DETERMINATION OF RATIONAL PARAMETERS OF LIQUID FINISHING OF LEATHER SEMI-FINISHED PRODUCT USING ACRYLIC POLYMER AND MODIFIED FATS

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Abstract: *A mathematical model of the processes of liquid finishing of semi-finished leather products using modern chemical materials in the form of acrylic polymer and modified fats has been obtained, revealing the influence of the consumption of these materials on the content of substances extracted by organic solvents (the so-called unbound fat), elongation at a stress of 10 MPa and the yield of leather by area. Rational parameters of liquid finishing have been determined, allowing for more efficient use of scarce raw materials while reducing the harmful burden on the environment.*

Key words: liquid finishing, mathematical model, rational parameters, acrylic polymer, modified fats, leather semi-finished product, leather.

ODREĐIVANJE RACIONALNIH PARAMETARA TEČNE ZAVRŠNE OBRADE POLUPROIZVODA OD KOŽE KOJI KORISTE AKRILNI POLIMER I MODIFIKOVANE MASTI

Apstrakt: *Dobijen je matematički model procesa tečne dorade poluproizvoda od kože korišćenjem savremenih hemijskih materijala u vidu akrilnog polimera i modifikovanih masti, koji otkriva uticaj potrošnje ovih materijala na sadržaj supstanci ekstrahovanih organskim rastvaračima. (tzv. nevezana mast), istezanje pri naponu od 10 MPa i prinos kože po površini. Utvrđeni su racionalni parametri tečne završne obrade, koji omogućavaju efikasnije korišćenje deficitarnih sirovina uz smanjenje štetnog opterećenja životne sredine.*

Ključne reči: tečna završna obrada, matematički model, racionalni parametri, akrilni polimer, modifikovane masti, kožni poluproizvod, koža.

1. INTRODUCTION

The production of genuine leather includes a number of stages during which physical-chemical processes and mechanical operations are performed with the addition of a number of chemical materials. Liquid (or wet) finishing is one of the key stages of this production. During liquid finishing, semi-finished leather and leather are given final properties (strength, elasticity, vapor permeability, appearance, etc.) through the use of vegetable and synthetic tanning agents, fats and dyes [1-2].

Based on the results of previous studies, the structure and properties of modern chemical materials have been established: acrylic polymer and modified fats of various origins, their compatibility with collagen and other chemical reagents intended for processing semi-finished leather products, as well as the feasibility of use during the processes of retanning, filling and fatliquoring [3-4].

The purpose of this work is mathematical and statistical modeling of the processes of liquid finishing of semi-finished leather products for shoe uppers in the presence of the specified means, followed by the determination of rational technological parameters.

2. THEORITICAL PART

When improving existing technologies or creating new ones, there is a constant need to find the best solution from a certain set of feasible solutions. At the same time, the task becomes significantly more complicated due to a significant number of parameters characterizing technological processes. In addition, there are a number of processes that require a special approach [5]. The latter include liquid physical and chemical processes of tanning production, the specificity of which is largely due to the biogenic origin of raw hides, the complex architecture of the microstructure of the dermis and its main component – collagen.

It is well known from the theory and practice of leather production that during liquid processes, diffusion and fixation of chemical materials in the structure of the dermis occur simultaneously, however, the formation of the desired consumer properties of the finished product requires gradual penetration and uniform distribution of reagents in the "collagen-chemical material" system [6]. And although the main formation of the structure and properties of leather occurs at the tanning stage, liquid finishing plays an equally important role in tanning technology. Liquid finishing is entrusted with a responsible mission: preserving the results of the previous (preparatory and pre-tanning) stages of leather processing, on the one hand, and the subsequent, post-tanning formation of its structure and consumer properties, on the other. Especially considering that currently the final finishing of leather is not always done in the form of top dyeing due to the use of more innovative methods: applying a laser pattern, embroidery, appliqué, etc. [7].

The traditional liquid finishing sequence involves neutralization, retanning-filling, dyeing, then fatliquoring, each of which may require more than one component. Although these treatments use different reagents and obviously different chemical processes, there are common principles and mechanisms, e.g. the mechanism of reagent fixation based on a heterogeneous reaction, often involving a sulfonate group [1].

The effectiveness of liquid finishing depends on many factors, including the type and nature of chemical materials [1, 8]. The lack of high-quality domestic means for liquid leather finishing forces manufacturers to use the products of foreign firms and companies, information about the structure and properties of which is unknown and does not always correspond to reality. Such a situation does not contribute to the conscious management of the technological process at an individual enterprise, the sustainable development of the leather industry as a whole. Thus, the development of the technology of liquid finishing of leather, including for the upper of shoes, with the justified use of modern chemical materials, remains relevant. Determining the rational parameters of the processes of liquid finishing of leather semi-finished products with such materials will allow to increase the quality of leather products with reduced consumption of raw and material resources, harmful load on the environment.

3. MATERIALS AND METHODS

Modern chemical materials manufactured by Smit & Zoon (Netherlands) were used in the work, intended for the production of natural leather: acrylic polymer Syntan RS-540 and modified fats in the form of Synthol LC based on natural and synthetic oils, sulfonated triglycerides, lecithin-containing mixture, as well as Sulphirol EG 60 based on sulfited natural and synthetic oils. The research was carried out on Wet blue leather semi-finished product, obtained from a Heifer according to a well-known method [9] and intended for the production of leather using the chrome tanning method for the upper of shoes. In order to exclude the influence of topographical areas, the groups were assembled according to the asymmetric fringe method.

Liquid finishing was carried out according to a technological map developed on the basis of previous experimental studies:

1. Washing: water Modern chemical materials manufactured by Smit & Zoon (Netherlands) were used in the work, intended for the production of natural leather: acrylic polymer Syntan RS-540 and modified fats in the form of Synthol LC based on natural and synthetic oils, sulfonated triglycerides, lecithin-containing mixture, as well as Sulphirol EG 60 based on sulfited natural and synthetic oils.

The research was carried out on Wet Blue leather semi-finished product, obtained from a half-hide according to a well-known method [9] and intended for the production of leather using the chrome tanning method for the upper of shoes. In order to exclude the influence of topographical areas, the groups were assembled according to the asymmetric fringe method.

Liquid finishing was carried out according to a technological map developed on the basis of previous experimental studies:

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

    tannins – 2.0%, 40-60 minutes.

The experiment was carried out in a laboratory setup that ensured proper temperature conditions with constant rotation of the equipment. The consumption of materials was determined taking into account the content of the active substance and the mass of the initial semi-finished product Vet blue. Fat emulsions were prepared with a concentration of 25% by gradually adding water (temperature 45-50 C), 2.0% surfactant and 0.5% (by weight of fat) ammonium hydroxide solution with a concentration of 10% to a sample of fat with constant stirring. The Crust (uncoated leather) obtained after liquid finishing was processed according to the traditional scheme: laying – drying - tempering - staking - setting out, and after modeling and determining rational parameters, cover dyeing was performed [9].The properties of the chemical and leather materials studied in the work were assessed using analysis methods common in the tanning industry [10] 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; DSTU 3376: 2022 (EN ISO 3376: 2020, IDT; ISO 3376: 2020, IDT) Leather - Physical and mechanical tests - determination of tensile strength and percentage elongation; 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 the coagulation temperature when heated to 100°C; DSTU EN ISO 14268: 2022 (EN ISO 14268: 2012, IDT; ISO 14268: 2012, IDT) Leather. Physical and mechanical tests. Determination of vapor permeability; DSTU EN ISO 4048: 2022 (EN ISO 4048: 2018, IDT; ISO 4048: 2018, IDT) Leather - Chemical tests. Method for determining substances soluble in dichloromethane; 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.

The successful conduct of an experiment largely depends on the correct choice of its plan, which determines the mathematical and statistical analysis of the results. The choice of a planning matrix in the form of a full factorial experiment (FFE), when using a first-stage polynomial as a model, ensures optimal planning based on the following properties: all calculations are carried out simply; regression coefficients are determined independently of each other; the variances of all regression coefficients are equal and minimal; the dispersion of the initial parameter does not depend on the rotation of the coordinate system in the center of the plan, but only on the radius of the studied sphere of the factor space (the rototability property). The most widespread planning of factors at two levels, when the upper and lower limits of the variation interval are used as levels. Setting up experiments according to plans is called a two-level full factorial experiment of type 2^n, where n is the number of factors [11].

Considering that liquid finishing processes (retanning-filling with acrylic polymer, fatliquoring with modified fats) influence, first of all, such factors (indicators) as the content of substances extracted with organic solvents (hereinafter simply "fat content"), elongation at stress of 10 MPa and area yield, we first used the method of full factorial experiment of type 2^3, which allows, with a limited number of experiments, to construct a mathematical model of the technology and determine its rational options.

The following were chosen as the most significant factors of the experiment: x_1 – consumption of Syntan RS-540, %; x_2 – consumption of Synthol LC, %; x_3 – consumption of Sulphirol EG 60%, as well as their levels and variation intervals (Table 1). The following were chosen as response functions: Y_1 – fat content *F* (more precisely, the mass fraction of substances extracted by organic solvents), %; Y_2 – elongation at 10 MPa *L10* (elongation at stress 10 MPa), %; Y_3 – yield in area ***ΔS*** relative to the area of the semi-finished product before liquid finishing, % (Table 3).

Table 1: Factors and their levels

Factor lower –		Level	
		upper	
		+	
x_1	- consumption of Syntan RS-540, %	3,0	6,0
x_2	- consumption of Synthol LC, %	3,0	6,0
x_3	- consumption of Sulphirol EG 60, %	3,0	6,0

Table 2: Matrix and experimental conditions

Group	x_1	x_2	x_2	Syntan RS-540, %	Synthol LC, %	Sulphirol EG 60, %
1	–	–	–	3,0	3,0	3,0
2	+	–	–	6,0	3,0	3,0
3	–	+	–	3,0	6,0	3,0
4	+	+	–	6,0	6,0	3,0
5	–	–	+	3,0	3,0	6,0
6	+	–	+	6,0	3,0	6,0
7	–	+	+	3,0	6,0	6,0
8	+	+	+	6,0	6,0	6,0

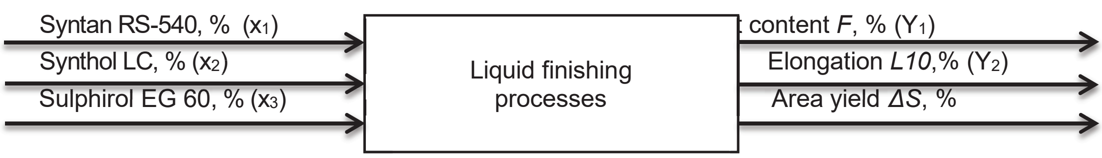


Table 3: Recall functions

Group	Fat content *F*, %			Elongation at 10 MPa *L10*, %			Area yield *ΔS*, %		
	$y1_1$	$y1_2$	$y1_{cep}$	$y2_1$	$y2_2$	$y2_{cep}$	$y3_1$	$y3_2$	$y3_{cep}$
1	4,56	4,88	4,72	44,5	47,5	46,0	104,0	106,0	105,0
2	4,50	4,70	4,60	42,0	43,0	42,5	104,7	105,9	105,3
3	4,42	4,20	4,31	42,0	44,0	43,0	105,9	104,7	105,3
4	4,21	4,44	4,33	46,5	49,5	48,0	100,5	101,9	101,2
5	3,98	4,15	4,07	50,5	49,5	50,0	108,0	106,4	107,2
6	3,66	3,39	3,53	44,0	45,5	44,8	83,9	85,6	84,8
7	5,61	5,45	5,53	38,5	40,5	39,5	92,8	94,3	93,6
8	5,33	5,42	5,38	39,5	41,0	40,3	100,6	102,0	101,3

If the mathematical model of the process is nonlinear, then it is approximated by a polynomial. However, when obtaining a mathematical model, the number of necessary experiments grows rapidly as the number of terms of this polynomial increases. In this regard, it is necessary to differently solve questions about the number of levels, the center of the experimental plan, and the principles of optimality of the plans used. These issues can be resolved using different methods. The method of central compositional planning is most used in engineering practice to describe a nonlinear region [11]. It was this method that was used to obtain a mathematical model and rational parameters for the liquid finishing of semi-finished leather products with acrylic polymer and modified fats.

4. RESULTS AND DESCUSION

There are complex relationships between given factors, so their influence on the effective attribute is complex, and not just the sum of isolated influences. To assess the degree of influence on the studied performance indicator of each of the factors introduced into the model, with a fixed position at the average level of other factors, a three-factor regression analysis of the experimental data was carried out. There was no functional connection between the factors.

As a result of checking the adequacy of the resulting linear model to the experimental data, it was decided to conduct the experiment according to a second-order plan [11-13]. After processing the experiment results, we obtained mathematical models in the form of three-factor, quadratic regression equations (1-3), which in coded units had the form:

$$Y_1 = b_0 + bx_1^2 + b_2x_2^2 + b_3x_3^2 + ε \quad (1)$$

$$Y_2 = b_0 + bx_1^2 + b_2x_2^2 + b_3x_3^2 + ε \quad (2)$$

$$Y_3 = b_0 + bx_1^2 + b_2x_2^2 + b_2x_3^2 + ε \quad (3)$$

where b_0 is a free term that determines the values of Y_1, Y_2, Y_3 in the case when all independent variables Xi are equal to 0; coefficients b_1, b_2, b_3 show how much the resulting characteristic Y_1, Y_2, Y_3 will change when each independent factor x_1, x_2 and x_3 changes by a unit of measurement; ε is a random variable characterizing the deviation of factors x_1, x_2 and x_3 from the regression line (residual variable). In our study, the mathematical expectation of the random deviation εi is 0 for all observations (M(εi) = 0).

To estimate the unknown parameters b_0, b_1, b_2, b_2, the least squares method (LSM) was used, according to which the function parameters are selected in such a way that the sum of the squared deviations of the experimental values Yi from their calculated values Y_{ip} is minimal, i.e.

Below are mathematical models of regression equations (5-7), which describe the dependence of the most significant indicators of Crust (uncoated leather) on the consumption of acrylic polymer and modified fats.

a) Regression equation for determining fat content:

From the interpretation of the regression coefficients, it was concluded that the constant shows the aggregated influence of other (except for those taken into account in the model x_i) factors on the result Y_1 and means that Y_1 in the absence of x_i was 3.7217. The coefficient b_1 shows that when x_1 increases by 1, Y_1 decreases by 0.00259. The coefficient b_2 indicates that when x_2 increases by 1, Y_1 increases by 0.03333. The coefficient b_3 indicates that when x_3 increases by 1, Y_1 increases by 0.00852.

Variances of model properties: $S_{b0} = \sqrt{0,0163} = 0,128$; $S_{b1} = S_{b2} = S_{b3} = \sqrt{10^{-5}} = 0,00309$. To assess the significance of the correlation coefficients t_i using the Student's table, we found t_{table} = (n - m - 1; a/2) = (4; 0,025) = 3,495. Because the $t_i = bi/S_{bi}$, all coefficients of equation (5) are statistically significant: t_0 = 29,173 > 3,495; t_1 = 8,038 > 3,495; t_2 = 10,776 > 3,495; t_3 = 3,754 > 3,495.

The adequacy of the regression equation was checked using the Fisher test. To do this, we first calculated the adjusted coefficient of determination: $R^2 = 1 - [S_i^2 / \sum_{i=1}^{n}(Y_i - \bar{Y})^2] = 1 - (0,0558 / 179) = 0,9689$.

F-statistic of Fisher distribution:

$F = [R^2/(1-R^2)] \cdot [(n-m-1)/m] =$

$[(0,9689) / (1 - 0,9689)] \cdot [(8 - 3 - 1) / 3] = 41,47$.

Table value for degrees of freedom:

$k_1 = 3$ i $k_2 = n - m - 1 = 8 - 3 - 1 = 4$,

$F_{kp}(3; 4) = 6,5914$.

Since the actual value of $F > F_{kp}$, the coefficient of determination is statistically significant and the regression equation is statistically reliable, that is, the coefficients bi are jointly significant.

$$S = \sum_{i=1}^{n}(Y_i - Y_{ip})^2 = \sum_{i=1}^{n}(Y_i - \varphi(x_i, b_0, b_1, \dots, b_k))^2 \longrightarrow \min \quad (4)$$

$$Y_1 = 3,7217 - 0,00259x_1^2 + 0,03333x_2^2 + 0,00852x_3^2 \quad (5)$$

Taking into account the rather high value of the coefficient of determination R2, it is possible to make a forecast regarding the rational ranges of values of independent factors: the costs of Syntan RS-540, Synthol LC, Sulphirol C, at which the "fat content" indicator after liquid finishing of a semi-finished leather product with acrylic polymer during retanning-filling, modified fats when fattening takes on the most acceptable value. Based on this, the rational ranges for changes in the main factors are: x_1 (consumption of Syntan RS-540) = 3,0 %; x_2 (consumption of Synthol LC) = 3,0 %; x_3 (consumption of Sulphirol EG 60) = 3,0 %. Under such conditions, Y_1 will be 4,75 % (Fig. 1).

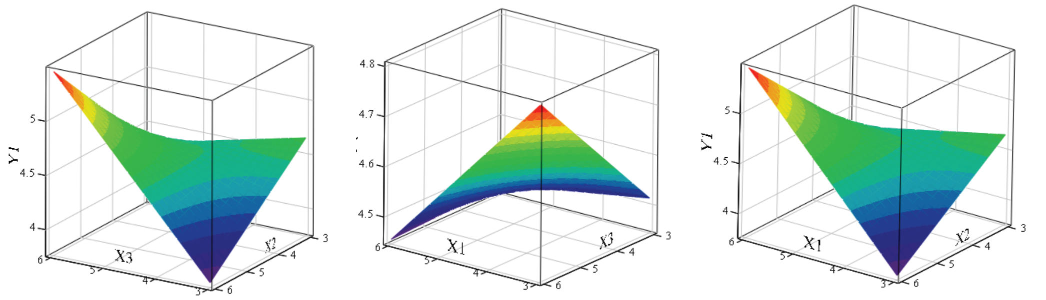
The adequacy of the regression equation was checked using the Fisher test. First, we calculated the adjusted coefficient of determination:

$$R^2 = 1 - [S_i^2 / \sum_{i=1}^{n}(Y_i - \bar{Y})^2] = 1 - (0{,}125 / 20{,}29) = 0{,}9938.$$

F-statistic of Fisher distribution:

$$F = [R^2/(1-R^2)] \cdot [(n-m-1)/m] = [(0{,}9938) / (1 - 0{,}9938)] \cdot [(8 - 3 - 1) / 3] = 215{,}321.$$

Table value for degrees of freedom: $k_1 = 3$ i $k_2 = n - m - 1 = 8 - 3 - 1 = 4$, F_{kp} (3; 4) = 6,5914. The actual value of $F > F_{kp}$, the coefficient of determination is statistically significant and the regression equation is statistically reliable, that is, the coefficients b_i are jointly significant.



a *b* *c*

Figure 1: Graphic 3D dependence of fat content:
a – on the consumption of Synthol LC and Sulphirol EG 60;
b – on the consumption of Syntan RS-540 and Sulphirol EG 60;
c – on the consumption of RS-540 and Synthol LC.

b) Regression equation for determining elongation at 10 MPa:

$$Y_2 = 48{,}0758 - 0.0294x_1^2 - 0{,}1076x_2^2 - 0{,}03722x_3^2 \quad (6)$$

From the interpretation of the regression coefficients, it was concluded that the constant evaluates the aggregated influence of other (except for those taken into account in the model xi) factors on the result Y_2 and means that Y_2 in the absence of x_i is 48.0758. Coefficient b_1 shows that when x_1 increases by 1, Y_2 decreases by 0.02944. The coefficient b_2 shows that when x_2 increases by 1, Y_2 decreases by 0.1076. Coefficient b_3 shows that as x_3 increases by 1, Y_2 decreases by 0.03722.

Variances of model properties: $S_{b0} = \sqrt{0{,}0364} = 0{,}191$; $S_{b1} = S_{b2} = S_{b3} = \sqrt{2{,}1 \cdot 10^{-5}} = 0{,}00463$. To assess the significance of the correlation coefficients t_i using the Student's table, we found $t_{table} = 3{,}495$. Therefore, all coefficients of equation (6) are statistically significant: $t_0 = 251{,}935 > 3{,}495$; $t_1 = 6{,}364 > 3{,}495$; $t_2 = 23{,}254 > 3{,}495$; $t_3 = 8{,}045 > 3{,}495$.

Based on the sufficiently high value of the coefficient of determination R_2, it is possible to make a prediction regarding the rational ranges of values of independent factors at which the indicator of "elongation at 10 MPa" after liquid finishing of a semi-finished leather product with acrylic polymer and modified fats acquires an acceptable value: x_1 (consumption of Syntan RS-540) = 3,0 %; x_2 (consumption of Synthol LC) = 3,0 %; x_3 (consumption of Sulphirol EG 60) = 3,0 %. Then Y_2 will be 46% (Fig. 2).

c) Regression equation for determining area yield ΔS:

$$Y_3 = 107{,}8792 - 0{,}01138x_1^2 + 0{,}4468x_2^2 - 0{,}2248x_3^2 \quad (7)$$

From the interpretation of the regression coefficients, it was concluded that the constant evaluates the aggregated influence of other (except for those taken into account in the model x_i) factors on the result Y_3 and means that Y_3 in the absence of xi would be 107.8792. Coefficient b_1 shows that when x_1 increases

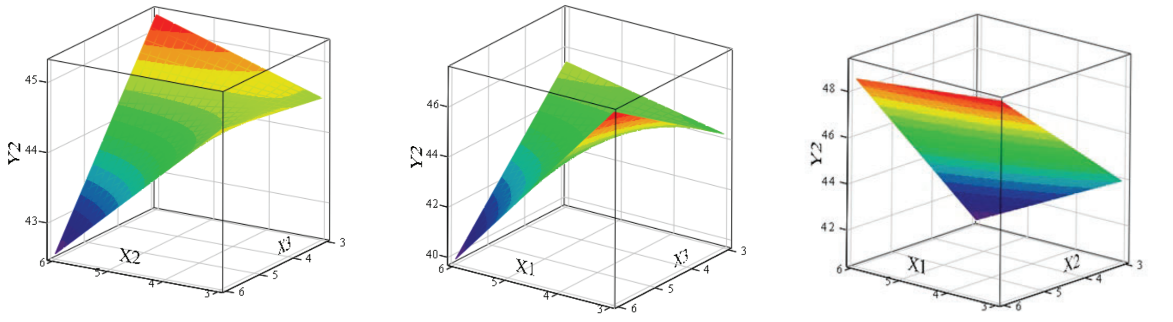


Figure 2: Graphic 3D dependence of elongation at 10 MPa:

a – on the consumption of Synthol LC and Sulphirol EG 60;

b – on the consumption of Syntan RS-540 and Sulphirol EG 60;

c – on the consumption of RS-540 and Synthol LC.

by 1, Y_3 decreases by 0.1183. The coefficient b_2 shows that when x_2 increases by 1, Y_3 increases by 0.04468. The coefficient b_3 shows that when x_3 increases by 1, Y_3 decreases by 0.2248.

Variances of model properties: $S_{b0} = \sqrt{4{,}78} = 2{,}186$ $S_{b1} = S_{b2} = S_{b3} = \sqrt{0{,}00281} = 0{,}053$. To assess the significance of the correlation coefficients t_i using the Student's table, we found $t_{table} = 3{,}495$. Based on this, all coefficients of equation (7) are statistically significant: $t_0 = 49{,}344 > 3{,}495$; $t_1 = 6{,}231 > 3{,}495$; $t_2 = 4{,}843 > 3{,}495$; $t_3 = 4{,}245 > 3{,}495$.

To check the adequacy of the regression equation, we calculate the adjusted coefficient of determination:

$$R^2 = 1 - [S_i^2 / \sum_{i=1}^{n} (Y_i - \bar{Y})^2] =$$
$$1 - (16{,}388 / 113{,}36) = 0{,}8554.$$

F-statistic of Fisher distribution:

$$F = [R^2/(1 - R^2)] \cdot [(n - m - 1)/m] =$$
$$[(0{,}8554) / (1 - 0{,}8554)] \cdot [(8 - 3 - 1) / 3] = 7{,}89.$$

Table value for degrees of freedom: $k_1 = 3$ i $k_2 = n - m - 1 = 8 - 3 - 1 = 4$, F_{kp} (3; 4) = 6,5914.

Since the actual value of $F > F_{kp}$, the coefficient of determination is statistically significant and the regression equation is statistically reliable, that is, the coefficients bi are jointly significant. Taking into account the rather high value of the coefficient of determination R_2, it is possible to predict rational ranges of values of independent factors in which the area yield of leather after liquid finishing with acrylic polymer and modified fats acquires an acceptable value Y_3 = 106% (Fig. 3): x_1 (consumption of Syntan RS-540) = 3.0%; x_2 (consumption of Synthol LC) = 3.0%; x_3 (consumption of Sulphirol EG 60) = 3.0%.

For a more complete characterization of liquid finishing processes when choosing rational parameters for liquid finishing processes, we additionally analyzed the performance of spent solutions after retanning-filling and fatliquoring. As can be seen from Table 4, an increase in material consumption worsens the processing of working solutions, as indicated by a change in the "dry residue" indicator. The lowest value of the latter is observed with a consumption of acrylic polymer and modified fats of 3.0% (3.12%; group 1), which is almost 1.5 times less than this indicator with a material consumption of 6.0% (4.64%); group 8).

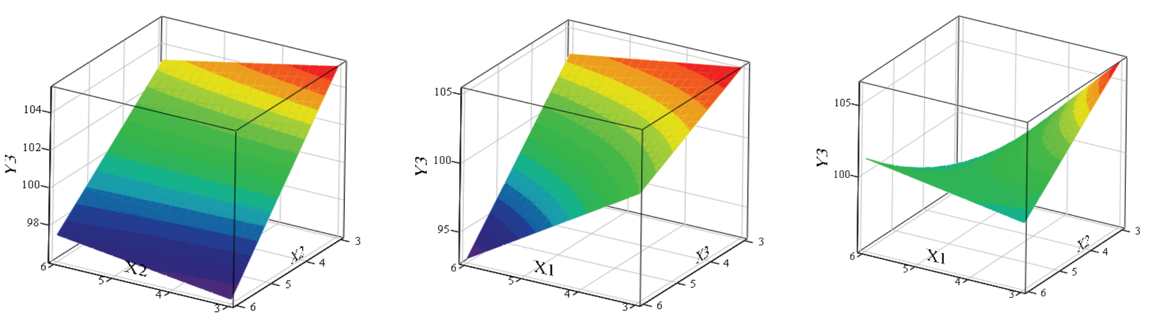


Figure 3: Graphical 3D dependence of yield by area:

a – on the consumption of Synthol LC and Sulphirol EG 60;

b – on the consumption of Syntan RS-540 and Sulphirol EG 60;

c – on the consumption of RS-540 and Synthol LC.

Table 4: Characteristics of spent solutions

Group	Liquid finishing conditions			Spent solution after			
	Syntan RS-540	Synthol LC	Sulphirol EG 60	retanning-filling		fatliquoring	
				density, g/cm³	dry residue,%	density, g/cm³	dry residue,%
1	3,0 %	3,0 %	3,0 %	1,006	3,98	0,996	3,12
2	6,0 %	3,0 %	3,0 %	1,007	4,36	0,996	3,15
3	3,0 %	6,0 %	3,0 %	1,006	3,98	1,000	3,46
4	6,0 %	6,0 %	3,0 %	1,007	4,36	1,000	4,50
5	3,0 %	3,0 %	6,0 %	1,006	3,98	0,999	3,78
6	6,0 %	3,0 %	6,0 %	1,006	3,37	0,999	4,16
7	3,0 %	6,0 %	6,0 %	1,006	3,98	1,012	3,94
8	6,0 %	6,0 %	6,0 %	1,007	4,36	1,016	4,64

The next series of experiments was devoted to determining the influence of the technological regulations of liquid finishing on the quality indicators of the finished leather. For this purpose, when retanning and filling the experimental group of the semi-finished product Vet blue from a Heifer, 3.0% acrylic polymer Syntan RS-540 was used, reducing the consumption of quebracho tannins from 4.0 to 2.0%; and fatliquoring – 3.0% each of the modified fats Synthol LC and Sulphirol EG 60. Retanning and filling of the control group was carried out using known technology [9] in the presence of 4.0% quebracho tannins, and fatliquoring was carried out with 6.0% of the well-known anionic fat Provol BA. No complications were identified during processing. The prototypes had a clean, velvety front surface and a pleasant neck.

The leather finishing after liquid treatment was carried out using the well-known technology for the production of chrome tanned leather for shoe uppers [9]. The final treatment in both groups was carried out by applying a coating twice with the following composition, wt. hour: Compound VR (30%) – 60; acrylic AM 146 (42.5%) – 80; Pockryl SW 4025 (40%) – 120; wax emulsion (20%) – 40; water – 200. Consumption – 80 g/m^2.

The results of chemical analysis and physical-mechanical testing (Table 5) showed the positive effect of liquid finishing using 3.0% acrylic polymer and 3.0% of each of the two modified fats involved on both the performance of the finished leather and the choice of chemical materials from the working materials. solutions, it is established:

- increasing the content of unbound fatty substances in the skin by 12.0%, which improves its elastic-plastic properties (the elongation rate at a stress of 10 MPa increases by 12.1%);
- increasing the strength of the leather as a whole by 6.0%, and the strength of its outer layer by 11.2%:
- improvement of hygienic properties (relative vapor permeability increases by 10.1%);
- reducing the anisotropy of the main indicators of physical and mechanical properties (increasing the coefficients of distribution uniformity in various directions of leather – tensile strength, stress when cracks appear in the facial layer and elongation at a stress of 10 MPa – by 1.2-1.4 times), which will determine more rational use of leather materials when cutting into shoe parts;
- reducing the difference between the strength of leather as a whole and the strength of its outer layer by 3.9 times, which indicates a more uniform distribution of chemical materials in the thickness of the dermis, and this, in turn, improves the elastic-plastic properties and yield of the leather over the area;
- increase in thickness and area yield by 1.6 and 6.3%, respectively;
- improving the quality of the coating on the leather (for example, the resistance of the coating to wet friction increases by 1.25 times), which will also have a positive effect on the consumer properties of leather products;
- improvement of the composition of industrial wastewater due to an increase in the degree of solution recovery by 5.3-11.6%.

Table 5: Indicators of finished leather and spent working solutions

Index	Experienced group	Control group	Regulatory document [14]
Leather:			
Mass fraction (on absolute dry matter), %: - chromium oxide	4,20	3,95	3,5
- substances extractable with organic solvents	5,15	4,60	3,7-10,0
Tensile strength σ_t, 10 MPa	1,93	1,82	1,5
Stress when cracks appear in the front layer σ_f, 10 MPa	1,89	1,70	1,3
$\Delta = 100 \cdot [(\sigma_t - \sigma_f) / \sigma_f]$, %	2,10	8,24	–
Elongation at stress 10 MPa *L10*, %	39,8	35,5	20-40
Uniformity coefficient $K_{\sigma t} / K_{\sigma f} / K_{L10}$	0,90 / 0,89 / 0,77	0,83 / 0,78 / 0,65	–
Temperature of shrinkage, ºC	115,5	112,0	–
Relative vapor permeability, %	85,2	77,4	–
Area yield, %	99,7	93,4	–
Output by thickness, %	89,5	87,9	–
Coating resistance to wet friction, speed	250	200	≥100
Resistance of the coating to repeated bending, points.	4	4	≥3
Color fastness, points: - to dry friction	5	5	≥4
- to wet friction	4	3	≥3
Spent solution:			
Degree of solution processing, %: - after retanning-filling	85,5	80,2	–
- after fatliquoring	87,1	75,5	–

5. CONCLUSION

A mathematical model of the processes of liquid finishing of semi-finished leather products using acrylic polymer and modified fats has been obtained, which reveals the influence of their consumption on the content of substances extracted by organic solvents (the so-called unbound fat), elongation at a stress of 10 MPa and area yield.

Based on mathematical modeling, rational parameters for liquid finishing have been determined, which include retanning and filling the semi-finished leather product Wet Blue with Syntan RS-540 acrylic polymer at a consumption of 3.0%, a temperature of 30-35 °C for 1.5-2 hours and fatliquoring with modified fats Sulphirol EG 60 and Synthol LC at a flow rate of 3.0%, temperature 45-50 C for 1.5-2 hours.

It has been established that, in comparison with the known technology, the developed liquid finishing technology makes it possible to improve the consumer and cutting properties of finished leather, as indicated by the results of chemical analysis and physical and mechanical tests, and to use raw materials more efficiently while reducing the harmful load on the environment.

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