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EVALUATION OF THE EFFICIENCY OF LIQUID LEATHER FINISHING USING POLYMERS AND MODIFIED FATS

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The efficiency of technological processes and the quality of leather products largely depend on the nature and technological capabilities of the chemical materials used. This is especially true for liquid finishing, which after tanning is responsible for the further formation of the structure and properties of the leather. Numerous publications note the advantages of using polyacrylates and modified fats in liquid finishing, however, there are references to a decrease in the strength and quality of leather dyeing when using polymers. The purpose of study was to determine the efficiency of liquid finishing of chrome leather for shoe uppers made from cattle raw materials using a new series of polymer compounds based on acrylic acid and modified fats during filling-retanning and fatliquoring. Using standard methods of studying the chemical composition, physical and mechanical characteristics and hygienic properties of the skin, as well as microscopic analysis of its structure, it was established, that the developed technology makes it possible to improve the consumer and cutting properties of leather, as indicated by an increase in many indicators: fat content, strength, elongation, yield in thickness and area, vapor permeability, resistance of the coating to wet friction, reduction of anisotropy of the main indicators of physical and mechanical properties, etc. In addition, taking into account the increasing degree of processing of solutions, the environmental load on the environment is reduced. The achieved result can be explained by the nature of the distribution and fixation of chemical materials in the structure of the dermis with the formation of strong and at the same time flexible bonds.

Keywords: liquid finishing, chemical materials, leather properties

INTRODUCTION

Active implementation of innovative developments in the production of leather, textile, non-woven materials and products allows to significantly improve the consumer properties of these materials, expand the range of their functional capabilities. The use of effective chemical materials in the form of polymer compounds, surfactants, etc. plays a significant role in this. Thanks to the physicochemical modification of structural elements and the surface, competitive products with optimized characteristics are developed. Examples include texturing, embossing, filling, which provide protection of the product from water and wind, abrasion resistance, volume, permeability of water vapor and gases, chemical resistance (Petrova *et al.*, 2023). Another example is the study of the fiber-forming properties of polymer blend melts: polypropylene-copolyamide (PP/CPA), polyoxymethylene-copolyamide (POM/CPA), POM-copolymer of ethylene and vinyl acetate (POM/EVAC), PP/EVAC, EVAC/CPA, polypropylene-polyvinyl alcohol (PP/PVA). The ability of melts of such mixtures to form fibers was assessed by the degree of longitudinal deformation of the polymer melt. The authors found that the fiber-forming properties of polymer melts can be controlled by changing the chemical nature of the mixture components, the processes of structure formation, and the introduction of various polymer additives and non-polymer additives into the binary mixture. Complex threads made from PP, POM, or EVAC microfibers have such excellent properties as high strength and initial modulus, high elasticity, exceptional softness, pleasant feel, adhesion, capacity, and wooliness without special textural procedures, high sorption of moisture, dyes, and other compounds (Tsebrenko et al., 2004).

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The efficiency of technological processes and the quality of leather goods also largely depend on the nature and technological capabilities of the materials used. This is especially true for liquid finishing, which after tanning is responsible for the further formation of the leather structure and properties. Traditional technologies for retanning and filling of semi-finished leather products include a wide range of plant, polymer and mineral compounds. At the same time, the limited production and high cost of plant tannins contributed to the development of synthetic compositions for retanning and filling, also with the aim of completely eliminating or partially replacing expensive plant tannins. Since there is insufficient information in the scientific literature on compositions that could fully reproduce the retanning and filling effect on the structure of semi-finished leather products, similar to the effect of plant tannins, the development of a new retanning and filling composition for leather production based on lignosulfonates and highly dispersed natural minerals has become relevant (Mokrousova, 2010).

A number of recent studies have noted the advantages of using polyacrylates (Zaiets & Andreyeva, 2023a; Canudas *et al*., 2019; Jin *et al*., 2019; Yi *et al*., 2024; Dudu *et al*., 2024) and modified fats (Zaiets & Andreyeva, 2023a; Sahu *et al*., 2021; Nkwor & Ukoha, 2023; Niyozova, 2023; Alam *et al*., 2024) for liquid finishing. However, there are some references to the fact that leathers retanned with acrylic polymers have lower color intensity and worse structural properties (strength) due to their high anionic activity, which changes the cationic surface of the leather, causing lower interaction of dyes and fatliquoring agents with the leather (Canudas *et al*., 2019; Jin *et al*., 2019; Yi *et al*., 2024). The purpose of this study was to determine the efficiency of liquid finishing of shoe upper leather from cattle hides using a new series of polymer compounds based on acrylic acid and modified fats during retanning-filling and fatliquoring.

MATERIALS AND METHODS

To carry out the dyeing and fatliquoring processes, a number of new generation chemical materials were used in the work:

- Syntan RS-540 (Smit&Zoon, the Netherlands) – a polymer resin based on acrylic acid;
- Synthol LC (Smit&Zoon, the Netherlands) – fatliquoring mixture based on natural and synthetic oils, sulfonated triglycerides, lecithin mixture;
- Sulphirol EG-60 (Smit&Zoon, the Netherlands) – fatliquoring mixture based on sulfated natural and synthetic oils;

as well as imported materials that are widely used in practice /quebracho tannins (China) for retanning-filling; Provol BA (Zschimmer&Schwarz, Germany) – a fatliquoring agent based on lecithin; Sanodal Black (Clariant Inc, Switzerland) – anionic black dye/ and domestic materials /sodium formate, bicarbonate and carbonate for neutralization, acetic acid to enhance the spreading of the fatliquoring emulsion and improve the distribution of fatliquoring materials in the dermis; ammonium hydroxide and nonionic surfactants to increase the stability of the emulsion/.

Based on previously conducted studies of the structure, physicochemical properties and technological capabilities of a number of modern polymer compounds and modified fatliquoring materials (Zaiets & Andreyeva, 2024a; 2024b; 2024c; 2023b), a process map was created for the liquid finishing of Wet Blue – a semi-finished product of the chrome tanning method for the shoe upper leather from cattle hides, the peculiarity of which is the implementation of the retanning-filling process using Syntan RS-540 with a halved consumption of vegetable tannins (quebracho tannins), and the fatliquoring process – using modified fats Synthol LC and Sulphirol EG-60 (Zaiets & Andreyeva, 2024d):

1. Washing: water – 100-150%, surfactant – 0.3%, acetic acid – 0.5%, temperature 30 ºC, duration 20 min.
2. Washing: water – 100-150%, temperature 30 ºC, duration 20 min.
3. Retanning: water – 150%, chrome tanning – 4.0%; temperature 30 ºC, duration 60 min; sodium bicarbonate – 0.2%, duration 60 min.
4. Washing: water – 100-150%, temperature 30 ºC, duration 20 min.
5. Neutralization: water – 200-250%, sodium bicarbonate – 0.5-0.7%, sodium formate – 0.5-0.7%, temperature 30-35 ºC, duration 60 min.
6. Washing: water – 100-150%, temperature 30 ºC, duration 20 min.
7. Retanning-filling: water – 150%, temperature 30-35 ºC, Syntan RS-540 – 3.0-6.0%; duration 40-60 min; quebracho tannins – 2.0%, 40-60 min.
8. Washing: water – 100-150%, temperature 30-50 ºC, duration 20 min.
9. Fatliquoring: water – 150%, temperature 45-50 ºC, duration 5 min; Synthol LC – 3.0-6.0%, Sulphirol EG-60 – 3.0-6.0%, duration 60 min; acetic acid – 1.0%, duration 60 min.
10. Washing: water – 100%, temperature 30 ºC, duration 10 min.

Liquid finishing processes are carried out with constant rotation of the equipment. The consumption of materials is calculated for the technical product. A fat emulsion with a concentration of 25% is prepared by gradually adding water (temperature 45-50 ºC), 2.0% surfactant and 0.5% of a 10% ammonium hydroxide solution (based on the weight of the fat) to the fat sample. Stirring is constant. After liquid finishing, the leather is processed using the traditional method of drying and tempering processes and operations and leather coating (Danilkovich & Mokrousova, 2009).

Subsequently, taking into account the created process map, rational parameters of liquid finishing were determined by mathematical modeling, providing for retanning-filling of the semi-finished product Wet blue with acrylic polymer Syntan RS-540 at a consumption of 3.0%, a temperature of 30-35 °C for 1-2 hours and fatliquoring with modified fats Sulphirol EG 60 and Synthol LC at a consumption of 3.0%, a temperature of 45-50 °C for 1.5-2 hours. The final finishing in the work was carried out by double application of a coating of the following composition, wt. parts: Compound VR (30%) – 60; acrylic AM 146 (42.5%) – 80; Rokril SW 4025 (40%) – 120; wax emulsion (20%) – 40; water – 200. Consumption – 80 g/m^2 (Zaiets & Andreyeva, 2024d).

The properties of the chemical and leather materials studied in the work were assessed using the analysis methods common in the leather industry (Danilkovich, 2006) in accordance with regulatory documentation, for example: DSTU EN ISO 2419: 2020 (EN ISO 2419: 2012, IDT; ISO 2419: 20 Leather. Physical and mechanical tests. Preparation and conditioning of samples; 3376: 2022 (EN ISO 3376: 2020, IDT; ISO 3376: 2020, IDT) Leather. Physical and mechanical tests. Determination of tensile strength and elongation in percent; DSTU EN ISO 17236: 2022 (EN ISO 17236: 2016, IDT; ISO 17236: 2016, IDT) Leather. Physical and mechanical tests. Determination of elongation set; DSTU ISO 3380:2022 (EN ISO 3380:2015, IDT; ISO 3380:2015, IDT) Leather. Method for determining shrinkage temperature; DSTU EN ISO 14268:2022 (EN ISO 14268:2012, IDT; ISO 14268:2012, IDT) Leather. Physical and mechanical tests. Determination of water vapour permeability; DSTU EN ISO 4048:2022 (EN ISO 4048:2018, IDT; ISO 4048:2018, IDT) Leather. Chemical tests. Method for determination of substances soluble in dichloroethane; EN ISO 5398-1:2022 (EN ISO 5398-1:2018, IDT; ISO 5398-1:2018, IDT) Leather – Chemical determination of chromium oxide content – Part 1: Quantitative determination by titration, etc.

It was experimentally established that, in comparison with the known technology, the developed technology of liquid finishing allows improving the strength, hygienic and elastic-plastic properties of finished leather, this is indicated by the results of chemical analysis and physical and mechanical tests (Zaiets & Andreyeva, 2024d). The importance of drum dyeing for the appearance of leather and its commercial value is well known from the theory and practice of tannery production. Based on this, this study was devoted to refining the process parameters and determining the efficiency of liquid finishing using polymers and modified fats, additionally including in the proposed process flow chart after retanning-filling the process of drum dyeing under the following conditions: consumption of anionic dye Sanodal Black 4.0% of the semi-finished product weight, duration 1 hour, temperature 30-40 ºC. During retanning-filling of experimental samples of Wet Blue from cow hide, 3.0% acrylic polymer Syntan RS-540 and 2.0% quebracho tannins were used; with fatliquoring with 3.0% of modified fats Synthol LC and Sulphirol EG 60. In the control group, 4.0% of quebracho tannins were used for retanning-filling, and 6.0% of the well-known anionic fat Provol BA were used for fatliquoring. The leather was processed after liquid finishing using the well-known method for producing shoe upper leather from cattle hides (Danilkovich & Mokrousova, 2009). The leather coating was carried out in the same way as indicated above.

RESULTS

No complications were observed during the experiment. The experimental leather samples were uniformly dyed and painted black, had a clean front surface, and a pleasant handle. The color of the control samples was black with a greenish tint.

The results of chemical analysis and physical and mechanical tests presented in Table 1 indicate a positive effect of liquid finishing using 3.0% acrylic polymer, 3.0% of each of the two modified fats involved in the work, and 4.0% Sanodal Black dye on the indicators of finished leather and the choice of chemical materials from solutions, since the following occur:

Table 1. Indicators of finished leather and the degree of processing of working solutions

Indicator	Experience	Control
Leather:		
Mass part (on abs dry matter), %:		
- chromium oxide	4.21	4.00
- substances extractable by organic solvents	5.00	4.47
Tensile strength σ_1, 10 MPa	1.89	1.78
Stress at appearance of cracks in the outer layer σ_2, 10 MPa	1.84	1.65
$\Delta = 100 \cdot [(\sigma_1 - \sigma_2) / \sigma_1]$, %	2.7	7.3
Elongation at 10 MPa stress *L10*, %	37.9	34.0
Uniformity coefficient $K\sigma\ \sigma_1 / K\ \sigma_2 / K_{L10}$	0.89/0.86/0.79	0.78/0.74/0.62
Shrinkage temperature, °C	114.0	112.5
Vapor permeability, %	83.9	77.0
Coloring, %	70.6	59.5
Colour resistance, points:		
- to dry friction	4	3
- to wet friction	4	3
Coating resistance to wet friction, rpm	240	200
Resistance of the coating to repeated bending, points.	4	4
Output by area, %	97.6	91.8
Output by thickness, %	90.1	88.3
Spent solution:		
Degree of processing, %, after:		
- retanning-filling	86.0	80.3
- drum dyeing	74.8	65.2
- fatliquoring	83.0	76.4

- increase in the content of unbound fatty substances (substances extractable by organic solvents) in the leather by 11.8%, which improves its elastic-plastic properties (the elongation at 10 MPa stress increases by 11.5%);
- increase in overall leather strength (tensile strength) by 6.2%, and in the strength of its outer layer by 11.5%;
- decrease in the difference between overall leather strength and the strength of its outer layer by 2.7 times, which indicates a more uniform distribution of chemical materials in the dermis, which in turn improves the elastic-plastic properties and output by area;
- decrease in the anisotropy of the main indicators of physical and mechanical properties (increase in the uniformity coefficients of distribution in different directions of the leather of the tensile strength, stress at the appearance of cracks in the outer layer and elongation at 10 MPa stress by 1.1-1.2 times), which will lead to a more rational use of leather materials when cutting into foot-wear components;
- improvement in leather dyeability by 18.7% rel.;
- increase in the resistance of dyeability to dry and wet friction by 1 point;
- improvement in hygienic properties (the vapor permeability index increases by 9.0%);
- increase in output by thickness and area by 1.8%abs and 5.8% abs, respectively;
- improvement in the quality of the coating on the leather (the coating resistance to wet friction increases by 1.2 times), which will also have a positive effect on the consumer properties of leather products;
- improvement in the composition of wastewater due to an increase in the degree of solution processing after retanning-filling by 7.0% rel., after drum dyeing – by 14.7% rel., after fatliquoring – by 8.6% rel.

Improvement of the degree of dye solution processing, dyeability and coloring of leather in the experimental group showed the possibility of more economical use of dye. An additional experiment confirmed this possibility, since with a decrease in the consumption of Sanodal Black dye from 4.0 to 3.0% (i.e. by 25%), the extraction of dye from the solution, dyeability and coloring of leather really improved, the strength and vapor permeability indicators, and the resistance of dye to dry and wet friction increased (Table 2).

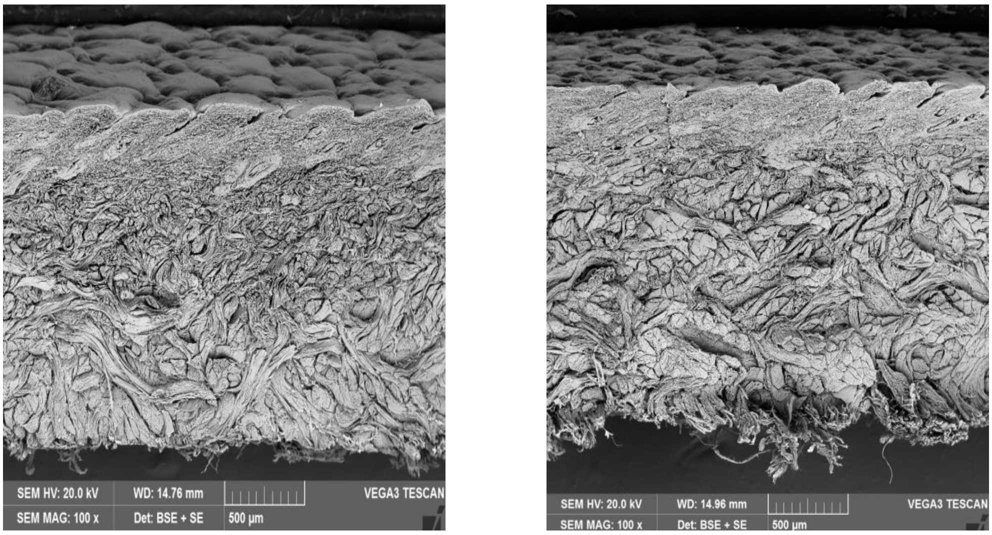
Table 2. Determining the possibility of reducing dye consumption

Indicator	Value for dye consumption	
	3.0%	4.0%
Degree of processing after drum dyeing, %	75.0	65.5
Coloring, %	80.1	60.2
Tensile strength σp, 10 MPa	2.00	1.80
Stress at appearance of cracks in the outer layer, 10 MPa	1.96	1.60
Elongation at 10 MPa stress *L10*, %	37.0	32.5
Vapor permeability, %	85.9	76.8
Colour resistance, points:		
- to dry friction	4	3
- to wet friction	4	3

Based on the results of the conducted research, the technology of liquid finishing using polymer and modified fats can be finally presented in the form of the following simplified scheme: washing 1,2 – retanning with chromium compounds – washing – neutralization – washing – retanning-filling with organic compounds (polymer Syntan RS + tannins quebracho with a 50% reduction in vegetable tannins consumption) – drum dyeing (reduction in dye consumption by 25%) – washing – fatliquoring with modified fats Synthol LC and Sulphirol EG 60 – washing.

Using a scanning electron microscope SEM JSM-6490-LV (GEOL, Japan), the effect of liquid finishing on the morphological structure of Crust (uncoated leather) was established, which manifests itself in a decrease in the spread of voids over the area, an increase in the density of the structure in the direction of the front surface during retanning-filling with polymer and fatliquoring with modified fats (Figure 1).

In the micrographs of the experimental samples, a more ordered structure of the dermis is observed – a more uniform separation of collagen fiber bundles and the location of interbundle spaces (Figure 1, a).



a *b*

Figure 1. Electron microscopic image of cross-sections of skin samples (x100): *a* – experiment; *b* – control

Industrial testing of the developed technology confirmed the results of laboratory studies. Based on the evaluation of the properties of finished leather made using acrylic polymer and modified fats during liquid finishing, it can be concluded that such treatment improves the properties of leather, avoiding problems with the strength and coloring of traditional acrylic resins. The use of Syntan RS-540 as a retanning agent promotes the absorption of dye and fatliquoring solutions, a more uniform distribution of materials in the structure of the dermis, and a reduction in the harmful environmental impact on the environment.

CONCLUSION

Based on a comprehensive study of the structure, properties and technological capabilities of a new series of polymer compositions and modified fats, their influence on the formation of the properties of leather for shoe uppers made of cattle hides, rational parameters of the liquid finishing technology have been established, providing for retanning-filling the semi-finished product Wet blue with acrylic polymer Syntan RS-540 at a consumption of 3.0%, a temperature of 30-35 °C for 1.5-2 hours and fatliquoring with modified fats Sulphir and Synthol LC at a consumption of 3.0%, a temperature of 45-50 °C for 1.5-2 hours. The developed technology allows to improve twofold the strength, hygienic, elastic-plastic, cutting properties and some other characteristics of the finished leather while reducing the consumption of vegetable tanning agents. After including the drum dyeing process using the anionic dye Sanodal Black in the process flow chart, the efficiency of the developed technology was assessed taking into account this process. Experiments have shown that leather is more evenly dyed black, that the dye and other reagents are more fully extracted from the working solution, and that many leather parameters are improved, including the color fastness to dry and wet friction, when using the developed technology. This result is maintained when the dye consumption is reduced from 4.0 to 3.0%, i.e. by 25%.

Industrial tests of the developed technology have confirmed the results of laboratory studies. Based on the evaluation of the properties of finished leather treated with acrylic polymer and modified fats, it can be concluded that such treatment improves the properties of leather, avoiding problems with the strength and drum dyeing of traditional acrylic resins. The use of Syntan RS-540 as a retanning agent promotes better absorption of dye and fat solutions, as well as a more uniform distribution of materials in the structure of the dermis. The obtained effect can be explained by the nature of the formation and ordering of the microstructure of the dermis under the influence of the polymer and modified fats with the formation of various, strong and at the same time flexible, mobile connections between the individual components of the "collagen-chemical material" system.

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