TECHNOLOGY DEVELOPMENT OF LIQUID FINISHING OF CHROME-TANNED GOATSKIN

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ABSTRACT. There has been developed resource-saving environmentally friendly technology for producing chrome-tanned goatskin for shoe upper using new synthetic materials, which involves neutralization in the presence of Politan BN – syntan-neutralizer based on naphthalene sulfonic acid (Codyeco S.p.a., Italy) in the amount of 3.6% (in terms of dry residue), fatliquoring with a mixture of drugs Sulphirol C – a fatliquoring drug based on sulfonated fish oil, resistant to electrolytes (Smit & Zoon, Netherlands) and SMX 473 – a semi-synthetic composition based on sulfonated and sulphated fats (Shebekinsky industrial chemistry, Russia) in the ratio of 70:30 with a total fat consumption of 5.0% (in terms of 100% fat), retanning-filling Retanal LMV 100 – retanning agent based on melamine (Cromogenia Units, Spain) in the amount of 4.5% (in terms of dry residue). This allows to expand the range of chemical materials for liquid finishing and increase production efficiency (conditional economic benefit is UAH 9.22 per 1 m^2 of finished products due to more rational use of raw and material resources), while increasing the uniformity of distribution of tensile strength in different areas of the skin, strength of surface, elongation at strain 10 MPa in 1.2-1.4 times, the skin yield by area increases by 1.8%, and its grade – by 0.7%; improve the physical, mechanical and hygienic properties of the skin; reduce the harmful load on the environment. The technology has passed production tests at PJSC "Chinbar" (Kyiv, Ukraine) and is ready for implementation at tanneries.

KEY WORDS: resource-saving technology, liquid finishing, leather for shoe upper

DEZVOLTAREA TEHNOLOGICĂ A UNUI FINISAJ LICHID PENTRU PIEI DE CAPRĂ TĂBĂCITE ÎN CROM

REZUMAT. S-a dezvoltat o tehnologie ecologică, cu economie de resurse, pentru fabricarea pielii de capră tăbăcită în crom pentru fețe de încălțăminte folosind materiale sintetice noi, care presupun neutralizarea în prezența Politan BN – sintan neutralizator pe bază de acid naftalen sulfonic (Codyeco S.p.a., Italia) în cantitate de 3,6% (reziduu uscat), ungere cu un amestec de Sulphirol C – un agent de ungere pe bază de ulei de pește sulfonat, rezistent la electroliți (Smit & Zoon, Olanda) și SMX 473 – o compoziție semi-sintetică pe bază de grăsimi sulfonate și sulfatate (Shebekinsky industrial chemistry, Rusia) în raport de 70:30 cu un consum total de grăsimi de 5,0% (raportat la 100% grăsime), agent de retăbăcire-umplere Retanal LMV 100 – agent de retăbăcire pe bază de melamină (Cromogenia Units, Spania) în cantitate de 4,5% (reziduu uscat). Acest lucru permite extinderea gamei de materiale chimice pentru finisaj lichid și creșterea eficienței producției (beneficiul economic condiționat este de 9,22 UAH pe 1 m^2 de produs finit datorită utilizării mai raționale a resurselor prime și materiale), crescând în același timp uniformitatea distribuției rezistenței la tracțiune în diferite zone ale pielii, tensionare la apariția fisurilor pe stratul exterior, alungire la deformare de 10 MPa de 1,2-1,4 ori, suprafața utilă a pielii crește cu 1,8%, iar calitatea sa – cu 0,7%; îmbunătățirea proprietăților fizice, mecanice și igienice ale pielii; reducerea poluării asupra mediului. Tehnologia a trecut testele de producție la PJSC „Chinbar" (Kiev, Ucraina) și este gata de implementare în tăbăcării.

CUVINTE CHEIE: tehnologie de economisire a resurselor, finisaj lichid, piele pentru fețe încălțăminte

DÉVELOPPEMENT TECHNOLOGIQUE D'UNE FINITION LIQUIDE POUR CUIR DE CHÈVRE TANNÉ AU CHROME

RÉSUMÉ. Une technologie respectueuse de l'environnement et économe en ressources a été développée pour la fabrication de la peau de chèvre tannée au chrome pour les tiges de chaussures en utilisant de nouveaux matériaux synthétiques, ce qui implique la neutralisation en présence de Politan BN - neutraliseur de syntan à base d'acide naphtalène sulfonique (Codyeco Spa, Italie) en quantité de 3,6% (en termes de résidus secs), graissage avec un mélange de Sulphirol C – un agent de graissage à base d'huile de poisson sulfonée, résistant aux électrolytes (Smit & Zoon, Pays-Bas) et SMX 473 – une composition semi-synthétique à base de graisses sulfonées et sulfatées (Shebekinsky industrial chemistry, Russie) dans le rapport 70:30 avec une consommation totale de graisse de 5,0% (en termes de 100% de graisse), retannage-remplissage Retanal LMV 100 – agent de retannage à base de mélamine (Cromogenia Units, Espagne) à hauteur de 4,5% (en termes de résidus secs). Cela permet d'élargir la gamme de matériaux chimiques pour la finition liquide et d'augmenter l'efficacité de la production (l'avantage économique conditionnel est de 9,22 UAH pour 1 m^2 de produits finis en raison d'une utilisation plus rationnelle des ressources brutes et matérielles), tout en augmentant l'uniformité de la répartition de la résistance à la traction dans différentes zones de la peau, déformation lors de l'apparition de fissures dans la couche externe, allongement lors de la déformation de 10 MPa 1,2-1,4 fois, la surface utile de la peau augmente de 1,8 % et sa qualité – de 0,7%; améliorer les propriétés physiques, mécaniques et hygiéniques de la peau; réduire la pollution de l'environnement. La technologie a passé les tests de production chez PJSC « Chinbar » (Kiev, Ukraine) et est prête à être mise en œuvre dans les tanneries.

MOTS CLÉS : technologie d'économie de ressources, finition liquide, cuir pour tige de chaussure

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INTRODUCTION

One of the common types of hides is goatskin, which has a fairly dense and strong dermis, and the leather made of it is soft and elastic, has a beautiful pattern of the surface grain (pattern) [1]. This determines the attractiveness of such leather as a material for manufacturing high quality model shoes, clothes, haberdashery, etc. That is why recently, in the competition for markets, foreign producers of soft, elastic leather goods from goatskin are increasingly entering the Ukrainian market, thus displacing the domestic producer. Therefore, the current problem is the creation of goatskin production technology with improved physical, mechanical and hygienic properties to meet the functional and operational requirements for footwear, and given the realities of the current state of the economy and ecology, – strengthening the resource-saving and environmental imperative of new development.

Skinners have known for a long time about the impact of dyeing-fatliquoring processes on the physical and mechanical, hygienic and other properties of the skin, the purpose of which is to further form the structure of the dermis after tanning. The composition and sequence of the individual stages of liquid finishing are different and depend on the type and purpose of the skin. The processes of retanning, filling, fatliquoring are precisely the processes that, after treatment with tannins, change the characteristics of leather products most significantly [2, 3].

Advanced reagents for retanning-filling are polymeric compounds obtained on the basis of acrylic and maleic acids [4-10], syntans with low formaldehyde content [11-19], as well as products of industrial waste modification [20, 21]. Improving the fatliquoring involves the use of more effective substances of both synthetic and natural origin individually and in the form of compositions (mixtures) [22-27], or in general with a change in the technological scheme, for example, by applying thermostable enzymes before fatliquoring [28].

According to the analysis of the literature and practical experience of enterprises in the industry, it has been established that the most part of all research to improve existing or develop innovative technologies is based on the search for and introduction of new modern chemical materials. At the same time, the effectiveness of the study is most clearly manifested at the stage of liquid finishing, during which there is an additional formation of the dermis structure and adding the desired properties to the skin. Based on the above, the purpose of this study has been formulated to develop resource-saving and environmentally friendly technology for liquid finishing of chrome-tanned goatskin.

EXPERIMENTAL

Materials and Methods

The study uses a semi-finished product from goatskin, as well as chemical materials common in leather production as a means for liquid finishing of the skin: Sulphirol C – a fatliquoring material based on sulfonated fish oil, resistant to electrolytes (Smit & Zoon, Netherlands); SMX 473 – semi-synthetic composition based on sulfonated and sulphated fats (Shebekinsky industrial chemistry, Russia); Politan BN – syntan-neutralizer based on naphthalene sulfonic acid (Codyeco S.p.a., Italy); Retanal LMV 100 – a melamine-based retanning agent (Cromogenia Units, Spain).

Microscopical Method

The impact of liquid finishing on the change of the supramolecular structure of the dermis collagen and the way of sedimentation of the chrome tanning agent in the supramolecular structure have been studied with the help of scanning electronic microscopy (SEM) using the device JSM-6490-LV, GEOL (Japan) and applying microprobe analyses based on energy- and wave dispersion spectrometers (EDS + WDS, OXFORD, UK) [29].

Methods of Studying the Skin Properties

Physical and mechanical trial runs and the chemical analysis of the leather have been done using the official IULTCS methods: sampling location (ISO 2417:2016), sample preparation and conditioning (ISO 2419:2012), shrinkage temperature (ISO 3380:2015), strength of surface (ISO 3379:2015), strength and percentage extension (ISO 3376:2011), apparent density (ISO 2420:2002), measurement of thickness (ISO 2589:2016), measurement of area (ISO

11646:2014), determination of tear load (ISO 3377-1:2011), water vapour permeability (ISO 14268:2012).

The margin of error of the test when studying physical and mechanical properties was at most 5 %, the one of chemical composition indices was at most 3%.

RESULTS AND DISCUSSIONS

The results of previous studies [29-34] have become the basis for developing technology for producing chrome-tanned goatskin for shoe upper by using selected synthetic and fatliquoring materials during liquid finishing. Technological parameters and sequence of physical and chemical processes are given below:

1. *Washing*: float ratio (FR) 1.5, temperature 30-35°C, duration 0.5 h;

2. *Neutralization*: FR 1.0, temperature 32-35°C, duration 1.0-1.5 h, consumption Politan BN 3.6% (in terms of dry residue). The end of the process is determined by the pH of the spent solution indicator bromocresol green;

3. *Washing*: FR 1.5, temperature 30°C, duration 0.5 h;

4. *Washing*: FR 1.5, temperature 30°C, non-ionic surfactant (e.g. Savenol NWP) 0.2%, duration 0.5 h;

5. *Dyeing*: FR 1.0, temperature 32-35°C, duration 2.0 h, consumption of dye diluted with water in a ratio of 1:10, 4.0%. After complete absorption of the dye, dilute (1:10) formic acid in the amount of 1.0% is added to the solution, the treatment is continued for another 30 minutes;

6. *Washing*: FR 1.5, temperature 50-55°C, duration 15 min;

7. *Fatliquoring*: FR 1.0, temperature 50-55°C, duration 1.0 h; a mixture of drugs Sulphirol C and SMX 473 in a ratio of 70:30 with a total fat consumption of 5.0% (in terms of 100% fat);

8. *Washing*: FR 1.5, temperature 35-40°C, duration 15 min;

9. *Retanning-filling*: FR 1.0, temperature 35-40°C, duration 1.0 h, Retanal LMV 100 4.5% (in terms of dry residue);

10. *Washing*: FR 1.5, temperature 35-40°C, duration 15 minutes.

The consumption of all materials is calculated from the shaved weight considering the activity (or dry residue) of the reagents used.

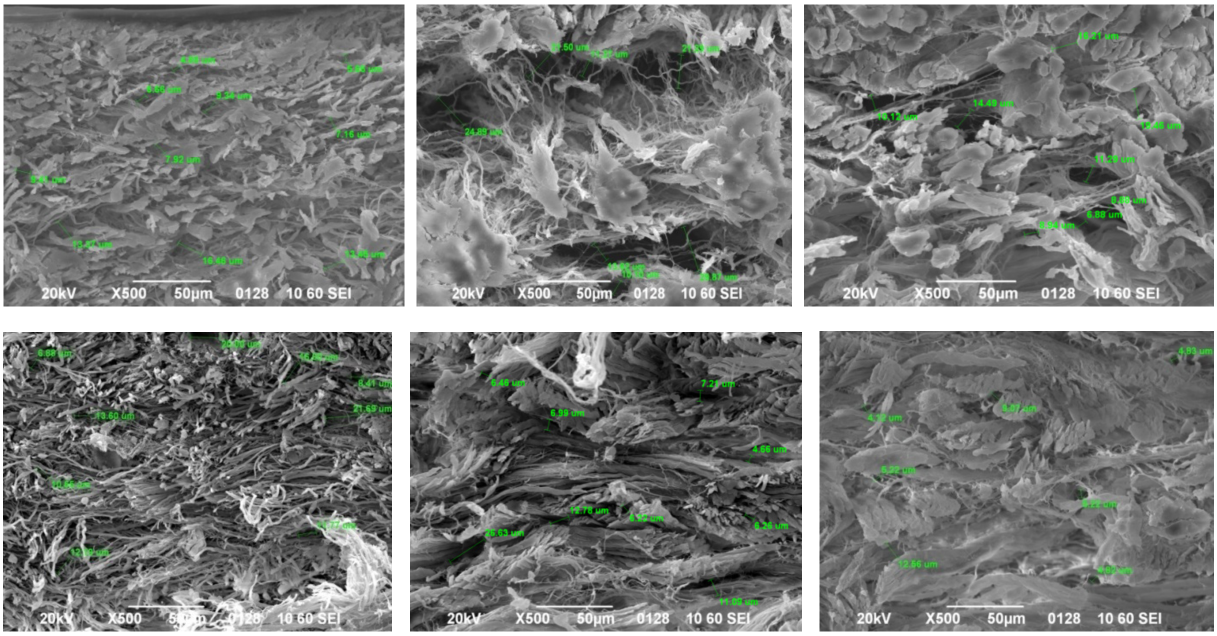
All previous and subsequent processes and operations are performed according to the known method of producing chrome-tanned goatskin for shoe upper [35].

The effectiveness of the new technology has been evaluated on the basis of analysis of photographs of microscopic sections, chemical composition and physical and mechanical tests of chrome-tanned leather from goatskin. For comparison, skin samples were used that were treated in the same sequence, but the neutralization process was performed with 0.6% carbonate and 1.5% sodium formate, the fatliquoring – using only the composition SMX 473 (consumption 5.0%), retanning-filling – Quebracho tannins (consumption of 4.5% by weight of samples).

After drying and moistening processes and operations, the final finishing of the skin was carried out by double coating of the following composition, wt. p. (consumption 70 ± 10 g/m^2): Codyeco RPI 4377 (18%) – 150; Acrylic 1755 (28.6%) – 100; casein (10%) – 50; wax emulsion (20%) – 40; water – 200. To fix the coating the composition was used, wt. p. (consumption 55 ± 10 g/m^2): nitro emulsion LE 5555 (80%) – 100; water – 100.

There were no complications during the treatment of the experimental group. According to organoleptic evaluation, the semi-finished product and finished leather had a pleasant neck and a clean, silky surface grain.

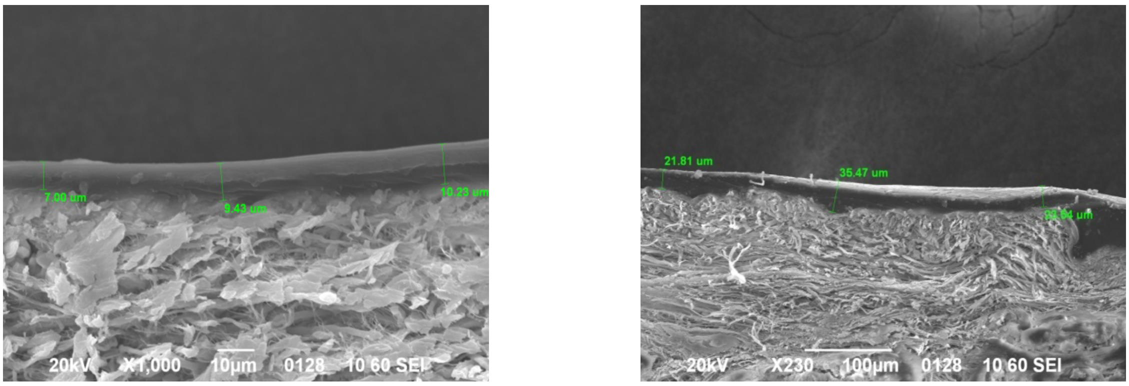
For microscopic examination and electron probe analysis, sections of skin samples were used, which were first dried with an alcohol-ether mixture, then, to provide electrical conductivity, they were coated with gold. As a result of the performed manipulations, microphotographs (Figure 1) were obtained, as well as spectrograms of the content and distribution of chromium compounds in the structure of the dermis (Figure 2).



b

Figure 1. Micrographs of the cross-section of the skins of the experimental (a) and control (b) groups (x 500)

From the obtained microphotographs (Figure 1) we can conclude that in skin samples there are morphological changes in the structure due to the nature of its formation, which is manifested in a more uniform, "layered" arrangement of individual structural elements, increasing the average distance between individual elements (L_{aver}) of experimental samples manufactured using the new technology (12.92 ± 6.24 µm) compared to the control ones (10.21 ± 5.72 µm).

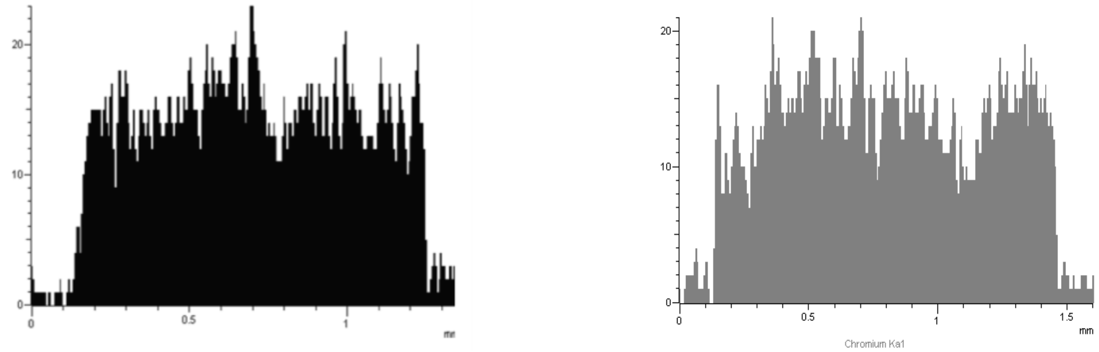


a b

Figure 2. Determination of coating thickness on skin microsections of the experimental (a) and control (b) groups (x 1000, x 230)

After measuring the thickness of the coating on micro cuts of the skin (Figure 2) a significant improvement of this indicator was found in the experimental group compared with the control group, because the average thickness of the coating (T_{aver}) on the experimental samples averages out 8.89 ± 1.37 µm, which 3,03 times less than the control indicator (26.94 ± 6.07 µm).

According to the results of electron probe analysis, it has been found out that in the experimental group, chromium tanning agent is distributed in the dermis, especially in its middle layers, more evenly than in the control group (Figure 3).



a b

Figure 3. WDS-analysis of the cross-section of the skins of the experimental (a) and control (b) groups

All of the above should increase the strength, elastic-plastic and hygienic properties of the skin, the quality of the coating on it, which is confirmed by the results of chemical analysis and physical and mechanical tests of the samples (Table 1).

To confirm the results of the laboratory tests, the new technology was tested in the production conditions of Kyiv leather enterprise PJSC "Chinbar" on a shaved semi-finished product Wet Blue, obtained by the current technology of production of chrome-tanned goatskin for shoe upper.

The weight of the experimental and control batches in the raw material was 400 kg. To obtain objective data, the method of alternating halves was used [36].

Table 1: Indicators of chrome-tanned goatskin for shoe upper (laboratory tests)

Index	Experimental group	Control group
Mass content, % (per completely dry substance), % – chromium oxide	4.6	4.4
– minerals	11.0	11.5
– substances, extracted with organic solvents	8.0	7.4
Tensile strength, MPa, σ_t	1.93	1.80
Strength of surface, MPa, σ_s	1.80	1.60
$\Delta\sigma = \sigma_t - \sigma_s$, MPa	0.13	0.20
Elongation at strain 10 MPa, %	30.0	25.0
Elongation at fracture, %	76.0	79.0
Distribution efficiency of tensile strength	0.82	0.46
Distribution efficiency of strength of surface	0.84	0.53
Distribution efficiency of percentage extension at 10 MPa	0.96	0.75
Distribution efficiency of elongation at fracture	0.87	0.85
Water vapour permeability, mg/sm^2 · h	2.11	1.89
Porosity, %	57.5	54.0
Yield on the thickness, %	92.0	90.8
Yield on the area, %	93.1	92.1
Volume yield, sm^3/100 g of protein	322.5	274.6
Shrinkage temperature, **°C**	105.5	104.0
Absorption drop of water, h	2.0	1.9
pH potassium chloride extract	4.7	4.3
Coating resistance to multiple bending, points	3.0	3.0
Coating resistance to wet friction, rotations	130.0	115.0
Adhesion of coating to the subsurface, H/m: – dry	450.0	430.0
– wet	110.0	100.0
Thickness of cover, g/mm^2	0.25	0.29

The semi-finished product of the experimental batch was processed according to the new technology, following the scheme: washing - neutralization - washing 1, 2 - dyeing - washing - fatliquoring - washing - retanning-filling - washing.

The semi-finished product of the control batch was neutralized with sodium carbonate and formate at a consumption of 0.6 and 1.5%, respectively, and fatliquoring was performed only with the drug SMX 473 at a consumption of 5.0%; retanning-filling was performed with Quebracho tannins in the amount of 4.5%.

The consumption of all materials was determined from the shaved weight. All subsequent processes and operations were performed according to the current technology.

As before, during laboratory tests, no complications occurred during the processing of the experimental batch. According to organoleptic evaluation, the semi-finished product and finished leather had a pleasant neck and a clean, silky surface grain. In addition, the tested skins not only met the requirements of regulatory documentation, but also improved physical, mechanical and hygienic properties compared to skins made by the current technology (Table 2). Thus, the content of minerals in the experimental skins is less by 3.5%, and substances extracted with organic solvents, on the contrary, more by 13.2%. The tensile strength during stretching increases by 4.5%, and the strain during the appearance of cracks in the front layer by 8.4%. Reducing the difference between the strength of the skin as a whole and the strength of its outer layer indicates a more uniform distribution of chemical reagents in the structure of the dermis, which has a positive effect on the elastic-plastic and hygienic properties, the area received. The use of new chemical materials at the stage of liquid finishing has a positive effect on the quality of the coating on the skin, the thickness of the coating film.

The advantages of the new technology are also revealed in reducing the fat content in the spent solution by 5.6%, improving the ratio of biological oxygen demand (BOD) and chemical oxygen demand (COD) to 71.4%, which will help green production, increase the likelihood of cleaning industrial effluents by biological methods.

The conditional economic benefit from introducing a new technology of liquid finishing of chrome-tanned leather from goatskin for the shoe upper will be equal to UAH 9.22 per 1 m^2 of finished products due to more rational use of raw and material resources, while the yield of leather by area increases by 1.8%, and its grade – by 0.7%.

Table 2: Comparative evaluation of new and current technologies for producing chrome-tanned goatskin for shoe upper (production tests)

Index	New technology	Current technology	DSTU 2726-94
Leather:			
Mass content, % (per completely dry substance), %			
– chromium oxide	4.5	4.2	no less 3.5
– minerals	10.9	11.3	–
– substances, extracted with organic solvents	8.3	7.2	3.7-10.0
Tensile strength, MPa	1.99	1.90	no less 1.80
Strength of surface, MPa	1.91	1.75	no less 1.50
Elongation at strain 10 MPa, %	32.0	27.0	15-35
Distribution efficiency of tensile strength	0.80	0.59	–
Distribution efficiency of strength of surface	0.81	0.63	–
Distribution efficiency of elongation at strain 10 MPa	0.90	0.72	–
Water vapour permeability, mg/$sm^2 \cdot h$	2.15	1.90	–
Yield on the thickness, %	91.5	89.7	–
Yield on the area, %	92.6	90.8	–
Coating resistance to multiple bending, points	4	3	no less 3
Coating resistance to wet friction, rotations	140	120	no less 100
Adhesion of coating to the dry/wet subsurface, H/m:	460/115	445/110	–
Grade, %	90.6	89.9	–
Waste solution after liquid finishing:			
Fat content, mg/dm^3	236.0	250.0	–
CSAA content, mg/dm^3	117.0	125.0	–
Biochemical oxygen demand / Chemical oxygen demand, %	71.4	68.3	–

CONCLUSIONS

Resource-saving environmentally friendly technology has been developed for producing chrome-tanned goatskin for shoe upper using new synthetic materials, which involves neutralization in the presence of Politan BN – syntan-neutralizer based on naphthalene sulfonic acid (Codyeco S.p.a., Italy) in the amount of 3.6% in terms of dry residue), fatliquoring with a mixture of drugs Sulphirol C – fatliquoring drug based on sulfonated fish oil, resistant to electrolytes (Smit & Zoon, Netherlands) and SMX 473 – semi-synthetic composition based on sulfonated and sulphated fats (Shebekinsky industrial chemistry, Russia) in the ratio of 70:30 with a total fat consumption of 5.0% (in terms of 100% fat), retanning-filling Retanal LMV 100 – retanning agent based on melamine (Cromogenia Units, Spain) in the amount of 4.5% (in terms of dry residue).

According to the results of laboratory studies using scanning electronic microscopy (SEM), electron probe and other methods of instrumental and chemical analysis, it was found that in comparison with the current technology, the new technology provides more efficient use of raw and material resources due to more orderly arrangement of chemical materials in the dermis forming strong and at the same time flexible bonds. This is confirmed by the results of production testing in the terms of Kyiv leather enterprise PJSC “Chinbar”, which established the following advantages of the new technology:

- reduction of mineral content in the skin by 3.5%, which will prevent the formation of salt spots during its operation in adverse climatic conditions in the form of precipitation;
- increase in the content of unbound fatty substances in the skin by 13.2%, which improves its elastic-plastic properties (elongation at strain 10 MPa increases by 15.6%) and the composition of wastewater (fat content in the spent solution decreases by 5.6%);
- increase of the strength of the skin as a whole by 4.5%, and its outer layer by 8.4%;
- improvement of hygienic properties (vapour permeability increases by 11.6%);
- reduction of the anisotropy of the main indicators of physical and mechanical properties (increasing the uniformity of distribution in different directions of the skin of tensile strength during tension, strain during cracking of the outer layer, elongation at strain 10 MPa in 1.2-1.4 times), that will cause more rational use of skin during cutting on details of footwear;
- increase in yield in thickness and area by 1.8%, respectively;
- improvement of the quality of the skin coating (indicators of resistance of the coating to repeated bending and wet friction, the adhesion of the coating film to the skin increases by 1.3, 1.2 and 1.1 times, respectively), which will also positively affect the consumer properties of leather products;
- improvement of the wastewater composition – in addition to the already mentioned reduction of fat content in the spent solution, the ratio of biochemical oxygen demand (BOD) and chemical oxygen demand (COD) increases to 71.4%, which will help green production, increase the likelihood of industrial wastewater treatment.

In case of introduction of new resource-saving technology into production, the expected economic benefit will be UAH 9.22. per 1 m^2 of finished products due to a more rational use of raw and material resources, while the skin yield by area will increase by 1.8%, and grade – by 0.7%.

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