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# TOWARDS OPTIMISATION OF HYDROPHOBIZING COMPOSITION IN THE FUR PRODUCTION

## К ОПТИМИЗАЦИИ ГИДРОФОБИЗИРУЮЩЕЙ КОМПОЗИЦИИ В ПРОИЗВОДСТВЕ МЕХА

**Danylkovych A.G. / Данилкович А.Г.**
*d.t.s., prof. / д.т.н., проф.*
*ORCID: 0000-0002-5707-0419*
*Kyiv National University of Technologies and Design, Kyiv, Nemirovicha-Danchenko, 2, 01011*
*Киевский национальный университет технологий и дизайна,*
*Киев, Немировича-Данченко, 2, 01011*
**Sanginova O. V. / Сангинова О.В.**
*c.t.s., as.prof. / к.т.н., доц.*
*ORCID: 0000-0001-6378-7718*
**Shakhnovsky A.M. / Шахновский А.М.**
*c.t.s., as.prof. / к.т.н., доц.*
*ORCID: 0000-0003-2963-4026*
*Igor Sikorsky Kyiv Polytechnic Institute, Kyiv, Prosp. Peremohy 37, 03056*
*КПИ им. Игоря Сикорского, Киев, пр.Победы 37, 03056*

*The present paper deals with response surface methodology based approach applied to development the optimal composition of filing and hydrophobizing mixture for the production of velor from nutria skins. Statistical models "qualitative characteristics of nutritia skins velour vs composition of hydrophobizing mixture" were constructed. The optimal composition of the filler-hydrophobic composition is determined by solving the problem of multi-purpose optimization using a method based on the Harrington desirability function. The composition of the filler-hydrophobizing mixture proposed according to the results of the research can be effectively used in the technologies of manufacturing sheepskin-fur and leather materials of high water resistance. The obtained hydrophobized nutria velor can be used for the production of uncovered sheepskin products for various purposes, which will be operated in extreme conditions.*

***Keywords:*** *multicriteria optimization, desirability function, nutria velour, velor properties, hydrophobization.*

**Problem statement**. Speaking of velor, one means a type of natural leather material obtained from dense small animal skins [1]. Usually, for this type of leather, raw materials are taken with defects on the front surface, as a result of which the outer side is not the smooth front side (grain of hide), but the inner side (flesh back of a hide). The inner side is sanded and a dense, low, monophonic pile is obtained. This is "flesh split velor". There is also a "front velor", with a ground surface with an abrasive cloth. In this way, it resembles nubuck, but for the latter, larger and coarser raw materials are used. This article will cover "fur velor" as the leather with a fur cover, dressed like velor. As is known, chrome tanning is used to make velor. Also, for tanning, zirconium or titanium salts are used, due to the effect of which the leather acquires good hairiness when sanded after tanning. Fillers are also used: albumins, starches, vegetable glues. To make the velor water-resistant, it is treated with aluminum or chrome soaps, silicone. Unfortunately, in the process of use, the surface of velor is prone to getting wet, dirty and losing its shape, therefore, it needs special processing and filling and impregnation.

The object of research in this work are filler and hydrophobic compositions for the treatment of natural materials, which are used to create products that are operated in conditions of high humidity.

Speaking of velor, one means a type of natural leather material obtained from dense small animal skins [1]. Usually, for this type of leather, raw materials are taken with defects on the front surface, as a result of which the outer side is not the smooth front side (grain of hide), but the inner side (flesh back of a hide). The inner side is sanded and a dense, low, monophonic pile is obtained. This is “flesh split velor”. There is also a “front velor”, with a ground surface with an abrasive cloth. In this way, it resembles nubuck, but for the latter, larger and coarser raw materials are used. This article will cover "fur velor" as the leather with a fur cover, dressed like velor. As is known, chrome tanning is used to make velor. Also, for tanning, zirconium or titanium salts are used, due to the effect of which the leather acquires good hairiness when sanded after tanning. Fillers are also used: albumins, starches, vegetable glues. To make the velor water-resistant, it is treated with aluminum or chrome soaps, silicone. Unfortunately, in the process of use, the surface of velor is prone to getting wet, dirty and losing its shape, therefore, it needs special processing and filling and impregnation.

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**Analysis of previous research**. The effectiveness of the use of water repellents significantly depends on the characteristics of the porous structure of the collagen-keratin material and its hair. Different parts of the semi-finished product (note than the fur semi-finished product is ultimately just a dressed and dyed (and sometimes cut) animal skins from which fur products have not yet been made) interact differently with impregnating agents, due to which finishing effects are created. It is known that hair has a denser structure compared to the skin, so the diffusion of impregnating agents into the thickness of the hair is more difficult. The hair is more hydrophobic, so it is better impregnated with agents soluble in hydrophobic media. Increasing the content of hydrophilic groups increases the solubility of impregnating agents.

Many mixtures of different chemical composition are widely used nowadays for hydrophobization of natural leather materials. particularly, the authors [2] use polymeric reagents (silanes, fluorocarbon resins, aluminum complexes with wax or paraffin). In [3] for water resistance, ductility and mechanical strength of leather semi-finished products used a copolymer of acrylic acid and acrylate monomers. An emulsion of a fluorine-containing copolymer based on maleic anhydride and natural of vegetable or fish oils with the addition of dodecafluoroheptanol and octadecyl alcohol also makes it possible to obtain a natural material of high water resistance [4]. There is information on the use to achieve the above objectives of polyfunctional polyurethanes with hydrophilic-hydrophobic radicals [5]. The increase in the strength of the material and water resistance is observed due to the combination of treatment of the material with organosilicon polymer and plasma treatment of the skin [6-9]. Thus, many mixtures and technologies for filling and hydrophobization of natural fur and leather materials have been proposed. However, the choice of the composition of the mixture usually is unsystematic.

**The purpose** of presented work is to study mathematical methods for developing optimal solutions for the alkenmalein-acrylsintane mixture in hydrophobized velor from nutria skins production.

A systematic approach to the development of filler-hydrophobic compositions in this work involved the use of the so-called "Response surface methodology" [2]. Response surface methodology (also RSM) examines the linkages between multiple explanatory variables and one or more response variables. The central idea of the RSM is to use systematically planned experiment results (in form of polynomial model(s)) to obtain an optimal "response" (ie, the best values of the characteristics of the studied process).

Some modifications of the original methodology [2] was related to the multiple response problems. Multiple-

**The main material**. Response problems are quite complex since the optimum for one criterion may not be optima for other criteria.

The development of optimal filler-hydrophobic compositions based on the response surface methodology included the following stages:

1) implementation the experimental part of the research in order to achieve maximum accuracy of measurements with the minimum possible number of experiments, while maintaining the statistical reliability of the results;

2) building experimental-statistical models that puts the factors of the filler-hydrophobic mixture in line with the properties of the studied material (in this case - with the properties of velor from nutria skins);

3) making reasonable optimal decisions on the basis of constructed mathematical models.

**1. Selection of input factors and output variables, synthesis of the experimental plan**

The composition of the hydrophobizing alkenmalein-acrylsintane mixture was investigated. This mixture is intended for the treatment of nutria skins with an area of 24–25 dm2 with coarse bristle hair after its epilation and tanning to a temperature not lower than 90 °C according to the technology [11].

The researched mixture included [11] alkenmaleic polymer synthesized on the basis of alpha-alkenes (with an average chain length of 20-24) and maleic anhydride with a molecular weight of 38·103 (on average), as well as polyacrylic emulsion and the synthesis of 2-naphthylsulfonic acid – sintan tanner BNS. The characteristics of the alkenmalein-acrylsintane mixture are determined by the following input factors: the amount of alkenmalein polymer (x1), the amount of polyacrylic emulsion (x2), the amount of sintered tannin BNS (x3), and the residual amount of alkenmalein polymer (x4).

The efficiency of the influence of alkenmalein-acrylsintane mixture formulation on the properties of nutria fur velor was evaluated by the following output variables:

- $y_1$ as the amount of mixture that diffused into the semi-finished product, wt. %;
- $y_2$ as duration of dynamic waterproofing of velor, sec;
- $y_3$ as yield of velor area, %.

It should be noted that in this case there was a planning of the experiment in the study of local areas of the diagrams "composition-property": the researchers were not interested in recipes in which there were no other components. In other words, the task was to study the dependence of properties on the composition not in the whole area of change in the concentration of components, but in the local area of the "composition-property" simplex diagram (fig. 1).

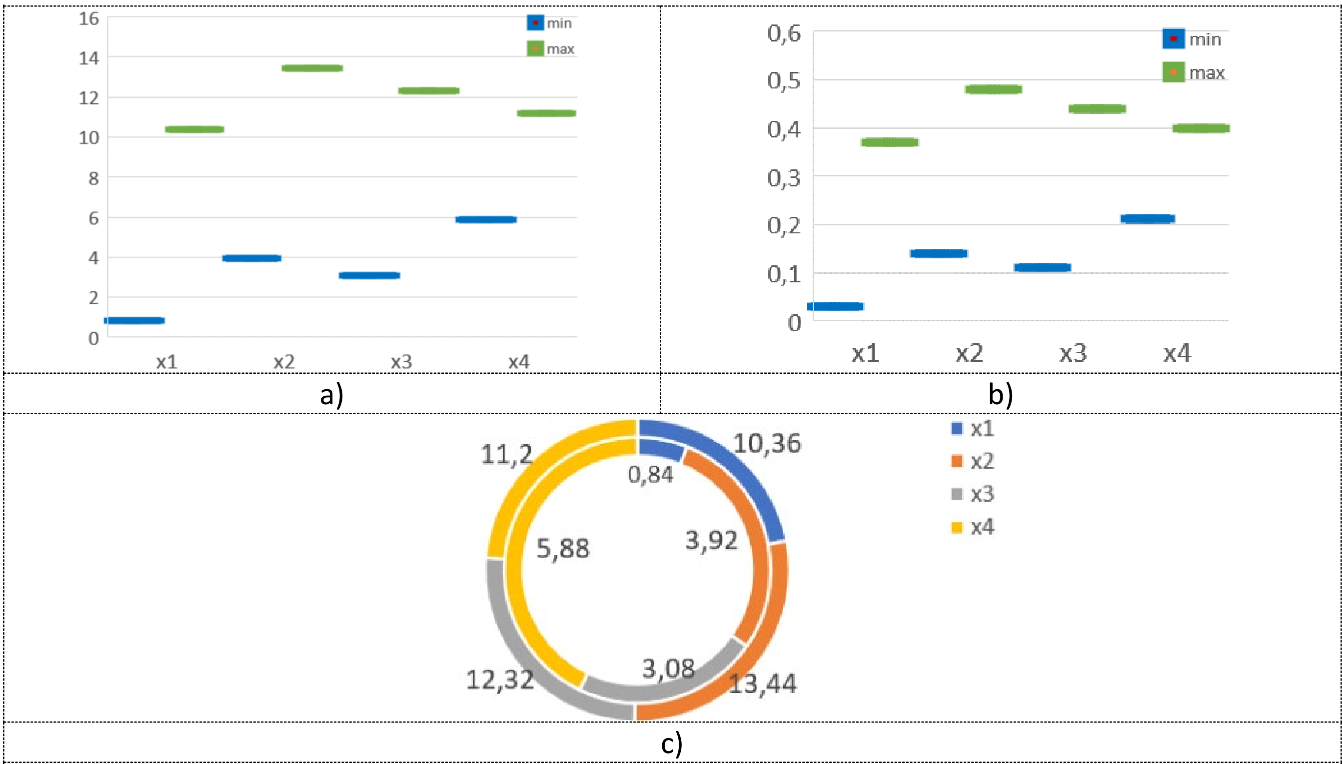



**Figure 1. Boundaries for the ingredients of the filler-hydrophobic mixture:**
a) - in natural values; b) - in coded values; c) – mixture representation (natural values).

**Table 1**

**Experimental design and results of its implementation**

| 0 | Input factors | | | | Output variables | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | x1 | x2 | x3 | x4 | y1 | | y2 | | y4 | |
| 1 | 0.210 | 0.140 | 0.440 | 0.210 | 79.2 | | 1390.0 | | 106.2 | |
| 2 | 0.200 | 0.480 | 0.110 | 0.210 | 88.5 | | 1260.0 | | 102.4 | |
| 3 | 0.030 | 0.460 | 0.110 | 0.400 | 73.4 | | 1630.0 | | 103.8 | |
| 4 | 0.030 | 0.320 | 0.440 | 0.210 | 78.6 | | 1370.0 | | 101.5 | |
| 5 | 0.030 | 0.140 | 0.440 | 0.390 | 65.3 | | 1840.0 | | 102.3 | |
| 6 | 0.370 | 0.140 | 0.110 | 0.380 | 87.1 | | 1565.0 | | 104.3 | |
| 7 | 0.190 | 0.140 | 0.270 | 0.400 | 89.4 | | 1780.0 | | 105.3 | |
| 8 | 0.370 | 0.225 | 0.195 | 0.210 | 88.3 | | 1353.0 | | 104.7 | |
| 9 | 0.030 | 0.480 | 0.195 | 0.295 | 79.1 | | 1410.0 | | 104.5 | |
| 10 | 0.225 | 0.335 | 0.110 | 0.330 | 93.0 | | 1560.0 | | 106.1 | |
| R1* | 0.036 | 0.321 | 0.250 | 0.393 | 82.9 | 83.4 | 2011 | 1990 | 106.7 | 106.3 |
| R2* | 0.036 | 0.393 | 0.250 | 0.321 | 87.1 | 86.8 | 1690 | 1681 | 106.1 | 106.0 |
| R3* | 0.072 | 0.393 | 0.214 | 0.321 | 89.7 | 90.2 | 1559 | 1562 | 104.6 | 104.1 |

*Note: *reference points*

Based on the referred above, the special type D-optimal simplex lattice experimental design (table 1) was synthesized according to a modified McLean-Anderson algorithm [11, 12].

After the implementation of the synthesized plan, experimental data (table 1) were obtained that characterize the effect of the composition of alkenmalein-acrylsintane mixture on the properties of nutria velor.

**2. Construction and verification of mathematical models.**

The coefficients of mathematical models were determined by approximating the experimental data by the method of least squares, assuming that the studied structural-determining qualitative characteristics of velor from nutria skins are continuous functions of factors and can be represented with sufficient accuracy by polynomials.

Mathematical models based on experiments (table 1) on the above three indicators of structural and defining properties of velor nutria, depending on the composition of alkenmalein-acrylsintane mixture have the form:

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

For statistical research of the received mathematical models (table 2) two parallel experiment runs in three reference points were realized.

Statistical verification of models (1) by Fisher's criterion (table 2) showed that all three obtained models (1) are adequate, and the model for the yield of fur velor area (y3) most accurately describes the experimental data.

**Table 2**

**The results of experimental and statistical verification of models**

| Descripion | y1 | y2 | y3 |
|---|---|---|---|
| Tabular value of F-test statistic Fт for 10% significance level and numbers of degrees of freedom f1 = 9 and f2 = 3 | 5,24 | 5,24 | 5,24 |
| Calculated value of F-test statistic Fp | 22,49 | 13,11 | 30,06 |
| General average | 792,90 | 1569,60 | 104,46 |
| Total variance | 66,08 | 63324,0 | 3,17 |
| Regression variance | 83,23 | 83182,0 | 4,43 |
| Residual variance | 3,85 | 6343,1 | 0,15 |

The obtained adequate mathematical models "composition of the composition vs properties of nutria velor" formed the basis of the optimization model to determine the optimal composition of alkenmalein-acrylsintan mixture in the fur velor nutria production.

### 3. Multicriteria optimization of the composition of alkenmalein-acrylsintane mixture

To find the optimal composition of the mixture for processing velor from nutria skins, it was necessary to find the optimum of the problem of multi-variable constrained programming (2):

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

where $\overline{X}$ 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.

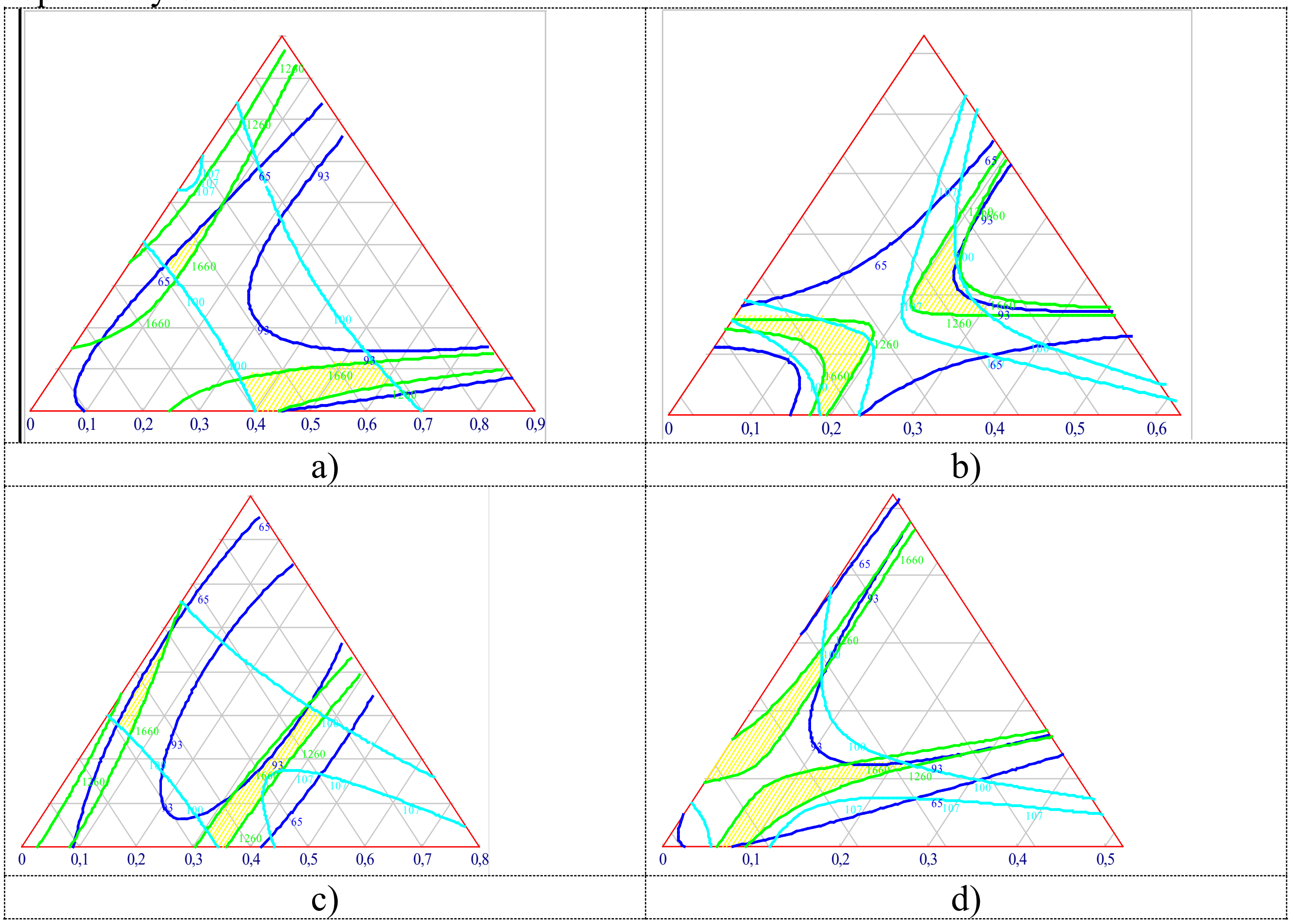
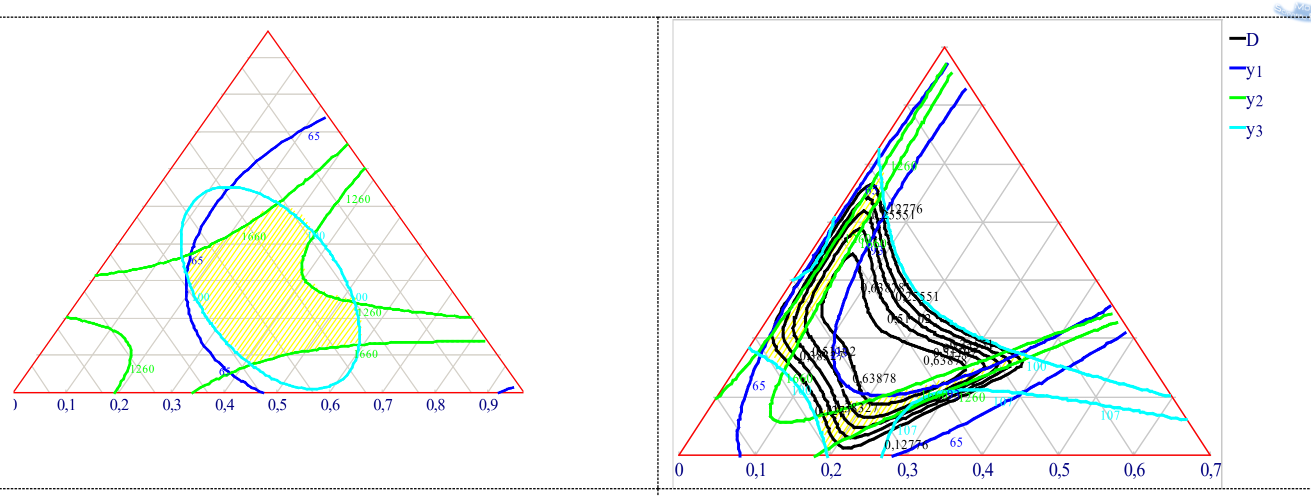



**Figure 2. "Composition-property" simplex diagram for the characteristics of the composition of alkenmalein-acrylsintan mixture:**

*a) the factor x1=0,1 was fixed; b) the factor x1=0,37 was fixed; c) the factor x2=0,2 was fixed; d) the factor x2=0,48 was fixed.*




a) b)

**Figure 3. Areas of compromise and desirability function for multicriteria the optimal composition of the alkenmalein-acrylsintane mixture:**
*a) areas of compromise (the factor x1=0,03 was fixed); b) desirability function graph (the factor x2=0,3 was fixed).*

As it was found out from the previous technological analysis of optimization criteria (2), criteria are conflicting (this fact one can also note from Fig. 1). Thus, the solution of problem (2) requires finding a compromise range of factor values.

In accordance with the research objective, the solution of the mathematical problem of optimization (2) was carried out by the method based on the Harrington desirability function [11, 13] – see fig. 3 and table 3as well as fig. 4. While solving the problem of optimizing the composition of the alkenmalein-acrylsintane mixture in accordance with the approach based on the desirability function, for the criterion of optimality y1 "bilateral" desirability profile was applied.

**Table 3**

**The results of optimization of the composition formulation**

| Composition formulation | | | | Output variables | | |
|---|---|---|---|---|---|---|
| x1 | x2 | x3 | x4 | y1, wt. % | y2, sec | y3, % |
| 0,03 | 0,303 | 0,31 | 0,357 | 82,97 | 1943,71 | 107,00 |

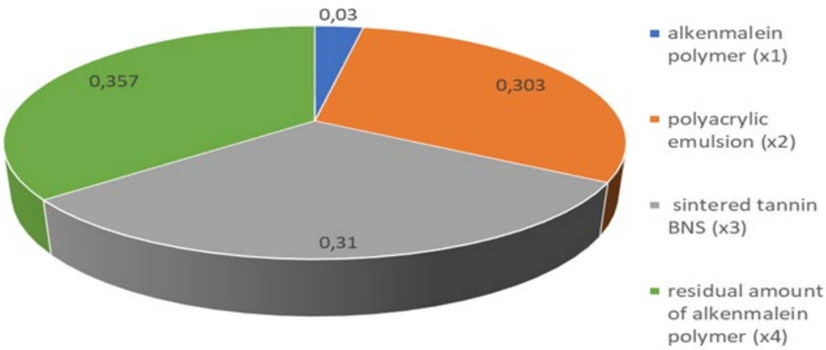



**Figure 4 –The optimal formulation of hydrophobizing alkenmalein-acrylsintane mixture**

Multicriteria optimization gave the result (Table 3, Fig. 4), which belongs to the desired compromise area (Fig. 3).

**Conclusions**. The approach based on response surface analysis methodology was applied to develop the optimal composition of alkenmalein-acrylsintan mixture for the production of hydrophobized velor from nutria skins with coarse hair. The optimal composition of the filler-hydrophobic composition is determined by solving the problem of multi-purpose optimization using a method based on the Harrington desirability function. The composition of the filler-hydrophobizing mixture proposed according to the results of the research can be effectively used in the technologies of manufacturing sheepskin-fur and leather materials of high water resistance. The obtained hydrophobized nutria velor can be used for the production of uncovered sheepskin products for various purposes, which will be operated in extreme conditions.

Prospects for further research. Further research in the direction of optimization of processes of filling and hydrophobization of fur material will include systematic study and improvement of hydrophobization processes, transition from "composition-properties" problems to "technology-properties" and "composition-technology-properties " problems.

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***Аннотация.*** *В данной статье рассматривается подход, основанный на методологии поверхности отклика, применяемый для разработки оптимального состава наполнительно-гидрофобизирующей смеси для производства велюра из шкур нутрии. Построены статистические модели «качественные характеристики велюровой шкурки нутрии в зависимости от состава гидрофобизирующей смеси». Оптимальный состав наполнителя-гидрофобного состава определяется путем решения задачи многоцелевой оптимизации с использованием метода, основанного на функции желательности Харрингтона. Предложенный по результатам исследований состав наполнитель-гидрофобизирующей смеси может быть эффективно использован в технологиях производства овчинно-меховых и кожевенных материалов повышенной водостойкости. Полученный гидрофобизированный велюр нутрии может быть использован для производства изделий из овчины без покрытия различного назначения, которые будут эксплуатироваться в экстремальных условиях.*

***Ключевые слова:*** *многокритериальная оптимизация, функция желательности, велюр нутрии, свойства велюра, гидрофобизация.*

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