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POLYMER COMPOSITION FOR HYDROPHOBIZATION OF FUR VELOUR

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Abstract. Using computer modeling and optimization methods, a formulation of alkenmalein-acrylsintan polymer mixture for hydrophobizing treatment of nutria fur velour was developed. The optimal composition of the filler-hydrophobic mixture (alkenmaleic polymer - 38.7 wt. %, polyacrylic emulsion Melio Resin A-821 - 30.3 wt. %, cintan NS-DS - 31.0 wt. %) was determined and validated.

Key words: fur velour, nutria skins, filling and hydrophobization, experimental design, multicriteria optimization, velour properties.

Modern innovative technologies are subject to strict requirements with respect to the profitability, as well as the use of new efficient reagents and chemicals, and environmental friendliness. This is particularly valuable for the development of new and improvement of existing material-intensive, multi-stage and labor-intensive technologies, which include technologies for processing leather and fur raw materials. The peculiarities of processing such raw materials into velour are the need for effective filling of the structure of the semi-finished product leather and, as a result, the formation of a pile surface that is resistant to external influences. This is especially important in the case of velour materials with high resistance to environmental moisture while maintaining the original physical, mechanical and hygienic properties. The hydrophobization of fur velour allows to expand essentially the range of the clothes and footwear suitable for operation in extreme conditions.

The processes of filling and hydrophobization occupy a special place in the technological cycle of production of leather and fur materials, including velour, because it mainly completes the formation of a stabilized fibrous structure with a set of basic properties. To this end, different authors offer a large number of chemical reagents in different technological conditions, depending on the objectives sought. Thus, the authors of [1] investigated the effect of bentonite acrylic hydrophilic polymer on the structure and complex of physical-mechanical and hygienic properties of natural materials. In [2] the authors present the results of a study of the effect of synths and fats on the features of the porous structure and properties of different skin types. It was found that the filling process occurs with a decrease in the size distribution of pores, which is 20.7% larger for shoe leathers compared to clothing. At the same time, the air permeability of shoe leathers is reduced to a greater extent by 42%. The authors of [3] investigated the effect of molecular weight up of acrylic polymer to $200 \cdot 10^3$ on the diffusion and properties of filled skin. The dominant influence on the process of diffusion of the polymer concentration and the charge of the semi-finished product has been established. The use of the polymer in combination with anionic agents is accompanied by an increase in the uniformity of diffusion over the area, but the increase in the molecular weight of the polymer leads to an increase in thickness and a decrease in elasticity. The particle size of the acrylic dispersion affects the strength-deformation properties of the skin in a similar way [4]. The influence of the chemical composition of aminofluoropolymers on the physical and mechanical properties was studied in [5]. With the optimal filling of the semi-finished product, an increase in its grinding ability and the necessary set of physical and mechanical properties of velour with low uniform pile is achieved. In the process of filling the semi-finished product with the use of hydrophobic reagents, the hydrophilic sites of macromolecules of the fibrillar structure of collagen are blocked. For this purpose, silanes, fluorine carbons, polydimethylsiloxane polymers, and complex aluminum compounds are used [6]. Copolymers of acrylic acid in combination with hydrophobic acrylic monomers are also used for hydrophobization of chromium tanning semi-finished products [7]. The high degree of filling-hydrophobization of natural material is achieved through the use of polymers with direct hydrocarbon molecules. In particular, the maximum degree of hydrophobization of the material is achieved when the chain length is greater than C_{16} [8]. The influence of the chemical composition of the fluoropolymer on the hydrophobic properties was studied in [9]. It is established that at 5% fluorine content in the copolymer modifier the required water resistance of the material under dynamic conditions is achieved. When using multifunctional urethane polymers [10], an increase in the hydrophobicity of the skin is achieved, but its stiffness is increased. The influence of co-use of copolymers with plasma modification of a semi-finished product from raw materials of cattle and sheeps has been studied [11, 12]. At the same time, it is established that at application of such technology increase of water resistance and durability is reached.

Thus, these works indicate the use of a wide range of chemical reagents for filling and hydrophobization of leather materials, but there are virtually no systematic studies of this type of processing of raw materials. To form high-quality natural materials with a set of operational and technological properties, it is necessary to conduct systematic research using computer simulation and multi-criteria optimization.

The aim of the work is to obtain and study computer models for the development of an optimized formulation of alkenmalein-acrylsintane mixture for the formation of waterproof velour from raw nutria skins.

Materials and methods of research. The raw material of male nutria skins with coarse spiny hair with an area of 24–25 dm^2 was used after hair removal by epilation and chromium-aluminum tanning of skins according to the technology [13] to the temperature of hydrothermal resistance of skin tissue 90 °C. The studied filling-hydrophobizing alkenmalein-acrylsintan (AM-AC) mixture includes an alkenmaleic (AM) polymer synthesized on the basis of α-alkenes $C_{20\text{-}24}$ and maleic anhydride with an average number of molecular weight $38 \cdot 10^3$; polyacrylic (PA) emulsion Melio Resin A-821 by "Clariant" (Germany) and the product of the synthesis of 2-naphthol sulfonic acid with dioxydiphenylsulfone (cintan NS-DS). The composition was dosed into a processing medium with a flow rate of 28 g per dm^3 at a 7/1 ratio of water to semi-finished product.

In the study of the process of filling-hydrophobization of nutria velour depending on the composition of the mixture AM-AS was carried out. Samples of tanned semi-finished sodium skins were taken by the method of proportional squares [14]. The efficiency of using the composition in the process of filling and doubling of semi-finished fur velor was determined as a percentage of the difference between the consumed composition AM-AS and its residue in the spent solution, water resistance of hydrophobized fur velour and its yield by area.

Optimization of the composition of the filler-hydrophobic mixture involved creating the D-optimal experimental design, obtaining a mathematical model "composition vs properties of velour" with subsequent determination of the optimal ingredient content by mathematical optimization methods.

Synthesis of the experimental plan and obtaining a mathematical model. The properties of AM-AS mixture for filling and hydrophobization of nutria fur velour are determined by quantitative parameters, such as: filling part of AM-polymer (x_1), weight fraction of PA-emulsion (x_2), weight fraction of cintan HC-DS (x_3) and hydrophobizing part of AM polymer (x_4).

Table 1

The experimental design

Code of experimental point*	2	3	4	5	10	12	14	27	29	34
Ingredient	The composition of the mixture at the experimental point									
x_1	0.210	0.200	0.030	0.030	0.030	0.370	0.190	0.370	0.030	0.225
x_2	0.140	0.480	0.460	0.320	0.140	0.140	0.140	0.225	0.480	0.335
x_3	0.440	0.110	0.110	0.440	0.440	0.110	0.270	0.195	0.195	0.110
x_4	0.210	0.210	0.400	0.210	0.390	0.380	0.400	0.210	0.295	0.330

Note: * Numbers of planned experimental runs selected from the total set by the criterion of D-optimality

The efficiency of the influence of the formulation on the properties of fur velour is evaluated by the parameters: y_1 (the the composition utilization efficiency, wt. %), y_2 (duration of dynamic water penetration of fur velour, sec) and y_3 (yield of fur velor area, %).

The D-optimal experimental design (Table 1) was synthesized according to a modified McLean-Anderson algorithm [15, 16].As a result of the implementation of the experimental design (Table 1) experimental data (Table 2) were obtained, which characterize the effect of the formulation of the AM-AC mixture on the properties of fur velorr.

Table 2

Properties of hydrophobized fur velour (measured data)

Quality indicator	The value of the indicator at the experimental points									
	2	3	4	5	10	12	14	27	29	34
y_1	79.2	88.5	73.4	78.6	65.3	87.1	89.4	88.3	79.1	93.0
y_2	1390.0	1260.0	1630.0	1370.0	1840.0	1565.0	1780.0	1353.0	1410.0	1560.0
y_3	106.2	102.4	103.8	101.5	102.3	104.3	105.3	104.7	104.5	106.1

The coefficients of the mathematical model [1] were determined on the basis of experimental data by the method of least squares. It was assumed that the studied characteristics of the nutria fur velour are continuous functions of the parameters x_i and can be represented with sufficient accuracy by polynomials.

$$\begin{cases} y_1 = -138{,}69x_1 - 13{,}344x_2 - 84{,}272x_3 + 398{,}29x_1x_2 + 429{,}7x_1x_3 + 535{,}01x_1x_4 + 468{,}02x_2x_3 + 225{,}52x_2x_4 + 305{,}51x_3x_4 + 625{,}12x_1x_2x_3 \\ y_2 = +765{,}9x_1 - 3599{,}7x_2 - 3315{,}8x_3 + 21850x_1x_2 + 24474x_1x_3 - 3662{,}3x_1x_4 + 15166x_2x_3 + 11914x_2x_4 + 12409x_3x_4 - 1{,}5364 \cdot 10^5 x_1x_2x_3 \\ y_3 = +78{,}871x_1 + 35{,}227x_2 + 30{,}294x_3 + 307{,}49x_1x_2 + 444{,}79x_1x_3 + 109{,}2x_1x_4 + 202{,}83x_2x_3 + 303{,}05x_2x_4 + 284{,}15x_3x_4 - 2418{,}5x_1x_2x_3 \end{cases} \rightarrow max, \quad (1)$$

$$\overline{X} \in Q(\overline{X}).$$

where x_i is the set of input optimization factors, $\overline{X} \Leftrightarrow x_i,\ i = 1,2,\ldots,k;$ $\overline{X} \in Q(\overline{X})$ is system of technological constraints of the optimization problem; m is number of optimality criteria.

Optimization of the mixture formulation by the desirability function method. The optimal composition of the mixture should correspond to the maximum duration of water-wetting of nutria velor, as well as the maximum yield of its area and the effective use of AM-AC mixture. Therefore, the goal of this study to develop the optimal composition of the water-repellent composition from a mathematical point of view is a multicriteria optimization problem. At the same time there is a problem of calculation of the generalized indicator of quality taking into account weight coefficients of unit indicators of physical and chemical properties of the investigated mixture. This problem has been effectively solved by an approach known as the "method of constructing a generalized desirability function" [17]. This mathematical method has proven itself well in the practice of optimization of complex multicriteria problems [18, 19, 20]; it allows one to convert the “real” values of the optimality criteria into a single dimensionless numerical scale with fixed limits from 0 to 1, followed by the conversion of partial quantitative scales into generalized scales of quality criteria.

When solving the problem of optimizing the AM-AC mixture formulation in accordance with the desirability function-based approach, the "bilateral" desirability profile was used for the y_1 criterion.

Multi-purpose optimization gave the result (Fig. 1), which belongs to the desired region of compromise.

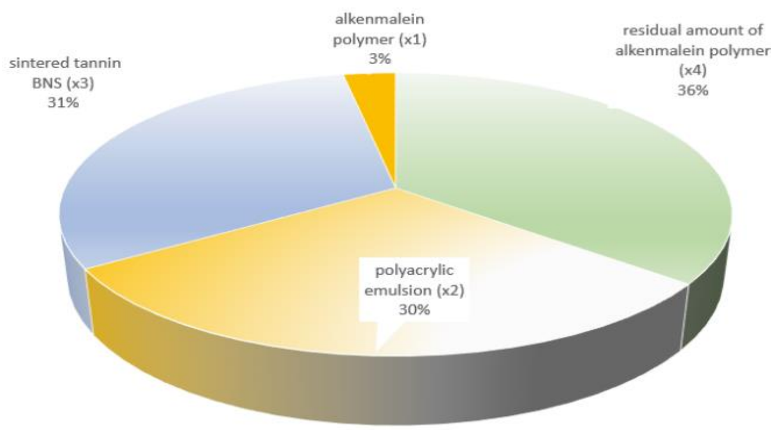

Fig. 1. The optimal formulation of the hydrophobizing AM-AS mixture.

Therefore, the consumption of the AM-AS mixture at a concentration of 28 g / dm^3 for filling and hydrophobization is 19.6 kg per 100 kg of semi-finished nutria skins. The properties of fur velour acquire values: the efficiency of the composition is 89.7%, the duration of dynamic water penetration is 1943.7 sec, the yield of the area of fur velour is 107.0%.

Approbation of technology of production of hydrophobized velor. The developed composition of alkenmalein-acrylsintan mixture for the formation of water-resistant velour from raw nutria skins was used in the industrial production of JSC "Chinbar" (Kyiv, Ukraine). Nutria skins after chromium-aluminum tanning and epilation of the hair was treated with a filler-hydrophobic composition at a 7/1 ratio of the mass of the processing medium and the semi-finished product. To hydrophobize the nutria velour, the ingredients of the AM-AS mixture at a temperature of 40–43 °C are sequentially dosed into the “processing medium – semi-finished product” system. Initially, an AM polymer was added to the paddle, and after 15–20 min, a filler mixture of Melio Resin A-821 polyacrylic emulsion and a copolymer of 2-naphthol sulfonic acid with dioxydiphenylsulfone was added. The remaining hydrophobizing AM polymer was added to the processing medium after 1.0 h. The total duration of the filling-hydrophobization process was 2.5 hours. Water was removed from the obtained fur semi-finished product by centrifugation to a humidity of 52–53%. Subsequently, drying and moisturizing processes and operations to the moisture content in the semi-finished product of 12–14%, as well as grinding of skin tissue were performed. After keeping the hydrophobized velour of nutria skins under standard conditions [13], its physicochemical tests were performed.

The "reference" method of nutria velour processing differed from the developed technology by the lack of processes of filling and hydrophobization. Fat liquoring of nutria velour was performed for 1 hour with an electrolyte-resistant emulsion of Trupol DL leather fat mixture by Trumpler (Germany) at a temperature of 38–40 °C at the concentration of 2.5 g per dm^3 of processing medium.

The results of determining the physicochemical properties of hydrophobized velour of nutria skins are given in table. 3. The efficiency of the process of hydrophobization of nutria velour using the composition AM-AS is to significantly increase the duration of water penetration in dynamic conditions (compared with the material obtained by the “reference” technology). This increases the efficiency of the composition of the AM-AC, as well as the yield of the material area. At the same time, there is an increase in the thickness of the skin tissue of hydrophobized nutria velour and, accordingly, the homogeneity of the material in topographic areas, which contributes to more efficient use of its cutting area in the manufacture of products. At the same time, the deformation properties of hydrophobized nutria velour are superior to the material obtained by the “reference” approach of processing.

Table 3

Physico-chemical properties of nutria fur velour

Indicator	Velor, which is obtained by technology	
	developed here	pre-existing
Water penetrationin (dynamic conditions), sec	1800±20	25±5
The efficiency of the mixture utilization,%	87.2±2.5	79.3±3.6
Yield area,%	105.6±0.3	100.0±0.3
Tensile strength, MPa	1.2±0.20	1.09±0.25
Elongation at break,%	62.0±5.0	59.0±5.0
Elongation at 4.9 MPa,%, complete	28.0±2.5	22.0±2.6
Porosity of skin tissue,%	62.0±3.0	65.0±4.3

Based on the research in the production conditions, authors can assume that the developed technology of forming hydrophobized nutria velour can be used to expand the range of velour materials for the manufacture of products operated in conditions of high humidity.

Conclusions. The formulation of alkenmalein-acrylsintan mixture and its use for the formation of hydrophobized nutria fur velour of the technological process were studied using computer modeling and optimization. The formulation of the filler-hydrophobizing mixture was determined by a modified McLean-Anderson method taking into account the type of mathematical model "composition-properties of hydrophobized material"; the optimization was performed using the Harrington desirability function. It was found that the optimal composition of the filler-hydrophobic mixture is (wt.%): Alkenmalein polymer - 38.7, polyacrylic emulsion Melio Resin A-821 - 30.3, and cintan NS-DS - 31.0. According to the developed technology combining filling and hydrophobization processes, nutria velour with a significant increase in the duration of dynamic water penetration as well as an increase in the yield of the material area by 7.0% (compared to the semi-finished chromium-aluminum tanning product) was obtained. Effective use of alkenmalein-acrylsintane composition provides the formation of elastic material, more homogeneous in topographic areas, from porous raw materials, technologically unsuitable for fur production. The hydrophobized nutria fur velour was which in terms of a set of properties is suitable for the manufacture of products for various purposes for use in extreme conditions.

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