Розроблено процес ензимної пластифікації напівфабрикату хромового дублення у технології виробництва еластичних шкір. Технології ензимної пластифікації напівфабрикату забезпечують формування шкір із підвищеними деформаційно-пластичними показниками, збільшення їх виходу за площею на 5,4–6,3 % та підвищення економічної ефективності на 1,20–1,86 і 3,35–4,45 тис. грн. відповідно для шкіри із сировини великої рогатої худоби та великих шкур свиней

Ключові слова: ензимна пластифікація, напівфабрикат хромового дублення, шкіряний матеріал, вихід площі

Разработан процесс энзимной пластификации полуфабриката хромового дубления в технологии производства эластичных кож. Технологии энзимной пластификации полуфабриката обеспечивают формирование кож с повышенными деформационно-пластическими показателями, увеличением их площади на 5,4–6,3 % и повышением экономической эффективности на 1,20–1,86 и 3,35–4,45 тыс. грн. соответственно для кожи с сырья крупного рогатого скота и крупных шкур свиней

Ключевые слова: энзимная пластификация, полуфабрикат хромового дубления, кожевенный материал, выход площади

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

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1. Introduction

Production of natural leather materials is characterised 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 rawhides, less processing through 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 weight and energy consumption, thus increasing productivity 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 features 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.

2. Analysis of previously published studies and the statement of the problem

Among the eco-efficient materials that are widely applied in various fields of industrial production, a special use is made of 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. In particular [8] describes the use of protosubtilin G3x, pectofoetidin P10x, and maltavamorin G10x to accelerate saturation of a dry raw material with fresh water. The action of enzymes of pectoavamorin P10x and pectofoetidin P10x together with non-ionic surfactants accelerates removal of lipids and hydrocarbons from the skin tissue as well as 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 enzyme preparations along with the lipid one produce protease and glycosidic effects.

Enzyme preparations accelerate the physicochemical processes of converting animal hides and skins into materials through soaking, degreasing, depilation, and softening. These processes significantly depend on the methods of preserving the natural material and the purpose of using it. The length of technological processing at the stage of soaking the raw material during its dry and moist fresh preservation is reduced by the use of amilosubtilin G3x, maltavamorin G10x, and pectofoetidin P10x [10]. Moreover, by increasing the plasticity of the skin tissue, the defects of rawhides are reduced during their mechanical processing.

While soaking hides in ash water, it is recommended to use enzyme preparations of proteolytic, glycosidic and lipolytic effects [11]. Herewith, the ash can be removed with the help of the enzyme preparations 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 depilated with the enzyme preparation called protosubtilin G10x [14, 15]. Proteolytic enzyme preparations and trypsin can be used even in the processing of secondary resources of producing chrome-tanned hides [16].

The effectiveness of using enzyme preparations also greatly depends on the pH and temperature of the environment, which requires careful monitoring of the technological processes. According to [17], the proteolytic activity of protosubtilin G3x at the optimal pH is maximized at temperatures of 45–55 °C, and it is reduced by 50 % at 30 °C and 65 °C. While the enzyme of lipavamorin G3x exhibits optimum performance at temperatures of 35–37 °C, it is completely inactivated at 55 °C. The temperature optimum of the activity of protomesenterin G3x is a range of 60–65 °C.

Thus, enzyme preparations greatly accelerate the biochemical ash-soaking and pre-tanning processes in treating leather and fur raw 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 enzyme preparations of high heat resistance. This makes it possible to expect a reduction in the duration of the technological process, a lower consumption of raw materials per unit area, and formation of supple leather materials.

3. The purpose and tasks of the study

The purpose 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 purpose, it is necessary to do the following tasks:

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

– 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.

4. 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 neutralization process. The material was derived from large raw hides of cattle (heifers) of an average heavy weight of 24.3 kg and LPH of an average area of 180 dm^2 (a weight of 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 while using protosubtilin G3x (EP-1) produced by the enterprise "Enzyme" (Ukraine), which is typically obtained by the method of submerged bacterial cultivation of Bacillus subtilis 103. One gram of the preparation contained the following activity units: neutral protease – 70, B-glucanase – 196, xylanase – 147, A-amylase – 298, and alkaline protease – 10.96 thousand.

Enzymatic plasticizing of semi-finished leather was conducted in a drum Dozemat DD-7.5 made by Dose Maschinenbau GmbH (Germany) with a drive capacity of 13.5 kW at a rate of 1 m^3 of water use per 1 tonne of the semi-finished product. Further mechanical plasticizing was held in a sliding drum Dose 4648.MI by Dose Maschinenbau GmbH (Germany) with the energy consumption of 9 kW per hour. With the developed technology, the process was carried out at a temperature of 53–55 °C and during the treatment time of 1 hour and 3 hours for semi-finished cattle hides and LPH, respectively. According to the technology of the PJSC "Chinbar", enzymatic plasticizing was carried out while using the preparation enzymaz 10TD (EP-2) by Cromogenie (Spain) at temperatures of 38–42 °C during the treatment time of 2–4 hours and 12–14 hours, respectively for the semi-finished products from cattle hides and LPH. Under the previously existing technology of producing supple leather in the absence of enzymatic plasticizing of structured semi-finished hides of cattle and LPH for footwear uppers [18], the duration of the mechanical plasticizing process increased significantly.

The technological efficiency of enzymatic plasticizing of semi-finished leather is proved by the results of the research on the output of finished leather for shoe uppers by the area and its physical and mechanical properties determined by specific methods [19]. The economic effect of the considered technologies was evaluated by the difference between the cost of increasing the area, weight, and energy use in producing leather by the developed technology and the one practised by the PJSC "Chinbar" versus the control technology, taking into account the cost of enzyme preparations:

$$E^{EP}=\frac{\left(\Delta S\cdot P_h-m_{en}\cdot P_{en}-E\cdot P_e\right)100}{L_c},$$

where E^{EP} is the economic effect of enzymatic plasticizing per 100 m^2 of leather, UAH; ΔS 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 preparation spent to process one tonne of semi-finished leather, kg; P_{en} is the price of 1 kg of enzyme preparation, UAH; E is the energy consumption for enzymatic and mechanical plasticizing of one tonne of semi-finished leather, kW/h; P_e is the price of 1 kW/h of energy, UAH; L_c is the output of leather from one tonne 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.

5. A comparative analysis of technologies used for enzymatic plasticizing of chrome-tanned semi-finished leather

The use of enzyme preparations in the technologies of physical and chemical treatments of hides in manufacturing supple leather materials (Fig. 1) can be significantly important in terms of preparing the fibrous structure of a chrome-tanned semi-finished product for further effective technological processing and primarily for filling with organic tannins.

The properties of the chrome-tanned semi-finished leather after an enzymatic plasticizing treatment (EPT) with protosubtilin G3x and enzymaz 10TD are shown in Table 1. The results indicate that with an increase in the processing temperature to 54 °C for both semi-finished cattle hides and LPH the duration of EPT is reduced three to four times compared with the technology used by the PJSC "Chinbar", whereas the physical and mechanical properties remain rather high. Besides, there is a maximum elongation at a tension of 10 MPa and a break of 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.

Table 1

The technology of an enzymatic plasticizing treatment of chrome-tanned semi-finished leather and its physical and mechanical properties

The indicators	The EPT technologies				The control technology
	The developed technology			The PJSC "Chinbar" technology	
	1	2	3		
Consumption of an enzyme preparation as to the initial activity of the bath: 0.1 ml of the n. solution of NaOH	1.1	0.9	0.9	1.0	–
the greasing substances as to the semi-finished product weight, %	0.4	0.6	0.8	–	–
The processing temperature, °C	37	54	58	40	–
The processing time, hours: – for cattle hides – for LPH	 1.5 4	 1 3	 1 3	 4 13	 – –
Greasing, %	6.6	6.4	6.2	7.0	7.0
Tensile strength, MPa	19.4/17.3	19.5/18.4	18.5/17.7	18.1/17.9	18.3/17.5
Elongation at a tension of 10 MPa, %	28.3/30.2	33.9/38.0	35.0/29.0	33.5/37,3	27.8/29.6
Relative elongation at a break, %	59.0/51.0	76.0/58.0	69.0/53.0	72.0/57.0	58.0/49.0

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

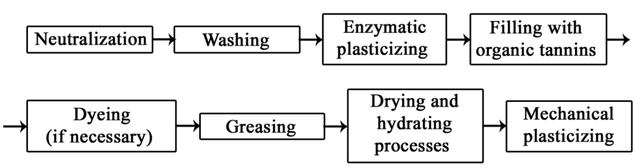
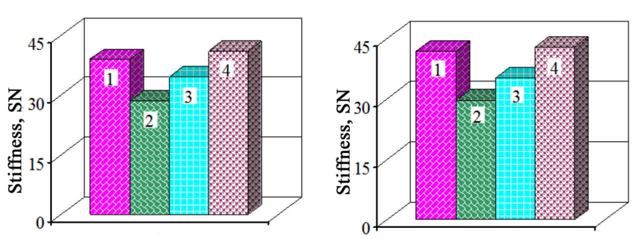


Fig. 1. A technological flowchart of producing leather by enzymatic plasticizing of a chrome-tanned semi-finished product

Evaluation of the semi-finished leather elasticity alongside its stiffness varies according to the deformation parameters obtained under uniaxial tension. 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 LPH. This effect is achieved with an active working solution of enzyme preparations such as protosubtilin G3x and enzymaz 10TD in the respective amounts of 0.9 mL and 1.0 mL 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 physical and mechanical properties.



a *b*

Fig. 2. A dependence of the stiffness of the semi-finished leather on the temperature of its enzymatic plasticizing, °C: 1 — 37; 2 — 54; 3 — 58; 4 — without processing with an enzyme; *a* — cattle hides; *b* — LPH

The technological and economic advantages of the developed technology and the one industrially practised by the PJSC "Chinbar" over the control technology are shown in Table 2. According to the results, the technologies that have been developed and industrially practised by the PJSC "Chinbar" provide a significantly larger output area of the finished leather material. The technology of the PJSC "Chinbar" and the developed technology can increase the output area of the leather material by 3.5–3.8 % and 5.1–5.9 %, respectively. Thus, the output of leather from rawhides according to the developed technology over the technology of the PJSC "Chinbar" increases by 1.8–2.2 %.

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

Taking into account the cost of increasing the area of the leather material, the consumption of enzyme preparations and the energy spent for enzymatic and mechanical plasticizing, the economic benefit from the technology of the PJSC "Chinbar" over the control technology is 1.2–3.3 thousand 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.

Table 2

The technological and economic efficiency of enzymatic plasticizing of one tonne of chrome-tanned semi-finished leather

The indicators	The technology		Efficiency	
	EPT	Control	technological (+, –)	economic, UAH (+, –)
The leather output, m^2				
after EP-1	346.0/412.1	325.5/391.0	20.5/21.1	14,477/7,293
EP-2	338.4/404.7	Ditto	12.9/13.7	10,898/4,671
Consumption of an enzyme, kg				
during EP-1	9/10	– / –	–9/–10	–1,148/–1,275
EP-2	10/10	– / –	–10/–10	–850/–850
Enzymatic plasticizing, hours:				
EP-1	1/3	– / –	–1/–3	–12.7/–77.0
EP-2	4/13	Ditto	–4/–13	–50.6/–164.3
mechanical, hours: EP-1 versus EP-2	9/12	20/24	11/12	188.1/205.2
EPT efficiency, UAH per 100 m^2				
during EP-1				4,448/1,865
EP-2				3,348/1,195

Notes: 1. EP-1 and EP-2 relate, respectively, to the technologies that have been developed and industrially practised by the PJSC "Chinbar". 2. The numerator and the denominator refer to the finished leather from cattle hides and LPH

6. The peculiarities of enzymatic plasticizing of structured semi-finished leather

The use of enzyme preparations at various stages of producing leather and fur materials is justified by their specific active influence 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 enzyme preparations when converting raw hides and fur into an appropriate material is predetermined by the similarities between their chemical nature and the dermis collagen. It should be noted that the stages of soaking, alkaline treatment (ashing and depilation), ash removal and softening the use of enzymes is predetermined by profound destructive changes in the semi-finished leather, which is connected with the destruction of covalent, ionic and hydrogen bonds between both macromolecules of the dermis collagen and with its components. In particular, the presence of enzymes at the stage of ashing significantly accelerates the process of destroying amide bonds in the lateral radicals of collagen.

The action 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 in the destruction of hydrogen and ionic bonds. The effectiveness of the active centre of the enzyme preparations of protosubtilin G3x 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 radicals of collagen macromolecules. Given the isoelectric point of proteins and the pH environment of 5.6–5.8, the radicals of these amino acids exist in a deprotonated form and exhibit their basic properties.

After the destruction of the intermediate enzyme-collagen complexes, the released functional groups of lateral radicals in collagen interact with particles of a fat emulsion, thereby increasing the mobility of the macromolecules of a structural protein. This helps realize the plasticizing and biocatalytic activities of an enzyme preparation. 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 the processes of 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 output areas, which testifies to an increase in the technological and economic efficiency of the technologies that we have studied.

7. Conclusions

1. We have developed a technology of enzymatic plasticizing of chrome-tanned semi-finished leather based on using protosubtilin G3x 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 deformation and plastic properties increased by 26.0–43.0 % and 28.0–44.0 %, respectively.

2. The technology of enzymatic plasticizing by the PJSC "Chinbar", which involves the use of enzymaz 10TD, provides an increase in the output area 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 3.3 thousand UAH and 1.2 thousand UAH per 100 m^2 of the finished material.

3. The developed technology of enzymatic plasticizing compared with the control technology helps increase the output area of the leather material by 6.3 % and 5.4 %, reduce the duration of mechanical plasticizing twice, and achieve the economic benefit of 4.45 thousand UAH and 1.86 thousand 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 rather promising for introduction into the manufacturing of supple leather materials.

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