in the solution is regulated, its gradual effect on the skin is carried out, as a result of which a more uniform distribution and better fixation of reagents in the structure of the dermis are ensured, strength indicators, and leather yield by area are increased.

The ecological imperative of the developed technology is based on a decrease in the amount or even complete elimination of environmentally hazardous materials from circulation. The expected economic effect from the introduction of the new technology will be UAH 1.97 per 1 m² due to a more rational use of scarce and expensive today raw leather and chemical materials.

CONCLUSION

The technology for the production of sheep parchment for various purposes (for the manufacture of musical instruments and souvenirs, for restoration work) has been improved. The developed technology was tested in the conditions of an existing tannery. The results of the work have a certain environmental and socio-economic effect since they provide:

- reducing the negative impact on the environment due to the exclusion of sodium sulfide from the technological cycle and reducing the consumption of calcium hydroxide;
- more rational use of raw materials and material resources.

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