Досліджено споживні властивості наповненого крупнопористого шкіряного напівфабрикату, отриманого за розробленою технологією з використанням електрохімічно активованих водних розчинів композиції, що включає ксантанакриламід. Сформований гідрофільний матеріал характеризується мікропористою структурою і підвищеними еластично-пластичними властивостями порівняно зі зразками діючої технології. Отриманий шкіряний матеріал рекомендується для внутрішніх деталей взуття і як обтиральний для видалення поверхневої вологи

Ключові слова: шкіряний напівфабрикат, наповнювання, активована вода, ксантанакриламід, пористість, гідрофільність, еластичність

Исследованы потребительские свойства наполненного крупнопористого кожевенного полуфабриката, полученного по разработанной технологии с использованием электрохимически активированных водных растворов композиции, включающей ксантанакриламид. Сформированный гидрофильный материал характеризуется микропористой структурой и повышенными эластично-пластическими свойствами по сравнению с образцами действующей технологии. Полученный кожевенный материал рекомендуется для внутренних деталей обуви и как обтирочный для удаления поверхностной влаги

Ключевые слова: кожевенный полуфабрикат, наполнение, активированная вода, ксантанакриламид, пористость, гидрофильность, эластичность

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RESEARCH OF CONSUMER PROPERTIES OF LEATHER FILLED WITH THE USE OF ELECTROACTIVATED WATER REAGENT SOLUTIONS

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1. Introduction

Expanding the range and improving the quality of the leather material 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, uniform density and thickness at different sections [1, 2]. This applies particularly to pig skins, which are characterized by the through pores in the dermis, resulting from the hair removal, intensive development of skin glands, 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 increased resistance to external influences, minimize losses of the hide surface when drying, increase the yield of full cut works, especially in the processing of low-quality raw materials and preparation of semi-finished products to the effective conduct of coating.

Thus, the process of filling is crucial in terms of the formation of technological and consumer properties of the finished material 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.

2. Literature review and problem statement

The use of a wide range of different chemical compositions for the semi-finished leather filling [4] is known, in which each component must have specific properties that first of all take into account the structural features of hides. For obtaining high-strength intensely colored chrome-tanned leather, out of raw hide, the filling process can be carried out using acryl amide in the presence of potassium persulfate [5] during oxidative polymerization 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 destruction products can be used. In particular, the use of compositions of aqueous dispersions of copolymers of diallyldimethylammonium chloride and maleic acid in an amount 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 minutes. The resulting semi-finished product is characterized by high 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 raw hide and subsequent retanning with organic tanning agent BNS is also known. Using 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 [9], the authors used anionic sulfite melamine formaldehyde oligomers with subsequent dyeing and fatliquoring for after-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 of [10] recommend the use of aminofurazan resin. Because its particles acquire a positive charge as a result of protonization, 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 higher physical and mechanical properties of leather material – abrasion resistance, transverse and longitudinal tensile and tearing strength, elasticity and reduction of the lost surface of semi-finished products after finishing compared with the control variant of treatment. According to the results of [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 after-tanning processes, filling materials of natural origin, including protein mixtures derived from whey in the manufacture of cheese with gelatin in a 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, and the resulting material for shoe uppers, transport upholstery, furniture and other decoration, filled with the protein/gelatin mixture has the improved coloration, flexibility and high drapery.

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, the physical and mechanical properties of the filled material are virtually identical to 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 is described in [14]. The resulting material is characterized by the uniform distribution of the complex filler in the semi-finished product structure, better organoleptic properties as to thickness and color compared to the control group of samples. At the same time, there is an increase in temperature of hydrothermal stability of semi-finished leather when using genipin-gelatin treatment. The results of research on the scanning electron microscope 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 the raw chrome-tanned hide filling 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 size yield, high elastic-plastic properties, 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. In [17, 18], it is shown that the use of activated water solutions of benzyl alcohol, glycerol, glyoxal can increase the flexibility of leather [17] and leather tissue of fur when hair dyeing [18]. Plasticizing of leather materials from raw hides with electrochemically activated water in wetting-drying processes of forming shoe uppers makes it possible to increase the deformation capacity 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 after-tanning formation of semi-finished products out of pig skins and especially with the use of 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.

3. The purpose and objectives of research

The aim was to study consumer properties of the chrome-tanned semi-finished leather from pig skins using electrochemically activated aqueous solutions of the filling composition comprising xanthan acrylamide EPAA-M.

To achieve this goal, the task was set to study the effect of the filling composition on consumer specifications of the shaved chrome-tanned semi-finished leather, including:

– porous structure;
– absorption properties;
– strain-relaxation dependencies;
– volume and areal yield of the material.

4. Materials and methods of study of consumer properties of semi-finished leather

For experiments, the chrome-tanned semi-finished pig skins (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 were selected.

Variants for the filling technology were practiced on three experimental groups of 120×150 mm samples each containing seven pieces packaged by the method of asymmetric flesh side [21]. Before the filling process, the semi-finished product was neutralized with formate (TU 21-249-00204168-92) and sodium carbonate in a ratio of 1:1. In the course of the semi-finished product filling, plasticization of using electrolyte resistive oil Trupol RA (Trumpler, Germany) was conducted.

The active component of the filling composition for the semi-finished product processing was a copolymer of exopolysaccharide of bacterial origin TU U 88-105-002-2000 – xanthan modified with acryl amide TU 6-01-1049-92 [22] (EPAA-M, Ukraine).

The semi-finished product was processed using the composition of xanthan acrylamide EPAA-M according to the current technology, instead of anionic acrylic-based polymer Retanal RCN-40 (Cromogenia-Units, Spain) in the electrochemically activated water environment – anolyte, catholyte [23].

Properties of the resulting semi-finished product were studied by the methods [21]. In particular, 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, hardness – on the PZHU-12M device. Relaxation and deformation properties of semi-finished leather were determined on the facility, described in [24]. The sample was under tension stress corresponding to 9.8 MPa. The duration of the sample under load was 30 minutes. After removing the tension, conventional elastic deformation was determined immediately, after 30 minutes – high elastic, and after 24 hours – residual deformation were determined.

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 (hide) substance (HS). 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 in percentage.

Water capacity of the semi-finished product samples was determined on a thermo-gravi-calorie-metric installation [25] in the mode of thermograms. For this purpose, the samples of the semi-finished product with the size of 40×40 mm were previously maximally moisturized within 24 hours at a temperature of 20 °C. The change in the mass of samples during moisture desorption was determined at 100 °C for 4 hours using modified analytical scales ADV-200, and the temperature of the sample – by 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 and moisturizing processes and operations relative to the unfilled semi-finished leather.

5. Effect of composition on the properties of the resulting semi-finished product

In the process of this study, filling compositions are used (Table 1), differing in types of the dispersion medium.

Unlike the current processing technology of semi-finished products, the experimental technology used the compositions based on xanthan acrylamide and electrochemically activated (ECA) types of water.

Table 1

Chemical components of filling composition

Component	Producing country	Consumption of materials, % of mass of shaved semi-finished product by technology			
		experimental			current
		1	2	3	
Trupol DL	Germany	2	2	2	2
Retanal RCN-40	Spain	–	–	–	3
EPAA-M	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 anolyte – catholyte; – distilled	Ukraine	+	+	+	tap water

The process of filling the chrome-tanned semi-finished leather was carried out after washing for 30 minutes at the ratio of water and semi-finished product 2:1 with increasing temperature from 35–40 to 55–60 °C and addition of the filling composition, the processing duration of 1 hour. The use of anolyte provided the pH of the working solution within 4.2–4.4, distilled water – 4.7–4.9 and catholyte – 6.7–7.0. Subsequently, for the structure plasticizing, processing of the semi-finished product with the fat liquor for 1 hour with the consumption of fat of 6 % was conducted. 10 minutes before the filling-fatliquoring process completion, fixing processing with 10 % formic acid with a flow rate of 1 % of the semi-finished product mass was performed.

Given the essential role of moisture exchange properties of chromium-tanned leather material made of pig skins 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

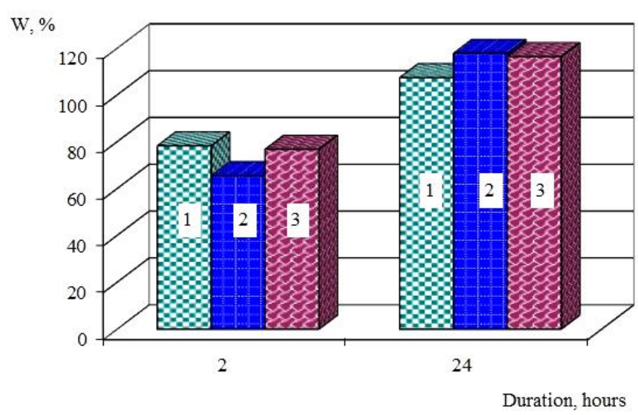

Fig. 1. Dependence of soaking of the filled semi-finished leather at 20 °C on the duration of the process using: 1 — anolyte; 2 — catholyte; 3 — distilled water

Water intake of 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.

Thus, at the initial stage of the interaction of the filled chrome-tanned semi-finished leather with water, the samples obtained from a composition where the dispersion medium is the anolyte display greater sorption capacity.

However, according to experimental results (Table 2), forming of semi-finished leather using EPAA-M in the anolyte provides a leather material with the volume yield greater by 19.0 % compared with the version of 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 when using the experimental composition based on distilled water, this technological index of the semi-finished product practically does not change. 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 2

Technological properties of the filled semi-finished leather

Indicator	Semi-finished leather obtained by technology			
	experimental			current
	1	2	3	
Volume yield, cm^3/100 g HS	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 organic bound ingredients (Table 3) 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 hardness by 12.0 %.

Table 3

Physical and chemical properties of semi-finished leather

Indicator	Semi-finished leather obtained by technology			
	experimental			current
	1	2	3	
Mass fraction in terms of absolutely dry substance, %				
– moisture;	14.1	13.9	13.5	13.4
– chromium oxide (III);	4.1	4.7	4.3	4.4
– substances extracted with OS;	89	7.9	8.1	8.3
– organic bound;	11.2	7.9	10.4	10.5
– hide substance	68.2	69.9	68.2	69.1
Shrinkage temperature, °C	115.0	112.0	114.0	114.0
Tensile strength, MPa	19.7	18.0	18.6	18.8
Elongation under a load of 10 MPa, %	35.8	28.0	32.0	33.2
Belly porosity, %	54.6	45.7	49.8	50.1
Relative air permeability, $cm^3/cm^2 \times hour$	324.0	269.0	301.0	308.0
Hardness, sN	37.0	48.0	42.0	43.0
Reduction of area, %	1.9	1.1	1.5	1.4

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 first case.

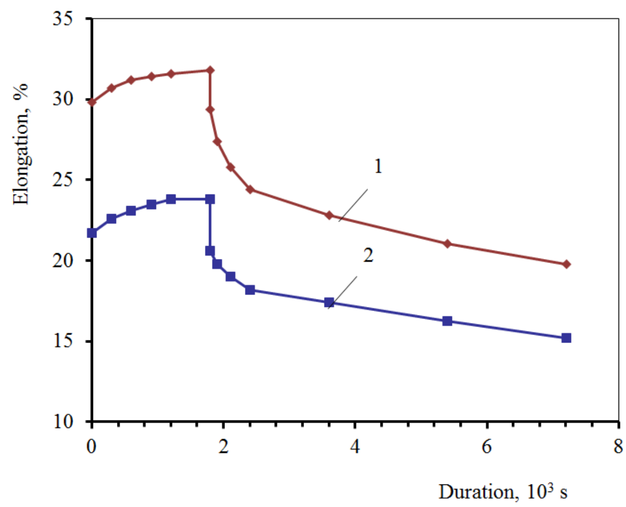

Fig. 2. Relative elongation of semi-finished leather before and after removal of the load using: 1 — anolyte; 2 — catholyte

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 obtained leather material. However, such an important technological indicator as the loss of area during drying and moisturizing processes (reduction of area) is minimal when using the anolyte in the experimental technology.

Given the essential sorption capacity of the leather material for the insides of shoes obtained from macroporous materials – pig skins, the study of differential porosity by the sections after filling of the chrome-tanned semi-finished leather by the experimental and current technologies is of considerable interest (Table 4). The above data show that the moisture intake of the samples of the semi-finished product filled using the experimental composition is characterized by lower values of moisture capacity and water of soaking compared to the samples of the current technology. The adsorption of water in the polylayer and monolayer in dense and loose areas is greater at lower values of these parameters in the first case.

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 watered 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.

Table 4

Differential moisture content of the filled semi-finished leather

Hide sections	Moisture intake, %	Water of soaking, %	Differential water, %			Specific pore volume, %, corresponding to water	
			hygroscopic	polylayer	monolayer	soaking	hygroscopic
Butt	107.2 / 113.0	51.9 / 60.6	55.3 / 52.4	18.1 / 14.2	4.6 / 4.1	48.41 / 53.63	51.59 / 46.37
Belly	121.4 / 130.6	66.5 / 75.8	54.9 / 53.8	21.8 / 16.3	4.8 / 3.7	54.78 / 58.81	45.22 / 41.19

Note: 1. The water of the polylayer and monolayer is part of the hygroscopic water. 2. Numerator – semi-finished leather samples filled using the anolyte and KSAA; denominator – control samples of semi-finished leather obtained by the technology of PJSC "Chinbar"

6. Physical and chemical 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 hydrophilic ability and porosity of the material is of significant importance. The effectiveness of the process increases with decreasing difference between the properties of solid and loose sections of the semi-finished product. Through the use of electrochemically activated aqueous solutions of reagents with negative oxidation-reduction potential, thermodynamic unbalance [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 out of raw material from heifers by using the xanthan acrylamide copolymer [28] in another 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-fat liquoring and after process water removal from the semi-finished product in the process of moisturizing-drying remains in a mobile state. This structure formation of the material enhances water absorption 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 destruction of the formed mainly hydrogen bonds, water absorption 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, 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 acrylamide in the anolyte solution.

7. Conclusions

1. 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 of the composition comprising acrylamide-modified xanthan were determined. Replacement of acrylic polymer in the current technology of PJSC "Chinbar" with xanthan 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.

2. 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.

3. 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.

4. Higher volume yield by 41.5 cm^3/100 g of proteins compared with the current technology contributes to the formation of a material with high hygienic properties and lower loss of area 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.

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