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Article

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Technology audit and production reserves

UDC 675.016-025.24
DOI: 10.15587/1729-4061.2023.290018

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AN EFFECTIVE INDICATOR DETERMINATION FOR THE LEATHER MATERIAL UNIFORMITY ASSESSMENT

The object of research is the process of determining the objective indicator of the degree of topographic homogeneity of the structure and properties of the leather material. The work defines a set of indicators of properties of semi-finished chrome tanning and leather materials. At the same time, when evaluating the homogeneity of the properties of leather materials, the difference between the values of the physical and mechanical indicators of the shabrack and the bottom is taken into account. At the same time, for a more homogeneous leather material, this difference should be minimal. The maximum differences between the determined physico-mechanical parameters of the semi-finished product of chrome tanning and the minimum for experimental and industrial leather materials were established. The given technological scheme for obtaining an experimental leather material by the technology of syntan-tannin filling-plasticization is more homogeneous with the use of syntan BNS TU 17-06-165-89, mimosa extract with a tannin content of 81.7 %, alkylcarboxyethanolamine of aliphatic acids, dye anionic black K, Fosfol L-1301 emulsions of Cromogenia Units, S.A. (Spain), aluminum potassium alum. For an objective assessment of the homogeneity of the properties of the leather material, a complex indicator is proposed – a coefficient that takes into account the meridian elongation at the crack of the face layer, the limit of strength of the material and its face layer at spherical deformation, which characterize the quality of the leather material according to DSTU 2726-94 «Leather for shoe uppers. Specifications». At the same time, the time-consuming nature of sample preparation and instrumental determination of the properties of leather material is taken into account. The determined complex coefficient of homogeneity of the experimental material is 0.88, and the industrial one is 0.82. This indicates greater homogeneity of the properties of the experimental leather material. A comprehensive analysis and evaluation of the homogeneity of the properties of the experimental leather material testify to the prospects of its use in the manufacture and operation of footwear products.

Keywords: *deformation properties of leather, strength properties of leather, syntane-tannin composition, filling-plasticization, homogeneity coefficient.*

Received date: 11.09.2023
Accepted date: 27.10.2023
Published date: 31.10.2023

How to cite
Danylkovych, A., Sanginova, O. (2023). An effective indicator determination for the leather material uniformity assessment. Technology Audit and Production Reserves, 5 (3 (73)), 6–10. doi: https://doi.org/10.15587/1729-4061.2023.290018

1. Introduction

Natural leather materials, thanks to the combination of high physical, mechanical and hygienic properties, are widely used in the national economy for the manufacture of various products, including footwear, clothing, and technical products. At the same time, it should be noted that leather raw materials are characterized by significant topographic heterogeneity of structure and properties. This heterogeneity of natural raw materials is due, first of all, to different diameters and lengths of elementary collagen fibers and the angle of inclination of their bundles to the leather surface. At the same time, the angle of inclination of the collagen bundles changes from the central spinal line of the shabrack to the peripheral areas – the bottom and groin of the hides from 70 % to 20 % and 5 %, respectively [1]. At the same time, their density and thickness decrease, which is characteristic of mammalian raw materials obtained from females. In this regard, to increase the homogeneity of the structure and properties of leather materials, the technological stage of duplicating and filling the semi-finished product is used [2] using a wide range of chemical reagents and optimized conditions of the process depending on the intended purpose of the leather material. As a result, there is a preferential diffusion of the ingredients of the filling composition into the areas of the semi-finished product of lower density with the filling of interstructural spaces. At the same time, the collagen fibers lengthen somewhat, the angles of inclination of their bundles and the thickness of the semi-finished product increase with the formation of a significant number of intermolecular bonds. At the same time, the topographic homogeneity of the leather material increases.

In this regard, the determination of the objective indicator of the leather material to assess the topographic homogeneity of its structure and properties is of practical importance. This makes it possible to rationally use leather material when cutting it, in particular for shoe parts, with differentiated consideration of the importance of individual parts and operating conditions.

To increase the uniformity of the structure and properties of leather materials in topographic areas, a wide range of reagents is used in the compositions. Thus, in work [3], the influence of polymers – acrylic, melaminoformaldehyde, phenolformaldehyde, and biopolymer on the topographic properties of leather material was studied. The dominant effect of melaminoformaldehyde and biopolymer on bottom areas was established. While the phenol-formaldehyde polymer increases the area yield of the material, and the biopolymer contributes to the alignment of its face layer. Aminopolymer synthesized using glyoxal aldehyde [4] increases the fullness, softness and appearance of the leather semi-finished product compared to samples tanned with aminopolymer containing residual formaldehyde. The authors of the paper [5] showed that amphoteric acrylic copolymer, in contrast to anionic acrylic polymer, increases the strength, softness, and dyeability of the leather semi-finished product. In [6], optical activation of acrylic polymer was carried out to establish its diffusion into the semi-finished product during its duplicating and filling. The diffusion of such a polymer into the structure increases with a decrease in the density of the semi-finished product. Polyacrylic acid/polyurethane surfactant copolymer was synthesized in [7]. An increase in the physical and mechanical properties of the leather material was established when using this copolymer for dubbing the semi-finished product. The obtained results can be used in the development of environmentally safe technology for the production of natural leather.

To retanning of the semi-finished product, the authors of [8] synthesized phosphorus-containing polyurethane modified with graphene nanocomposite oxide. Obtained leathers with increased hydrothermal resistance, physical and mechanical properties and fire resistance. Collagen powder was used [9] to modify water-soluble polyurethane. A product with a uniform distribution of particles with an average size of 70 nm was obtained. Modified polyurethane when duplicating the semi-finished product shows effective filling, especially in the areas of its bottom, and contributes to increasing the hydrothermal resistance and strength of the leather material. The synthesized composition of syntin/tanids/hydrolyzed collagen [10]. It was established that it diffuses mainly into the peripheral topographic areas of the semi-finished product, which contributes to obtaining leather of a more uniform thickness. The effect of mineral, synthetic, vegetable tannins and aldehyde on the properties of semi-finished product Krust was studied [11]. The effect of the type of reagent on the hydrothermal stability, elasticity and vapor permeability of the leather material was established.

Therefore, the analysis of literary sources shows that in order to effectively fill the structure of the leather semi-finished product and level the topographical properties of the leather, the authors take into account both the diffusion properties of the reagents and the chemical activity of the individual ingredients of the composition when developing new technologies. In the works, insufficient attention is paid to the influence of the semi-finished product forming technology on the topographic homogeneity and uniformity of the structure and properties of leather materials.

The aim of research is to determine an effective indicator for evaluating the homogeneity and uniformity of the structure and properties of natural leather material.

2. Materials and Methods

The object of research is the process of determining the objective indicator of the degree of topographic homogeneity of the structure and properties of the leather material.

The work used a leather semi-finished product of chrome tanning with a thickness of 0.9–1.1 mm after planing, obtained from a beef weighing 13 kg, and a material made from it with a thickness of 1.2–1.3 mm. The used semi-finished product is characterized by topographic heterogeneity of structure and properties, which gradually decreases in the multi-stage process of forming the leather material for the upper of shoes (Fig. 1).

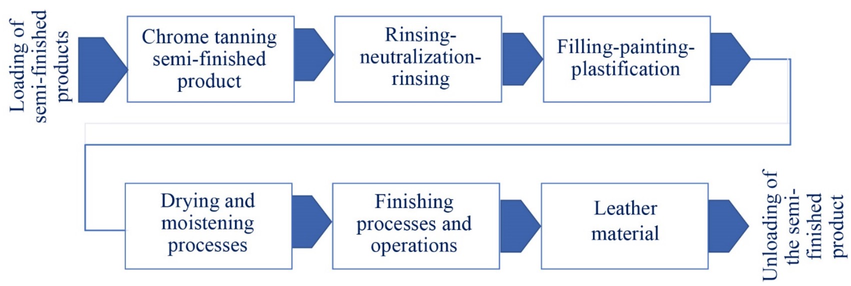

Fig. 1. Technological diagram of the formation of leather material

All technological processes of the formation of leather material at the stage of filling and plasticization were carried out at the private enterprise of Chynbar JSC (Kyiv, Ukraine) in the drum of the experimental workshop of the company Doze (Germany) with a volume of 0.39 m^3. Other technological processes and operations are performed on the enterprise's equipment using industrial technology. It should be noted that for effective leveling of the structure and properties of the experimental leather semi-finished product after its neutralization, a syntan-tannin composition was used, which included: syntan BNS TU 17-06-165-89, mimosa extract with a tannin content of 81.7 %, alkylcarboxyethanolamine of aliphatic acids, anionic black K dye, Fosfol L-1301 emulsion from Cromogenia Units, S.A. (Spain), aluminum potassium alum of Allbiz company, Ukraine. For this purpose, the semi-finished product of the industrial batch was used after the soaking-ash and tanning processes. At the same time, the control option was leather material obtained by industrial technology.

The homogeneity of semi-finished chrome tanning and leather material was assessed based on a complex of physical and mechanical characteristics in topographical sections according to methods [12]. Uniaxial deformation of the samples to determine their strength and elongation was performed on a RT-250M tensile machine at a speed of movement of the lower clamp of 0.09 $m \cdot min^{-1}$. The stiffness, elasticity, and plasticity of the semi-finished product and the material were determined on PZhU-12M and POVSh devices (Ukraine). At the same time, the stiffness on the PZhU-12M was measured in sN by loading a 20–160 mm leather sample bent into a ring to its deflection by 1/3 of the diameter.

Elasticity as a reverse deformation is set in % by the ratio of the amount of straightening of the leather sample after removing the load to the amount of its deflection. Duration of holding the sample under load and after unloading for 30 s. Stiffness was measured at POVSh [13] in *H* by the value of the material's resistance to deformation to a depth of 8 mm under the action of a punch with a sphere with a radius of 5 mm. Plasticity on this device is set in % after determining stiffness by residual deformation. Physico-mechanical indicators, determined during uniaxial deformation and on PZhU-12M, were estimated as the arithmetic mean of their values obtained in the central and four diagonally opposite points of each topographic section according to samples of transverse and longitudinal orientation.

3. Results and Discussion

The results of determining the physical and mechanical parameters of the semi-finished product and leather obtained by experimental and industrial technologies are shown in Table 1. At the same time, the physical and mechanical indicators that determine the quality of the leather material are taken into account in [14]. Taking into account the significant share of the area of the topographical areas – shabrack and bottom of the leather of the calf and the angle of inclination of the bundles of collagen fibers, further studies of the properties were carried out on these areas. The leather produced according to the research technology in the areas of the shabrack and bottom is characterized by higher strength indicators compared to semi-finished chrome tanning, in particular by 6.4 and 8.4 MPa, respectively. Leather obtained by industrial technology is also characterized by higher values of this indicator at 5.1 and 6.1 MPa. At the same time, the difference in the values of this indicator between the shabrack and the bottom of the experimental technology is smaller compared to the industrial technology. The given results testify to the higher efficiency of the research technology processes and the production of leather material with a more uniform structure and properties. In a similar way, the deformation indicators of the shabrack and bottom areas for experimental and industrial hides change compared to semi-finished chrome tanning. At the same time, the difference in indicators between these areas is smaller for the material of the experimental technology, which when deformed with a stress of 10 MPa and the tensile stress is 4.5 and 6.5 and 4 and 7 %, respectively.

Table 1

Physico-mechanical characteristics of leather material under uniaxial deformation

Indicator		Chrome tanning semi-finished product	Leather material	
No.	Name		experimental	industrial
1.1	Limit of leather strength, MPa	18.6/13.1	25.0/21.5	23.5/19.2
1.2	Stress at the appearance of cracks in the face layer, MPa	19.0/25.0	25.0/29.5	25.5/32.0
1.3	Elongation at a stress of 10 MPa, %	19.0/25.0	25.0/29.5	25.5/32.0
1.4	Elongation at break, %	24.0/31.0	55.0/59.0	53.0/60.0

Note: the numerator and denominator correspond to the indicators of the shabrack and bottom

To study the resistance of various topographic areas of the leather material when it is loaded/unloaded, stiffness and elasticity were determined (Figs. 2 and 3). From the obtained data, it can be seen that the difference between the hardness indicators for the areas of the shabrack and the bottom of the experimental leather is also smaller compared to the industrial material, namely by 1.8 times. At the same time, lower absolute values of this indicator in the first case indicate higher elasticity and homogeneity of the test material. High recovery of the deformed leather material is indicated by the obtained elasticity indicators (Fig. 3). And in this case, the difference between the sections of the shabrack and the bottom according to this indicator compared to the industrial material is significantly smaller for the material of the experimental technology by 1.6 times.

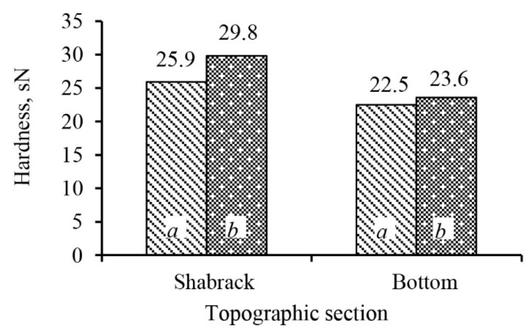

Fig. 2. Dependence of stiffness on the topographical area of the leather: *a* – research, *b* – industrial

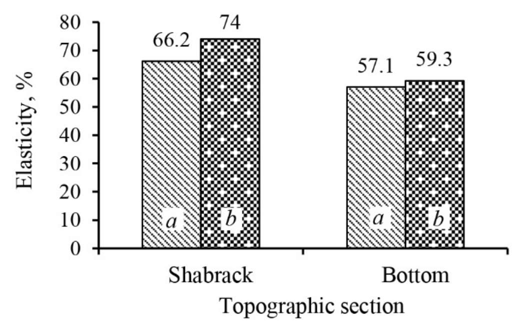

Fig. 3. Dependence of elasticity on the topographical area of the leather: *a* – experimental, *b* – industrial

The results of the study of physical and mechanical indicators in the areas of the shabrack and bottom during spherical deformation of the semi-finished product and the obtained leathers are shown in the Table 2. It should be noted that, in contrast to uniaxial deformation, during spherical deformation, there is a more even distribution of stresses in the sample, especially in the front layer, where their maximum concentration occurs, which increases with the thickness of the leather. At the same time, it is possible to determine the indicator on any topographical area of the leather material without cutting down the samples.

In a similar way, the properties between experimental and industrial materials changed in relation to the semi-finished product. At the same time, smaller differences between the values of the indicators of the areas of the shabrack and bottom were observed for the material of the experimental technology. This especially applies to meridian elongation, in which the differences between the indicators are 1.8 times.

For a more effective and objective characterization of the homogeneity of the semi-finished product and the leather material, the coefficient of homogeneity K_o can be used, which reaches 1.0 in the case of the same values of the determined indicators in the areas of the shabrack and bottom. At the same time, in order to determine this indicator, it is necessary to take the ratio of the smaller value of the physical and mechanical indicator of one topographic section to its larger value of the second section. The results of the study K_o of semi-finished products and leather materials, calculated according to their deformation-strength properties, are shown in Table 3. It should be noted that the chrome tanning semi-finished product has a minimum value $K_o^{\min}$ determined by indicator 2.2 – the appearance of cracks during spherical deformation. At the same time, for experimental and industrial materials $K_o^{\min}$ corresponds to a stiffness index of 2.5 during spherical deformation.

From the obtained data, it can be seen that a significant difference between the minimum values of the coefficients of deformation and strength groups, as well as between their minimum and maximum values in the semi-finished product, indicates its significant heterogeneity. A significantly smaller difference between these indicators and their higher absolute values also indicate an increase in their homogeneity after the filling-plasticization and drying-moistening processes. It should be noted that the research material is characterized by higher homogeneity coefficients. Taking into account the correlation K_o according to the deformation and strength properties of the materials, as well as the high values of the coefficients and, accordingly, according to the elongation at break and at a stress of 10 MPa of the experimental leather material, it can be considered that for an objective assessment of the homogeneity of the properties of leather materials, it is necessary to use a comprehensive assessment of them by topographical areas.

It should be noted that the physical and mechanical parameters determined during spherical deformation of the material play a particularly important role both in the manufacture of footwear products and in their operation.

The obtained results can be used to improve the filling-plasticization processes of leather semi-finished products. The proposed coefficient of homogeneity of leather materials establishes a relationship between the structural and physical-mechanical properties of topographic areas of leather material and is an effective indicator of the quality of filling and plasticizing processes.

Optimization of finishing processes requires the development of mathematical models of the composition-property type and the conduct of additional experiments in production conditions, which, under the conditions of martial law in Ukraine, is a significant limitation of this study.

Prospects for further research are to optimize the composition of syntane-tannin compositions for filling and plasticizing the semi-finished product, taking into account the homogeneity of the leather material.

4. Conclusions

A set of indicators of properties of semi-finished chrome tanning and leather materials has been determined. At the same time, when evaluating the homogeneity of the properties of leather materials, the difference between the values of the physical and mechanical indicators of the shabrack and the floor is taken into account. At the same time, for a more homogeneous leather material, this difference should be minimal. The maximum differences between the determined physical and mechanical parameters of the chrome tanning semi-finished product and the minimum for experimental and industrial leather materials were established. The experimental leather material was obtained by the technology of syntan-tannin filling-plasticization. For an objective assessment of the homogeneity of the properties of the leather material, a complex indicator is proposed – a coefficient that takes into account the meridian elongation at the crack of the face layer, the limit of strength of the material and its face layer at spherical deformation, which characterize the quality of the leather material according to DSTU 2726-94 «Leather for shoe uppers. Specifications». At the same time, the time-consuming nature of sample preparation and instrumental determination of the properties of leather material is taken into account. The calculated complex coefficient of homogeneity of the experimental material is 0.88, and the industrial one is 0.82. This indicates greater homogeneity of the properties of the experimental leather material. A comprehensive analysis and assessment of the homogeneity of the properties of the experimental leather material indicate the prospects of its use in the manufacture and operation of footwear.

Table 2

Physico-mechanical characteristics of leather material under spherical deformation

Indicator		Chrome tanning semi-finished product	Leather material	
No.	Name		experimental	industrial
2.1	Limit of leather strength, N	630/390	1030/890	950/770
2.2	Strength limit of the face layer, N	540/310	980/870	890/740
2.3	Meridian elongation at the appearance of a crack in the face layer, %	46/63	54/60	51/62
2.4	Meridian elongation during leather breakdown, %	48/67	55/61	52/63
2.5	Rigidity, N	43/36	23/18	27/21.5
2.6	Plasticity, %	31/43	33/38	32/39

Note: the numerator and denominator correspond to the indicators of the head and gender

Table 3

Homogeneity coefficients of leather materials

Material	Homogeneity coefficients by indicator groups							
	deformation				strength			
	No.	$K_o^{\min}$	No.	$K_o^{\max}$	No.	$K_o^{\min}$	No.	$K_o^{\max}$
Semi-finished product	2.4, 2.6	0.72	1.4	0.78	2.2	0.57	2.5	0.84
Experimental leather	1.3	0.85	1.4	0.93	2.5	0.78	2.2	0.89
Industrial leather	1.3	0.80	1.4	0.85	2.5	0.80	2.1, 2.4	0.83

ISSN 2664-9969

Conflict of interest

The authors declare that they have no conflict of interest in relation to this study, including financial, personal, authorship, or any other, that could affect the study and its results presented in this article.

Financing

The study was conducted without financial support.

Data availability

The manuscript has no associated data.

Use of artificial intelligence

The authors confirm that they did not use artificial intelligence technologies when creating the presented work.

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