Increasing of Skin Consumer Properties by Optimization of Filling Composition in its Manufacturing Technology

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ABSTRACT

The filling process is studied in the manufacture of elastic skin by optimizing the filling composition. At the same time, the four-component composition includes oligomers and polymers of natural and synthetic origin. The process of filling the tannery is carried out using the technology of private joint-stock company "Chinbar" (Ukraine, Kiev). The aim of research is producing highly elastic leather from the semi-finished product of chrome tanning, obtained from the raw materials of pig skins, with a complex of improved consumer properties by optimizing the composition of the filling composition.

Investigation of the composition consists in using a mathematical model for the four-component composition, developing a multithreaded program using the McLean-Anderson method, taking into account the type of model, determining the experimental compositions by the D-optimality criterion. The optimum composition is established at the maximum of the desirability function, which corresponded to the best compromise value of the consumer skin indices - volume yield of the material, its stiffness and imaginary specific mass.

The technology of filling is developed to ensure the formation of more homogeneous topographic patches of skin material from pig skins with a complex of high consumer properties. At the same time, the received leather material by conditional module exceeds 15% of the skin, manufactured using the technology of PJSC "Chinbar", and according to physical and mechanical characteristics it meets the requirements for the properties of garments in accordance with GOST 3115-95 and the quality management system according to interstate standards "ISO 9001:2008 ".

Keywords: MacLean-Anderson method, design synthesis, filling composition, composition optimization, consumer properties, leather material.

INTRODUCTION

Increasing consumer properties of leather material in recent years is given particular importance in connection with the expansion of markets for both leather materials and products from them. At the same time, much attention is paid to the complex of their quality indicators. This is especially important for leather materials produced from a specific micro porous raw material, in particular, pig skins. Moreover, leather materials from such raw materials occupy the second place in terms of production volume [1] after materials obtained from raw cattle. It should be noted that the raw materials of pig skins are characterized by a considerable heterogeneity of the structure along topographic sections. In this connection, the problem arises of the formation of a qualitative material by area, which can be achieved, first of all, by efficiently performing the process of filling the structure of a semi-finished product using scientifically valid composite reagents. In this case, the chemical composition of the filler composition should be optimized using mathematical modeling using the MacLean-Anderson method [2], improved by authors, and the desirability function [3]. Due to the complex differential distribution of the pores of pig skin in size in the structure of the leather semi-finished chrome tanning and the impossibility of changing the content of the components of the filling composition within the range of 0-1, the optimization of the composition "composition-properties" should be related to obtaining an experiment design with the McLean-Anderson method taking into account the mathematical model.
Literature review and problem statement

In the technology of manufacturing of elastic leather materials, the stage of filling the structure of the semi-finished product is especially important, since after tannic processes an effective yield of the material over the area is achieved. At the same time, a complex of sorption-mechanical properties of natural material is formed.

A wide range of chemical reagents of synthetic and natural origin is used to fill the leather semi-finished product [4]. From an ecological point of view, the technology of filling a tannery with a mixture of sodium goatinate, obtained from waste products of the food industry, with gelatin in a ratio of 10:1 can be considered a promising coenzyme [5,6]. In this case, the use of microbial trans-glutaminase for gelatin modification speeds up the process four times, and the resulting material is characterized by high density, smoothness of the face, elasticity and draping ability. The resulting leather material when filling with gelatin modified with genipin [7] is characterized by a uniform distribution of the complex filler in the semi-finished product due to its sorption on the fibers of the fibrillar structure of the skin. The use of genipin-gelatin processing of the semi-finished product also contributes to the increase in the hydrothermal stability of the material.

Topographic uniformity of the structure of the dermal semi-finished product of chrome tanning can be improved by filling the sulphonated oligomers based on melanin and formaldehyde [8]. In a study used a copolymer of styrene and butyl acrylate to fill the tanning semi-finished product of chrome tanning [9]. Filling the tannery with aqueous dispersions of synthesized copolymers with nano-sized particles makes it possible to form a leather material with increased hydrothermal resistance and physical and mechanical characteristics.

Elastic leather materials obtained by filling the semi-finished chrome tanned montmorillonite, modified by sodium polyphosphate and sodium carbonate with basic chromium sulphate [10,11], gain increased yield by volume, high elastic-plastic and sanitary-hygienic properties. It is shown [12] that the use of a copolymer of the sodium salt of maleic acid and 10% of polyoxyethylene lauryl makes it possible to form an elastic semi-finished product from the raw material of pig skins. The resulting material has enhanced physical and mechanical performance and yield area compared to control technology.

Thus, the analysis of the literature sources of information indicates the use of a wide range of chemical reagents in the composition for filling the tannery semi-finished chrome tanning. In this case, the consumer properties of the material depend on the kind of composition and the ratio of the components, so the search for a quasi-optimal composition is performed using a passive experiment. Investigation of a material that is structurally heterogeneous in topographic areas with both porosity and physical and mechanical properties can be considered promising in the use of mathematical modeling, imposing restrictions on the components of the composition with subsequent multi-criteria optimization.

The aim and objectives of research

The aim of research is production of a highly elastic leather material from a semi-finished chrome tanning product obtained from the raw material of pig skin, with a complex of improved consumer properties by optimizing the composition of the filling composition. To achieve this aim, the following tasks are set:

Synthesis of the experiment design "composition of filler composition - properties of leather material" by the method of MacLean-Anderson;

Analysis of obtaining an adequate mathematical model of the experiment on the basis of experimental data and establishing the optimal composition of the filling composition using the desirability function;

Determination and analysis of physical and mechanical properties of the filling leather material obtained at the experimental points of the synthesized design.

Materials and methods of research of filling composition

In the work samples of the semi-finished chrome tanning product (TU U 00302391-03-98) are used after its designing for the thickness (1.3-1.4) × 10⁻³ m. Semi-finished product according to the method of the private joint stock company Chinbar (Ukraine, Kyiv). According to the method of asymmetric fringe [13], 14 groups of samples measuring (20 × 120) × 10⁻³ m in size of 12 pieces in each group are formed from the semi-finished product. In this case, each group consists of samples of semi-finished products selected from the site of the belly and the coupon (6 pieces each).
Samples of the semi-finished product neutralized sodium formate TU 21-249-00204168-92 and sodium bicarbonate GOST 2156-76 in the ratio 1:1 by weight.

To study the process of filling the tannery, a composition with components is used:

- Copolymer of exopolysaccharide of bacterial origin TU U 88-105-002-2000 - xanthan modified with acrylamide TU 6-01-1049-92 (EPAA-M) [14] (Ukraine);
- Trupotan AG of Trumpler (Germany) - preparation based on a modified design extract and pyrocatechin;
- Tergotan SMU of Clariant (Poland) - copolymer based on synthetic and natural reagents;
- Quebracho extract (China).

In the control technology "Chinbar" instead of the copolymer EPAA-M, the anionic acrylic polymer Retanal RCN-40 from Cromogenia-Units (Spain) is used.

The process of filling the tannery takes place in the environment of electrochemically activated water - catholyte [15]. Control technology in laboratory filling conditions is realized in a distilled water environment. The total consumption of the components is 11.5 % of the weight of the pressed samples of the semi-finished product at a water / half-finished product ratio of 1.2/1.0. The temperature of the medium and the duration of the process correspond to the production technology and are 28-30°C and 2.0 h with constant mixing of the components at a rate of 8-10 min⁻¹. The obtained samples are treated with a fat emulsion at a rate of 7 % by weight of the semi-finished product, dried in a free state at a temperature of 20-23 °C, kneaded, pressed, kept in a desiccator over calcium chloride and tested in laboratory conditions.

Consumer properties of tanning semi-finished products are determined by the methods [13] on samples obtained from the belly area, since it is more structurally and kinetically sensitive to the filling process. In this case, it is determined: the volume yield of the material in terms of the volume of the semi-finished product per 100 g of protein, the stiffness - ПЖУ-12М device, and also the apparent specific gravity.

The physical and mechanical properties of the samples from the section of the leather material croupon are determined on the PM-250M machine at a deformation rate of 80 × 10⁻³m/min⁻¹, since this is stipulated in the standard for leather for garments (DSTU 3115-95). At the same time, the samples obtained at all experimental points of the design according to the indices are analyzed:

\[ \sigma_s \] - Tensile strength, MPa;
\[ \varepsilon_t \] - Elongation at a strength of 9.8 MPa, %;
\[ \varepsilon_b \] - Breaking elongation, %.

Previous studies [16] establish the possible intervals of expenditure of the components of the filling composition (Table 1) for the filling process.

**Table 1:** Restriction of the components of the filling composition

<table>
<thead>
<tr>
<th>( I )</th>
<th>Limits of the filling composition components, in the values of natural ( X_i )</th>
<th>encoded ( x_i )</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>min</td>
<td>Max</td>
</tr>
<tr>
<td>1</td>
<td>2</td>
<td>6</td>
</tr>
<tr>
<td>2</td>
<td>1</td>
<td>3</td>
</tr>
<tr>
<td>3</td>
<td>1</td>
<td>3</td>
</tr>
<tr>
<td>4</td>
<td>2</td>
<td>5</td>
</tr>
</tbody>
</table>

Note 1: The sequence number of the component of the composition; natural components are given in% of the weight of the semi-finished product.

Since \( \sum_{i=1}^{k} X_i = 1 \), where \( k \) - the number of components, the "composition-property" problem is reduced to encoded factors \( X_i \) by the dependence:

\[ X_i = 1.337 \cdot 10^{-10} + 11.500 x_i \]
The composition of the filler composition is determined by a second-order mathematical model:

\[ \hat{y} = \sum_{i=1}^{k} b_i x_i + \sum_{i=1}^{k-1} \sum_{j=i+1}^{k} b_{ij} x_i x_j , \]

Where, \( \hat{y} \) - the forecast value of the output variable; \( b_i, b_{ij} \) - coefficients of the model; \( i, j \) - the sequence numbers of the components.

In the above model, the normalization condition is used:

\[ \sum_{i=1}^{k} x_i = 1 . \]

In experiments for technological reasons, restrictions are imposed on the numerical values of the \( x_i \) components:

\[ 0 \leq x_i^{\min} \leq x_i \leq x_i^{\max} \leq 1 \ (i = 1, 2, ..., k), \]

The mathematical model of a general form for a four-component composition acquires the form:

\[ \hat{y}_i = b_{1i} x_1 + b_{2i} x_2 + b_{3i} x_3 + b_{4i} x_4 + b_{12ij} x_1 x_2 + b_{13ij} x_1 x_3 + b_{14ij} x_1 x_4 + b_{23ij} x_2 x_3 + b_{24ij} x_2 x_4 + b_{34ij} x_3 x_4 , \]

Where, \( \hat{y}_i \) - the predicted value of the consumer property of the leather material, \( i = 1-3; \)

- \( x_1 \) - copolymer EPAA-M;
- \( x_2 \) - preparation Trupotan AG;
- \( x_3 \) - copolymer Tergotan SMU;
- \( x_4 \) - quebracho extract.

The effectiveness of the effect of the composition of the filling composition on the consumer properties of the leather material is evaluated according to the following indicators:

- \( y_1 \) - volumetric yield of leather material, cm³/100 g of protein;
- \( y_2 \) - material stiffness, cN;
- \( y_3 \) - imaginary specific mass of samples, kg/m³;

To obtain a mathematical model that describes the consumer properties of the leather material depending on the composition of the composition, it is necessary to synthesize the experiment design according to the D-optimality criterion with imposed restrictions on the components of the composition. After the implementation of the experiment design and the processing of the obtained data, the coefficients of the model are calculated and its adequacy at the control points is checked. The obtained "composition-property" models are used to optimize the composition of the composition by the desirability function.

**Obtaining a mathematical model of the composition of the filling composition**

Previous studies [16] make it possible to determine the boundaries of the variation of these components in the composition of the filling composition, parts (Table 1).

To obtain the coefficients of the model (4) according to certain theoretical points by the candidates (Table 2), according to the MacLean-Anderson algorithm, based on the maximum distance from the design center and from each other [2] and the developed multithread program, let's synthesize the experiment design. To do this, let's select from N theoretical points the best n experimental points of the design according to the D-optimality criterion.
In order to determine the experimental points of the design, all possible combinations from N to n points in number
\[ \tilde{n}_N = \frac{N!}{n!(N-n)!} \]
and a combination is calculated in which the determinant
\[ \det|D| \rightarrow \min \]
where, \( D \) is the dispersion matrix of the current design;
\( F \) is the matrix of the experimental design \( X \), generalized by the form of the model \( \text{f}^T(\bar{x}) \) of size \( n \times l \);
\( l \) is the number of model coefficients;
\( T \) is the matrix transpose operation.

To obtain the coefficients of the four-component composition model, an optimal experimental design is synthesized (Table 3) in a limited region of the simplex (Table 1), taking into account the normalization condition.

Thus, from the theoretical points obtained by the MacLean-Anderson method and the D-optimality criterion, ten experimental points are selected for further research.

The obtained experimental results of the influence of the composition of the filling composition according to the design of Table 3 in consumer properties of leather material are given in Table 4.

The coefficients of the four-component mathematical model are determined by the method of least squares in the matrix form.
\[ B = (F^T F)^{-1} F^T Y. \]

Where, \( B \) - the vector of the required coefficients;

\( Y \) - column of the values of the dependent variable, which are observed in the experiments.

The adequacy of the model is verified by the Student's criterion [2] at each control point that the researcher is interested in.

To test the adequacy of the mathematical model, two parallel experiments are performed at three arbitrarily chosen control points (Table 5).

**Table 5: Physical and chemical properties of the filling leather material in control points of the composition**

<table>
<thead>
<tr>
<th>Control point</th>
<th>Composition</th>
<th>Technological indicators</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( x_1 )</td>
<td>( x_2 )</td>
</tr>
<tr>
<td>1</td>
<td>0.3478</td>
<td>0.087</td>
</tr>
<tr>
<td>2</td>
<td>0.2609</td>
<td>0.087</td>
</tr>
<tr>
<td>3</td>
<td>0.4348</td>
<td>0.1739</td>
</tr>
</tbody>
</table>

Table 1 shows the experimental and control data. 4 and 5 with the use of a computer, a nonlinear mathematical model of the dependences of the technological consumer properties of leather material on the composition of the filling composition is obtained:

\[
\begin{align*}
\hat{y}_1 &= 200.40724066 + 817.28417467 x_1 + 794.77256631 x_2 + 1156.82205723 x_3 + 281.52425942 x_4 - 222.17434727 x_1 x_2 - 2008.642258 x_2^2 - 2586.624701 x_3^2 - 2367.360642 x_4^2 - 1842.679728 x_1 x_3 x_4; \\
\hat{y}_2 &= 33.33857263 - 182.04460653 x_1 + 102.52437199 x_2 - 69.85634247 x_3 + 287.94133639 x_4 + 587.645514 x_1 x_2 + 184.1415527 x_2 x_3 + 252.7588175 x_3 x_4 + 440.0149701 x_4 x_1 x_2 x_3 x_4; \\
\hat{y}_3 &= 0.524937846 + 0.380750396 x_1 + 0.412988324 x_2 + 0.705938768 x_3 + 0.134947823 x_4 + 0.737231397 x_1 x_2 + 1.435059291 x_1 x_3 + 1.1690889 x_1 x_2 x_3 x_4.
\end{align*}
\]

Determination of the adequacy of the mathematical model of the "composition of the filling composition - the properties of the leather material" at the control points is given in Table 6.

Thus, from Table 6, it can be seen that the obtained mathematical model adequately describes the consumer properties of the leather material of the corresponding composition of the filling composition.

**Table 6: Results of checking the adequacy of the mathematical mode**

| \( y_{ij} \) | \( \hat{y}_{ij} \)  | \( \hat{y}_{ij} \)  | \( \Xi \) | \( |\hat{y}_{ij} - y_{ij}| \) | \( t_p \) | adequacy |
|--------------|------------------|-------------------|-----|-------------------|------|--------|
| y11          | 187.8            | 192.5             | 1.4 | 4.7               | 1.425| 1      |
| y12          | 28.6             | 29                | 1.3 | 0.4               | 0.307| 1      |
| y13          | 0.628            | 0.626             | 1.5 | 0.002             | 0.667| 1      |
| y21          | 229.4            | 233.5             | 1.4 | 4.1               | 1.261| 1      |
| y22          | 25.3             | 23.5              | 1.3 | 1.8               | 1.421| 1      |
| y23          | 0.603            | 0.597             | 1.5 | 0.007             | 2.522| 1      |
| y31          | 141.8            | 150               | 1.4 | 8.2               | 2.42 | 1      |
| y32          | 36.7             | 34                | 1.3 | 2.7               | 2.015| 1      |
| y33          | 0.645            | 0.641             | 1.5 | 0.004             | 1.523| 1      |

Optimization of the composition of the filling composition

To optimize the composition of the four-component composition \( \bar{x} = \| x_1, x_2, x_3, x_4 \| \) which is characterized by \( g \) output of the received mathematical model by consumer indicators, the desirability function [3] is used:
\[ D_f = \prod_{i=1}^{g} d_i d_2 \ldots d_g \cdot \]

Where, \( d_i \) \((i = 1, 2, \ldots, g)\) - a partial function of the property desirability of the leather material \( y_i \), which takes values in the interval \([0; 1]\) and is determined by the dependence:

\[ d_i = \exp[-\exp(-y_i')] \cdot \]

Where, \( y_i' \) - dimensionless value of the material property \( y_i' \) - which is determined by the linear relationship:

\[ y_i' = b_0^{(i)} + b_1^{(i)} y_i \cdot \]

The coefficients \( b_0^{(i)} \), \( b_1^{(i)} \) from the above equation are determined from the following system of equations:

\[
\begin{align*}
    y_i^{(worse)} &= b_0^{(i)} + b_1^{(i)} y_i^{(worse)} \\
    y_i^{(better)} &= b_0^{(i)} + b_1^{(i)} y_i^{(better)},
\end{align*}
\]

where \( y_i^{(worse)} \), \( y_i^{(better)} \) - worse and better value of the criterion \( y_i \), which is established by the researcher according to the consumer properties of the material, is correspondingly worse and better, and can’t be reduced or increased;

\[
\begin{align*}
    y_i^{(worse)} &= -\ln(-\ln d_i^{(worse)}) \\
    y_i^{(better)} &= -\ln(-\ln d_i^{(better)}),
\end{align*}
\]

Where, \( d_i^{(worse)} \), \( d_i^{(better)} \) - worse and better value of individual desirability functions; accordingly, the values 0.2 and 0.8 are adopted.

The maximum of the desirability function \( D_f \) corresponds to the optimal composition \( \mathbf{x}^{opt} \), has the best compromise values of the consumer indicators \( y_i \).

So, on the basis of the desirability function, the optimal composition of the filling composition is determined, which is characterized by three best consumer properties. At the same time, the high yield of the material and the minimum values of the imaginary specific gravity and stiffness are considered as the best values.

The obtained mathematical models of consumer properties are used for multicriteria search of the optimal composition of the filling composition with the help of the generalized desirability function, compiled from the corresponding mathematical models in x-coordinates with constraints on the output variables corresponding to the worst and best values: \( y_1 \) - 200 and 260, \( y_2 \) - 30 and 22, \( y_3 \) - 0.630 and 0.580. Using the scanning method [17] in 0.01 increments, the optimum composition of the composition, wt. parts: \( x_1 = 0.222 \), \( x_2 = 0.087 \), \( x_3 = 0.257 \), \( x_4 = 0.434 \), or as a percentage of the weight of the semi-finished product: \( X_1 = 2.55 \), \( X_2 = 1.00 \), \( X_3 = 2.96 \), \( X_4 = 4.99 \). In this case, the consumer properties of the leather material take the values: \( y_1 = 257.4 \) cm\(^3\)/100 g of protein, \( y_2 = 22.1 \) cN, \( y_3 = 0.581 \) kg/m\(^3\) as a desirability function \( D_f = 0.7896 \) with the number of calculations of its values-7734 times.

**Physical and mechanical properties of the filling leather material**

The research results of the physical and mechanical properties of the obtained samples at ten experimental points (Table 3) of the composition of the filling composition are given in Table 7. It can be seen from the obtained data that the deformation capacity is the most sensitive indicator of the leather material characterizing its consumer properties in the investigated interval of the composition of the filling composition. At the same time, the deformation of the material samples at strength of 9.8 MPa increases by 47% with a change in the composition of the filling composition, while the tensile strength changes 2.6 times less. It should be noted that the volumetric yield and stiffness of the material obtained from the belly area, respectively, change by 64 and 68%.

**Table 7: Physical and mechanical properties of the filling leather material**

<table>
<thead>
<tr>
<th>Indicator</th>
<th>Experimental point</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2</td>
</tr>
<tr>
<td>( \sigma ), MPa</td>
<td>\text{19 ± 0.9}</td>
</tr>
<tr>
<td>( \varepsilon ), %</td>
<td>\text{34 ± 2.0}</td>
</tr>
<tr>
<td>( \varepsilon_g ), %</td>
<td>\text{66 ± 4.6}</td>
</tr>
</tbody>
</table>
With the optimum composition of the filling composition, which practically corresponds to the first experimental point, the physical and mechanical parameters reach the maximum values.

The research results of the physical and mechanical properties of the filling semi-finished product with the developed and control composition of the composition (using the technology of PJSC Chinbar) are shown in the Figure 1.

![Figure 1](image_url)

**Figure 1**: Physical and mechanical characteristics of leather material obtained using the optimized composition of the composition (left) and the control (right): 1 - tensile strength, σs, MPa, 2 - elongation at 9.8 MPa %, 3 - breaking elongation ɛb, %

Comparative analysis of samples obtained using the developed technology using the optimal composition of the filling composition and the control technology of PJSC Chinbar, demonstrates the advantages of replacing the anionic acrylic polymer Retanal RCN-40 with a copolymer of exopolysaccharide of bacterial origin, xanthan modified with acrylamide. At the same time, the deformation capacity at strength of 9.8 MPa of the material obtained by the optimized technology exceeds the control samples by 15%.

Thus, according to the set of consumer characteristics, the optimal composition of the filling composition is established on the basis of the obtained mathematical model and the generalized desirability function. The developed composition provides an efficient filling process in the production of elastic leather material of chrome tanning from pig skins with a complex of high performance properties.

**CONCLUSION**

For the formation of leather material from the semi-finished chrome tanning of pig skin with high consumer properties, an experiment design for the composition of the filling composition by the improved MacLean-Anderson method is synthesized and implemented, taking into account the type of the mathematical model using the developed multithread program, which reduces the duration of synthesis of the D-optimal design in two times compared to a single-threaded program, and is 24 hours.

On the basis of the calculated mathematical model for consumer properties of leather material, a multifactor optimization of the composition of the filling composition using the desirability function is carried out.

The optimal composition of the four-component filling composition is established, which ensures the formation of a topographically more homogeneous leather material with a complex of high consumer properties. According to physical and mechanical characteristics, the obtained material meets the requirements for the properties of garments in accordance with GOST 3115-95 and the quality management system according to interstate standards "ISO 9001:2008".

**REFERENCES**


