MULTICRITERIA COMPROMISE OPTIMIZATION FOR LEATHER AND FUR SKIN MATERIALS TANNING TECHNOLOGY

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ABSTRACT. The work is devoted to the study of the influence of electro-activated aqueous solutions on the technological cycle of leather and fur skin materials production and footwear made of them. The influence of electro-activated aqueous solutions on the physicochemical transformations of the structure of skin tissue collagen is exemplified by rabbit fur skins used for shoe production. The spectral characteristics of changes in the structure and composition of dermal collagen are determined and optimal modes of tanning process of leather and fur skin materials based on multicriteria compromise optimization are determined.

KEY WORDS: electro-activated aqueous solutions, anolyte, catholyte, leather and fur skin materials, footwear

INTRODUCTION

Technologies that provide the manufacture of leather and fur skin materials imply the retention of beneficial properties of both the skin tissues and its hair-covering, and ensure permanency of these materials during continuous exploitation of products made of them. The most toilful and time-consuming processes in the leather and fur skin manufacturing cycle are preparatory and tanning stages. These processes are carried out with significant water consumption, while water is acting as a solvent for chemical reagents, and their utilization requires significant costs in the future [1].

The most promising solution to the problem of reducing water consumption and material consumption of fur production are methods that activate chemical reagents in water such as usage of electric current. The effect of the latter is widely studied by a number of scientists [2, 3], but the nature and action mechanism of the water being treated by electricity has not been sufficiently studied yet.

Liquid processes in the production of leather and fur skin materials are fully associated with the presence in the water solution of electrolytes formed in the result of the dissociation of ions of chemical formations in the protein structure, hydrolysis of bonds, the carriers of which are structural elements of the protein, as well as relatively free ions. At the same time, ions introduced with water as a solvent
of chemical components, in particular Na\(^+\)Cl\(^-\) ions, are involved. Natural (tap) and distilled water has minimal electrical conductivity in its structure, and electro-activated water (anolyte and catholyte) has 2-3 times greater electrical conductivity, that indicates that the conductivity in these solutions is provided not only by Na\(^+\)Cl\(^-\) but also by ions formed by the excess of mobile ions with a positive or negative charge that may be carried by groups with water molecules.

One of the most common forms of polymeric material study is their physical and mechanical testing, as their physical and mechanical properties are widely used in light industry to evaluate the quality of fully processed products. Studies of the relaxation and deformation characteristics of materials are of considerable scientific and practical interest. The results of such experiments allow to record simultaneously during one experiment the following kinetic curves [4]: the curve of development and relaxation and deformation in the sample, changes in its linear dimensions and hygroscopicity.

It is known [5] that objects with complex curvilinear surface shape (foot, shoe pad, shoe upper parts) are of the greatest complexity for design, because anatomical structure of the foot and the properties of the leather and fur skin materials from which the footwear is made must be taken into account in order to ensure their proper quality. However, in the conditions of production of leather and fur skin materials, most often according to the existing technological schemes and instructions it is not possible to determine the optimal combination of technological factors by which in particular case it is possible to achieve the maximum approximation to the required properties of the prefabricated leather component at the minimum cost of chemical materials.

Solving the problems of optimization and mathematical modeling of complex technological systems is characterized by significant particular characteristics due to the narrow application orientation of the obtained solutions, sometimes by the lack of sufficient information about the mechanisms occurring inside the system. At the same time the solution of such problems leads to the random nature of the change of optimality criteria and some factors with a considerable number of quality indicators (optimization criteria) and as well as to factors that are taken into account in optimization and modeling [6].

The applied methodology for solving these problem classes provides various recommendations for the nature of this study. According to the classical, i.e. theoretical and analytical approach [7], it is recommended to obtain a mathematical model and then, using it, to find the optimal conditions.

**EXPERIMENTAL**

**Materials and Methods**

Rabbit skins that differ in the way they had been made were selected as the object of the study. Thus, for the manufacture of skins at all stages of the technological cycle electro-activated aqueous media was used. Skins, tanned by the standard technology were used to control the initial performance indicators of the dermis and to compare them.

The change in the structure and chemical composition of the rabbit dermis collagen was evaluated by the results of IR spectroscopy (Bruker TENSOR spectrometer) within the spectral range of 4000-400 cm\(^{-1}\). The test specimens were prepared in the form of a tablet which contained potassium bromine (KBr) with a sample of ground tissue 0.5-1 mg. The IR spectra of the studied materials were described on the basis of reference data [8–10].

The IR spectra of rabbit skin tissue in the range of 3800-2600 cm\(^{-1}\) and 1800-400 cm\(^{-1}\) were studied. The nature of the interaction of the studied systems was evaluated by the disappearance, displacement and intensity change of the corresponding characteristics of bandwidths. The bandwidths in the IR spectra of the initial materials and the products of their interaction were assigned according to the bandwidths of the characteristic bonds of C–C atoms group and \(\text{CH}_2\).

The influence of the electrical conductivity of water on the basic chemical parameters of rabbit fur skin was evaluated by the content of fat in the skin tissue, its welding temperature and the indicator of the formation of dermal volume in samples that were tanned using the appropriate technologies [11].
RESULTS AND DISCUSSIONS

To make a quantitative study of changes in protein functional groups and skin-forming components within certain characteristic waves, the optical density was determined using the baseline method [8]. The bands of 2854 cm$^{-1}$ and 1454 cm$^{-1}$ were selected as the internal standard due to the valence vibrations of the methylene groups - CH$_2$ and carbon chain C-C groups (Fig. 1). Characteristic wave frequencies for the collagen dermis of rabbit skin tissue that relate to the characteristic wave frequencies of certain functional groups or their interactions were taken into account.
Figure 1. Experiment spectrum where the following substance was used in the technological processes: a – water formed in the result of passage of current on a negative electrode (anolyte); b – water formed in the result of passage of current on a positive electrode (catholyte); c – distilled water; d – technical water

Tables 1, 2 show the oscillation frequencies of characteristic groups that change in the skin tissue during the manufacturing cycle of fur production. In all cases the content of neutral salts per NaCl was the same and was equal to 0.2 g/l.

### Table 1: Optical density of skin tissue samples IR spectra in the range 3800-2600 cm\(^{-1}\)

| Water source                          | Electrical conductivity, µS/cm | Optical density at wave frequency |
|---------------------------------------|-------------------------------|----------------------------------|
| Near anion electrode (anolyte)        | 2800                          | 0,86, 0,932, 1,02, 0,582, 1,45, 1,00 |
| Near cationic electrode (catholyte)   | 1270                          | 1,390, 1,51, 1,35, 0,89, 1,49, 1,00 |
| Distilled water                       | 710                           | 0,481, 0,641, 0,689, 0,489, 0,71, 0,87 |
| Technical water                       | 750                           | 0,894, 0,975, 0,867, 0,59, 1,45, 1,00 |

### Table 2: Optical density of samples IR spectra in the range of 1800-400 cm\(^{-1}\)

| Water source                          | Electrical conductivity, µS/cm | Optical density at wave frequency |
|---------------------------------------|-------------------------------|----------------------------------|
| Near anion electrode (anolyte)        | 2800                          | 1,59, 1,19, 0,76, 0,63, 0,82, 0,71, 0,57, 0,46, 0,36 |
| Near cationic electrode (catholyte)   | 1270                          | 1,67, 1,25, 0,78, 0,65, 0,76, 0,61, 0,58, 0,43, 0,40 |
| Distilled water                       | 710                           | 1,50, 1,06, 0,71, 0,57, 0,85, 0,82, 0,60, 0,50, 0,37 |
| Technical water                       | 750                           | 1,58, 1,17, 0,75, 0,64, 0,84, 0,77, 0,61, 0,51, 0,41 |
Based on the obtained data it can be stated that water of different origin affects the spectra of rabbit skin tissue differently in the range of the spectra of 3800-2600 cm\(^{-1}\) and 1800-400 cm\(^{-1}\). These spectra are characteristic for dermis collagen tanned with basic chromium salts. Specific features of the spectrum include the appearance of 1663 cm\(^{-1}\) wavelength which is inherent to the valence oscillation C = O of medium intensity, and wave of 1036 cm\(^{-1}\) which is inherent to the deformation oscillation C – O – C of medium intensity, which corresponds directly to the aldehyde group and the product of its interaction with the carbon chain, resulting in the emergence of heat-resistant bonds. The appearance of thermo-resistant bonds of the dermis with chromium salt can be estimated by changing the optical density at a wavelength of 1084 cm\(^{-1}\).

The study results proved that the technological processes of production of leather and fur skin materials, such as wetting, pickling (using technical and distilled water), tanning, greasing and drying are significantly influenced by the general characteristics of water, that can be reduced to its electrical conductivity (Tables 1-2), and the main indicators of the finished product (Fig. 2) with of the square values of the correlation ratio \(R\) greater than 0.8.
Figure 2. Water electrical conductivity effect on: a) skin tissue fat content; b) welding temperature; c) dermal volume formation

Using water with different electrical conductivity as a solvent, it was discovered that it significantly affects the degree of the polar part of both soluble substances and directly hydrophobic and hydrophilic balance inside the dermis. This leads to different interactions of the functional groups both in solution itself and between the water-soluble compounds and the active groups that are present in the dermis. The result of this interaction is a change in the analytic characteristics of the skin tissue and the index of the dermis volume formation. The positive charge of amino groups can be stated on the basis of the existence of characteristic waves with length of 3410 cm\(^{-1}\) and 1663 cm\(^{-1}\) especially in acidic environment during pickling (Fig. 3). With a certain electrical conductivity, the maximum value of the optical density can be observed. Increasing and decreasing leads to a deviation in the downward direction of the optical density when the wave oscillation frequency is of 3410 cm\(^{-1}\) and 1663 cm\(^{-1}\).
Wavelengths of 3410 cm\(^{-1}\) and 1663 cm\(^{-1}\) are associated with the formation of hydrogen bonds, a great number of which significantly affects the dermal collagen welding temperature. The essence of these connections means that after breaking in one place, they are re-formed in another place, that provides to some extent the possibility of deformation and fixing of the residual deformation.

A distinctive feature of the process of forming heat-resistant bonds in the dermis is the result of several, at first glance, opposite reactions. First of all, the normal formation of heat-resistant bonds is due to the carboxyl group being included in the chromium complex. And the interaction of the fat molecule with the chromium complexes prevents the further formation of a heat-resistant bridge. Thus, the thermal resistance of the skin tissue decreases (Fig. 4).

Figure 3. Water electrical conductivity effect on optical density at the wave spectrum: a) 3410 cm\(^{-1}\); b) 1663 cm\(^{-1}\)
However, this interpretation does not explain why the properties of the skin are restored during a short period of time after welding. This phenomenon is observed when the skin is being tanned with aldehyde compounds. The appearance of C-O-C groups with a wavelength of 1084 cm\(^{-1}\) (Fig. 5) in the structure of the derma is a consequence of the interaction of dialdehyde compounds with protein. The aldehyde groups appear due to the presence of a large number of oxidants or reducing agents in the catholyte and anolyte in the system respectively.

![Figure 4](image1.png)

**Figure 4.** Relationship between dermal welding temperature and: a) the fat content; b) the content of chromium salts

The wavelength of 1663 cm\(^{-1}\) corresponds to the carbonyl groups, that is conditioned by their presence in proteins and fatty substances in the form of triglycerides. Meanwhile, this wave is characteristic for the fluctuations of the N-H protein groups, that can be manifested as a result of the transformation of the general restructuring of the protein structure in the spectrum (Fig. 6). The imprint of the restructuring (deformation under load) on the vibrations of the groups N – H and C = O, that corresponds to the model of change in the deformation of the tensile under load and after its removal allows us to confirm the correctness of the physical model to the full extent [11].

![Figure 5](image2.png)

**Figure 5.** Relationship between dermal welding temperature and optical density wavelength 1084 cm\(^{-1}\)
Negative OH\(^{-}\) groups that are a part of the complex chromium sphere are dominated in catholyte, can result in the formation of neutral or negative charge tanner particles. The latter is most likely when using catholyte during tanning. Therefore, the negatively charged chromium molecule interacts with the positively charged NH\(^{2+}\) amino group, that results in the partial neutralization of the negatively charged chromium complex, freeing the coordination center in the chromium to interact with other groups having the ability of entering the complex sphere of chromium atoms. It is possible to form heat-resistant bonds in both cases that provide the effect of tanning (welding temperature increase). In the presence of trivalent chromium in a highly saturated with oxygen (in the form of OH\(^{-}\) ions medium), the processes of oxidation of hydrocarbons with the formation of aldehydes are possible, which form heat-resistant bonds, that are destroyed at a temperature in the aqueous medium above 65°C, and at a lower temperature below the specified level they are being restored. The appearance of such bonds is evidenced by the presence of C-O-C groups at wave frequencies of 1166 cm\(^{-1}\), 1036 cm\(^{-1}\) and 1084 cm\(^{-1}\), that are the result of the interaction of dialdehyde compounds with the protein. The wave frequency of 1036 cm\(^{-1}\) can be partially attributed to the OH alcohol group (Fig. 7).

Bearing in mind that the OH and C-O-C groups have a high affinity for the formation of complex compounds, it can be deduced that this effect (restoration of the sample after welding during cooling) causes the restoration of heat-resistant samples.
The practical solution to the optimization problem is done almost approximate due to a large number of factors that are responsible for the results of manufacturing products and their quality. The methodology of multicriteria compromise optimization was used to final solution of the technology optimization problem. This methodology is used when there are more than two quality criteria according to which compromise optimization is performed [6].

Performing multicriteria compromise optimization requires finding a target function that looks like:

\[ \gamma_{w,r} = \sqrt{\sum_{j=1}^{n} (1-D_j)^2 \cdot W_j^2}, \]  

where \( \gamma_{w,r} \) is the value of the generalized
MULTICRITERIA COMPROMISE OPTIMIZATION FOR LEATHER AND FUR SKIN MATERIALS TANNING TECHNOLOGY

objective function for the r-th experiment experience, which in the case of finding the optimum tends to 0 ($\gamma_{opt} \rightarrow 0$) and is a value of the proximity of this point to the hypothetical optimal value in coded form which is equal to 1;

$D_j$ - reduced to the interval 0 ... 1 the value of the j-th response (quality criterion) in the r-th experiment experience, depending on the target quality selected for a specific criterion this value is calculated by different formulas;

$W_j$ - weight of the j-th quality criterion (response);

practically equals to $\sum_{m=1}^{m} \gamma$;

$m$ - the number of quality response criteria.

To find a generalized criterion for the quality of leather and fur skin materials an array of data was created which consists of analytical indicators and indicators characterizing the porous structure and deformation properties. The results of the calculation are shown in Table 3.

Table 3: Basic data to calculate the objective response function

| Group            | Fat content, % | Chromium salts content, % | Derma volume formation, cm$^3$ | Derma collagen welding temperature, °C | Macropores volume, $\times 10^{-5}$, kg/m$^3$ | Micropores volume, $\times 10^{-5}$, kg/m$^3$ | Total pore volume, $\times 10^{-5}$, kg/m$^3$ | Components of deformation, % | Overall objective response function $\gamma$ |
|------------------|----------------|---------------------------|---------------------------------|----------------------------------------|-----------------------------------------------|-----------------------------------------------|---------------------------------------------|-----------------------------------------------|-----------------------------------------------|
| Anolyte          | 25,4           | 0,76                      | 308,1                           | 76                                     | 81,55                                         | 38,37                                         | 137,05                                      | 2,9                                           | 5,3                                           | 9,6                                           | 1,4                                           | 4,6                                           | 0,09                                         |
| Catholyte        | 20             | 0,70                      | 254,5                           | 67                                     | 34,51                                         | 34,46                                         | 96,39                                       | 1,4                                           | 2,9                                           | 5,4                                           | 1,1                                           | 1,9                                           | 0,21                                         |
| Distillate       | 27,5           | 0,76                      | 435,9                           | 68                                     | 30,62                                         | 35,96                                         | 91,93                                       | 1,5                                           | 2,7                                           | 5,2                                           | 0,9                                           | 2,3                                           | 0,16                                         |
| Technical water  | 31,4           | 0,83                      | 499,6                           | 66                                     | 29,92                                         | 34,13                                         | 92,21                                       | 1,7                                           | 1,9                                           | 4,6                                           | 0,9                                           | 1,9                                           | 0,26                                         |

As it is seen from the Table 3, the smallest value of the generalized quality criterion $\gamma$ (0.09) is observed in the anolyte treatment method which corresponds to the point of the factor space closest to the hypothetically optimal one.

There is a generalized dependence between the objective function, which characterizes the porous structure of the skin tissue, its analytical parameters (fat content, chromium oxide, volume formation, derma welding temperature), deformation characteristics and electrical conductivity values of the water that was used (Fig. 9).
Figure 9. Effect of electrical conductivity on a generalized objective function, which is characterized by: 1 - porous structure of skin tissue ($R^2 = 0.9298$); 2 - analytical indicators of skin tissue ($R^2 = 0.0927$); 3 - spectral characteristics ($R^2 = 0.9205$); 4 - deformation characteristics ($R^2 = 0.5613$); 5 - generalized set of indicators inherent to rabbit skin ($R^2 = 0.6480$)

The spectral characteristics do not define the quality of the material, but mainly reflect the presence of functional groups that affect the parameters that characterize the quality of the finished skin. The deviation of the generalized objective function, which characterizes the spectral and analytical characteristics of rabbit skin tissue, is not significant; that is why this optimization is not taken into account.

The porosity characteristics (curve 1) and the deformation characteristics (curve 4) of skin tissue made on the basis of technologies involving the use of electro-activated water (anolyte with an electrical conductivity of 2800 $\mu$S/cm, catholyte with a catalyst of 2800 $\mu$S/cm) are most significantly influenced by the value of the generalized objective function (Fig. 15) with electrical conductivity of 1270 $\mu$S/cm and not activated water (with electrical conductivity of 710-750 $\mu$S/cm). When searching for the optimum, the smallest values of the generalized objective function correspond to the anolyte.

The most significant contribution to the disclosure of the essence of transformations in the skin tissue derma in the process of its manufacture is made by its spectral characteristics and porosity characteristics.

The presence of C-O-C groups (Fig. 10), which arise from the interaction of electro-activated water with the protein and the formation of aldehydes in the protein structure, which are subsequently transformed into simple heat-resistant ether bonds, has the influence on the overall objective function of the spectrum.
The obtained optical density values (Fig. 10), which are lower than 0 (curves 2–4), are extrapolated. They are not taken into account in the analysis because they are imaginary. Optical density limits at conductivity values up to 1260 μS/cm and greater than 2400 μS/cm are significant.

CONCLUSIONS

The treatment of leather and fur skin materials with electro-activated water in the technological cycle of their production significantly affects the quantitative indicators that objectively characterize the quality of the skin tissue (skin fat content, dermal welding temperature) and participate in the formation of skin structure (volume formation indicator), and also contributes to the elastic and plastic properties of the skin that must be taken into account when making footwear from materials with predicted properties.

The most probable reactions of the rabbit skin tissue using water with different conductivity characteristics when natural salt is present (industrial water), distilled water when table salt is present, and distilled water in the presence of table salt formed on the cathode and anode (catholyte and anolyte) are considered. The latter have shown their specificity in influencing the technological processes of fur skin production from rabbit skins. The properties of the finished skins depend entirely on the content of the components that may be the carriers of the electric charge.

The specificity of electro-activated water is that in the process of its manufacture in the anolyte an excess of electrons is observed, and in the catholyte, on the contrary, their lack is observed. This leads to the formation of compounds that have a reactive activity, that means that they interact with each other and with other active groups of collagen, which provides the appearance of cross-links in the irrigated derma that largely resistant to temperature as well as changing elastic and plastic properties of skin tissue. Thus, advanced technology can be used in industry as an effective method of leather and fur skin materials with specific properties tanning that can be predicted at the stage of their manufacture.
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