PRODUCTION OF ELASTIC LEATHERS FROM HORSE RAW MATERIAL USING ACTIVATED AQUEOUS SOLUTIONS OF AGENT

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ABSTRACT. A step-by-step technology of formation of leather material made of horse raw materials using electrochemically activated aqueous solutions of chemical agents has been developed. Effective implementation of the leather raw material soaking process has been established due to the use of the optimal ratio of catholyte and anolyte. At the same time, environmentally hazardous agents are excluded from the process and its duration is reduced by two times compared to the current technology. The use of working solutions at the stages of liming and tanning with the use of catholyte and anolyte respectively, ensures the exclusion of environmentally hazardous chemical agents and the reduction of the processes duration. The developed technology of production of leather materials, unlike the existing ones, is characterized by simultaneous treatment of all anatomical areas of the hide.

KEY WORDS: horse hide, electrochemically activated water, activated agent solutions, technology, leather properties

REALIZAREA DE PIEI ELASTICE FOLOSIND CA MATRIE PRIMĂ PIELE DE CAL ȘI SOLUȚII APOASE CU AGENȚI DE ACTIVARE

REZUMAT. S-a dezvoltat pas cu pas o tehnologie de obținere a pielii folosind ca materie primă piele de cal și soluții apoase activate electrochimic de agenți chimici. Implementarea eficientă a procesului de înmuiere a pielii s-a datorat utilizării raportului optim de catolit și anolit. În același timp, agenții periculoși pentru mediu sunt excluși din proces, iar durata acestuia este redusă de două ori comparativ cu tehnologia actuală. Utilizarea soluțiilor de lucru în etapele de cenușărire și tăbăcire, folosind catolitul, respectiv anolitul, asigură excluderea agenților chimici periculoși pentru mediu și reducerea duratei proceselor. Tehnologia de obținere a pielii dezvoltată, spre deosebire de cele existente, este caracterizată de tratarea simultană a tuturor zonelor anatomice ale pielii.

CUVINTE CHEIE: piele de cal, apă activată electrochimic, soluții cu agent de activare, tehnologie, proprietăți ale pielii

FABRICATION DE CUIRS ÉLASTIQUES À PARTIR DE MATIÈRE PREMIÈRE DE CHEVAL À L'AIDE DE SOLUTIONS AQUEUSES AVEC DES AGENTS ACTIVANTS

RÉSUMÉ. Une technologie d'obtention du cuir a été développée étape par étape en utilisant le cuir de cheval comme matière première et des solutions aqueuses activées électrochimiquement par des agents chimiques. La mise en œuvre efficace du processus de trempage de la peau était due à l'utilisation du rapport optimal entre le catholyte et l'anolyte. Dans le même temps, les agents dangereux pour l'environnement sont exclus du processus et sa durée est réduite de deux fois par rapport à la technologie actuelle. L'utilisation de solutions de travail dans les étapes de pelanage et de tannage, utilisant respectivement le catholyte et l'anolyte, garantit l'exclusion des agents chimiques dangereux pour l'environnement et la réduction de la durée des processus. La technologie d'obtention de la peau développée, contrairement à celles existantes, se caractérise par le traitement simultané de toutes les zones anatomiques de la peau.

MOTS CLÉS : cuir de cheval, eau activée électrochimiquement, solutions avec des agents activants, technologie, propriétés du cuir

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INTRODUCTION

One of the effective ways to improve existing technologies is the use of new chemical agents, including activated water and its solutions. Various methods are used to obtain activated water [1, 2]: under the influence of thermal, magnetic, ultrasonic and electric fields. At the same time, electrochemically activated (ECA) water has advantages compared to the use of other types of liquid treatments in leather materials manufacturing technologies. This concerns the high redox potential, the thermodynamic imbalance of such technological solutions stored for a long time and causing intensification of biotechnological processes [3, 4]. Another advantage of ECA solutions is the possibility of effective regulation of their properties. The use of ECA water in technologies of leather and fur raw materials processing can be considered particularly effective. Taking into account the significant volume of working solutions and the need to protect natural raw materials from biological damage caused by microorganisms, the use of ECA solutions of agents in the multi-component and multi-stage technology of leather materials production can be considered promising. At the same time, an urgent issue is to reduce the consumption of environmentally harmful agents and the duration of individual step-by-step physical and chemical treatments via development of chemical composition of working solutions and the conditions for their effective use for production of high-quality leather materials.

ECA water is known to be used in medicine, electronic industry, agriculture, food and light industries, and other industries [5]. At the same time, many works use different fractions of ECA water: catholyte and anolyte that are characterized by specific properties in relation to pH, available chemically active radicals and ions, and high redox potential [1]. In works [6, 7], the authors identified effective bactericidal properties of anolyte in relation to the vital activity of pathogenic microorganisms. In this case, lack of habituation of microorganisms to such disinfectants despite their environmental safety has been shown. The authors [8] identified bactericidal properties of anolyte on test organisms. In the furfural synthesis technology, the authors [9] showed the possibility of using anolyte as a catalyst instead of acid agents.

In paper [10], peculiarities of ECA water diffusion into the structure of protein raw materials were studied. In this case, glycosaminoglycans and lipids are effectively removed from the structure of leather raw materials. At the same time, catholyte exhibits an intense extractive effect during the processing of plant raw materials [11]. The specific properties of the effect of ECA aqueous solutions on physical and chemical transformations of the collagen structure of rabbit skin tissue were studied in [12]. It was established that catholyte and anolyte significantly increase the volume formation and deformation characteristics of hide tissue. In paper [13], the plasticizing effect of catholyte on the structure of leather material during the formation of shoe products was established. At the same time, efficiency of using the material area increases. The authors [14] report the improvement of physical and mechanical as well as deformation characteristics of the hide after tanning processes: re-tanning, re-dyeing and greasing. However, re-tanning significantly reduces the elongation of the material, while the coefficient of its homogeneity decreased as a result of greasing. The use of THPS prior to plant tanning [15] reduces consumption of chromium compounds during tanning, increases heat resistance of the hide and the elastic and plastic properties of the dermis.

Thus, the analysis of scientific and technical references on the study of the properties and use of fractions of electrochemically activated water: anolyte and catholyte of different chemical composition in technological processes proves their high bactericidal and physicochemical properties. This gives grounds for the prospects of practical application in leather production technologies.

The aim of the research is to study the influence of electrochemically activated solutions of chemical agents on the processes of formation of elastic leather material from raw horsehide and its properties.

EXPERIMENTAL

Materials and Methods

The research is carried out using halves of wet-salted horsehide with a mass of 6.6 kg after fleshing in raw materials with a moisture content of 45.3–51.8 and a thickness of 1.7–6.2 in different anatomical areas of the hide (Table 1).

Table 1: Changes in content of moisture and dermis thickness by anatomical areas of horsehide

Area name	Moisture, % of dermis mass	Thickness, mm
Head	68.1 / 49.9	1.7
Neck	66.7 / 48.6	1.9
Back	63.9 / 45.3	4.1
Loin	64.7 / 46.8	5.4
Flank	69.2 / 50.1	3.3
Dock	64.6 / 46.4	6.1
Croup	65.3 / 46.9	5.7
Legs	70.1 / 50.8	2.8
Stifle	66.4 / 47.2	3.7
Barrel	71.3 / 51.8	2.3
Average	67.03 / 48.38	3.7

Note: The numerator and denominator show moisture content in the dermis of fresh hide respectively, without taking into account the hair preserved by brining

Table 1 shows that the maximum moisture content of fresh horsehide is observed in peripheral areas. Central anatomical areas are characterized by minimal moisture content. The uneven distribution of moisture in the anatomical areas of the horsehides stays even after they have been brined. The same refers to thickness distribution.

In research on the technology of formation of elastic hides from horse raw materials, two fractions of ECA water: anolyte and catholyte and a number of chemical agents of different composition were used. ECA fractions of water are obtained in the research laboratory of the National University of Food Technologies at the semi-production flow-type installation «Izumrud KFTO» (RF, Petersburg) with a capacity of 60-70 dm^3/h. Anolyte and catholyte are characterized by a pH of 2.7-3.6 and 9.0-10.8, respectively, and a redox potential of 300-1500 and –100…–700 mV. It should be noted that under the conditions of storage in closed rooms without an air layer, the hydrogen index and the redox potential of the catholyte and anolyte relax to a quasi-stable state within 50 hours by 3% and 16–18%, respectively [16].

Among the other technological agents, the following ones should be noted:

– technical pancreatin of polyfunctional action (OCT 49-167-81), which contains a number of proteolytic enzymes;

– chrome tanning agent (TU 2141-033-541386-2003) with a basicity of 35-42%;

– acrylic polymer Retanal RCN-40 from the company «Cromogenia-Units, S.A.» (Spain);

– Quebracho extract with a tannin content of 70% from the company «Plasma» (Ukraine);

– Trupol RA lubricating material as a mixture of sulfated and sulfited synthetic and natural anionic fats with an active substance content of 70%, pH 10% emulsion 7.5 manufactured by Trumpler company (Germany);

– potassium alum $KAl(SO_4)_2 \cdot 12H_2O$.

Unlike the developed technology of processing leather raw materials by the current technology [17], nonionic surfactant SPK-50 (TU 2484-014-22284995-99), sodium carbonate and sodium sulfide % of sample mass: 0.25, 0.45 and 0.3, respectively, are used at the soaking stage.

The water content in raw materials is determined by the gravimetric method at a temperature of 102 ± 2 °C; the pH of water and technological solutions is measured with a pH-meter of the pH-340 brand. Before weighing the samples on electronic scales (AXIS, AD200, Poland), surface moisture was carefully removed with filter paper.

Characterization of the samples of the obtained hides is carried out according to the complex of physical and chemical properties after their preliminary conditioning [18] by the exsiccation method under normal conditions at a temperature of 20±2 °C and a relative humidity of 65 ± 5%. Heat resistance of hide samples is characterized by hydrothermal shrinkage of collagen molecules during its denaturation (welding temperature), which is established by heating the sample at a rate of 2–3 °C/min in a mixture of glycerin and water with a weight ratio of 4:1 (ASTM D6076-18 and DSTU (National Standard of Ukraine) 2726- 94). The content of chromium tanning compounds in the semi-finished product is determined by iodometric titration and is expressed as the mass fraction of chromium (III) oxide. Substances extracted with organic solvents (SEOS) are determined in Zaychenko's apparatus using tetrachloromethane and trichloroethylene in a ratio of 1:1, followed by drying at temperatures of 128-130 °C for 1.5 and 1.0 hours, respectively.

Bound organic tannins (BOT) in leather are calculated by the formula:

$$BOT = LS - PS, \quad (1)$$

where LS = 100 – (TA + OS + OWS) is the mass fraction of leather substances calculated on the dry basis;

TA – the mass fraction of total ash (DSTU ISO 4047:2006);

OS – the mass fraction of organic substances, extracted with organic solvents (DSTU EN ISO 20344);

OWS – the mass fraction of organic water-soluble substances (DSTU ISO 4098:2020);

PS – the mass fraction of hide (protein) substance in the leather in terms of completely dry leather. It is determined by the nitrogen content by the Kjeldahl method (DSTU ISO 937:2005).

Hide density is determined by the ratio of its mass to the total volume. Mechanical properties of the leather samples are measured on the PM-250M tearing machine (RF) at a distance between the clamps of 50 mm with a deformation rate of 90 mm/min. The hide area is determined on an electromechanical action machine model 07484/P1 produced by the Svit company (Czech Republic).

RESULTS AND DISCUSSION

All technological processes of leather raw materials processing are carried out at Chinbar PJSC (Ukraine, Kyiv) using a drum of the Doze company (Germany) with a volume of 0.39 m^3. Soaking of horse raw materials with a significant difference in properties in different anatomical areas of the hide is carried out taking into account the results of previous studies and the use of anolyte and catholyte [19]. It should be noted that in the catholyte/anolyte mixture in the soaking processes, it is necessary to take into account the nature of the pH change and the antiseptic properties of the working solution.

The soaking process of canned raw materials is carried out in a catholyte/anolyte mixture under the conditions listed in Table 2.

To determine the optimal catholyte/anolyte ratio, a study of the effect of mixture composition on water absorption by the anatomical area: the croup, taking into account the high pH of the subsequent liming process was carried out. The choice of this area of hide is due to its increased density and the convenience of controlling the moisture content.

Table 2: Technology of soaking and liming, and tanning processes

Process	Agent/consumption, % of raw material mass	Mode
Washing	Water 26-28 °C – 150	60-min rotation; drain
Soaking	Catholyte /anolyte = 5/1-3/1 26-28 °C – 130	pH 8.2-9.5, rotation (rev.) 2 hrs.; then every hour revolutions 5 min for 4 hrs., drain
Liming	Catholyte 26-28 °C – 30 Calcium hydroxide – 0.7 Sodium hydrosulfide – 0.6 Sodium sulfide – 0.6 Calcium hydroxide – 0.4 Catholyte 28 °C – 80	 40 min. rev./ 20 min. idle/ 30 min. rev. 30 min. rev., pH ~ 12 30 min об. 10 min/hrs., 7,5-8 hrs., pH ~ 12.2
Washing	Water 24-26 °C – 2×150	2 times 15 min. Each
Fleshing	Fleshing machine	
Unusable areas removal	Table	Removal of unusable areas of hide
Doubling		Thickness of hide 2.2-2.3 mm
Identification of mass of hide		The entire batch is weighed
Washing	Water 32-34 °C – 150	20 min. rev. of the drum
Deliming-softening	Catholyte 36-38 °C= 5/1 – 20 Ammonium sulfate – 3.0 Pancreatin – 0.05	 60 min. rev.; pH 8.2-8.5 30 min. rev., drain
Washing	Water 18-20°C – 2×150	Two times 20 min. rev. each, drain
Pickling	Anolyte 25-27 °C – 40 Sodium chloride – 2.5 Sodium formate – 0.4 Sulfuric acid – 0.6 Formic acid 85% – 0.3	 15 min. rev. 30 min. rev. 3 hrs. rev., pH 2.6-2.8
Tanning	Chromium sulfate with a basicity of 37-42% – 4 Sodium formate – 0.25 Catholyte/anolyte 7/1 45 °C – 30 Magnesium oxide – 0.4	 2,5 hrs. rev. 4–4,5 hrs. rev., pH 3.6–3.8

According to the obtained data, the optimal catholyte/anolyte ratio corresponds to the minimum duration of reaching the moisture content as close as possible to its content in fresh hide after having been soaked for 5-6 hours. At the same time, there is no strip of dark color in thickness of the croup when it is cut near the rump, which indicates the completion of the process. Therefore, with a ratio of catholyte/anolyte of 7/1-5/1, the duration of the soaking process is reduced by 2.5 times when excluding environmentally hazardous agents.

At the same time, the need to exclude environmentally hazardous antiseptic agents from the working solution is taken into account. Shall the pH value in the soaking process according to the current technology decrease from 10.7, with available sodium sulfide, sodium carbonate, and surfactant to 7.3 (Table 3) upon completion of this process in 14 hours, according to the developed technology, at a lower initial pH value, this process is completed in 5.0-5.5 h without the use of an environmentally hazardous agent. When determining the optimal ratio, condition of the raw materials is taken into account. Completion of the soaking process takes place under control of the moisture content that should be close to the moisture content of the fresh raw material in the area of the croup.

Table 3: Change in pH of technological solution at soaking of horse raw hides

Working solution	pH from the start of soaking, hrs.				
	0	0.15	1.0	5	14
Catholyte/anolyte 1/0	10.6	8.4	7.6	7.2	7.2
1/1	6.7	7.1	7.1	7.1	7.1
5/1	8.3	7.7	7.3	7.1	7.1
7/1	9.5	8.2	7.4	7.2	7.2
Distilled water	6.6	7.0	7.1	7.1	7.1
Current technology	10.7	8.5	7.7	7.4	7.3

After the raw material has been soaked, it is limed (Table 2) using only catholyte, which creates a working environment when it is consumed, initially 30% of the mass of the raw material, and after 3.5 hours another 80% is added. The total duration of the process is 10.0-10.5 hours. After washing the received half-finished hides, its physicochemical properties are determined (Table 4).

Table 4: Properties of limed horse raw hides

Index	Researched technology		Current technology	
	Back	croup	back	croup
The temperature of the moisturized dermis, °C	49.0	56.0	52.0	59.0
The density of the semi-finished product, g/cm^3	1.019	1.113	1.032	1.125
Mineral substances, %	1.37	1.12	1.17	0.89

The obtained results indicate a higher content of mineral substances in the experimental samples both in the area of the croup and the back by 26.0% and 17.0% respectively, compared to the samples of the current technology. This proves increased activity of chemical agents during their interaction with collagen of the dermis with available catholyte, while their consumption is three times lower. This primarily concerns calcium hydroxide. Interaction of alkaline agents with collagen of the dermis is accompanied by a decrease in the welding temperature of the hide and its density. This may be the result of effective defibrillation of the hide structure when treated with an alkaline solution based on catholyte.

After washing, doubling, washing, de-liming-softening and washing, the obtained hide is pickled with available 40% of anolyte with a reduced consumption of sodium chloride by two times compared to the current technology and replacing 50% of sulfuric acid with 25% formic acid. The process of leather tanning is carried out on a spent pickling solution with the masking of the basic chromium sulfate with sodium formate, which contributes to its effective diffusion. At the same time, consumption of chromium compounds is reduced by 20% compared to the current technology. After 2.5 hours, a 30% catholyte/anolyte mixture and magnesium oxide base are added to continue tanning. Tanning is completed at the welding temperature of the samples of 107 °C.

Subsequently, the tanned semi-finished product is adjusted to a thickness of 1.1-1.2 mm, washed with 150% of water at a temperature of 35 °C. Further, the semi-finished product is doubled with available anolyte and basic chromium sulfate 100% and 1.6% of the mass of the semi-finished product respectively, neutralized with a mixture of formate and sodium bicarbonate in a ratio of 4:1 to pH 6.0-6.5. After washing the obtained semi-finished product with 150% of water at a temperature of 55 °C, the semi-finished product is filled with organic compounds with consumption of 4% of acrylic polymer Retanal RCN-40 and 4% of quebracho extract, and plasticized with 7% of Trupol RA lubricating material. Fixation of filling and plasticizing agents in the structure of the semi-finished product is carried out by 0.4-0.5% of aluminum-potassium alum to pH 4.2. The technology is completed by washing with 150% of water at a temperature of 30 °C. After drying and moisturizing processes, the samples of the obtained leather material are kneaded on a vibrating stretching and softening machine «Mollisa» produced by Svit company (Czech Republic).

The current technology [17] differs from the developed one by additional plasticization of the semi-finished product after neutralization and washing of the semi-finished product using an enzyme preparation and surfactant.

The obtained half hides were analyzed for chemical composition and physical and mechanical properties (Table 5) after the completion of drying and moisturizing treatments. A comparative analysis of leather samples of experimental and current technologies indicates a higher content of chromium tanning compounds and bound organic substances in the first case. At the same time, higher welding temperature, strength and deformation capacity of the samples are observed. This may indicate a more effective implementation of the chemical structuring process due to the use of activated aqueous solutions of agents for the technology of manufacturing leather material from horse raw materials. At the same time, compared to the current technology, there are 6.9 and 15% more of unbound fatty substances for the back and croup areas, respectively.

Table 5: Physical and chemical characteristics of leather

Index	Technology			
	researched		current	
	back	croup	back	croup
Mass share, %				
– chromium oxide (III)	4.21	3.58	4.02	3.37
– SEOS	8.67	6.76	8.11	5.86
– BOT	12.79	8.75	12.04	7.78
Welding temperature, °C	115.0	111.0	112.0	109.0
Density, g/cm^3	0.62	0.66	0.64	0.69
Breaking strength limit, MPa	18.6	23.1	16.9	21.3
Elongation under load 10 MPa, %	38.0	27.0	33.0	23.0
Elongation at break, %	66.0	49.0	61.0	45.0
Area output, dm^2/10 kg of raw material	153.0		146.2	

The higher content of fatty substances in the structure of the semi-finished product of the researched technology helps to increase the mobility of fibrillar structure of leather material during its deformation. This is confirmed by some decrease in density and increase in elastic and plastic properties of the hide. This especially applies to the strength and deformation capacity at low loads on experimental hides, which increase by 8.5-10.0 and 15.0-17.0%, respectively. This is also evidenced by the increase in the yield of leather by area by 6.8 dm^2 from 10 kg of raw material. According to the set of properties, the obtained leathers meet the DSTU requirements and can be used for the manufacture of footwear, clothing and haberdashery products, taking into account the properties of anatomical areas of horsehide.

CONCLUSIONS

A step-by-step technology for formation of leather material from horse raw materials using electrochemically activated aqueous solutions of chemical agents has been developed. A complex of physical and chemical properties in different anatomical areas of horsehide has been studied. The effect of the ratio of fractions of electrochemically activated aqueous solutions of catholyte and anolyte on the complex of physical and chemical properties of leather material at different stages of its formation has been determined. Effective implementation of leather raw material soaking process has been shown due to the use of the optimal ratio of catholyte and anolyte. At the same time, environmentally hazardous agents are excluded from the process; its duration is reduced by 2.5 times compared to the current technology.

The use of working solutions based on catholyte at the liming stage of leather raw materials ensures a three-fold reduction in the consumption of environmentally hazardous chemical agents. At the same time, when implementing the developed tanning process using anolyte, consumption of environmentally hazardous chromium compounds is reduced by 20% and the duration of the process is reduced by 1.7 times.

Taking into account the specific influence of different fractions of electrochemically activated aqueous solutions of chemical agents on the formation of leather material ensures obtaining a complex of increased elastic and plastic properties while saving natural raw materials by 4.6% compared to the current technology. At the same time, the developed technology of the production of leather materials, unlike the existing ones, is characterized by the simultaneous treatment of all anatomical areas of the hide. The obtained leather material meets the requirements of DSTU 3115-95 Leather for sewing products – General technical characteristics and ISO 9001:2008 international standard of quality management systems requirements and can be effectively used in manufacturing of a wide range of products. At the same time, we may recommend areas of the back and croup of horse leather to be used in production of shoe parts, and the remaining areas for haberdashery and accessories.

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