DEVELOPMENT OF THE ELASTIC LEATHER MATERIALS PRODUCTION TECHNOLOGY

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Abstract: *The filling-fatliquoring technology of chrome tanned semi-processed leather at the production of elastic leather materials from the raw bull hides with the use of the optimized fatliquor composition is developed. The influence of the fatliquor composition on the physical and chemical properties of elastic leather material is studied. The formula composition was optimized using the global criterion method, which allowed to reduce the problem of multicriteria optimization to single-criteria. A D-optimal plan is designed and implemented by the modified McLean-Anderson method and an adequate mathematical model of the filling-fatliquoring process is obtained. The main parameters of optimization of the constructed model were: yield of leather material, its strength limit and stiffness. A computing module was developed in Visual Basic for Application to automate the calculation; the module allows to determine the optimal process parameters and can be used to optimize similar technological processes. The optimised fatliquor composition provides highly elastic properties of leather material, which in terms of technological properties surpasses the material formed by production technology, respectively, elongation at a stress of 9.81 MPa greater by 21.0% and lower stiffness by 27.0%. A significant increase in the yield of the obtained material ensures the efficient use of raw hides and meets the requirements of DSTU 3115-95 “Garment leather. General technical conditions”. The industrial testing results of the developed filling-fatliquoring processes suggest their effective use in new and improved technologies of elastic leather materials production from other types of raw hides and skins.*

Keywords: *semi-finished leather, filling-fatliquoring technology, elastic leather material, fatliquor composition, McLean-Anderson method, optimization, global criterion method.*

1 INTRODUCTION

Widening the variety of elastic leather materials requires the development of innovative technologies through the gradual improvement of chemical reagents or their compositions using new environmentally friendly materials [1, 2]. As a result of structural transformations in the filling and fatliquoring processes in the interaction of active chemical reagents with microfibrillar structural elements of the collagen is their dispersion and increase the mobility of the whole structure. It is essential to stabilize the collagen structure at the filling-fatliquoring stage. Collagen structure stability should be maintained after finishing drying and wetting processes and after processing stages of semi-processed leather products. Maintaining the above-mentioned effects is important for the next technological stages such as vacuum drying, pressing and others. At the same time, when improving a particular technological process, special attention should be paid to minimize the technogenic impact of both waste solutions and manufactured material on the environment [2]. In this regard, the issue of computer optimization of the composition and their effective use at all stages of the technological cycle of leather materials in the development of new technologies or the improvement of existing technologies is essential.

When filling and fatliquoring semi-processed leather materials, a wide range of chemical reagents and their composition of Ukrainian and imported production is suggested. Specifically, to increase the elasticity of leather for garment, the authors of [3] recommend the use of modified palm oil. For the same purpose, the company "TFL" recommends a plasticizing composition based on lecithin "Coripol ALF" for the manufacture of elastic leather materials [4]. Also, high stability of properties is provided, light and heat resistance of the received natural material increases.

The use of highly dispersed minerals, mainly in a modified form [5, 6] is a very promising direction in the process of filling in leather materials production. The increase of physical and mechanical properties and volume yield of leather materials when using modified montmorillonite is shown. The authors of [7] consider silica nanoparticles to be an effective filler of semi-processed leather products due to their high colloid-chemical properties. According to [8], the use of silica nanoparticles increases the physical and mechanical properties of leather, its ageing resistance and resistance to environmental effects. Modification of silica nanoparticles with polymethacrylic acid made it possible to use it also in the tanning process. Moreover, the colored silica nanoparticles are recommended by Ramalingam and co-authors [9] to be used to obtain a stable skin color. When filling the semi-processed leather product [10], natural aluminosilicate modified with acrylic polymer was used. Due to the effective compatibility of the modified highly dispersed montmorillonite with the collagen fibers [11], the process of structuring and filling-plasticization of the leather material takes place simultaneously. The obtained leather materials were characterized by increased strength, softness and volume yield. To determine the effect of synthetic polymers and plant extracts on the properties of white skins, a fluorocarbon compound was used [12]. The highest effect is achieved using tannins and a dispersing agent Inditan RS.

To increase the elastic properties of leather materials, fatliquoring reagents are added to the filling compositions. Thus, Manich and co-workers [13] study the impact of fatliquors based on triglycerides of colza oil and fish oil on the mechanism of water diffusion into the structure of the treated semi-processed product and its properties. Different aspects of sorption capacity in a semi-processed leather product depending on humidity are established. Thus, the vast majority of the selected papers are mainly empirical, in which the effective use of chemical reagents and compositions requires additional scientific research and optimization of their use in elastic leather materials production.

In this study, the development of the filling-fatliquoring process technology in elastic leather materials production is carried out by simulating the optimal composition of reagents. In the furtherance of this aim, the following problems are solved: filling and fatliquoring process conditions determination in the production technology of elastic leather materials; designing of experiments by the McLean-Anderson method; obtaining an adequate mathematical model of fatliquoring composition to technological properties; determining the optimal fatliquoring composition; testing of the developed technology in the field operating conditions.

2 EXPERIMENTAL

2.1 Materials and methods

The research object is the optimization process of the filling and fatliquoring composition and its effective use in the formation of highly elastic leather materials. For the study, a semi-processed product from the scalp area of the wet-salted and chromium tanned skins with a welding temperature of 107°C after splitting to a thickness of 1.4 mm was used. To optimize the composition are completed groups of samples of 5 pcs size 13×20 cm. The samples were prepared by the method of asymmetric fringe [14]. The control group of samples was processed according to the current technology [15].

The process of filling the semi-processed leather product is carried out after its neutralization [16] using reagents: acrylic polymer Retanal RCN-40 company "Cromogenia Units, S.A." (Spain), synthetic tanning agent Relugan D from BASF (Germany) and quebracho extract (China).

The following reagents were used to carry out the fatliquoring process:

- montmorillonite 85 % $(OH)_4Si_8Al_4O_{20}\cdot{}_nH_2O$ [14] modified with 5% sodium sulfite (x_1);
- technical cattle fat of light brown color with acid value of 51 mg of KOH/g, iodine value of 67 g of iodine/100 g of fat, and freezing point 13°C (x_2);
- unrefined sunflower oil with acid value of 6.0 mg of KOH/g, iodine value of 143 g of iodine/100 g of oil (x_3);
- nonionic surfactant SPK-50 TU 2488-014-22284955-99 / sodium alkylsulfonate $R\text{-}SO_2ONa$ C11–C18 TU 6-01-5763450-10 in the ratio 1:2 (x_4). The mass fraction of the basic substance in sodium alkylsulfonate is not less than 60%, and the pH of 1% aqueous solution is 8.1.

The effect of the fatliquoring composition on the process of forming the leather material is determined by the physico-chemical and technological properties of the obtained leather according to the methods [14]. Mineral substance is determined by the weight method by oxidizing the samples in air in porcelain crucibles at a temperature not exceeding 600°C until a constant mass is reached. The content of chromium compounds is determined by the iodometric titration and is expressed as a mass fraction of Cr_2O_3. A mixture of carbon tetrachloride and trichlorethylene in a ratio of 1:1 is used to establish substances that are extracted with organic solvents.

Physical and mechanical properties of the obtained material are determined after their preliminary conditioning at 20±2°C and humidity of 65±5% on the universal testing machine RT-250M (RF) at a deformation rate of 90 mm.min^{-1}. The hardness of leather is tested on the device PZhU-12M (RF), density - by pycnometric method. Adhesion of the coating is defined by using an 18% solution of polymethylacrylamide in alcohol and toluene 1:9. The leather area is measured on a Svit 07484/P1 machine (Czech Republic) after drying and conditioning processes.

2.2 A mathematical model development

All groups of samples were washed simultaneously, neutralized with a mixture of formate and sodium bicarbonate in a ratio of 1:1 to the pH 5.8-6.0 of the semi-processed product in a wooden drum with a volume of 18 dm^3 at a ratio of working solution: semi-processed product equal to 1:1 with liquid ratio (LR) is 1.0 at a temperature of 40-42°C and constant rotation at a speed of 18-20 min^{-1} for 60 min. After 10 min of washing, the semi-processed product is treated for 80 min with a filling composition with the consumption of ingredients, respectively, wt.% planed semi-processed product: acrylic polymer Retanal RCN-40, synthetic tanning agent Relugan D and Quebracho extract - 3, 5, 6. For fatliquoring, the samples are sorted into subgroups.

Based on previous studies, the variation limits of the fatliquoring composition ingredients are set (Table 1).

Table 1 Variation limits of the fatliquoring composition ingredients x_i

Ingredient number [x_i]	Constraints of the composition ingredients	
	low limit a_i	***upper limit b_i***
1	0.14	0.23
2	0.25	0.40
3	0.33	0.50
4	0.06	0.14

Note. Variation limits of the composition ingredients:

$$0 \le a_i \le x_i \le b_i \le 1 \text{ (i = 1, 2,.., k)} \quad (1)$$

It should be noted that the following rationing condition should be maintained:

$$\sum_{i=1}^{k} x_i = 1 \quad (2)$$

The effectiveness of the fatliquoring composition on the technological properties of the leather material is evaluated by the following variables: y_1 – the yield of the area of the leather material to the control group of samples [%]; y_2 – leather material strength limit [MPa]; y_3 – stiffness [cN].

According to the McLean-Anderson algorithm [17], 40 theoretical points were selected to obtain a plan for the experiment. To establish the experimental points, all theoretical points are sequentially sorted by the D-optimality criterion:

$$\det|D| \to \min \quad (3)$$

where: $D=(F^T.F)^{-1}$ – dispersion matrix of the current plan; F – the plan of experiment matrix X obtained by the type of mathematical mode $\tilde{f}^T(\bar{x})$ of size n x l; l – the number of the model coefficients; n – number of selected points; T – matrix transposition operation.

In this paper, for the synthesis of the optimal plan of the experiment, all possible combinations of theoretical points are obtained, from which the best 10 are selected under condition (3).

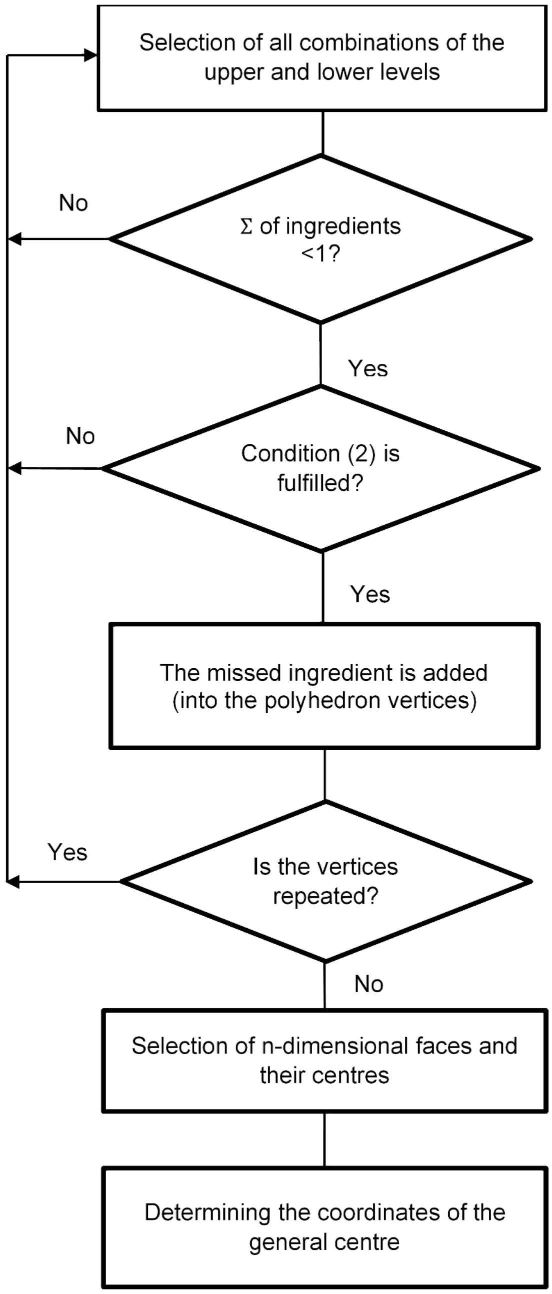

Figure 1 Experimental point selection algorithm by the modified McLean-Anderson method

According to the algorithm shown in Figure 1, the procedure for obtaining the optimal plan is as follows:

- for each ingredient of the composition, all possible combinations of lower and upper levels included in condition (1) are selected;
- from all combinations of ingredients, those are selected in which the sum of ingredients is less than 1 (according to condition 2) and the missed ingredient is added to them, but only if condition (2) is fulfilled. In this case, the combination with the added ingredient that also satisfies condition (1) is the coordinate of the vertices of the desired polyhedron;

- the condition for vertex repeatability is checked and repeated vertices are omitted; the dimension of the obtained polyhedron is always equal to k-1;
- the n-dimensional polyhedron faces are selected and the coordinates of the centres of all selected n-dimensional polyhedron faces are determined as the average values of the vertices coordinates that form the corresponding face;
- the coordinates of the general centre of a polyhedron are determined as the average value of the coordinates of all vertices of this polyhedron.

The presented algorithm is the basis of a software module implemented in the Visual Basic for Application (VBA). The obtained plan of the optimal experiment of the semi-processed product fatliquoring in a limited area of the simplex using the ingredient restrictions (Table 1) is shown in Table 2.

The fatliquoring process of the filled semi-processed product is carried out using a fatliquoring composition at a temperature of 52-55°C at LR 1.2 in a 10 dm^3 glass drum with constant rotation at a speed of 18-20 min^{-1}. The fatliquoring composition [18] is dosed into the drum according to the experimental point with a consumption of 7% by weight of the splitted semi-processed product at pH 8. After 40 min of rotation, alum in the amount of 04-0.5% and sodium formate in the amount of 0.3-0.4% is added to the process solution. Stirring is continued for another 20 min. The treatment is completed at pH 4.2. Further drying and wetting operations of the semi-processed product are performed according to the current technology. The defined properties of the filled-fat semi-processed product are shown in Table 3.

The coefficients of the four-component mathematical model of the fatliquoring composition are determined by the method of least squares in matrix form

$$B = (X^T X)^{-1} . XT^Y$$

where: B – vector of required coefficients; Y – vector-column of the dependent variables observed in the experiments.

Based on these experiments, the mathematical model is obtained for the above mentioned three technological indicators of the filled and fatliquored semi-processed product depending on the fatliquoring composition:

$$\begin{aligned} y_1 = {} & -180.197x_1 - 303.613x_2 - 341.419x_3 - 160.131x_4 - \\ & - 3.167x_1x_2 + 1.828x_1x_3 + 0.175x_1x_4 - \\ & - 0.444x_2x_3 + 0.743x_2x_4 - 0.1758x_3x_4 \\ y_2 = {} & -40.706x_1 - 68.008x_2 - 75.616x_3 - 35.966x_4 + \\ & + 1.723x_1x_2 + 1.016x_1x_3 + 0.552x_1x_4 - \\ & - 0.161x_2x_3 + 1.152x_2x_4 + 0.613x_3x_4 \\ y_3 = {} & -41.911x_1 - 68.383x_2 - 78.833x_3 - 36.929x_4 - \\ & - 3.878x_1x_2 - 2.477x_1x_3 + 0.316x_1x_4 - \\ & - 0.557x_2x_3 - 1.51x_2x_4 - 0.2x_3x_4 \end{aligned} \quad (4)$$

To perform calculations on the obtained model, the ingredients are coded as follows:

$$\bar{x}_i = \frac{x_i - x_{0i}}{dx_i}, \; x_{0i} = \frac{a_i - b_i}{2}$$

where: a_i, b_i – the limits of the composition ingredients given in Table 1.

Experimental and statistical goodness of fit of the regression equations of the mathematical model by comparing the calculated values of the Fisher test with tabular at a p-value of 0.95 proved that the model adequately describes the studied process.

2.3 *Optimization of the fatliquoring composition by the global criterion method*

Determining the optimal fatliquoring composition using the obtained mathematical model based on the global criterion method. According to [17, 19], the method is used when it is possible to select one of the criteria as the main one. This method is quite simple and often used in solving technical and economic problems of optimization. In this case, the initial variables are subject to restrictions (Table 4), corresponding to the worst and best values of technological indicators.

Table 2 Plan of experiment

Ingredient	The composition formulation at the experimental point									
	1	*2*	*3*	*4*	*5*	*6*	*7*	*8*	*9*	*10*
x_1	0.23	0.14	0.14	0.23	0.23	0.14	0.14	0.23	0.23	0.14
x_2	0.30	0.39	0.30	0.38	0.25	0.25	0.40	0.25	0.28	0.35
x_3	0.33	0.33	0.50	0.33	0.38	0.47	0.40	0.46	0.36	0.45
x_4	0.14	0.14	0.06	0.06	0.14	0.14	0.06	0.06	0.14	0.06

Table 3 Technological properties of filled and fatliquored semi-processed leather product

Technological indicator	The value of technological properties of semi-processed leather products									
	1	*2*	*3*	*4*	*5*	*6*	*7*	*8*	*9*	*10*
y_1	101.5	100	98.7	100.2	102	95.6	100.8	99.5	98.3	100.4
y_2	24.5	21.3	18.4	22	24.8	18.9	24	22.5	21.2	22.5
y_3	21.2	25	27.4	24.5	21.5	29.7	22.6	23.2	25.6	23

Table 4 Technological indicators constraints of the filled-fatliquored semi-processed product

Indicator number y_i	Technological indicators constraints	
	min	***max***
1	102.0	103.0
2	21.0	23.0
3	21.2	25.0

Based on the economic and technological requirements for the technological process, the initial values of y_1 and y_2 should be maximized, and the value of y_3 should be minimized. The optimization of the composition for fattening a filled semi-processed leather product as a task of multicriteria optimization is estimated by the vector function of the form:

$$f(\bar{x}) = (f_1(\bar{x}), f_2(\bar{x}), \ldots f_k(\bar{x})) \quad (5)$$

components of which ($f(\bar{x})$ (i=1,2,…,k) are given functions of the vector $\bar{x} = (x_1, x_2, \ldots, x_n)$.

Constraints (Table 1) are imposed on variables x_i (i= 1,2,…,n). In this case, the vector $\bar{x}$ belongs to the set of possible values. It is necessary to find a point $\bar{x}^* \in X$ that will provide the optimal value of the functions $f_1(\bar{x}), f_2(\bar{x}), \ldots f_k(\bar{x})$.

One of the approaches to finding an optimal solution is to reduce it to the single-objective optimization problem. Therefore, according to the chosen global criterion method, one of the considered criteria $f_1(\bar{x})$ is chosen as the global one, and the other objective functions are replaced by constraints. Next, the single-objective optimization problem for the maximum (minimum) of the function $f_1(\bar{x})$ is solved, provided that other criteria will be greater than or equal to the specified control values of G_i:

$$f_1(\bar{x}) \to \max$$
$$f_i \geq G_i, \quad i = 2,3,\ldots k \quad (6)$$

In this case, all values $\bar{x}$ must belong to an admissible set.

When solving the problem of finding the optimal fatliquoring composition, the global criterion for expert evaluation is the function y_1, which determines the yield of the area of leather material to the extruded semi-processed product [%], for which the maximization problem is solved.

To solve the above-mentioned optimization problem, a computational module in the VBA has been developed, which implements the global criterion method. The number of inputs and outputs of the applied model, limit values of parameters, coefficients of the corresponding equations of the mathematical model are used as initial data for the calculation of optimal fatliquoring composition.

The main window of the computing module with the entered initial data and the obtained results for the optimal fatliquoring composition are shown in Figure 2.

To perform calculations, the number of inputs and outputs (*n* and *k* respectively) in the appropriate cells should be indicated; also, the coefficients of the equations of the mathematical model in the pre-prepared cells for y_1, y_2, y_3 both with the limits of variables x_i, y_i should be entered.

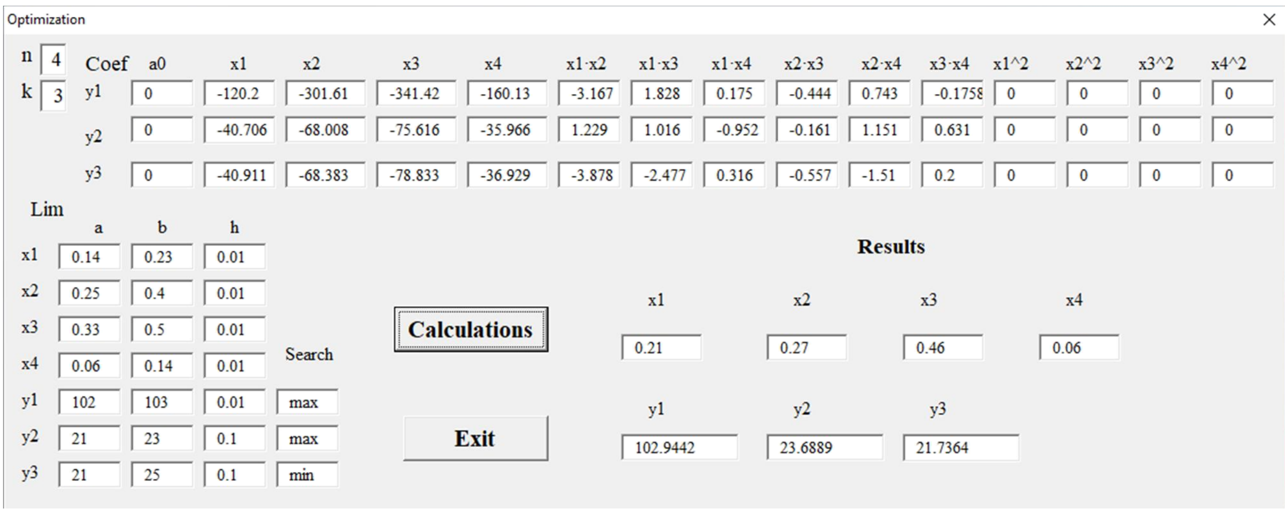

Figure 2 The main window of the computing module for calculating the optimal fatliquoring composition

After entering the required data and clicking the Calculations button, the results of calculations of the optimal composition will be displayed in the corresponding windows in the Results area. Pressing the Exit button ends the work with the program.

Thus, the optimal values of the fatliquoring composition ingredients for the technology of forming semi-processed elastic leather product were found. They are, wt.%: modified montmorillonite - 21, beef fat - 27, sunflower oil - 46, non-ionic surfactant SPK-50 - 6. The following technological indicators are achieved: the yield of the leather area to samples of control technology is 102.99%, the strength of leather material is 23.67 MPa and its stiffness 21.74 cN. All the results obtained are met the requirements on the input and output parameters, specified in Tables 1 and 4.

The use of a certain composition at the manufacturing of semi-processed leather products will improve the quality of the elastic leather material.

3 APPROBATION OF THE DEVELOPED TECHNOLOGY

The developed technology of filling and fatliquoring in the production of elastic leather materials was tested with optimal fatliquoring composition in the semi-production conditions of PJSC "Chinbar" (Ukraine). For this purpose, the wet-salted bull hides were used after soaking, deliming and tanning processes in the drum “Vulcan” of the Olcina Group (Spain) with a volume of 21.0 m^3, assembled in two batches by the method of alternating halves of 5 pcs each after splitting to a thickness of 1.4 mm [14]. The obtained semi-processed product was neutralized and filled similarly to test samples in a drum “Doze” (Germany) with a volume of 0.39 m^3.

The optimized fatliquoring composition with a consumption of 7% by weight of the semi-processed leather at pH 8.0 was dosed into the spent filling solution after raising the temperature from 40-42°C to 53-55°C by adding hot water to LR 1.2. The control halves set of the filled semi-processed product were fatliquored according to the current technology [15] using the emulsion of the FOSFOL L-1301 fatliquoring agent from Cromogenia Units, S.A. (Spain). Fixation of reagents in the structure of the semi-processed product was carried out with 10% formic acid with a consumption of 0.5% by weight of the semi-processed product to pH 4.0. Further processing of the fatliquored semi-processed product, including the application of the acrylic coating is performed according to the current technology.

The physical and chemical properties of the obtained leather materials are given in Table 5. The obtained leather materials according to the developed technology are characterized by an increased content of unbound fatty substances and a significant increase in elastic properties. Especially it concerns elongation at 9.81 MPa, skin stiffness and coating adhesion.

The determined physical and chemical properties of the leather obtained by the developed technology indicate a regular distribution of fat substances, which are fixed at the fibrillar level of the semi-processed product. The front layer of the leather has a non-oily surface. A significant increase in the yield of the leather material relative to the control sample is caused by the plasticization effect due to the use of an optimized fatliquoring composition.

Table 5 Physical and chemical properties of elastic leather material

Indicator	Leathers are obtained by the technology	
	Developed	***Proving***
The mass fraction [%] - Cr_2O_3 - mineral substances - substances extracted with organic solvents	 4.2±0.02 6.4±0.06 8.3±0.17	 4.3±0.03 5.6±0.04 7.7±0.15
Tensile strength [MPa]	23.0±1.2	19.3±1.3
Elongation at 9.81 MPa [%]	34.0±1.7	28.0±1.9
Elongation before break [%]	51.0±4	62.0±4.7
Stiffness [cN]	23.0±0.9	31.5±1.6
Coating adhesion [Н/м] - to dry leather - to wet leather	 390±2.5 196±3.9	 193±3.6 98±4.1
Density [g/cm^3]	0.616±0.02	0.659±0.03
Yield of leather material [%]	104.9 ±3.0	100.0 ±3.0

Note. The mass fraction of leather components are given in terms of solid matter.

4 CONCLUSIONS

The fatliquoring composition for chrome-tanned leather materials processing has been optimized. The optimization was carried out by the method of global criteria, which made it possible to reduce the problem of multicriteria optimization to the problem of single-criteria. An adequate mathematical model of the filling- fatliquoring process was obtained using the D-optimal plan, which was developed by the modified McLean-Anderson method. The optimal process parameters are calculated using the developed computational module in the Visual Basic for Application, which can be used to optimize similar technological processes.

A filling-fatliquoring technology has been developed to obtain a highly elastic leather material, which, in terms of technological properties, prevails over the material obtained by the existing technology and meets the requirements of DSTU 3115-95 “Sewing leather. General technical conditions". An improvement was achieved in the following parameters: the elongation at a stress of 9.81 MPa was 21.0% higher and the stiffness was 27.0% lower. The industrial test results of the developed filling-fatliquoring technology provide the basis for their effective use in new and improved technologies for the elastic leather production from other types of skins and hides.

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