IMPROVEMENT OF STRUCTURE DETERMINING QUALITATIVE CHARACTERISTICS OF HYDROPHOBIZED VELOUR

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***Abstract**: The paper studies optimization of formulation of the alkenmalein-acrylsyntane composition in manufacturing of hydrophobized nutria fur velour with high structural and defining characteristics. A modified McLean and Anderson method was used to synthesize the experimental design. Mathematical modeling approach as well as a hierarchical technique of multi-objective optimization led to the identification the optimal formulation of the filling and hydrophobicizing composition. Based on the experimental results, an adequate non-linear mathematical model "formulation of the alkenmalein-acrylsyntane composition vs properties of fur velour" was constructed. The hierarchical method of successive concessions (epsilon constrained method) allowed to optimize the composition formulation. The optimal composition comprises 37.7 % m/m of alkenmalein polymer, 34.0 % m/m of polyacrylic emulsion Melio Resin A-821, and 28.3 % m/m of BNS synthane tannin. Developed technology ensures high consumer properties of nutria fur velour. The studies of water resistance have shown a significant increase in resistance of fur velour to the action of water in dynamic conditions. The developed technology has the great benefit of increasing the yield of fur velour area by 6.7% in comparison with the intermediate product of chrom-aluminum retanning. Taking into account considerable porosity and heterogeneity of the fiber structure of the raw material, an increase in yield is significant. The optimized formulation of the filling and hydrophobicizing composition can be used effectively in the technologies of manufacturing limed hide and leather materials of high water resistance. With the combination of properties the obtained hydrophobized nutria velour is suitable for the production of pickled leather products, which will be operated in extreme conditions.*

***Keywords**: nutria velour, filling, velour properties, hydrophobization, McLean-Anderson method, multicriteria optimization, hierarchical method of successive concessions.*

1 INTRODUCTION

In order to improve the physico-chemical properties of fur during its operation in extreme conditions, new effective modification methods must be found. Particularly, an important task is the preparation of natural materials for goods used in conditions of high humidity. Various chemical reagents can be used for such preparation to hydrophobize materials containing protein. The effectiveness of hydrophobic substances depends essentially on the features of the porous structure of the collagen-keratin material and its pelage. It should be noted that the increased porosity of the fur semi-finished product significantly complicates the process of its hydrophobization, since it requires additional physico-chemical processes and mechanical operations to form the proper operational and technological properties.

In particular, greater attention should be given to the use of new hydrophobic mixtures, as well as suitable filling agents, to create high water-resisting materials for pickled leather products. The completion of that task is of both scientific and technical significance. In this regard, the possibility of using natural rawhide materials unsuitable for fur production [1] is of great relevance. Expanding the range of products from fur semi-finished products with high water-resisting properties is possible due to the use of coarse-pored raw material with coarse pelage. New filler-hydrophobic compositions and processing modes should be developed for the effective use of this rawhide. The use of mathematical modeling and optimization methods is the necessary condition for successful development of scientifically grounded processes of forming a semi-finished product in the high water-resistance velour manufacturing. It is especially important to take into account the physico-chemical and technological properties of both the structure of the semi-finished product and the ingredients of the developed compositions.

2 LITERATURE REVIEW

In elastic leather and fur velour production technology, the processes of filling and hydrophobization play a significant role in the formation of materials with high performance properties. This is particularly true in case of raw materials with a specific irregular and coarse-pored structure.

Various synthetic polymers can be used for levelling of uneven and porous surface of the topographic areas of the skins. Polyacrylic or polymethacrylic acid, polyvinyl alcohol, copolymer of styrene and maleic anhydride, epoxy resins, polyisocyanates and especially amino resins may be used to fill the collagen-containing semi-finished product. In particular, the authors of [2, 3] as a result of filling have received natural materials with uniform properties in thickness, density, water resistance, increased strength and resistance to friction due to the use of water-soluble polymers. The synthesized copolymer based on butadiene and styrene at a ratio of 3 to 1 provided an opportunity to obtain elastic skin of a sufficiently filled and mobile structure [4].

The influence of the particle size of acrylic acid copolymers aqueous dispersions on the physico-mechanical properties of a semi-finished product was studied in [5]. The increase of thermal stability, strength and elasticity due to the use of aqueous emulsions of copolymers of butyl acrylate and styrene was identified.

To fill the leather semi-finished product with an aqueous dispersion of the acrylic copolymer, copolymers of acrylamide of methacrylic acid, nitrile of acrylic acid, maleic anhydride, vinyl acetate and butyl acetate were used in [6]. Compositions with different ratios of components were investigated, within the limits of their consumption 3.0-6.9% by weight of the semi-finished product.

In [7], a significant influence of the aminopolymers on the semi-finished product properties was proved. The aminopolymers mixture was based on dimethylurea and its modified derivatives synthesized by condensation of aldehydes with urea, melanin and dicyandiamide.

The resulting semi-finished product is characterized by high physical and mechanical properties, high grinding ability with the formation of low uniform pile. To fill the semi-finished product, sulfo-aromatic polymers were synthesized on the basis of polycondensation of sulfonated resorcinol and urea-formaldehyde resin with a particle size of aqueous dispersion of 0.7-1.4 μm [8]. The high diffusion capacity of synthesized polymers in the structure of a chromium semi-finished product is also shown. This diffusive ability ensures an increased degree of filling of the semi-finished product and its high elastic-plastic characteristics. Compared with the modified aminofurazan-formaldehyde polymer, the use of a sulfitated melamine-formaldehyde oligomer for filling the semi-finished product makes it possible to increase its density and elasticity. However, the presence of up to 10 mg/kg of free environmentally harmful formaldehyde in the product might be considered as a disadvantage.

Increasing the water-resistance of natural collagen-containing materials is achieved by filling the semi-finished product with reagents of a certain chemical composition. For example, monomeric and polymeric reagents [9] are used for this purpose, in particular silanes, fluorocarbon resins, polydimethylsiloxane rubbers, complex compounds of aluminum with wax or paraffin. Derivatives of oxycarboxylic acids, esters of fatty acids, etc. are also used. The authors [10] have studied the influence of fat emulsions based on triglycerides of rapeseed oil and fish oil on the sorption-desorption process as well as on the mechanism of water diffusion into the structure of the processed skin.

In [11], an acrylic acid copolymer and hydrophobic acrylate monomers were used to hydrophobize a chromium semi-finished product. Using this composition led to the increase in the degree of filling, water resistance, ductility and mechanical strength of the material. Copolymers with normal carbon chains have been proved to be effective in improving these properties. The greatest hydrophobic effect is achieved when the side chain length of the modifier is not less than C_{16}.

An emulsion of a fluorine-containing copolymer based on maleic anhydride, rapeseed oil or fish liver oil with the addition of dodecafluoroheptanol and octadecyl alcohol is also used to obtain a natural material of high water resistance [12]. The obtained material is characterized by a wetting angle of 155°, by dynamic water penetration of 55 min and by a static water absorption coefficient of 9 wt.%. The maximum hydrophobic effect is achieved at 5% fluorine content in the copolymer molecules. The use of hybrid polyfunctional polyurethanes with hydrophilic-hydrophobic radicals to increase water resistance and dirt repellency of materials has also been proposed [13]. However, after such modification, the rigidity of the material increases and its appearance deteriorates.

In [14-16], the complex effect of organosilicon polymer A-187 and plasma processing on the physico-mechanical and hygienic properties of skin was studied. This led to increase in the water resistance of the skin, as well as an increase in the strength of the material by 23%. The efficiency of hydrophobization of the material, determined by the duration of suction of a drop of water, is evidenced by an 86% increase in the duration of absorption of a drop of water [16] while reducing its hygroscopicity by 87 and 76%, for sheepskins and cattlehides, respectively.

Thus, one can use a wide range of reagents and compositions for filling and hydrophobization of natural materials. However, the practical application of the above-mentioned reagents is mainly empirical. The reactivity of the structure and properties of collagen-keratin material requires proper scientific substantiation.

Due to the expansion of the range of raw materials with a specific structure for the production of quality natural materials, further study of the effective formulations of filler & hydrophobic compositions is necessary. Taking into account the specificities of collagen-keratin structure, topographic unevenness of skin tissue, features of its porosity and low strength in the formation of nutria skins velour, it is necessary to develop an optimized formulation of filler-hydrophobic composition and determine the conditions of its effective use.

3 OBJECTIVES AND PURPOSE OF THE STUDY

The aim of the work is to study the process of forming hydrophobized nutria skins velour with coarse hair using the alkenmalein-acrylsyntane (AM-AS) composition. For this purpose, the following specific objectives have been set:

- determination of structurally sensitive quality characteristics of hydrophobized velour depending on the formulation of the filler-hydrophobizing composition;
- mathematical synthesis of the optimal plan of experiments for the study of formulations of mixtures;
- processing the results of experiments and identification of the mathematical model "formulation of filling composition vs velour properties";
- determination of the optimal formulation of the filling-hydrophobizing composition for the production of hydrophobized velour using the "composition formulation vs velour properties" model.

4 RESEARCH METHODOLOGY

The object of the study was the ways optimize the formulation of the filling-hydrophobic composition AM-AS for skins of male nutria with an area of 24-25 dm^2 with coarse beard hair after epilation and tanning (temperature not lower than 90°C) by technology [1]. The composition studied included an alkenmalein (AM) polymer synthesized on the basis of α-alkenes $C_{20–24}$ and maleic anhydride with an average molecular weight of 38.10^3, polyacrylic (PA) emulsion Melio Resin A-821, offered by “Clariant International Ltd” company and the product of the synthesis of 2-naphthylsulfonic acid with dioxydiphenylsulfon - BNS synthane tannin (in accordance with Ukrainian standard specifications TU 17-06-165-89).

During the tanned nutria skins processing, after water removal and epilating, the semi-finished product was subjected to chrom-aluminum retanning. The ratio of the weight of water and semi-finished product is equal to 7 with the following consumptions: chromium tanner in terms of chromium oxide (III) 4 g/dm^3, alumokalum branch 7 g/dm^3. The retanning should be carried out at 40-42°C for 6 hours in a 15 dm^3 laboratory paddle. The filling and hydrophobization of a nutria semi-finished product skin tissue should be done at 40-43°C by successive addition the AM-AS composition to the system of ingredients. First, the AM-polymer was dosed into the paddle, after 15-20 minutes, a filling mixture (Melio Resin A-821 polyacrylic emulsion and BNB tanner) was added to the processing medium. After another 1.0 hour, the remaining hydrophobic AM polymer was added. The total duration of the process did not exceed 2.5 hours. The semi-finished product was hydroextracted in a centrifuge to a humidity of 52-53% and then underwent the process of drying and humidification until the moisture content of 12-14% had been reached.

Experimental data were obtained by implementing the D-optimal experimental plan, synthesized by the modified McLean and Anderson method [17], which involves limiting the quantitative content of its ingredients due to their physico-chemical and technological features. For the experiment, samples of nutria skins were selected by the method of proportional squares [18].

The efficiency of technological processing of tanned semi-finished nutria skins was determined by the following parameters:

- the difference between the volume of the AM-AS composition, spent in the process and the remainder of the composition in the exhausted solution;
- water-resisting properties of hydrophobized fur velour;
- yield of hydrophobized fur velour by area.

The water resistance of velour was estimated under dynamic conditions by the duration of water wetting on the PVD-2 device (Russia) during the deformation of the samples at a rate of 70 min^{-1}. The hydrothermal stability of the velour was evaluated by the initial reduction of the sample length, the porosity was determined by the ratio of the pore and sample volumes. Physico-mechanical properties of velour were evaluated according to the methodology [18] on a tensile testing machine RT-250M (scale A, 0-0.50 kN) at a deformation rate of 80 mm/min. The yield of the velour area was estimated by the ratio of the areas of hydrophobized and chromium-aluminum tanned [1] semi-finished product under standard conditions. Based on the experimental results, nonlinear polynomial mathematical models “formulation of the filler-hydrophobizing composition vs properties of velour” were obtained. These models were subsequently used to find the optimal formulation of the AM-AS composition by the hierarchical method of successive concessions [19-21].

5 OBTAINING A MATHEMATICAL MODEL "FORMULATION OF THE FILLER-HYDROPHOBIZING COMPOSITION VS PROPERTIES OF NUTRIA VELOUR"

A nonlinear mathematical polynomial model (1) was used to optimize the formulation of the AM-AS composition:

$$\hat{y} = \sum_{i=1}^{k} b_i x_i + \sum_{i=1}^{k-1} \sum_{j=i+1}^{k} b_{ij} x_i x_j + \\ + \sum_{l=1}^{k-2} \sum_{i=l}^{k-1} \sum_{j=i+1}^{k} b_{l\,ij} x_i x_j , \quad (1)$$

where $\hat{y}$ is predicted value of the output variables; b_i, b_{ij} are model coefficients; x_i are designation of ingredients of the composition (in coded dimensionless form), i = 1, 2, …, k; k is number of ingredients; l, i, j are enumerators of ingredients.

It is important to emphasize that model (1) should retain the condition of normalization of the composition of the mixture:

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

During the experiments, the limiting variation range of ingredients X_i (3) was observed. The limits of change of ingredients mass in the mixture (X_i [g/dm^3]) at a total consumption of the mixture of 28 g/dm^3, determined by the results of previous studies, are shown in Table 1.

$$0 \le X_i^{\min} \le X_i \le X_i^{\max} \le 1 \quad (i = 1, 2, ..., k) \quad (3)$$

where X_i are designations of ingredients of the composition (in natural form); $X_i^{\min}$ and $X_i^{\max}$ are variation range limits (lower and upper respectively).

Table 1 Limits of variation of ingredients of the filler-hydrophobic composition

i	Limits of ingredients variation			
	natural values X_i [g/dm^3]		encoded values x_i	
	min	*max*	*min*	*max*
1	0.84	10.36	0.03	0.37
2	3.92	13.44	0.14	0.48
3	3.08	12.32	0.11	0.44
4	5.88	11.20	0.21	0.40

According to the results of previous studies, the general mathematical model (1) was reduced to the form:

$$\hat{y}_i = b_1 x_1 + b_2 x_2 + b_3 x_3 + b_{12} x_1 x_2 + \\ + b_{13} x_1 x_3 + b_{14} x_1 x_4 + b_{23} x_2 x_3 + b_{24} x_2 x_4 + \\ + b_{34} x_3 x_4 + b_{123} x_1 x_2 x_3 \quad (4)$$

where $\hat{y}_i$ are predicted values of the structural and determining indicators of the quality of fur velour, i = 1÷3; x_1, x_2, x_3, x_4 are encoded values of mixture ratio factors (respectively, the amount of AM polymer that acts as an activator of the filling process, the amount of PA emulsion, the amount of BNS synthane tannin and the amount of AM polymer as a hydrophobisator in the final stage of processing).

The effectiveness of the formulation of the AM-AS composition was evaluated by the following quality indicators:

- y_1 is the amount of composition that diffused to the semi-finished product [%];
- y_2 is duration of dynamic water penetration of fur velour [sec];
- y_3 is the yield of the area of fur velour [%].

According to the principles of mathematical statistics, the coefficients of the regression model (4) can be determined by approximating the experimental data. For data acquisition, experiments were performed according to the synthesized plan. The task of planning the experiment was to obtain the maximum theoretically possible amount of information for a given number of experiments, taking into account the condition of normalization of the composition of the mixture (2), as well as the important requirement (5) of availability of all ingredients in the mixture:

$$x_i > 0, i = 1,2,\ldots,k. \quad (5)$$

The experimental design was synthesized according to the previously developed algorithm [17]. This algorithm is summarized as follows:

1) According to the McLean and Anderson algorithm [22], N theoretical candidate points are selected (in this case, N=41). Selection is carried out in such a way as to ensure the maximum mutual distance of the experimental points, as well as the distance of the experimental points to the center of the plan;
2) The best experimental design in terms of D-optimality (6) is selected from n experimental points by exhaustive search of all possible combinations of candidate points:

$$\det|D| \to \min \quad (6)$$

where $D=(F^T \cdot F)^{-1}$ is the dispersion matrix of the combination of candidate points on the current iteration of the synthesis of the experimental plan; F is experimental design matrix, dimension of the matrix is $n \times t$; t is the number of coefficients of the model.

Selection of the n most desirable variants of the formulation composition among the N candidate points (n<N) requires n-combination search of a subset of n distinct elements of the candidate points set, which has N elements. The total number of required combinations (7) can be estimated by methods of probability theory:

$$c_N^n = \frac{N!}{n!\,(N-n)!} \quad (7)$$

To find the coefficients of model (4), the synthesized experimental design must contain at least 10 experimental points (n=10).

As follows from (7), the synthesis of such a plan requires more than 10^9 different combinations. Thus, the synthesis of the experimental design requires significant computational resources. Therefore, during the search of experimental plan points, an algorithm of parallel (multithreaded) calculations was implemented. In the present case, 23.86 hours were spent on the computer synthesis of the optimal experimental design (Table 2) in a limited area of factor space (Table 1).

Table 2 The experimental design

Experimental points		Mixture ratio			
No	*laboratory records code*	x_1	x_2	x_3	x_4
1	2	0.210	0.140	0.440	0.210
2	3	0.200	0.480	0.110	0.210
3	4	0.030	0.460	0.110	0.400
4	5	0.030	0.320	0.440	0.210
5	10	0.030	0.140	0.440	0.390
6	12	0.370	0.140	0.110	0.380
7	14	0.190	0.140	0.270	0.400
8	27	0.370	0.225	0.195	0.210
9	29	0.030	0.480	0.195	0.295
10	34	0.225	0.335	0.110	0.330

Table 3 Properties of hydrophobized fur velour

Experimental point		Quality measures		
No	*laboratory records code*	y_1	y_2	y_4
1	2	79.2	1390.0	106.2
2	3	88.5	1260.0	102.4
3	4	73.4	1630.0	103.8
4	5	78.6	1370.0	101.5
5	10	65.3	1840.0	102.3
6	12	87.1	1565.0	104.3
7	14	89.4	1780.0	105.3
8	27	88.3	1353.0	104.7
9	29	79.1	1410.0	104.5
10	34	93.0	1560.0	106.1

After the implementation of the synthesized plan, experimental data were obtained. They characterize the effect of the formulation of the AM-AS filling-hydrophobizing composition on the properties of nutria velour (Table 3).

The coefficients of the mathematical model (4) were determined by approximating the experimental data (Table 2 and Table 3) by the least square method. Mathematical models are built for the three above-mentioned quality indicators of nutria velour depending on the formulation of the AM-AS composition. After parametric identification, the models have the form (8):

$$\begin{aligned}
\hat{y}_1 &= -138.69x_1 - 13.34x_2 - 84.27x_3 + 398.29x_1x_2 + \\
&+ 429.70x_1x_3 + 535.01x_1x_4 + 468.02x_2x_3 + 225.52x_2x_4 + \\
&+ 305.51x_3x_4 + 625.12x_1x_2x_3; \\
\hat{y}_2 &= 765.90x_1 - 3599.70x_2 - 3315.80x_3 + 21850.00x_1x_2 + \\
&+ 24474.00x_1x_3 + 3662.30x_1x_4 + 15166.00x_2x_3 + 11914.00x_2x_4 + \\
&+ 12409.00x_3x_4 - 153640.00x_1x_2x_3; \\
\hat{y}_3 &= 78.871x_1 + 35.227x_2 + 30.294x_3 + 307.490x_1x_2 - \\
&+ 444.790x_1x_3 + 102.200x_1x_4 + 202.830x_2x_3 + 303.050x_2x_4 + \\
&+ 284.150x_3x_4 - 2418.500x_1x_2x_3.
\end{aligned} \quad (8)$$

The obtained mathematical models (8) should be used only after confirmation of their adequacy. To study the adequacy, two parallel experiments were additionally conducted at three experimental testpoints (Table 4). The testpoints were randomly selected from among the candidate points that were not included in the synthesized experimental design.

The validity check shows, that all three obtained models are adequate, though the model for the yield of the area of fur velour (y_3) most accurately describes the experimental data.

Thus, the obtained adequate mathematical models "composition formulation vs nutria velour properties" can be further used to optimize the alkenmalein-acrylsyntane composition in the manufacture of nutria fur velour. The validation of models for adequacy (Table 5) was performed according to Fisher's statistical test (F-test).

Table 4 Structural and defining measures of hydrophobized nutria velour at the testpoints

Testpoint No	Mixture ratio				Quality measures					
	x_1	x_2	x_3	x_4	y_1		y_2		y_3	
1	0.036	0.321	0.250	0.393	82.9	83.4	2011	1990	106.7	106.3
2	0.036	0.393	0.250	0.321	87.1	86.8	1690	1681	106.1	106.0
3	0.072	0.393	0.214	0.321	89.7	90.2	1559	1562	104.6	104.1

Table 5 The results of validation of models for adequacy

Quality measures	Values of the F-distribution for mathematical models		Adequateness (F_c>F_T)
	tabular value F_T*	*computed value* F_c	
y_1	5.24	15.127	Yes
y_2	5.24	13.114	Yes
y_3	5.24	468.67	Yes

*For the level of significance q = 0.1 and the number of degrees of freedom f_1 = 9, f_2 = 3.

6 OPTIMIZATION OF THE FORMULATION OF THE COMPOSITION BY THE METHOD OF SUCCESSIVE CONCESSIONS

Mathematical programming methods were used to find the optimal formulation of the AM-AS composition for the processing of nutria fur velour skins. The optimization model (9) belongs to the class of multigoal nonlinear constrained programming problems:

$$\begin{aligned} &\{y_i(\overline{X})\} \to \max, \\ &\overline{X} \in Q. \end{aligned} \tag{9}$$

where $y_i(\overline{X})$ are optimality criteria based on models (8). *i*=1,2,…*m*; $\overline{X}$ is the set of optimization factors, $\overline{X} \Leftrightarrow x_i, i = 1,2,\ldots,k$; $\overline{X} \in Q(\overline{X})$ is the system of constraints of the optimization problem based on conditions (2), (3), (5); m is the number of optimality criteria.

Simultaneous optimization approaches are most often used to solve models (9), an example of such approaches is desirability function based methods [17, 23].

However, in this study it was decided to use a hierarchical approach to multigoal optimization, as this approach enables to control the optimization process step by step. The applied procedure for finding the optimal solution of problem (9) is based on the hierarchical method of successive concessions (also called Constraint Method) [19-21].

Optimization of the formulation of the filling-hydrophobic AM-AS composition was performed according to the following procedure:

1) Carrying out a qualitative analysis of the relative importance of the criteria $y_i(\overline{X})$, *i*=1,2,…*m*. Construction of a hierarchical list of criteria (10) in descending order of importance:

$$\{y^{[1]}(\overline{X}), y^{[2]}(\overline{X}), \ldots, y^{[m]}(\overline{X})\} \tag{10}$$

where $y^{[i]}(\overline{X})$ is optimality criterion, which is in the *i-th* place in the hierarchical list (10).

2) Setting the criterion $y^{[1]}(\overline{X})$ as the "current" criterion.
3) Solving a single-criteria optimization problem taking into account the "current" criterion as an objective function:

$$y^{[1]}(\overline{X}) \to \max, \quad \overline{X} \in Q,$$

and determining the optimum $y^{[1]}_{\max}(\overline{X})$ by the current criterion.

4) Set assignment (i.e. allowable deviation) value $\delta^{[1]} \geq 0$ for the criterion $y^{[1]}(\overline{X})$.
5) Setting the criterion $y^{[2]}(\overline{X})$ as the "current" criterion.

   Adding a criterion $y^{[1]}(\overline{X})$ to the system of constraints taking into account the values $y^{[1]}_{\max}(\overline{X})$ and $\delta^{[1]}$:

$$y^{[2]}(\overline{X}) \to \max,$$
$$y^{[1]}(\overline{X}) \leq y^{[1]}_{\max}(\overline{X}) - \delta^{[1]}$$
$$\overline{X} \in Q,$$

6) Solving a single-criteria optimization problem for the "current" criterion.
7) Repeating steps 4, 5, 6 of this procedure until the hierarchical list is exhausted (11).

In the optimization procedure used by the authors, the successive concessions method is combined with the evolutionary method of nonlinear optimization - a genetic algorithm of the GENOCOP type [24]. The GENOCOP algorithm ensures the achievement of the global optimum by multiple solution of a single-criteria problem for the "current" criterion. According to the mentioned procedure, the optimization problem of the composition formulation was solved (Table 6).

As a result of optimization the optimal formulation of the composition was obtained (wt. parts): x_1=0.031, x_2=0.371, x_3=0.253, x_4=0.345 (see Table 6). The expected values of the output variables are y_1=84.0%, y_2=1838.0 sec, y_3=107.0%.

Therefore, the following procedure can be considered effective for filling and hydrophobizing the semi-finished product. Per 100 kg of retanned and epilated semi-finished nutria product after its centrifugation one should take 19.6 kg of alkenmalein-acrylsyntane composition, including: 6.664 kg of PA emulsion, 5.547 kg of BNS synthane tannin, 7.389 kg of AM polymer. It is necessary to spend 0.588 kg of alkenmalein polymer to activate the filling process.

Table 6 Optimization of composition formulation

Step No	Mixing proportion				"Current" criterion		
	x_1	x_2	x_3	x_4	*notation*	*optimum*	*assignment*
0	0.030	0.140	0.110	0.210	-	-	-
1	0.030	0.258	0.312	0.400	y2	2041.9	1837.7
2	0.030	0.340	0.283	0.347	y3	107.11	106.95
3	0.031	0.371	0.253	0.345	y1	84.4	-

7 TESTING THE TECHNOLOGY OF HYDROPHOBIZATION OF NUTRIA FUR VELOUR BY ALKENMALEIN-ACRYL-SYNTHANE COMPOSITION

The optimized formulation of the filling and hydrophobizing AM-AS composition was used to provide the technology of hydrophobized nutria fur velour production. Physico-chemical tests of hydrophobized nutria velour were conducted under standard conditions [18]. Reference method of nutria velour processing differed from the developed technology in the absence of the filling-hydrophobization process. In this case, the electrolyte-resistant emulsion Trupol DL (by Trumpler GmbH&Co., Germany) was used for the fat-liquoring of nutria velour. The process was carried out at 38-40°C with a fat consumption of 2.5 g/dm^3 for 1 hour.

The results of the study of the hydrophobized nutria fur velour physico-chemical properties are given in Table 7. Comparison of nutria fur velour obtained by the technology proposed by the authors with the product obtained by the reference technology (i.e., pre-existing technology) leads to the following conclusions. The hydrophobic effect is manifested in significant increase in the duration of dynamic water penetration compared to the material obtained by the reference technology. Considering the high cost of fur velour and a significant increase in area yield, it's possible to increase performance of a process and to reduce the cost of production.

Increasing the thickness of the skin tissue of hydrophobized nutria velour and, thus, increasing the uniformity of the material in topographic areas, promotes the more efficient use of semi-finished product in the manufacture of products. At the same time, the hydrophobized nutria fur velour obtained by the baseline technology is better in terms of deformation properties.

The laboratory studies show that the technology of hydrophobized velour formation allows to expand the range of water-resisting rawhide materials. The developed technology can be used without significant changes for the processing of other types of rawhides in the production of velour materials with high operational properties.

8 RESULTS

1. The optimization of the alkenmalein-acrylsynthane composition formulation in manufacturing of hydrophobized fur velour from epilated nutria rawhides with high structural and defining characteristics was investigated. A modified McLean and Anderson method was used to synthesize the design of experiments, taking into account "composition formulation vs properties of hydrophobized product" model. The hierarchical technique of multi-objective optimization was applied in order to find the optimal formulation of the filling and hydrophobicizing composition.
2. The optimal formulation of the filling and hydrophobising composition was developed. The optimal composition comprises 37.7 % m/m of alkenmalein polymer, 34.0 % m/m of polyacrylic emulsion Melio Resin A-821, and 28.3 % m/m of BNS synthane tannin. The consumption of composition ingredients are: alkenmalein polymer 7.3892%, polyacrylic emulsion Melio Resin A-821 6.664%, BNS synthane tannin 5.5468% (presented values are given as a percentage of the weight of the pressed semi-finished product). The ratio of semi-finished product to processing medium is 1:7.
3. The developed technology involves the combination of filling and hydrophobization processes. The advantage of such technology is the production of fur nutria velour with a significant increase in water resistance under dynamic conditions, as well as a larger area yield of 6.7% compared to intermediate product of chrom-aluminum retanning. This result is significant, considering the considerable porosity and heterogeneity of the fibrous structure of the skin.
4. The optimized formulation of the filling and hydrophobizing composition can be effectively used in the high water-resisting leather manufacturing technologies. The obtained hydrophobized nutria fur velour, on the totality of properties, is suitable for the production of pickled leather products of various purposes, which will be operated in extreme conditions.

Table 7 Physico-chemical properties of hydrophobized nutria fur velour

Indicator	Nutria velour obtained by developed here technology	Nutria velour obtained by reference technology
Dynamic water penetration [sec]	1800±17	25±5
Yield of area [%]	106.7±0.3	100.0±0.3
Skin thickness [mm]	1.18±0.4	1.06±0.7
Ultimate tensile strength [MPa]	1.17±0.20	1.09±0.25
Percent elongation at failure [%]	63.0±6.0	59.0±5.0
Total percent elongation of skin tissue at the load 4.9 MPa [%]	29.0±2.5	21.0±2.6
– elastic elongation [%]	18.5±1.6	12.0±1.2
– residual elongation [%]	10.5±0.9	9.0±0.8
Porousness of skin tissue [%]	63.0±3.0	67.0±4.5

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